Journal Pre-proof

Insights into coacervative and dispersive liquid-phase microextraction strategies with hydrophilic media – A review

Idaira Pacheco-Fernández, Raúl González-Martín, Francisca A. e Silva, Mara G. Freire, Verónica Pino

PII: S0003-2670(20)30855-2

DOI: https://doi.org/10.1016/j.aca.2020.08.022

Reference: ACA 237895

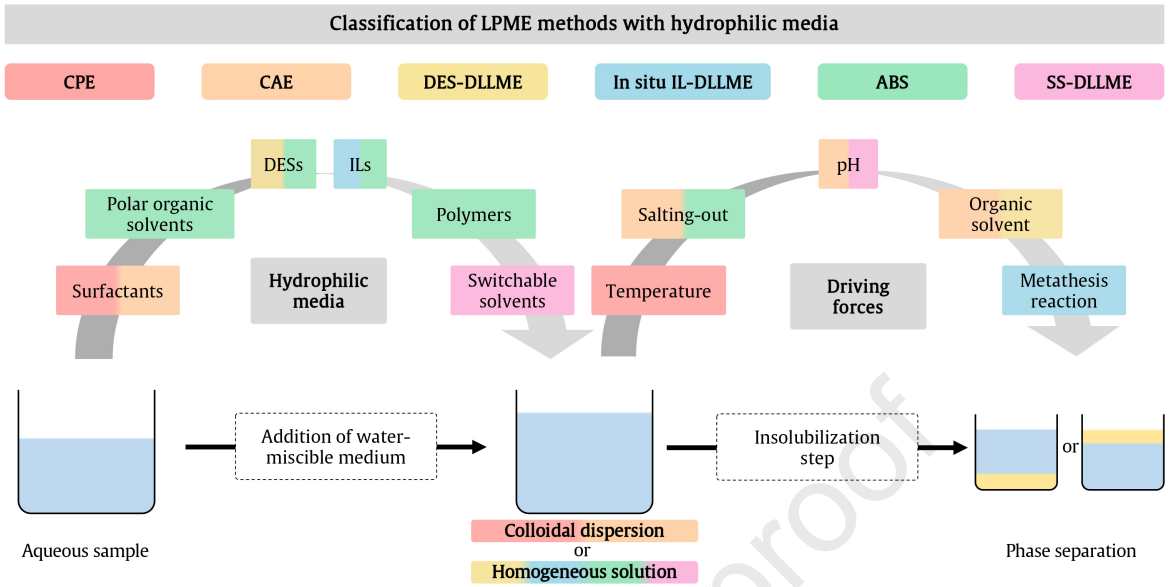
To appear in: *Analytica Chimica Acta*

Received Date: 23 June 2020

Revised Date: 10 August 2020

Accepted Date: 12 August 2020

Please cite this article as: I. Pacheco-Fernández, R. González-Martín, F.A. e Silva, M.G. Freire, V. Pino, Insights into coacervative and dispersive liquid-phase microextraction strategies with hydrophilic media – A review, *Analytica Chimica Acta*, https://doi.org/10.1016/j.aca.2020.08.022.



Insights into coacervative and dispersive liquid-phase microextraction strategies with hydrophilic media – A review

Idaira Pacheco-Fernández[1,2,#], Raúl González-Martín[1,#], Francisca A. e Silva[3], Mara G. Freire[3,], Verónica Pino[1,2,*]**

[1]Laboratorio de Materiales para Análisis Químicos (MAT4LL), Departamento de Química, Unidad Departamental de Química Analítica, Universidad de La Laguna (ULL), Tenerife, 38206, Spain
[2]Instituto Universitario de Enfermedades Tropicales y Salud Pública de Canarias, Universidad de La Laguna (ULL), Tenerife, 38206, Spain
[3]CICECO — Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

Abstract

Since the development of liquid-phase microextraction (LPME), different LPME modes depending on the experimental set-up to carry out the extraction have been described. Dispersive liquid-liquid microextraction (DLLME), in which a small amount of the water-insoluble extraction solvent is dispersed in the sample, is the most successful mode in terms of number of applications reported. Advances within DLLME have been mainly shifted to the incorporation of green, smart and tunable materials as extraction solvents to improve the sustainability and efficiency of the method. In this sense, hydrophilic media represent a promising alternative since the water-miscibility of these substances increases the mass transfer of the analytes to the extraction media, leading to higher extraction efficiencies. Considering the variety of hydrophilic media that have been incorporated in LPME approaches resembling DLLME, this review aims to classify these methods in order to clarify the confusing terminology used for some of the strategies. Hydrophilic media covered in this review comprise surfactants, polar organic solvents, deep eutectic solvents, ionic liquids, water-miscible polymers, and switchable solvents. Different physicochemical mechanisms of phase separation are discussed for each LPME method, including the coacervation phenomena and other driving forces, such as pH, temperature, salting-out effect, metathesis reaction and organic solvents. LPME modes are classified (in cloud-point extraction, coacervative extraction, aqueous biphasic systems, and different DLLME modes depending on the extraction medium) according to both the nature of the water-miscible extraction phase and the driving force of the separation. In addition, the main advances and analytical applications of these methods in the last three years are described.

Keywords: liquid-phase microextraction, aqueous biphasic system, surfactant, deep eutectic solvent, ionic liquid, switchable solvent

*Corresponding author: Email: veropino@ull.edu.es
**Co-corresponding author: Email: maragfreire@ua.pt

[#]Both authors contributed equally to this work

I. Pacheco-Fernández ipacheco@ull.edu.es
R. González-Martín raul.gonzalez.26@ull.edu.es
F. A. e Silva francisca.silva@ua.pt

Contents

1. Introduction

Liquid-phase microextraction (LPME) undoubtedly constitutes one of the most exploited strategies within modern analytical microextraction methods [1]. It emerged as a miniaturized version of the conventional liquid-liquid extraction, based on the isolation of analytes from the sample matrix to an extracting micro-liquid phase. In this sense, LPME entails a non-exhaustive extraction process [2] if considering the low volume of extraction solvent involved in the procedure (few microliters, < 100 µL), but quantitative recoveries can be achieved under certain conditions. The use of such low volumes of extraction solvent together with large sample volumes leads to high preconcentration factors, which allow the determination of trace amounts of analytes, being this one of the key aspects justifying its success. Other interesting features of LPME include low consumption of extraction solvent (and thus low generation of laboratory wastes), simplicity, low cost, low energy consumption, and negligible carry-over, while making possible (in most cases) the direct injection of the solvent containing the extracted and preconcentrated target compounds in the analytical system [1].

There is not a single mode of LPME; indeed, many different modes have been developed [1,3]. Existing LPME methods can be classified in three main categories depending on the experimental set-up to carry out the extraction: single-drop microextraction (SDME) – which requires a droplet (microliters) of extraction solvent suspended in the sample –, membrane-based LPME (including hollow fiber LPME – HF-LPME –, and electro-driven separations) – which requires an inert membrane to stabilize relatively higher amounts of extraction solvent (still in the microliters range) –, and dispersive liquid-liquid microextraction (DLLME) – which requires proper

dispersion of the extraction solvent (microliters) into the sample. Other classifications are also possible, but this simple division simplifies the overview on LPME.

DLLME, which was introduced by Rezaee *et al.* in 2006 [4], has become the most widely utilized LPME approach among all these strategies due to its simplicity, efficiency, and fastness. The conventional mode of DLLME bases on the dispersion of the extraction solvent in the sample with the aid of a dispersive solvent. The operational mode of this method involves the use of a mixture of the extraction solvent, immiscible with the sample, and the dispersion solvent, miscible with both the extraction solvent and the sample. The latter allows the formation of small microdroplets of extraction solvent through the sample, which increases the mass transfer of the analytes and therefore improves the extraction efficiency [5]. This mode of operation overcomes the drawbacks of SDME associated to the stability of the microdroplet, and those of HF-LPME related to the slow diffusion of the analytes to the extraction phase located in the pores or in the lumen of the hollow fiber. Figure 1 shows a general scheme of the conventional DLLME procedure, together with a summary of the main variations to improve the operational of this LPME method.

Since the incorporation of the Green Analytical Chemistry (GAC) guidelines in the sample preparation stage, the search of new solvents with the aim of improving the environmentally friendliness of DLLME (and other LPME methods) is one of the most important research lines in the field [6]. Therefore, efforts focus on the design of green, smart, and tunable solvents as an alternative to the conventional, toxic and expensive organic solvents commonly used in DLLME [7] while seeking not only the development of sustainable procedures but also selective and more efficient approaches. Within this trend, the use of hydrophilic media has been one of the explored strategies. The resulting methods take advantage of the hydrophilicity of the solvent/material to

increase the mass transfer and extraction efficiency of the target compounds, thanks to the enhanced dispersion of the extraction medium. Despite the water-miscibility of these extraction media, all the LPME methods resemble DLLME but including an additional insolubilization step to separate the final phase with the extracted/preconcentrated analytes from the remaining sample and non-extracted components.

Considering the variety of emerged hydrophilic media and their incorporation in different LPME approaches resembling DLLME, with *a priori* important similarities among all methods, and with confusing terminology in several cases, this review aims to classify all reported LPME methods using water-miscible media. This classification takes into account both the nature of the medium and the driving force responsible for the phase separation, as summarized in Figure 2. Special attention is paid to the mechanisms that take place during the insolubilization process. The advances within these strategies reported in the last three years (from 2017 to 2019) are also described, together with a summary of the most relevant analytical applications.

2. Coacervation phenomena-based liquid-phase microextraction methods

LPME methods with hydrophilic media driven by the coacervation phenomena deserve special mention due to the impressive number of applications. Clearly, it is essential to define several concepts related to colloidal chemistry with the aim of establishing the physicochemical mechanisms involved in the phase separation phenomena of the different coacervation-based LPME methods.

Coacervation-based LPME methods require the formation of colloids. A colloidal dispersion is a homogeneous mixture in which one solute composed of microscopic particles (1 nm – 1 µm) is dispersed into a continuous phase, generally a liquid (the

liquid dispersion) [8]. The coacervation phenomenon is observed when a specific environmental condition of the colloidal dispersion is modified. Thus, coacervation is the self-assembly or association between colloids, which generates a new insoluble phase rich in colloids that can be separated from the liquid dispersion [9]. The final insoluble phase after coacervation is a nano-structured liquid, also termed supramolecular solvent since it is made up of supramolecular aggregates.

In general, the first step of coacervation-based LPME methods occurs when a homogeneous solution becomes a colloidal dispersion above the critical aggregation concentration (CAC) of the extraction medium [10]. The second step is the coacervation, which leads to the formation of an insoluble supramolecular aggregate containing the extracted analytes, which can be then easily separated from the initial aqueous phase.

Among all extraction media useful for coacervation-based LPME methods, surfactants are the most known substances able to form supramolecular aggregates after coacervation. Surfactants are amphiphilic compounds formed by a hydrophobic tail (usually a hydrocarbon chain) and a hydrophilic head (a polar or an ionic group). The use of surfactants in extraction schemes has been extensively reported in Analytical Chemistry due to their ability to form micelles above the critical micelle concentration (CMC) [11,12]. More recently, other types of compounds have also been found to form supramolecular aggregates, such as long chain alcohols [13], long chain carboxylic acids [14], and primary amines [15]

This section will cover only coacervation-based LPME techniques that use hydrophilic media to form a colloid dispersion prior to coacervation. The different techniques are classified according to the type of hydrophilic medium involved and the driving force responsible of the coacervation. In this sense, two techniques will be

reviewed: cloud point extraction (CPE), using non-ionic or zwitterionic surfactants; and conventional coacervative extraction (CAE), with ionic surfactants. The use of long chain alcohols and long chain carboxylic acids in non-conventional coacervation phenomena-based LPME [16] are out of the scope of this review since these substances are hydrophobic, but they will be briefly discussed.

2.1. Cloud point extraction

CPE was introduced for the first time by Watanabe *et al*. in 1976 [17] as a promising green extraction technique. CPE is based on the coacervation that occurs when the aqueous solution of a non-ionic or zwitterionic surfactant (used at a concentration higher than its CMC) is heated above the cloud point temperature (CPT) of the surfactant. The CPT depends on the surfactant structure and concentration, and it is affected by the presence of additives [18]. Therefore, the coacervation is induced by temperature in CPE, which leads to a reversible micellar aggregation of the surfactant. Under the appropriate conditions, the polar moieties of the surfactant are dehydrated, leading to a decrease of inter-micelle repulsions and the formation of a water-insoluble surfactant-rich phase [19]. Furthermore, there is a competition between different physicochemical parameters that affect the CPE mechanism: enthalpy, entropy, and miscibility of the micelles in the aqueous medium [12].

The conventional procedure of CPE involves firstly the formation of micelles by adding the surfactant to the aqueous medium (ensuring a final concentration of the surfactant above its CMC). Then, the mixture is incubated at a temperature above the CPT during a certain time until a cloudy solution is formed. Centrifugation is then usually applied to promote the separation, leading to the formation of two coexisting phases: a water-rich phase and a water-insoluble surfactant rich-phase containing the

194 extracted analytes, as shown schematically in Figure 3 (A). The water-rich phase is
195 discarded, whereas the surfactant-rich phase is subjected to the analytical determination
196 [19].

197 One of the main disadvantages of CPE may be the high consumption of energy to
198 reach the desirable temperature for the phase separation (against GAC requirements).
199 Thus, recent trends focus on developing modifications of the conventional CPE method
200 to decrease the CPT [18]. Moreover, the high viscosity of the resulting surfactant-rich
201 phase has also hampered the application of this method, since the sensitivity is reduced
202 due to the required dilution of the final extract to ensure compatibility with the
203 analytical determination technique.

204 At this point, it is important to mention that conventional CPE was not initially
205 considered a microextraction method. However, most recent CPE applications are
206 indeed micro-CPE methods, if considering for example that a high number of studies
207 report the use of low volumes of surfactant solutions (~µL). In all these works, a high-
208 concentrated surfactant solution is added to the sample, so that the CMC is reached
209 despite the use of low volumes of surfactant solution [20–43]. Furthermore, a high value
210 of the aqueous sample to final extract volume ratio is obtained in many cases, thus
211 leading to the development of preconcentration methods based on CPE [28,30–
212 32,35,40,42,44–57].

213 In any case, non-ionic or zwitterionic surfactants used in CPE approaches must be
214 carefully selected to ensure the separation with the minimum energy consumption
215 possible. Therefore, surfactants with a CPT around room temperature and with low
216 CMC values are preferred [11,12]. Triton X-114 has been the most used non-ionic
217 surfactant in CPE approaches given its low CPT in a relatively wide range of
218 concentrations [21–24,27,29–32,35–40,42,45,50–52,55,58–74]. In fact, the cloud point-

concentration curve of this surfactant in water shows CPT values ranging from 27 to 30 ºC for concentrations between 0% (w/v) and 9% (w/v) [75]. This explains why most of the recent CPE methods report concentrations of Triton X-114 below 5% (w/v) [27,30,31,35–38,41,50,55,58,61,62,67,68,70,72]. This surfactant belongs to polyethylene oxide-derived family of surfactants, which are commercially available, stable, cheap, and non-volatile, thus favoring their use in environmental-friendly extraction strategies. Given these interesting features, Triton X-100 [28,33,34,41,44,46,76–82] and Triton X-45 [43,83], have also been used in recent CPE applications. Other surfactants have been commonly reported, like nonylphenol ethoxylate-based surfactants (Tergitol) [48,49,53,84–86], which provide versatile solubility characteristics, and other less common surfactants are PEG 6000 [56,87,88], Brij-35 [47,54], Tween 80 [89], and PONPE-20 [90].

Mixed-micellar media have been also successfully used in CPE methods since the combination of ionic and non-ionic surfactants leads to a synergistic effect that improves the extraction efficiency of the entire procedure. The use of non-ionic polyethylene oxide-derived surfactants (mainly Triton X-114 and Triton X-100) is frequently reported in combination with different ionic surfactants, being cetyltrimethylammonium bromide (CTAB) [26,57,91,92], sodium dodecyl sulfate (SDS) [20,91], and cetylpyridinium bromide (CPB) [93] the most commonly used in the recent years.

With respect to the effect of the ionic strength, the addition of inorganic electrolytes is quite important in CPE since the phase separation is improved due to the preferential hydration of the salt ions *versus* the surfactant (salting-out effect), leading to a decrease in the CPT [18]. Therefore, the addition of salts has been a common strategy in CPE applications [21,26,27,29,32,34,35,37,38,44–46,49,50,52–57,59,61–

64,67,68,70,71,76,78,80,84,86–89,91–93], with NaCl [26,27,37,44,46,53,54,59,68,70,80] and Na_2SO_4 [45,50,52,57,84,86–88] as the most common salts reported.

Incubation temperature and time are closely interconnected parameters, which directly depend on the CPT of the surfactant. Considering that several analytes can undergo thermal degradation, incubation temperature must be carefully optimized. In general, temperatures 15–20 ºC above the CPT are used in most cases to ensure the formation of the cloudy solution after a certain time [19]. Room temperature is the most desirable temperature for incubation, allowing the performance of the CPE method without any additional energy consumption. Thus, several studies have focused on the addition of different substances to decrease the incubation temperature to 25 ºC, mainly organic acids and alcohols. These substances have been selected due to their ability to establish hydrogen-bond interactions with water, thus favoring the dehydration of the surfactant and speeding up the phase separation without any heating process. The addition of salicylic acid [78] and ascorbic acid [65] has been reported to perform the extraction at room temperature using surfactants belonging to the Triton family (Triton X-100 and Triton X-114). More recently, acetonitrile has been incorporated in a CPE method to decrease the CPT of PEG 6000 [88]. Furthermore, it has also been described the use of a surfactant combined with an alcohol. Lei *et al.* reported the use of Triton X-114 combined with octanol [66], while Xu *et al.* [79] and Chen *et al.* [47] proposed the incorporation of hexafluoroisopropanol (HFIP) as additive to decrease de CPT.

With respect to the incubation time, 10 min is usually enough to reach the cloud point. In fact, times between 5 and 15 min are the most common reported [21,23,25,28,30,32,34,36,38,40,41,43,45,49,54–56,61,64–67,71–73,80,82,83,85,86,88,89,92–94].

The incubation process has been commonly performed in a water bath. Recently, the use of ultrasounds to reach the desired temperature has been reported, leading to the development of ultrasound-assisted CPE (US-CPE) [20,38,50,53,54,56,60,61,64–67,71,80,83,89,94]. US-CPE applications intend to decrease the incubation time required to form the cloudy solution, thus favoring the fastness and effectiveness of the method.

In CPE, complete phase separation is usually achieved by centrifugation, but most of the recent studies have reported an additional step of cooling. This increases the viscosity of the surfactant-rich phase and allows discarding the water-rich phase by simple decantation. In general, cooling is performed in an ice water bath for few minutes [20,21,23,30,31,33,37,41,42,51,54,55,57,58,67,69,71–74,76,77,90,92].

It is interesting to mention dual-cloud point extraction (d-CPE), an alternative mode of CPE, reported for the first time by Wei *et al.* in 2008 [95]. d-CPE involves two consecutive CPE steps: a conventional CPE followed by the back-extraction of the analytes from the surfactant-rich phase by another CPE procedure using a new aqueous solution. In the last three years, different d-CPE methods have been reported, using as back-extracting reagents acidic solutions (HNO_3 or HCl) [36,58,64,72], or alkaline solutions (NaOH) [39].

2.2. Conventional coacervative extraction

CAE is based on a procedure similar to CPE but using anionic or cationic surfactants as extractants. While in CPE the separation is induced by the temperature, in CAE the coacervation occurs due to the salting-out effect or in response to other parameters, such as the addition of an organic solvent or changes in the pH, as shown

schematically in Figure 3 (B) [96]. Surfactants must be added to the aqueous solution in a concentration above their respective CMC, as it occurs in CPE.

It is important to highlight that micelles of ionic surfactants suffer electrostatic repulsions between them that can negatively affect their aggregation [96]. For this reason, CAE method must be carefully optimized in order to guarantee proper inter-micelle interactions, thus ensuring the formation of the supramolecular aggregate. The surfactant structure, mainly its hydrophobic chain, plays an important role in the extraction process. Moreover, the nature of the surfactant (anionic or cationic) is often related with the experimental parameter that induces the coacervation [12]. Thus, cationic surfactants with a long hydrophobic chain are preferred due to the presence of stronger hydrophobic interactions between their micelles, which minimizes the electrostatic repulsion effect. Furthermore, cationic surfactants can experience coacervation in the presence of a salt [12]. In this sense, CAE methods using cationic surfactants reported in the recent literature use the salting-out effect as the driving force to induce the separation. Gissawong *et al.* reported the use of a mixture of two long-tailed cationic surfactants [97], while Salamat *et al*. used a mixture of a cationic and an anionic surfactant [98], both with NaCl, to induce the coacervation. Dodecyltrimethyl ammonium bromide [97] and dodecylmethyl imidazolium bromide [98] are the most representative cationic surfactants used in CAE approaches.

In anionic micellar media, the phase separation is mainly induced by modifications of the pH [12]. Recent CAE applications report the use of SDS as a single anionic surfactant [99], or include a mixed micellar medium together with a cationic surfactant to take advantage of the characteristics of both surfactants [100–102]. Nevertheless, in these studies the coacervation is not induced by pH, since other driving

forces prevail: the addition of an organic solvent or a coacervation-inducing agent, depending on the case.

Several studies describe the use of alcohols as organic solvents to induce coacervation. Specifically, HFIP [100,101] and propanol [103] have been used to coacervate solutions of tetraalkylammonium-type surfactants. Alcohols establish hydrogen-bond interactions with water, thus dehydrating ionic surfactants and promoting the coacervation.

Recent studies have reported a CAE method that incorporates a coprecipitation agent as a coacervation-inducing agent rather than using the salting-out effect, modifying pH or adding organic solvents as it is frequently reported. Furthermore, Mammana *et al.* reported a coprecipitation-assisted CAE using $Al_2(SO_4)_3$ as precursor of the coprecipitation agent for SDS [99], while $AlCl_3$ has also been used to promote the coacervation in a mixed-micellar medium composed of SDS and tetrabutylammonium bromide (TBAB) [102].

As it happens with CPE, it is important to mention that recent applications of CAE were developed with preconcentration purposes, given the low volume obtained of the coacervative phase (~µL) [99,104] compared with the volume of the initial aqueous sample (□10 mL) [99–101].

2.3. Non-conventional coacervative extraction

Apart from surfactants, in 2007, Rubio *et al*. demonstrated that other amphiphilic compounds were able to form supramolecular aggregates: alkanols and alkanoic acids with long chains [13,14]. These compounds form a colloid dispersion of reverse micelles in protic and aprotic solvents (e.g., tetrahydrofuran (THF) or acetonitrile) at concentrations higher than their respective CAC. The coacervation and subsequent

formation of the hydrophobic supramolecular solvent is induced with the addition of water, as shown schematically in Figure 3 (C). This phenomenon has been exploited for the development of a LPME method, termed supramolecular solvent-based microextraction (SUPRAS). The alcohols and carboxylic acids used in this LPME method are water-insoluble and, indeed, they have been used as solvents in conventional DLLME applications [105]. However, the addition of the protic or aprotic solvent favors the formation of self-assembled aggregates, which exhibit higher solvation characteristics and consequently, better extraction performance [14]. Given the hydrophobicity of alkanols and alkanoic acids used as extraction solvents in SUPRAS, this review will not cover this highly interesting mode of microextraction [106–108].

More recently, in 2020, Bogdanova *et al*. [15] also demonstrated the formation of supramolecular aggregates of primary amines with long hydrocarbon chains when using monoterpenoids as coacervation-inducing agent. The amines form positively charged amphiphiles when dissolved in water due to their hydration and dissociation. Terpenoids, negatively charged once added to these amine aqueous solutions, interact with the amphiphiles and induce the coacervation phenomenon. Thus, authors used the spontaneous formation of a coacervate of 1-decylamine when adding thymol for the development of a SUPRAS method for the extraction of sulfonamides from biological fluids.

3. Additional hydrophilic media-based liquid-phase microextraction methods

In the recent years there has been an increasing incorporation of new solvents inLPME methods to substitute halogenated organic solvents [6,7]. With respect to new hydrophilic media, deep eutectic solvents (DESs), ionic liquids (ILs), and switchable

solvents (SSs) have been explored. Moreover, water-miscible organic solvents have also been used in these LPME methods in which the extraction medium is directly added to the aqueous sample. Traditionally, these methods have been included within homogeneous liquid-liquid microextraction [109]. However, this classification is very general and the comprehension on the phenomena responsible of phase separation has been neglected. Therefore, it is essential to provide an insight into the unique set of physicochemical characteristics of these media to gain a better understanding on the variables affecting the phase separation process, which further helps in finding a rationale on their classification. In this section, the LPME methods using these hydrophilic media that do not experiment coacervation will be described. They are classified consideringboth the separation mechanism and the nature of the hydrophilic medium used as extraction solvent since the phase separation for the same medium can be accomplished by different strategies, leading to different LPME methods. Thus, DLLME using hydrophilic DESs, ILs and SSs, and ABSs using different media (i.e. ILs and DESs) will be reviewed.

3.1. Hydrophilic deep eutectic solvent-based dispersive liquid-liquid microextraction

Deep eutectic solvents (DESs) are a group of relatively new solvents formed by the combination of a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA) at different ratios [110]. These mixtures do not follow an ideal solid-liquid phase behavior and present melting points significantly lower than the melting temperature of the individual initial components. The resulting DES from such mixtures does not require any additional purification step. Main features of these solvents, if properly designed, may include low toxicity and high biodegradability, and they are cheap and

easy to prepare. These solvents are also versatile, because their physicochemical properties can be tuned by selecting the adequate combination of HBD and HBA species [7,110,111].

Given these characteristics, it is not surprising the impressive increase in the use of hydrophobic DESs in LPME, particularly in DLLME methods, in the recent years [111–113]. More recently, in 2015, Khezeli *et al.* developed for the first time a microextraction strategy based on the use of a water-miscible DES (formed by cholinium chloride and phenol) as initial extraction medium [114], which resembled a combination of DLLME and CAE. The method, termed as DES-DLLME in the current review, requires the addition of the hydrophilic DES as extraction solvent to the aqueous sample, obtaining a homogeneous solution. In this case, the formation of the final insoluble phase is induced by the addition of aprotic solvents. After centrifugation, the water-immiscible phase is obtained containing the target analytes as shown schematically in Figure 3 (D).

It has been suggested that π-π, hydrogen bonding and charge transfer interactions among DES components are the main responsible for their self-assembly and consequent insolubilization. Despite the common utilization of terms such as supramolecular aggregates and emulsification when referring to hydrophilic DESs in these methods, it is the opinion of the authors of the current review that more studies are required to ensure the presence of the coacervation phenomena when using these solvents. Indeed, a recent study has reported that the DES formed by cholinium chloride and phenol suffers decomposition once it is dissolved in aqueous media due to the destruction of the hydrogen bonds between its components (i.e. the starting components will be preferentially hydrated by water) [115]. The addition of the aprotic solvent (THF in this case) to the aqueous sample containing the hydrophilic DES leads to the

insolubilization of an organic phase mainly composed of phenol, THF and water. Therefore, this study demonstrates that the DES formed by cholinium chloride and phenol has been wrongly termed as extraction solvent in these DES-DLLME methods. It also highlights the need for evaluating the stability of DESs in water to elucidate the mechanism in these methods when using other hydrophilic or "quasy-hydrophobic" DESs [113]

Despite this recent breakthrough, this review will cover all hydrophilic DESs-based DLLME methods, even those with the DES composed by cholinium chloride and phenol. After all, the extraction phase used in these methods is added to the aqueous sample as a DES, and the decomposition only takes place when it interacts with water. In fact, after reporting this study, same authors took advantage of the decomposition of DESs to improve the dispersion of the extraction solvent into the aqueous medium and simplify the extraction procedure [116]. The method consists in an effervescence-assisted DLLME using the DES formed by menthol (water-insoluble) and formic acid (hydrophilic) as initial extraction solvent. When it is added to the aqueous sample containing sodium carbonate, the DES decomposes in its individual components. The reaction between the carbonate and formic acid generates carbon dioxide, which leads to the effervescence that enhances the dispersion of the water-insoluble menthol. In this case, the menthol acts as extraction phase, but it is important to point out that it is added to the sample in the form of a DES combined with formic acid. Even though the decomposition of the DESs occurs, the use of hydrophilic or DESs increases the mass transfer of the analytes to the extraction medium due to its enhanced dispersion in the aqueous sample in comparison with hydrophobic DESs. However, it is important to point out that in both cases the addition of a water-miscible organic solvent is required for the separation and dispersion of the extraction phase, respectively.

Many applications of hydrophilic DESs in this DES-DLLME method have been reported since the first published work in 2015 [114]. DESs composed of cholinium chloride as HBA and phenol as HBD have been the most comm[on [117–131]. Other alcohols and carboxylic acids have been used as HBDs in combination with cholinium chloride, such as 2-chlorophenol [132], oxalic acid [133], *p*-cresol [134], glycerol [135], and 5,6,7,8-tetrahydro-5,5,8,8-tetramethylnaphthalen-2-ol [136]. The use of the hydrophilic DESs obtained after the mixture of tetrabutylammonium chloride as HBA and decanoic acid as HBD has also been reported [137–139]. Depending on the composition of the DES, the water-insoluble phase is obtained as the upper or the bottom phase after the separation.

Following current trends within the preparation of materials with higher biodegradability [140], natural DESs (NADESs) synthesized by using natural products have also been used in this LPME method [141–143], for example NADESs prepared with sucrose as HBA and citric acid as HBD [141], among others.

As abovementioned, the synthesis of DESs is quite simple, implying a mixture of both components, followed by stirring at temperatures up to the mixture melting. It is interesting to mention that, in general, the optimum DESs to perform the microextraction procedure were those obtained with a higher content of HBD, with common HBA:HBD molar ratios of 1:2 and 1:4. This may be related to the higher hydrophobicity of the HBDs and the viscosity of the resulting DESs with higher concentrations of HBD. The amount of hydrophilic DESs used in these studies ranged between 50 [134] and 1000 µL [128], while the volumes of aqueous sample analyzed were high enough to ensure preconcentration.

In the vast majority of the studies, THF was employed as agent to induce the phase separation [117–133,136–139,141,143,144]. However, the use of acetonitrile

[135,142], and acetone [134], has also been reported. It is also quite common the application of ultrasounds immediately after the addition of the organic solvent, with the aim of facilitating the insolubilization while enhancing the dispersion of the hydrophobic phase formed [117,118,124,126–131,134,137–139,141–143].

Another common strategy to favor the insolubilization and increase the extraction efficiency is the incorporation of agitation cycles. This has been carried out by the aspiration and ejection of the mixture using a syringe [120,123–125,135,136]. As a step forward, the research group of Bulatov described the development of automated flow air-assisted DES-DLLME methods by using an eight-port valve connected to: a peristaltic pump, a mixing chamber where the extraction is accomplished, a syringe pump for the air-assistance, the analytical instrument to perform the on-line analytical determination, and the containers of the solvents and sample [120,135]. In order to avoid the tedious centrifugation steps, Li *et al*. incorporated ferrite magnetic nanoparticles (MNPs) to the mixture after the addition of THF to insolubilize the extraction medium [123]. The formed microdroplets were adsorbed on the surface of the MNPs due to hydrophobic interactions, which allowed the separation of the water-immiscible-phase containing the analytes by using of an external magnet. The only drawback of this approach is the necessity of an additional back-extraction step in the procedure to desorb the analytes from the composite.

3.2. *In situ* ionic liquid-based dispersive liquid-liquid microextraction

Ionic liquids (ILs) undoubtedly merit highlighting among the new solvents explored as extraction solvents in DLLME applications [145]. Indeed, it is the microextraction strategy (IL-DLLME) in which ILs have been most successfully used in recent years [146]. ILs are a group of salts with melting points below 100 □, mainly

formed by the combination of a bulky asymmetric organic cation and an organic or inorganic anion. They present negligible vapor pressure at room temperature, high conductivity, and high thermal and electrochemical stabilities. The most attractive feature of ILs is their impressive synthetic versatility and tuneability, which leads to drastic changes in their physicochemical properties by small modifications in their structure and composition. Thus, viscosity, solubility, and solvation properties of ILs can be easily tuned by properly selecting the nature of the cation and the anion [147].

Depending on the characteristics of the ILs and the assistance during the DLLME procedure by using materials with specific properties or specific instrumentation, different IL-DLLME modes can be distinguished [148,149]. This classification includes temperature-controlled IL-DLLME, vortex or ultrasounds-assisted IL-DLLME, magnetic IL-DLLME, among others. In 2009, Baghdadi and Shemirani [150] took advantage of the tuneability of ILs to describe a DLLME mode exclusively applicable when ILs are used as extraction solvent, termed mostly *in situ* IL-DLLME. In this approach, a hydrophilic IL is used. Then, an anion-exchange reagent is added to the aqueous sample containing the water-soluble IL. This reagent promotes a metathesis reaction in which the anion moiety of the IL is exchanged to obtain a hydrophobic IL, as it is schematically shown in Figure 3 (E).Due to the miscibility of the initial IL with water, the generated water-insoluble IL is dispersed all over the sample, leading to the formation of an emulsion (turbid solution). Finally, as in the conventional DLLME strategy, the mixture is centrifuged to obtain a microdroplet of the hydrophobic IL containing the analytes. In the study reported by Yao and Anderson also in 2009 [151], authors demonstrated the superiority of the *in situ* IL-DLLME approach compared to conventional IL-DLLME and IL-SDME. By using this strategy, the method is

simplified, the extraction time is shortened, and the extraction efficiencies are increased due to the enhanced dispersion of IL in aqueous sample in the initial stage.

The most common ILs used as extraction solvents in *in situ* IL-DLLME contain dialkylimidazolium cations, paired with chloride, bromide or tetrafluoroborate anions [152–170]. Hydrophilic ILs with other cations have been reported, such as alkylguanidinium of low cytotoxicity [157,171,172], tetraalkylammonium [173,174], and tetraalkylphosphonium [175]. Structurally tuned ILs, incorporating functional groups in the cation, have also been assessed in this microextraction approach for the extraction of specific analytes. In this sense, ILs with imidazolium cations containing hydroxyl and/or benzyl groups demonstrated good analytical performance for the determination of polychlorinated biphenyls (PCBs) and acrylamide in food samples [167]. Sadeghi and Sarrafi [160] reported the use of the 1-chloroethyl-methylimidazolium chloride IL functionalized with 8-hydroxyquinoline, which serves simultaneously as extraction solvent and as chelation reagent for the selective extraction of Cd(II) in complex samples. It is also interesting to mention the use of a hydrophilic acidic IL composed of an imidazolium cation and hydrogen sulfate anion, which acts as both extraction solvent and reagent to generate carbon dioxide during the extraction to assist the dispersion [153]. In all cases, the amount of IL used in the method was of a few µL or mg, which compared with the relatively high volume of initial sample, complies with typical high preconcentration factors achieved within DLLME applications.

With respect to the anion-exchange reagent, salts with bis(trifluoromethanesulfonyl)imide ($[NTf_2^-]$) [152,155,157,159,161,167,169,171,176] and hexafluorophosphate anions [153,154,156,159,160,162–166,170,174] are the most common. With the aim of avoiding the use of these highly toxic salts, fluorine-free

alternatives have emerged to promote the anion-exchange reaction, such as dicyanamide [175] and perchlorate salts [172,173].

The incorporation of magnetic ILs (MILs) in the *in situ* IL-DLLME procedure (*in situ* MIL-DLLME) is the most recent improvement within this method [177–179]. Hydrophobic MILs have been previously used in IL-DLLME, in which the typical centrifugation step is avoided since the paramagnetic properties of the extraction solvent allow its separation from the sample with the aid of an external magnet [149,180]. The MILs initially reported were not suitable for the *in situ* IL-DLLME approach since they were prepared using paramagnetic anions, which would be exchanged during the metathesis reaction thus losing the MIL. In 2019, Trujillo-Rodríguez *et al.* [177–179] proposed a new generation of hydrophilic MILs containing paramagnetic cations, which can undergo insolubilization by exchanging the anion moiety. The MILs were composed of cations with Ni(II) or Co(II) centers coordinated with four ligands of *N*-alkylimidazole and chloride anions, while Li-NTf_2 was used as anion-exchange reagent. In this case, after the addition of the metathesis reagent in the *in situ* IL-DLLME procedure, the solution was vortexed to accomplish the reaction and the hydrophobic MIL was collected using a magnet. The water-insoluble MIL formed by this method was also collected using a rod magnet previously inserted in the sample, which resembled to stir bar sorptive dispersive microextraction [178]. In this case, the magnet also served as stirring device to assist the metathesis reaction. Once the stirring was stopped, the *in situ* formed MIL was settled in the rod magnet, which was then transferred to another vial to perform the thermal desorption of the analytes.

In general, the *in situ* IL-DLLME mode does not require a dispersive solvent in contrast to conventional IL-DLLME, due to the initial miscibility of the IL with the aqueous sample. However, given the viscosity of the *in situ* generated hydrophobic IL,

the addition of organic solvents (methanol, acetone, acetonitrile, or THF of has been reported to favor its dispersion [157,166]. This is particularly necessary when dealing with the *in situ* MIL-DLLME [177–179]. This drawback has also been overcome using a non-ionic surfactant as both anti-sticking agent and dispersive solvent, such as Triton X-114 [160], or sodium bicarbonate as effervescent agent [153]. Another interesting study was reported by Su *et al.* [170] with an imidazolium-based hydrophobic IL used as extraction solvent in a microwave-assisted IL-DLLME method, and with a hydrophilic IL added as dispersive agent. Authors also performed a metathesis reaction to transform the IL used as dispersive solvent into a water-immiscible IL thus improving the recovery of the IL phase, with both ILs participating in the extraction of the analytes.

One of the main operational disadvantages of the *in situ* IL-DLLME approach is the requirement of centrifugation steps, together with the sampling of the IL microdroplet, which normally settles at the bottom of the sample container. In order to simplify these steps, MNPs have been incorporated in the *in situ* IL-DLLME procedure [154,155,169,173,175]. The MNPs can be added before or after the metathesis reaction. Once the reaction is accomplished, the water-insoluble IL containing the analytes covers the surface of the MNPs due to hydrophobic and electrostatic interactions. In 2018, Wu *et al*. described the preparation of magnetic effervescent tablets, which contained the MNPs, the effervescent agent and the hydrophilic IL [154]. Instead of MNPs, Wang *et al.* proposed the use of magnetic hollow fibers to collect the hydrophobic IL prepared *in situ* in the sample solution [163]. In this case, the hollow fiber pieces (containing a stainless steel wire) were added to the sample after the metathesis reaction, and then the water-immiscible IL impregnated the pores of the fibers after stirring. Despite the use of an external magnet enormously facilitates the separation of the IL phase from the

sample, the main drawback of these magnetic-assisted *in situ* IL-DLLME methods is the tedious back-extraction step. This step must be integrated into the procedure to desorb the analytes from the magnetic composite, which again increases the total analysis time. In this sense, the *in situ* MIL-DLLME method turns up to be the most promising strategy.

Other strategies have been reported to simplify the *in situ* IL-DLLME method, such as the solidification of the formed hydrophobic IL by the synergetic effect of cooling the mixture and the addition of NaCl [174]. NaCl is a widely used salting-out agent due to its high affinity towards water. Thus, NaCl induces the dehydration of the IL, which improves its separation from the aqueous sample and its subsequent solidification after placing the mixture in an ice bath. In this study, the whole extraction procedure was also performed in a syringe. A nonwoven polypropylene sheet was introduced in the syringe needle as a filter to collect the solidified IL-phase and discard the aqueous sample. In a similar way, Molaei *et al*. [165] presented an on-line separation of the IL-phase from the sample by passing the cloudy solution obtained after the metathesis reaction through a PTFE filter, which was placed in a six-port valve coupled to a peristaltic pump. The hydrophobic IL was isolated in the filter, and the analyte was then desorbed by using an organic solvent, followed by its injection in the analytical system.

3.3. Aqueous biphasic systems

Aqueous biphasic systems (ABSs) were first proposed by Albertsson in the 50's as more biocompatible separation alternatives to traditional liquid-liquid extraction techniques involving volatile organic solvents [181]. Given their biocompatible and eco-friendly nature, the application of ABSs rapidly evolved not only in the extraction

and purification of a plethora of (bio)molecules from the most diverse sources [182,183] but also as sample cleanup and preconcentration techniques for analytical purposes [184–217].

ABSs are water-rich liquid-liquid extraction systems, whose genesis builds up on the formation of two coexisting phases when at least two incompatible solutes (e.g., polymers, salts, sugars, amino acids, ILs, DESs, polar organic solvents, among others) are mixed in aqueous medium above given concentrations and under specific conditions (e.g., temperature, pH). The molecular-level mechanisms behind the formation of ABSs are highly contingent on the pair of phase-forming components used [218,219].

Under the scope of the present review, the most recent investigated pairs of ABSs phase-forming components are polymer/salt, polar organic solvent/salt, polar organic solvent/sugars, IL/salt, IL/polymer, IL/surfactant, IL/salt/surfactant, DES/salt, DES/polymer, DES/polyol, DES/amino acid and DES/DES [184–217]. In these cases, the liquid-liquid demixing is driven by a “salting-out” effect, where the creation of complexes between water and the salts/ILs/DESs ions induces the dehydration of the remaining ABSs components [218,219]. Each coexisting phase is enriched in each one of the solutes, so that ABSs are formed by two water-rich layers with different properties, as sketched in Figure 3 (F). Thus, it is possible to finely tune the properties and affinities of the ABSs phases by the cautious selection of ABS phase-forming components and operational conditions. In this way, it is possible to develop efficient liquid-phase microextraction strategies and to attest compatibility with analytical equipment. For most common ABSs, i.e. those bearing an inorganic salt as a salting-out agent, the bottom (denser) phase is commonly salt-rich, while the top phase is enriched in the other solute (e.g., polymer, IL, DES, polar organic solvent). It should thus be

mentioned that most often, because of the salting-out effect, the phase containing the preconcentrated analytes is the top phase, as shown in Figure 3.

To apply ABSs in liquid-phase microextraction, and given that they are ternary systems, it is vital to gather previous knowledge on both ABSs ternary phase diagrams and partitioning behavior of target analytes among the coexisting phases. ABS phase diagrams allow identifying mixture compositions that form two-phases. Each phase diagram entails two major components, as shown in Figure 4 in an orthogonal representation (where the amount of water corresponds to that required to reach 100 wt% for a given mixture composition): (i) the coexistence binodal curve (green full line), and (ii) the tie-lines (TLs, orange dashed lines). The binodal curve corresponds to the boundary between the monophasic and biphasic regimes and it is usually established using the cloud-point titration method (related experimental data represented by green diamonds). TLs indicate the composition of each phase (at the endpoints that intersect the binodal curve, orange circles) for a specific biphasic mixture composition (orange diamonds). The TL length (TLL) denotes the distance between the two phases composition. Any mixture composition lying on the same TL has the same phases' composition, whereas the volumetric or mass ratios between the coexisting phases varies. This possibility allows thus to tailor the mixture composition to reach target enrichment factors, which can be carried out by the application of the lever-arm rule, being the most relevant aspect in the development of preconcentration techniques using ABSs (cf. CF_1, CF_2 and CF_3 in Figure 4) [184,186,197,201,206].

Having the biphasic zone defined, mixture compositions yielding two-phases can be used to address the partitioning behavior of the target analytes and to carry out optimization studies [182]. Mixtures are prepared by adding the appropriate amounts of phase-forming components, vigorously stirred and left to equilibrate and/or centrifuged

665 to achieve the equilibrium. After, the phases are separated and collected to analytical
666 quantification, where extraction of the target analyte towards one phase is aimed. By
667 balancing the properties of the ABSs components and of the target analytes, it is
668 possible to shed light on the interactions governing partition, therefore enabling a
669 rational design of efficient extraction and preconcentration methods based on ABSs.

670 A wide range of polymers and salts have been used in the development of
671 liquid-phase microextraction strategies based on ABSs. Conventionally, even though
672 polyethylene glycols (PEGs) bearing distinct molecular weights are the most recurrently
673 used polymers [184–186], others such as PEG-block-poly(propylene glycol)-block-PEG
674 (Pluronics®) [187] and polyoxyethylene cetyl ether (Brij®, POELE20) [188] have also
675 been considered. These have been combined with either organic (e.g., citrates and
676 tartrates) and inorganic (e.g., phosphates and sulfates) salts to form ABSs [184–188].
677 The ABS operational conditions, namely the nature of the polymer and the salt, TL,
678 temperature, pH, extractant addition and phases' volumetric ratio, were shown to
679 significantly impact on the partitioning behavior of the target analytes [184–188]. As
680 such, a cautious optimization of the ABS operational conditions is usually necessary to
681 obtain the quantitative extraction to a single phase. It should be remarked that although
682 being of utmost importance to develop efficient sample pretreatment and
683 preconcentration techniques, the optimization of incubation times as well as
684 minimization of the ABS components quantities were seldom addressed [185–188].

685 Conventional ABSs may afford appropriate analyte enrichment factors
686 [184,186,188] as well as compatibility with analytical equipment (e.g., ICP-OES, LC-
687 UV and UV-Vis) [185–188] and point-of-use microfluidic immunoassays [184]. It
688 should be however remarked that these advantages depend on the ABS phase-forming
689 components used, mixture compositions, target analyte and respective concentration and

dilutions/solvent employed before proceeding for analytical quantification. So far, the quantitative extraction to a given ABS phase is somehow limited and/or dependent on the use of additional extractants [185,187] and the determination of enrichment factors has been often neglected [185,187]. Moreover, the wide application of these more conventional ABSs, i.e. mainly polymer-based, is hampered by: (i) the high viscosity of the polymer-rich phase, (ii) the low speed of the phases' separation and (iii) the unbalanced polarity difference between the coexisting phases which limits selectivity. Aiming to surpass these shortcomings, several strategies have been outlined by implementing polar organic solvents [189–196], ILs [197–212] and DESs [213–217] as ABS phase-forming components.

The substitution of polymers by polar organic solvents can overwhelm viscosity, increase phase separation velocity and polarity range. Within this framework, the development of this type of alternative ABSs has mostly relied on the use of salts combined with short-chain alcohols, such as ethanol and/or propanol [189–194]. Additionally, combinations of glycerol/salts [195] and tetrahydrofuran/sugars [196] have also been reported. As with polymeric ABSs, a high influence is exerted by operational conditions on the partition patterns of the target analytes [189–196]. Particularly, the incubation time was optimized [189–194], with minimum values of 8 min being achievable by integrating microwave-assisted extraction with ABS [189]. Overall, these systems provide efficient extraction as well as good compatibility with analytical equipment, mostly with LC coupled with various detectors [189–196]. Even though concentration factors remain an underexplored parameter, a maximum 200-fold was reported with tetrahydrofuran/fructose ABS [196].

Disclosed by Rogers *et al*. in 2003 [220], evolution of IL-based ABS concept has led to significant progress in extraction and separation fields [219]. By virtue of

their “designer solvent” character [221], ILs are indeed the ABSs components of election in the development of sample cleanup and preconcentration techniques. IL-based ABSs entail mostly IL/salts [197–207], but also IL/polymers [208], IL/surfactants [209,210], and IL/salts/surfactants [211,212]. Various IL cation-anion combinations have been covered to appraise the role of the IL structure on the partition of target analytes: (i) cations bearing distinct alkyl chains lengths or functionalization based on either nitrogen-based cyclic (e.g., imidazolium, pyrrolidinium and piperidinium) or acyclic (e.g., quaternary ammonium, phosphonium, guanidinium and cholinium) compounds; (ii) anions of multiple nature, ranging from the most common chloride, bromide, tetrafluoroborate, trifluoromethanesulfonate, dicyanamide, thiocyanate, TEMPO-sulfate and alkylsulfates to the ones derived from natural sources (e.g., alkanoates, aminoates, salicylates, acesulfamate and saccharinate) [197–212]. Like polymer- and polar-organic-solvent-based ABSs, compatibility with analytical equipment, mostly LC with different detectors, may be enabled with IL-based ABSs [197–212]. Also, the design of efficient extraction and preconcentration processes highly counts on the proper optimization of operational variables, namely the nature and mass of the phase-forming agents, water ratio, TLL, temperature, pH, time, phases’ volumetric ratio and ultrasound-assistance [197–204,206–209,211,212]. Some authors further reinforced the key role played by the IL structure in providing quantitative extraction of the target analytes towards the IL-rich phase [197,198,201,202,204,211,212]. Additionally, the correct selection of the phase-forming components may lead to suitable preconcentration factors, where strong salting-out species, such as K_3PO_4, $C_6H_5K_3O_7$, K_2HPO_4, and Na_2CO_3, should be prioritized [197,199–201,203,204,206]. Remarkably, using low amounts of ILs, i.e. typically <5 wt% in ABSs, concentration factors over 20000-fold were estimated to be achievable

with ABSs formed by ILs and salts, which in some cases are well-beyond the values needed [197,199–201,203,204,206]. The major advantage of IL-based ABSs is the high solvation capacity afforded by the IL-rich phase, avoiding the phase saturation with the target analyte. On the other hand, when combining ILs and salts in ABSs, there is a strong salting-out effect exerted by the salt, leading to the quantitative extraction of the target analyte to the IL-rich phase. Furthermore, whenever required, ILs can be easily recovered and reused in subsequent extractions/preconcentration steps, thus decreasing the cost of the overall technology [197]. It should be further highlighted that the "designer solvent" status of ILs further allowed the synthesis of MILs and their incorporation in ABSs, which speeds up extraction and facilitates phase separation [199]. By simply employing a magnetic external field, MIL-based ABSs shorten the time required to achieve equilibrium and dismiss the need for a centrifugation step.

In 2014, DESs were for the first time considered alternative ABS phase-forming components by Zeng *et al*. [222]. As with ILs, this was triggered by the DESs features: (i) high degree of structural diversity afforded by the plethora of starting materials and stoichiometric ratios that can be used for their preparation; and (ii) cost-effectiveness as their preparation mostly relies on cheap and naturally occurring starting materials, not requiring reaction and purification steps [223,224]. Opposing to the hype with IL-based ABSs within the scope of liquid-phase microextraction strategies, the application of DES-based ABSs has seldom been addressed [213–217]. So far, ABSs formulated by DESs/salts, DESs/polymers, DESs/amino acids, DESs/sugars, DESs/amino acids and DESs/DESs were covered [213–217]. Various HBD-HBA pairs have been studied regarding the influence of DESs components on the partition of target analytes: (i) ammonium salts (e.g., cholinium chloride and tetrabutylammonium halides) and amino acids (e.g., lysine and proline) as HBA and (ii) polyols (e.g., glycerol, 1,4-butanediol,

765 ethylene glycol, propylene glycol, xylitol and sorbitol), monosaccharides (e.g, glucose),
766 organic acids (e.g., acetic, glycolic, lactic, malic and citric acids) and phenols (e.g.,
767 phenol, pyrocathecol, resorcinol and phloroglucinol) as the HBD [213–217]. As with
768 polymer-, polar organic solvent- and IL-based ABSs, compatibility with LC and UV-
769 Vis analytical equipment was demonstrated [213–217]. The extraction efficiency was
770 shown to be contingent on the operational conditions, such as amount and nature of both
771 DESs and remaining phase-forming agent, phases' volumetric ratio, temperature, pH,
772 ultrasound time, separation time and addition of extra salt [213–217]. As revealed with
773 ILs, most authors disclosed the impact of the DESs HBD-HBA pair on the partition of
774 target analytes [213,214,216,217]. Furthermore, some authors highlighted how the ABS
775 phase-forming pair selection drives the extraction success [215,216]. Among the
776 available options, i.e. ABSs composed of DESs/salts, DESs/amino acids, DESs/sugars,
777 DESs/amino acids and DESs/DESs, those entailing strong salting-out agents (e.g.
778 Na_2CO_3 and Na_2SO_4), are generally the most efficient [215]. Yet, DESs/DESs and
779 DESs/polyols exhibited high capacity to simultaneously extract target analytes of
780 distinct nature, as shown with three proteins [216]. Even though no enrichment factors
781 were reported [213–217], volumes of DESs as low as 200 µL allowed the successful
782 extraction and quantification of the target analytes [214]. Remarkably, DES-based
783 ABSs were shown to outperform the extraction efficiency of either DLLME with
784 hydrophobic DESs [214] and polymer/salt-based ABSs [215].

785 Based on the exposed, and if properly designed, ABSs join high
786 extraction/preconcentration efficiency, compatibility with analytical equipment and low
787 environmental impact. Given the major accomplishments within the ABS domain, IL-
788 based approaches seem to be the most encouraging ones to be followed since they
789 allow: (i) fast separation and low viscosity of the IL-rich phase [205]; (ii) use of low

amounts of IL (in the order of μL) [206]; (iii) high preconcentration factors [201]; (iv) alternatives to speed up and facilitate phase separation/collection can be applied [199]; (v) high solvation ability of the IL-rich phase that allows the complete extraction of the target analyte from the sample (with no losses, thus given more accurate results); (vi) and saturation of the IL-rich phase is difficultly achieved at the levels that target analytes are being analyzed within an analytical perspective.

The same rational used for ILs can be followed while considering DES-based ABSs as useful routes for the extraction and preconcentration of target analytes. However, it should be kept in mind that the DES integrity may be compromised during ABS formation, as hydrogen-bonding between the two components is destroyed [225]. From an analytical viewpoint, this phenomenon may compromise quantification accuracy and the compatibility with analytical equipment. Since an adequate choice of the DESs and the remaining-phase forming component may overcome such disintegration issues [226], authors should appraise DESs integrity in their studies.

3.4. Switchable solvents-based dispersive liquid-liquid microextraction

Switchable solvents (SSs) are water-insoluble media that can be easily and reversibly transformed to a water-miscible solvent by a simple change in the system under mild conditions [227].

The first description of these solvents in 2005 involved the use of a water-insoluble mixture of 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU) and 1-hexanol [228]. After the exposure to gaseous CO_2 at room temperature and atmospheric pressure, the mixture rapidly changed its polarity and a homogeneous solution was obtained. This change in miscibility was due to an acid-base reaction in which the DBU was protonated and the hydrophilic carbonate salt of the alcohol was obtained. The reaction

could be easily reversed by evacuation of CO_2 from the mixture, leading to insolubilization. Since then, different compounds have been identified as SSs, including amidine and ternary amines of low polarity [227,229], and fatty acids [230].

In the case of amines (insoluble in aqueous solutions), the hydrophilic carbonate protonated form of the amine is obtained when CO_2 is added. This change in the polarity can be easily reversed by increasing the pH, which leads to deprotonation of the amine. In some cases, this phenomenon is also observed without the addition of CO_2 because the switching between the protonated and deprotonated form of the amine is accomplished by modifying the pH. Fatty acids (initially water-insoluble) generate the hydrophilic form when ionized (as salt, or as the carbonate when CO_2 is used) at high pH values. Thus, acidic pH values solubilize amines and basic pH values solubilize fatty acids.

In 2015, Lasarte-Aragonés *et al*. were the first to propose the use of SSs in microextraction, in a procedure quite similar to DLLME [231]. In this approach, an aqueous solution of the carbonate protonated amine (*N*,*N*-dimethylcyclohexylamine) is prepared by adding dry ice until a homogeneous phase is obtained. This mixture is used as extraction media, which is easily insolubilized by increasing the pH (with a concentrated NaOH solution). Once formed the emulsion, the upper deprotonated amine-rich phase easily separates from the aqueous sample as it is schematically shown in Figure 3 (G). Since this first application of amine-based SSs in LPME (SS-DLLME), different methods have been described following the same strategy. The original SS, composed of the mixture of DBU and an alcohol, has been used in this microextraction strategy by dissolving them in aqueous sample in presence of CO_2 (as dry ice or gas), followed by the insolubilization with an increase of the pH [232,233]. Carbonate protonated amines have been the most explored SSs [234–257]. In all cases, the

hydrophilic amine is previously obtained using dry ice, but some studies reported the bubbling of gaseous CO_2 instead [234,258]. Among all the amines that have been used, *N*,*N*-dimethylbenzylamine [236,238–241,245,251,259,260], and triethylamine [244,247–250,255,261] are the most common ones, and in less extent *N*,*N*-dimethylcyclohexylamine [237,246,252]. *N*,*N*-dipropylamine has been mainly used as SS by changing from the protonated and deprotonated form without adding CO_2 [262–264]. In this case, the hydrophilic amine is obtained *in situ* by simultaneously adding the amine and HCl to the aqueous sample solution. *N*,*N*-dimethylcyclohexylamine was also used following the same strategy [265], but in this case the amine was previously mixed with an aqueous acidic solution to obtain the water-miscible phase. In all above-mentioned studies, concentrated NaOH solutions were used to increase the pH and induce the phase separation. More recently, *N*,*N*-dipropylamine has also been used in a temperature-controlled SS-DLLME method [266]. In this approach, the initial hydrophobic tertiary amine was solubilized in the aqueous sample by decreasing the temperature due to the strong hydrogen bonding interactions between the amine and water molecules at 5 □, which was reversed to obtain the phase separation by increasing the temperature to 25 □. Therefore, the miscibility in water of the amine could be tuned without requiring protonation and deprotonation, thus facilitating the experimental procedure.

With respect to the use of long chain fatty acids in SS-DLLME, hexanoic acid [267–269], nonanoic acid [270,271], and decanoic acid [272,273] have been used. Two different approaches have been proposed when dealing with this type of SS: the use of hydrophilic solutions of the fatty acid salt (ionized form) as extraction solvent [267,269,272,273], or the use of carbonates as both effervescent reagent and as a basic medium to ionize the acidic form with the purpose of obtaining the hydrophilic phase

[268,270,271]. In the first case, sodium salts of the carboxylic acids were dissolved in the aqueous sample or NaOH was added to ionize and solubilize the fatty acid. When dealing with effervescent-assisted methods, the carboxylic acid and Na_2CO_3 are simultaneously added to the aqueous sample to form in situ the miscible solvent and thus increasing the dispersion (due to the effervescency caused by the carbonate) [268,270]. Shishov *et al*. described the preparation of an effervescent tablet taking advantage of the solid nature of all the reagents involved in the microextraction process. The tablet included the carbonate salt as effervescent reagent, the sodium salt of the fatty acid as extraction solvent, and oxalic acid as the agent to promote the insolubilization [271]. Therefore, the SS-DLLME only required the addition of two tablets to the aqueous sample, thus enormously simplifying the whole procedure. In the remaining cases using this type of SS, concentrated H_2SO_4 solutions were used to switch the solvent to their respective water-insoluble forms.

In some cases, DLLME methods are assisted by vortex stirring [235,238–241,243,249,251–254,258,261,264,270], or ultrasounds [233,244,250,257,260,269], once the hydrophilic solvent was switched to its water-insoluble form. These strong stirring media favor the dispersion and increase the extraction efficiency. It has also been reported the incorporation of ionic surfactants (e.g. Aliquat 336 and SDS) with the purpose of forming an ion-pair complex with the charged analytes - due to low extreme pH conditions used in the switching process -, ultimately improving the extraction performance of the method [247,249,250]. Some other strategies have been proposed with the aim of simplifying the extraction procedure and facilitating the collection of the formed hydrophobic phase. As examples, the solidification of the SS by cooling the mixture [235,270], or the use of a syringe to perform the entire SS-DLLME method [272,274]. The performance in a syringe device can be also performed in a fully

automated strategy with a syringe pump, as reported by Pochivalov *et al.* [274]. It is also interesting to mention the stir membrane device recently reported by Lebedinets *et al.* [267]. The stir disk required placing an iron wire between two poly(vinylidene fluoride-co-tetrafluoroethylene) membranes, which are then glued to close the device. The disk was added to the sample before switching the solvent to its water-insoluble form. Thanks to the iron wire, the disk could be rotated and assisted the dispersion of the solvent, while at the same time due to the porosity and hydrophobicity of the membrane disk, the SS was retained on its surface. Finally, the analytes were desorbed by immersing the membrane in methanol.

In all the reported applications, the amounts of the "precursors" of the SS (the pure amine added to an acidic aqueous sample, the pure fatty acid added to a basic aqueous sample, the acidic aqueous solution of the amine, the basic aqueous solution of the fatty acid, or the mixture water+amine+dry ice) are low enough to ensure a final switchable hydrophobic phase of a few µL. This led to high preconcentration factors if considering the relatively high volumes of sample (around 5–10 mL).

4. Analytical applications

LPME methods reviewed in this article have been widely used in different analytical applications within the last three years. Figure 5 shows the number of publications for each method in the period between 2017 and 2019. Among the different LPME methods with hydrophilic media, it is interesting to highlight the increase in the number of studies that incorporate newer and greener hydrophilic media. Indeed, the number of applications of hydrophilic DES-DLLME and SS-DLLME has significantly increased in the last year. This may be related to the facile synthesis, low toxicity and impressive tuneability of DESs, together with the interesting features of SSs, which

915 simplify the microextraction procedure and improve the sustainability. Furthermore,
916 despite CPE is a well-known steady technique, it still presents the higher number of
917 applications in the recent years. With respect to ABSs, their use as a LPME approach
918 with different hydrophilic components has been progressively extended in the last three
919 years, thus increasing the analytical applications of these ternary systems.

920 Figure 5 also includes a summary of the nature of the analytes extracted using
921 hydrophilic media, as well as the type of samples analyzed, with environmental waters
922 as the most common sample matrix. In those applications dealing with more complex
923 samples, in general, authors dilute the matrices with ultrapure water prior to the LPME
924 method, while previous extraction or digestion steps are required when analyzing solid
925 samples. It is important to highlight that there has not been found a rationale between
926 the nature of the target analytes and the characteristics and properties of the selected
927 hydrophilic extraction media. Indeed, the same hydrophilic media have been
928 successfully used for the extraction of totally different analytes: metal ions, polar
929 analytes and even highly hydrophobic organic compounds. Therefore, despite the wide
930 variety of extraction media and the tunable properties of some of them (i.e. ILs and
931 DESs), in general, the most common and well-known media have been applied in
932 different applications. Thus, poor attention has been paid to the design of the
933 hydrophilic extraction phase, while the selectivity of the analysis has been mainly based
934 on the analytical separation instrumentation.

935 Moreover, it is important to highlight some common issues amongst all the
936 methods that limit their real application: (i) the scarce number of applications using LC
937 coupled to mass spectrometry (MS), which may be due to the low compatibility of the
938 final extraction-phase with the MS system in the ionization interface; and (ii) the tricky
939 collection of the final extraction phase, which requires particular expertise of the

operator due to its small volume and high viscosity in most cases. In this section, the analytical applications in which these methodologies have found practical utility will be discussed below for each method, with emphasis in those hydrophilic media and techniques with higher number of applications, while Table 1 includes some representative examples for each method.

4.1. CPE

With respect to CPE, it has been developed for the extraction of both organic compounds and heavy metals, with the determination of metal species the most successful application as shown in Figure 5. This is probably related to the fact that most nonionic surfactants absorb UV-Vis radiation, thus generating interfering signals in chromatograms when LC-UV-Vis is used for organics.

V(IV) [32,61] and V(V) [32,61,67] , U(VI) [26,57,63,93], Cu(II) [21,82,84], Hg(II) [34,58,64,94] and $[CH_3Hg]^+$ [58,64,94] are some of the heavy metals determined in the recent years. In these cases, the addition of a chelating agent is necessary to form an extractable heavy metal ion complex prior to the CPE procedure [19]. This justifies that the pH of the aqueous sample is the main factor to be carefully optimized in the procedure.

A wide variety of organic compounds has also been extracted using a CPE method, including phenols [54,59,60,86,88], vitamins [49,56,80] and pharmaceuticals [24,44,46].

CPE has been mainly devoted to the extraction of analytes from environmental samples, with water the most studied matrix. Nevertheless, the development of CPE in complex matrices has also been reported in the recent years, including biological samples (mainly urine) [21,23,39,46,53,74,77,80] and food samples

965 [45,49,60,61,72,87,89,92,94]. d-CPE has been especially successful for the speciation
966 of metals, such as Hg species [58,64] and As(III) and As(V) [36], and even for the
967 determination of selenium in food samples [72]

968 The analytical technique employed after CPE depends on the analyte and it is also
969 conditioned by the compatibility of the surfactant-rich phase with the analytical
970 instrument. Thus, UV-Vis spectrophotometric applications prevails in these years
971 [21,23,26–28,34,41,45,48,51,52,54,57,59,61,62,67–69,71,74,76,78,83,92,94,275] while
972 LC is also quite common [24,38,39,44,46,49,50,53,55,56,60,70,79,86–88]. Only a
973 recent work has reported the coupling of the CPE method with GC by an ultrasound-
974 assisted back extraction with isooctane [38]. Inductively coupled plasma (ICP) has also
975 been successfully used in some of the applications of CPE for the determination of
976 heavy metals, in combination with optical emission spectroscopy (OES) [20,36,93] or
977 MS [22,77,91]. Prior to the analytical determination after CPE, the surfactant-rich phase
978 is often pretreated to ensure the compatibility with the instrument. Given the high
979 viscosity of the surfactant-rich phase, organic solvents are commonly selected to
980 dissolve it or to minimize its viscosity, with ethanol, methanol and acetonitrile the most
981 frequently used [21,23,24,27,34,44–46,48,50,52–56,67–69,71,79,80,82,83,85–87,93].
982 Several (few) studies intended for the determination of metal species also reported the
983 use of HNO_3 solutions [20,33,35,36] or even a mixture of methanol and HNO_3 solutions
984 in this dilution step of the surfactant-rich phase[30,40,42,51,57,73]. In some cases, the
985 direct injection of the surfactant-rich phase in the analytical system without the addition
986 of any solvent after filtration has been reported [32,47,65,81,88].
987

988 ***4.2. Conventional CAE***

With respect to conventional CAE, as observed in Figure 5, most of the applications in the last three years focused on the determination of organic compounds in water [99,102,203,276], food samples [97,98,101] and biological samples [104], using LC with UV-Vis detection [97–99,101–104,276]. CAE has also been used for the extraction of proteins. Specifically, Xu *et al.* have reported the extraction of lysozyme using a CAE-assisted method with HFIP in combination with capillary electrophoresis (CE) [100]. The resulting supramolecular aggregate obtained after the CAE is generally filtered or dissolved in methanol to reduce the viscosity prior to the analytical determination [99,104].

4.3. DES-DLLME

Hydrophilic DESs in DLLME have been used for the extraction of metals as often as for the extraction of organic compounds, as shown in Figure 5.

Among the metal species determined, Pb(II) [124,132,137,141], Cd(II) [119,127,141], Hg species [117,142], As(III) [133,143], and Se(IV,VI) [143,129] have been the most common ones, present in environmental waters or in food samples. The determination was accomplished either using UV-Vis spectrophotometry [118,142,144] or atomic absorption spectroscopy (AAS) techniques with different atomization methods, mainly electrothermal (ETAAS) [117,122,127–129] and flame AAS (FAAS) [119,132,137,141]. In general, the formed DES-rich phase after the microextraction method is directly injected in the instrument or diluted with an acidic aqueous solution of ethanol or methanol.

With respect to the determination of organic analytes with DES-DLLME, the extraction of drugs and pharmaceuticals from waters and biological fluids has been the main field of application [120,125,131,135,136], as examples: antibiotics in river waters

[131], methadone in plasma and urine [136], and anti-depressant drugs in plasma and pharmaceutical wastewaters [125]. Other contaminants have been extracted from environmental water samples using DES-DLLME methods, such as dyes [130,139], pesticides [121], and phenols [134]. Analytical determination has been accomplished mainly using LC with UV-Vis detection [120,121,123,125,131] or spectrophotometric techniques [126,130,135,138,139] after the dilution of the DES-rich phase due to its high viscosity. It is interesting to highlight that in those applications in which the microextraction method was performed in combination with GC, the DES-rich phase is directly injected in the GC system without requiring any evaporation and reconstitution step or dilution [134,136].

4.4. In situ IL-DLLME

Most of the *in situ* IL-DLLME methods have been proposed for the extraction of organic compounds (Figure 5), including a high variety of pesticides from environmental waters [155,159,163,169,175] and food samples [153,170,174]; persistent and emerging pollutants (UV filters and plasticizers) from environmental waters [161,167,177,178]; and pharmaceuticals [156] and biomarkers [172] from biological fluids. These methods have been mainly coupled with LC and different detectors depending on the nature of the analytes [153–156,158,163–175,177], with only one application using MS as detection technique for the determination of alkaloids in plants [168]. In some of those cases where the hydrophobic IL (or diluted with an organic solvent) was directly injected in the LC system, the compatibility with the mobile phase and the chromatographic column was ensured [171,172,177]. When dealing with GC coupled with different detectors, mainly MS, the analytes were

thermally desorbed from the hydrophobic IL using a headspace sampler [161,167,178] or a thermal desorption unit [159].

It is interesting to highlight the application of the *in situ* MIL-DLLME method proposed by Bowers *et al*. for the extraction of different sized fragments of DNA [179]. In this case, the amount of extracted DNA was indirectly determined (by injecting in the LC system or by measurement in the spectrofluorometer the supernatant obtained after the extraction procedure) leading to extraction efficiencies between 42 and 99%.

With respect to the determination of metals by *in situ* IL-DLLME, representative examples include Cd(II) and Cu(II) from water [157,162,166] and food samples [160]; cobalt [164], mercury [165], uranium [152], and nickel and zinc [166], mainly in environmental samples. In general, all these methods are coupled with FAAS after the dilution of the hydrophobic IL with an organic solvent (to reduce the viscosity of the IL and facilitate the aspiration of the extract into the instrument).

4.5. ABSs

Concerning the application of ABSs and as sketched in Figure 5, organic compounds represent the most explored type of analytes, followed by metals, proteins, and bacteria (one work). Among the organic compounds addressed, pharmaceuticals are the most studied, due to either their emergence as environmental pollutants [185,186,188,190,191,195,197,199–201,214] and food contaminants [211] or due to the need of screening drug quality [200] and concentration levels in biological fluids [200,212]. Other applications envisioned the determination of mycotoxins [184], carcinogens [192] and dyes [207,209,215] in food, feed and drinks, of pesticides in either environmental and food samples [194,196,198,203,208,210], of polycyclic aromatic hydrocarbons (PAHs) in tap water [206], and of flavonoids [189], ginsenosides

[213] and alkaloids [193,202] in biomass. Environmental samples, including water (e.g., river, lake, tap water, wastewater treatment plant (WWTP) effluents) and soil-based matrices, are the most focused matrices [187,188,190,191,196,197,199,201,203,204,206,214], followed by food samples [184,192,194,207–209,211,217], biological fluids [200,204,212] and others such as biomass [189,193], pharmaceutical formulations [200,213] and porcine crude extract [216]. However, it should be remarked that a significant amount of studies resort to synthetic samples, failing to address real case scenarios where the matrix effect on both analyte extraction and quantification plays a pivotal role [185,186,195,198,202,205,210,215].

Regardless the ABS constitution, LC has been the preferred analytical technique for the quantification of organic compounds. Depending on the target analyte nature and/or limits of detection needed, UV, DAD, FD or MS detectors have been used [188–191,193,196–201,203,206–208,210–214]. Other analytical techniques have been additionally adopted, namely UV-Vis spectroscopy [185,186,195,202,209,215], GC-MS [192], 2D-LC [194] and immunoassays [184,205]. Given the remarkable ABSs compatibility with analytical equipment, the direct analysis of the analyte-enriched phase, either undiluted or diluted in an appropriate solvent, is usually enabled [184–186,188–203,205–215]. Similarly, ABSs, if properly designed, assure compatibility with analytical techniques for metal ions (e.g., HG-ICP OES and DPASV) [187,204] and proteins (UV-Vis) [216,217] determination.

It should be finally highlighted that ABSs can be used with microfluidic and lateral flow immunoassays providing sensitive and rapid results for organic compounds, proteins and bacteria determination, which represents a steppingstone to off-site and point-of-care analysis [184,205].

4.6. SS-DLLME

The variety of analytes extracted using SS-DLLME is wider considering the higher number of publications with this method compared with the remaining methodologies, except for CPE (see Figure 5).

With regards to metal ions, Ni(II) [254,255,257,261], Co(II) [242,253,257,259], Cd(II) [245,248,257], Pd(II) [241,252], and Pb(II) [235,257] have been the most commonly determined in a wide variety of samples, including foods [235,242,248,253,254,257,259,261,272,277] cigarettes [253,254], waters from different sources [241,245,252,255,257,261], and urine [257].

Most applications of SS-DLLME have been shifted to the determination of drugs and pharmaceuticals from biological fluids (mainly urine) [243,249,258,263–265,267,274] or environmental samples [237,270]. The extraction of dyes from food [247,269], pesticides from waters or food samples [238,240,244,260], and disrupting compounds from environmental waters, including phenols [236,239,246,251], hormones [236,251,260,271], PAHs [273], and phthalic acid esters [266] have also been reported. The analytical determination in all cases was accomplished either by LC or GC techniques, depending on the nature of the analytes and the sensitivity required.

In most cases, the resulting hydrophobic phase was directly injected in the LC, GC, ASS or spectrophoto/fluoro-metric systems [233,236,238–240,243,247,249,251,256,258,260,264,266,268–270,273], but the dilution of the switchable phase with an adequate solvent has also been a common strategy [142,237,241,242,245,248,252–254,259,261,271,272,274,277].

Some studies also reported the evaporation of the SS followed by the reconstitution with a solvent more compatible with the analytical system

[244,246,250,255,257,262,263,265]. It is interesting to mention the studies reported by Afridi *et al.*, in which the extracted metal ions were desorbed from the hydrophobic phase, which allowed the reusability of the SS up to 6 times [232,234].

5. Conclusions and future perspectives

The incorporation of hydrophilic media within LPME methods undoubtedly constitutes a step forward to improve the efficiency and sustainability of these techniques. Hydrophilic media enhance the dispersion of the extraction phase into the sample, thus leading to an enhancement of the mass transfer of the analytes in comparison with the use of water-insoluble extraction phases, thus justifying the high number and variety of applications appearing in the past years.

In this particular research topic within LPME, advances in the last years have been mainly shifted to the design of new hydrophilic materials to develop greener and more efficient LPME modes. Due to the wide variety of exploited water-soluble materials (as alternative to conventional extraction phases) and the different pathways that may be followed for their insolubilization, this review articles aimed to establish a classification to avoid confusions in the scientific terminology. This classification is based on an understanding of the physicochemical mechanism that takes place during the phase separation, which is also useful for determining the main parameters that have a major influence in the performance of the method (and therefore should be optimized). The proposed classification of LPME methods using hydrophilic media considers both the nature of the water-soluble material and the driving force responsible of the phase separation. Thus, methods based on coacervation (e.g.; CPE and CAE) and other phenomena, including dehydration of the components (e.g., ABSs and DES-DLLME) and structural changes on the extraction material (e.g., *in situ* IL-DLLME and SS-

DLLME), have been developed. This classification aimed to improve the scientific criteria for a reasonable use of emerging hydrophilic materials, such as ILs, DESs and SSs, while pointing out some features about well-known materials that are still widely used, like surfactants.

Among the reviewed hydrophilic media within LPME approaches, surfactants are still quite successful in coacervation-based LPME methods, mainly for the extraction of metals. Besides, specific conditions to induce the phase separation when using surfactants are mild, particularly if they are compared with the parameters responsible for the separation in other strategies, such as extreme pH values in SS-DLLME and high amounts of salting-out agent in some of ABSs applications. In addition to conventional inorganic salts/electrolytes that are commonly used to decrease or tailor the cloud point temperature, there are recent evidences that ILs can be used for such a purpose, although not investigated up to date within the analytical chemistry perspective. Accordingly, the introduction of ILs, or even DESs, as new “electrolytes” in coacervation-based LPME methods deserves to be investigated in more detail given their tunability. Furthermore, it is important to highlight the easily operational of SS-DLLME, which only requires the modification of the pH of the sample (using common basic or acid solutions) to achieve the phase separation.

In the case of ABSs, and although less investigated within analytical chemistry applications, their remarkable extraction capacity and enrichment factors should not be discarded and more investigations in this field are encouraged. In particular, ABSs involving ILs and inorganic salts have been reported as the most promising, in which high extraction efficiencies are afforded by both the salting-out effect of the inorganic salts and high solvation ability of ILs. Although DESs have been also reported as ABS phase-forming components, special caution should be placed when dealing with such

mixtures since hydrogen-bonding interactions between the HBD and HBA species are broken and the concept of DES is lost. This does not mean that they will not work in this field or that should not be applied; only additional attention should be given to the DES definition and it should be taken into account that at least quaternary ABSs are being applied in these examples. Independently of the phase-forming components, to successfully apply ABSs as preconcentration techniques it is of major relevance to determine the respective phase diagrams and apply the lever-arm rule, which will provide an estimate of the appropriate mixture composition for a given enrichment factor.

With respect to ILs and DESs, their tuneability constitutes their most useful feature, since it leads to the design of more selective and sustainable hydrophilic extraction phases. Particularly for ILs, their high solvation ability is the main responsible for the high enrichment factors and extraction efficiencies reported. Furthermore, it is interesting to mention the preparation and use of hydrophilic MILs, which enormously facilitates the complex sampling of the water-insoluble phase prior to the analytical determination. In any case, functionalized ILs or ILs with safer toxicological profiles should be incorporated in these methods. In the case of hydrophilic DESs, it is important to take into account the possible decomposition of these solvents when they are dissolved in aqueous media, as it was highlighted before. Thus, the composition of the DES and the characterization of the initial and final extraction-phases is essential to understand the phenomena that take place in the LPME method, which would help in selecting the best DES composition while determining the main variables to optimize to obtain better extraction performance.

In conclusion, the rising use of all these water-miscible materials in LPME methods together with the understanding of the physicochemical driving forces of phase

separation can contribute to the rational development of effective LPME methods, opening a wide range of analytical applications still to be exploited. Future studies should also focus on improving the design and selection of the hydrophilic media to improve the performance for target analytical applications. Furthermore, the sustainable character of the methods applied should be carefully acknowledged, particularly when considering the necessity of incorporating additional organic solvents in the procedure for inducing the phase separation or diluting the final phase to ensure compatibility with the analytical instrument.

Acknowledgements

I. P.-F. thanks the Canary Agency of Research and Innovation (ACIISI), co-funded by the European Social Fund, for her FPI PhD fellowship. V.P. thanks the Spanish Ministry of Economy and Competitiveness (MINECO) for the project MAT2017-89207-R. This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/50011/2020, financed by national funds through the Portuguese Foundation for Science and Technology/MCTES. This article is also based upon work from the Sample Preparation Task Force and Network supported by the Division of Analytical Chemistry of the European Chemical Society.

Abbreviations

$[C_{10}Gu^+]$	decylguanidinium
$[C_4C_4Im^+]$	dibutylimidazolium
$[C_4Gu^+]$	butylguanidinium
$[C_4MIm^+]$	butylmethylimidazolium
$[C_5MIm^+]$	pentylmethylimidazolium
$[Chol^+]$	cholinium
$[N_{4444}{}^+]$	tetrabutylammonium
$[Ni(BeIm)_4{}^{2+}]$	tetra(*N*-benzylimidazolium)nickelate(II)
$[Ni(C_4Im)_4{}^{2+}]$	tetra(*N*-butylimidazolium)nickelate(II)
$[NTf_2{}^-]$	bis(trifluoromethanesulfonyl)imide

1218	[Sac^-]	saccharinate
1219	[Sal^-]	salicylate
1220	ABS(s)	aqueous biphasic system(s)
1221	CAE	coacervative extraction
1222	CPB	cetylpyridinium bromide
1223	CPE	cloud point extraction
1224	CPT	cloud point temperature
1225	CTAB	cetyltrimethylammonium bromide
1226	DBU	1,8-diazabicyclo-[5.4.0]-undec-7-ene
1227	DES(s)	deep eutectic solvent(s)
1228	DES-DLLME	deep eutectic solvent-based dispersive liquid-liquid microextraction
1229	diDDAB	didodecyldimethylammonium bromide
1230	DLLME	dispersive liquid-liquid microextraction
1231	DPASV	differential pulse anodic stripping voltammetry
1232	DTAB	dodecyltrimethylammonium bromide
1233	E_F	enrichment factor
1234	FD	fluorescence detection
1235	GAC	green analytical chemistry
1236	GFAAS	graphite furnace atomic absorption spectroscopy
1237	HBA	hydrogen bond acceptor
1238	HBD	hydrogen bond donor
1239	HF-LPME	hollow fiber liquid-phase microextraction
1240	HFIP	hexafluoroisopropanol
1241	IL(s)	ionic liquid(s)
1242	IL-DLLME	ionic liquid-based dispersive liquid-liquid microextraction
1243	LPME	liquid-phase microextraction
1244	MIL	magnetic ionic liquid
1245	MNP	magnetic nanoparticles
1246	NADES(s)	natural deep eutectic solvent(s)
1247	OH-PAHs	monohydroxylated polycyclic aromatic hydrocarbons
1248	PAHs	polycyclic aromatic hydrocarbons
1249	PCBs	polychlorinated biphenyls
1250	RSD_{max}	maximum relative standard deviation value
1251	SDME	single-drop microextraction
1252	SS(s)	switchable solvent(s)
1253	SS-DLLME	switchable solvents-based dispersive liquid-liquid microextraction
1254	SUPRAS	supramolecular solvent-based microextraction
1255	TBAB	tetrabutylammonium bromide
1256	TEMPO	2,2,6,6-tetramethylpiperidine-1-oxyl
1257	TL	tie-line
1258	TLL	tie-line length
1259	TNO	5,6,7,8-tetrahydro-5,5,8,8-tetramethylnaphthalen-2-ol
1260	WWTP	wastewater treatment plant
1261		

References

[1] Y. Yamini, M. Rezazadeh, S. Seidi, Liquid-phase microextraction – The different principles and configurations, Trac-Trends Anal. Chem. 112 (2019) 264–272.

[2] C. Poole, Z. Mester, M. Miró, S. Pedersen-Bjergaard, J. Pawliszyn, Glossary of terms used in extraction (IUPAC Recommendations 2016), Pure Appl. Chem. 88 (2016) 517–558.

[3] E. Carasek, J. Merib, Membrane-based microextraction techniques in analytical chemistry: A review, Anal. Chim. Acta 880 (2015) 8–25.

[4] M. Rezaee, Y. Assadi, M.-R.M. Hosseini, E. Aghaee, F. Ahmadi, S. Berijani, Determination of organic compounds in water using dispersive liquid–liquid microextraction, J. Chromatogr. A 1116 (2006) 1–9.

[5] M. Rutkowskaa, J. Płotka-Wasylka, M. Sajid, V. Andruch, Liquid-phase microextraction: A review of reviews, Microchem. J. 149 (2019) 103989.

[6] S. Armenta, S. Garrigues, F.A. Esteve-Turrillas, M. de la Guardia, Green extraction techniques in green analytical chemistry, Trac-Trends Anal. Chem. 116 (2019) 248–253.

[7] I. Pacheco-Fernández, V. Pino, Green solvents in analytical chemistry, Curr. Opin. Green Sustain. Chem. 18 (2019) 42–50.

[8] Colloidal Dispersions, in: R. Chhabra, M.G. Basavaraj (Eds.), Coulson and Richardson's Chemical Engineering: Volume 2A: Particulate Systems and Particle Technology, Sixth Edition, Butterworth-Heinemann, 2019, pp. 693–737.

[9] Y.P. Timilsena, T.O. Akanbi, N. Khalid, B. Adhikari, C.J. Barrow, Complex coacervation: Principles, mechanisms and applications in microencapsulation, Int. J. Biol. Macromol. 121 (2019) 1276–1286.

[10] K. Szutkowski, Z. Kołodziejska, Z. Pietrali, I. Zhukov, A. Skrzypczak, K. Maternad, M. Kozak, Clear distinction between CAC and CMC revealed by high-resolution NMR diffusometry for a series of bis-imidazolium gemini surfactants in aqueous solutions, RSC Adv. 8 (2018) 38470–38482.

[11] A.S. Yazdi, Surfactant-based extraction methods, Trac-Trends Anal. Chem. 30 (2011) 918–929.

[12] M. Moradi, Y. Yamini, Surfactant roles in modern sample preparation techniques: A review, J. Sep. Sci. 35 (2012) 2319–2340.

[13] A. Ballesteros-Gómez, S. Rubio, Environment-Responsive Alkanol-Based Supramolecular Solvents: Characterization and Potential as Restricted Access Property and Mixed-Mode Extractants, Anal Chem. 84 (2012) 342–349.

[14] F.-J. Ruiz, S. Rubio, D. Pérez-Bendito, Water-Induced Coacervation of Alkyl Carboxylic Acid Reverse Micelles: Phenomenon Description and Potential for the Extraction of Organic Compounds, Anal. Chem. 79 (2007) 7473–7484.

[15] P. Bogdanova, A. Pochivalov, C. Vakh, A. Bulatov, Supramolecular solvents formation in aqueous solutions containing primary amine and monoterpenoid compound: Liquid phase microextraction of sulfonamides, Talanta 216 (2020) 120992.

[16] C. Caballo, M.D. Sicilia, S. Rubio, Supramolecular Solvents for Green Chemistry, in: F. Pena-Pereira, M. Tobiszewski (Eds.), The Application of Green Solvents in Separation Processes, Elsevier, 2017, pp. 111–137.

[17] J. Mitira, H. Ishii, H. Watanabe, Extraction and separation of nickel chelate of 1-(2-thiazolylazo)-2-naphthol in nonionic surfactant solution, Bunseki Kagaku 25 (1976) 808–809.

[18] S.S. Arya, A.M. Kaimal, M. Chib, S.K. Sonawane, P.L. Show, Novel, energy efficient and green cloud point extraction: technology and applications in food processing, J. Food Sci. Technol. 56 (2019) 524–534.
[19] P. Samaddar, K. Sen, Cloud point extraction: A sustainable method of elemental preconcentration and speciation, J. Ind. Eng. Chem. 20 (2014) 1209–1219.
[20] N.R. Biata, G.P. Mashile, J. Ramontja, N. Mketo, P.N. Nomngongo, Application of ultrasound-assisted cloud point extraction for preconcentration of antimony, tin and thallium in food and water samples prior to ICP-OES determination, J. Food Compos. Anal. 76 (2019) 14–21.
[21] M.K. Hassan, A.F. Khudhair, Analysis and Cloud Point Extraction of Trace Copper (II) in Urine of Occupational Workers, Asian J. Chem. 31 (2019) 353–359.
[22] L. Torrent, F. Laborda, E. Marguí, M. Hidalgo, M. Iglesias, Combination of cloud point extraction with single particle inductively coupled plasma mass spectrometry to characterize silver nanoparticles in soil leachates, Anal. Bioanal. Chem. 411 (2019) 5317–5329.
[23] A.F. Khudhair, M.K. Hassan, H.F. Alesary, A.S. Abbas, A Simple Pre-concentration Method for the Determination of Nickel(II) in Urine Samples Using UV-Vis Spectrophotometry and Flame Atomic Absorption Spectrometry Techniques, Indones. J. Chem. 19 (2019) 638–649.
[24] G. Kojro, P.J. Rudzki, D.M. Pisklak, J. Giebułtowicz, Matrix effect screening for cloud-point extraction combined with liquid chromatography coupled to mass spectrometry: Bioanalysis of pharmaceuticals, J. Chromatogr. A 1591 (2019) 44–54.
[25] K.R. Kumar, P. Shyamala, Catanionic mixed micellar cloud point extraction of metal ions in coal fly ash samples and their determination by CS-ETAAS, J. Environ. Chem. Eng. 7 (2019) 103119.
[26] A. Saha, S. Neogy, D.R.M. Rao, S.B. Deb, M.K. Saxena, B.S. Tomar, Colorimetric and visual determination of ultratrace uranium concentrations based on the aggregation of amidoxime functionalized gold nanoparticles, Microchim. Acta 186 (2019) 183.
[27] A.F.O. Silva, W.V. Castro, F.P. Andrade, Development of spectrophotometric method for iron determination in fortified wheat and maize flours, Food Chem. 242 (2018) 205–210.
[28] M.A. Abdel-Fadeel, H.M. Al-Saidi, A.A. El-Bindary, A.Z. El-Sonbati, S.S. Alharthi, Cloud point extraction – Microvolume spectrophotometry for extraction and determination of bismuth in waters and roadside soil, J. Mol. Liq. 249 (2018) 963–969.
[29] L. Torrent, M. Iglesias, M. Hidalgo, E. Margui, Determination of silver nanoparticles in complex aqueous matrices by total reflection X-ray fluorescence spectrometry combined with cloud point extraction, J. Anal. At. Spectrom. 33 (2018) 383–394.
[30] Q. Han, Y. Huo, L. Yang, X. Yang, Y. He, J. Wu, Determination of Trace Nickel in Water Samples by Graphite Furnace Atomic Absorption Spectrometry after Mixed Micelle-Mediated Cloud Point Extraction, Molecules 23 (2018) 2597.
[31] Q. Han, Y. Huo, X. Yang, Y. He, J. Wu, H. Cai, Determination of ultra-trace levels of cobalt in water and wheat flour samples using cloud point extraction coupled with laser thermal lens spectrometry, Anal. Methods 10 (2018) 634–640.
[32] I. López-García, J.J. Marín-Hernández, M. Hernández-Córdoba, Graphite furnace atomic absorption spectrometric determination of vanadium after cloud point

extraction in the presence of graphene oxide, Spectroc. Acta Pt. B-Atom. Spectr. 143 (2018) 42–47.

[33] M.A. Iturbide-Casas, G. Molina-Recio, F. Cámara-Martos, Manganese Preconcentration and Speciation in Bioaccessible Fraction of Enteral Nutrition Formulas by Cloud Point Extraction (CPE) and Atomic Absorption Spectroscopy, Food Anal. Meth. 11 (2018) 2758–2766.

[34] S.K. Jawad, M.U. Kadhium, E.A. Azooz, Separation and Spectrophotometric Determination of Iron (III) and Mercury (II) via Cloud Point Extraction with New Azo-Derivative, Eurasian J. Anal. Chem. 13 (2018) 48.

[35] Z. Bahadir, L. Torrent, M. Hidalgo, E. Marguí, Simultaneous determination of silver and gold nanoparticles by cloud point extraction and total reflection X-ray fluorescence analysis, Spectroc. Acta Pt. B-Atom. Spectr. 149 (2018) 22–29.

[36] S. Wen, X. Zhu, Speciation of inorganic arsenic(III) and arsenic(V) by a facile dual-cloud point extraction coupled with inductively plasma-optical emission spectrometry, Talanta 181 (2018) 265–270.

[37] X. Li, N. Song, W. Feng, Q. Jia, Cloud point extraction of rare earths and zinc using 1,10-phenanthroline and Triton X-114 coupled with microwave plasma torch-atomic emission spectrometry, Anal. Methods 9 (2017) 5333–5338.

[38] P. Berton, S.B. Mammana, D.A. Locatelli, N.B. Lana, M.B. Hapon, A.B. Camargo, J.C. Altamirano, Determination of polybrominated diphenyl ethers in milk samples. Development of green extraction coupled techniques for sample preparation, Electrophoresis 38 (2017) 460–468.

[39] C. Nong, Z. Niu, P. Li, C. Wang, W. Li, Y. Wen, Dual-cloud point extraction coupled to high performance liquid chromatography for simultaneous determination of trace sulfonamide antimicrobials in urine and water samples, J. Chromatogr. B 1051 (2017) 9–16.

[40] Q. Han, Y. Huo, J. Wu, Y. He, X. Yang, L. Yang, Determination of Ultra-trace Rhodium in Water Samples by Graphite Furnace Atomic Absorption Spectrometry after Cloud Point Extraction Using 2-(5-Iodo-2-Pyridylazo)-5-Dimethylaminoaniline as a Chelating Agent, Molecules 22 (2017) 487.

[41] Y. Bazel, A. Tupys, Y. Ostapiuk, O. Tymoshuk, V. Matiychuk, A green cloud-point microextraction method for spectrophotometric determination of Ni(II) ions with 1-[(5-benzyl-1,3-thiazol-2-yl)diazenyl]naphthalene-2-ol, J. Mol. Liq. 242 (2017) 471–477.

[42] X. Yang, Z. Jia, X. Yang, G. Li, X. Liao, Cloud point extraction-flame atomic absorption spectrometry for pre-concentration and determination of trace amounts of silver ions in water samples, Saudi J. Biol. Sci. 24 (2017) 589–594.

[43] I. López-García, M.J. Muñoz-Sandoval, M. Hernández-Córdoba, Cloud point microextraction involving graphene oxide for the speciation of very low amounts of chromium in waters, Talanta 172 (2017) 8–14.

[44] O.G. Makukha, L.A. Ivashchenko, O.A. Zaporozhets, V.O. Doroschuk, Cloud point extraction combined with HPLC–MS for the determination of nimesulide in biological samples, Chem. Pap. 73 (2019) 693–699.

[45] R. Khani, R. Sheykhi, G. Bagherzade, An environmentally friendly method based on micro-cloud point extraction for determination of trace amount of quercetin in food and fruit juice samples, Food Chem. 293 (2019) 220–225.

[46] V.O. Doroschuk, I.Y. Matsenko, Y.S. Mandzyuk, O.G. Makukha, N.O. Grytsyk, Cloud Point Extraction Combined with Liquid Chromatography Coupled to Tandem Mass Spectrometry for the Determination of Verapamil in Urine, J. Anal. Chem. 74 (2019) 701–706.

[47] J. Chen. W. Deng, X. Li, X. Wang, Y. Xiao, Hexafluoroisopropanol/Brij-35 based supramolecular solvent for liquid-phase microextraction of parabens in different matrix samples, J. Chromatogr. A 1591 (2019) 33–43.
[48] A.T. Bişgin, Y. Sürme, M. Uçan, İ. Narin, Separation, Preconcentration and Spectrophotometric Determination of Rhodamine B in Industrial, Cosmetic and Water Samples by Cloud Point and Solid Phase Extraction, J. Anal. Chem. 73 (2018) 452–458.
[49] S. Ulusoy, M. Akçay, Simultaneous Determination of Vitamins B1 and B2 in Food Samples by Modified Cloud Point Extraction Method and HPLC-DAD, Food Anal. Meth. 11 (2018) 260–269.
[50] R. Kachangoon, J. Vichapong, R. Burakham, Y. Santaladchaiyakit, S. Srijaranai, Ultrasonically Modified Amended-Cloud Point Extraction for Simultaneous Pre-Concentration of Neonicotinoid Insecticide Residues, Molecules 23 (2018) 1165.
[51] F. Nekouei, H. Kargarzadeh, S. Nekouei, F. Keshtpour, A.S.H. Makhlouf, Efficient method for determination of methylene blue dye in water samples based on a combined dispersive solid phase and cloud point extraction using $Cu(OH)_2$ nanoflakes: central composite design optimization, Anal. Bioanal. Chem. 409 (2017) 1079–1092.
[52] E. Ghasemi, M. Kaykhaii, Determination of Zinc, Copper, and Mercury in Water Samples by Using Novel Micro Cloud Point Extraction and UV-Vis Spectrophotometry, Eurasian J. Anal. Chem. 12 (2017) 313–324.
[53] K.P. Amorim, L.S. Andrade, Development and application of a cloud point method for the extraction of natural estrogens E1 and E2 from urine samples and their simultaneous determination by HPLC-EC using a BDD electrode, Anal. Methods 9 (2017) 1627–1633.
[54] E. Yıldırım, R. Gürkan, N. Altunay, A New Ultrasonic Thermostatic-Assisted Cloud Point Extraction/Spectrophotometric Method for the Preconcentration and Determination of Bisphenol A in Food, Milk, and Water Samples in Contact with Plastic Products, Food Anal. Meth. 10 (2017) 1765–1776.
[55] J. Vichapong, R. Burakham, S. Srijaranai, Air-Agitated Cloud-Point Extraction Coupled with High-Performance Liquid Chromatography for Determination of Heterocyclic Aromatic Amines in Smoked Sausages, Food Anal. Meth. 10 (2017) 1645–1652.
[56] H.I. Ulusoy, H. Acıdereli, S. Ulusoy, S. Erdoğan, Development of a New Methodology for Determination of Vitamin B9 at Trace Levels by Ultrasonic-Assisted Cloud Point Extraction Prior to HPLC, Food Anal. Meth. 10 (2017) 799–808.
[57] W.I. Mortada, I.M.M. Kenawy, G.G. El-Gamal, S.M.N. Moalla, A micro mixed micelle-mediated preconcentration procedure for spectrophotometric determination of uranium in real and synthetic samples, J. Radioanal. Nucl. Chem. 313 (2017) 69–77.
[58] H. Zheng, J. Hong, X. Luo, S. Li, M. Wang, B. Yang, M. Wang, Combination of sequential cloud point extraction and hydride generation atomic fluorescence spectrometry for preconcentration and determination of inorganic and methyl mercury in water samples, Microchem. J. 145 (2019) 806–812.
[59] P.R. More, S.S. Arya, A novel, green cloud point extraction and separation of phenols and flavonoids from pomegranate peel: An optimization study using RCCD, J. Environ. Chem. Eng. 7 (2019) 103306.
[60] N. Guo, Y.-W. Jiang, P. Kou, Z.-M. Liu, T. Efferth, Y.-Y. Li, Y-J. Fu, Application of integrative cloud point extraction and concentration for the

analysis of polyphenols and alkaloids in mulberry leaves, J. Pharm. Biomed. Anal. 167 (2019) 132–139.

[61] N.K. Temel, B. Kuş, R. Gürkan, A new ion-pair ultrasound assisted-cloud point extraction approach for determination of trace V(V) and V(IV) in edible vegetal oils and vinegar by spectrophotometry, Microchem. J. 150 (2019) 104139.

[62] A. Shokrollahi, M. Refahi, Development of cloud point extraction-scanometry, for the preconcentration and determination of colorless species: application for the determination of phenylalanine, Quim. Nova 42 (2019) 36–41.

[63] H. Liang, Q. Chen, C. Xu, X. Shen, Selective cloud point extraction of uranium from thorium and lanthanides using Cyanex 301 as extractant, Sep. Purif. Technol. 210 (2019) 835–842.

[64] A. Thongsaw, R. Sananmuang, Y. Udnan, G.M. Ross, W.C. Chaiyasith, Dual-cloud point extraction for speciation of mercury in water and fish samples by electrothermal atomic absorption spectrometry, Spectroc. Acta Pt. B-Atom. Spectr. 160 (2019) 105685.

[65] L. Chen, Z. Lei, K. Hu, S. Yang, X. Wen, Non-aqueous phase hydride generation and determination of trace bismuth by atomic fluorescence spectrometry, Microchem. J. 137 (2018) 329–333.

[66] Z. Lei, L. Chen, K. Hu, S. Yang, X. Wen, Non-aqueous phase cold vapor generation and determination of trace cadmium by atomic fluorescence spectrometry, Spectroc. Acta Pt. A-Molec. Biomolec. Spectr. 203 (2018) 522–527.

[67] N.K. Temel, R. Gürkan, Preconcentration and Determination of Trace Vanadium(V) in Beverages by Combination of Ultrasound Assisted-cloud Point Extraction with Spectrophotometry, Acta Chim. Slov. 65 (2018) 138–149.

[68] M. Masrournia, A. Vaziry, Preconcentration of Ti(IV) in Ore and Water by Cloud Point Extraction and Determination by UV-Vis Spectrophotometry, J. Anal. Chem. 73 (2018) 128–132.

[69] L. Khalafi, P. Doolittle, J. Wright, Speciation and Determination of Low Concentration of Iron in Beer Samples by Cloud Point Extraction, J. Chem. Educ. 95 (2018) 463–467.

[70] R.P. Urio, J.C. Masini, Determination of Simazine and Atrazine in River Water by Cloud Point Extraction and High-Performance Liquid Chromatography, Anal. Lett. 50 (2017) 1065–1074.

[71] N.K. Temel, R. Gürkan, Extraction, Preconcentration, and Quantification of Low Levels of Free Formaldehyde from Some Beverage Matrices by Combination of Ultrasound-Assisted-Cloud Point Extraction with Spectrophotometry, Food Anal. Meth. 10 (2017) 4024–4037.

[72] M. Wang, Y. Zhong, J. Qin, Z. Zhang, S. Li, B. Yang, Determination of total selenium in food samples by d-CPE and HG-AFS, Food Chem. 227 (2017) 329–334.

[73] J.K. Andrade, C.K. Andrade, M.L. Felsner, S.P. Quináia, V.E. Anjos, Pre-concentration and speciation of inorganic antimony in bottled water and natural water by cloud point extraction with Electrothermal Atomic Absorption Spectrometry, Microchem. J. 133 (2017) 222–230.

[74] E. Kazemi, S. Dadfarnia, A.M.H. Shabani, M.R. Fattahi, J. Khodaveisi, Indirect spectrophotometric determination of sulfadiazine based on localized surface plasmon resonance peak of silver nanoparticles after cloud point extraction, Spectroc. Acta Pt. A-Molec. Biomolec. Spectr. 187 (2017) 30–35.

[75] V.C. Santos-Ebinuma, A.M. Lopes, A. Converti, A.P. Júnior, C.O. Rangel-Yagui, Behavior of Triton X-114 cloud point in the presence of inorganic electrolytes, Fluid Phase Equilib. 360 (2013) 435–438.
[76] M.M. Hamed, R.F. Aglan, Removal of Arsenazo□III from liquid radioactive waste by cloud point extraction, J. Radioanal. Nucl. Chem. 321 (2019) 917–926.
[77] J. Gui, C. Huang, J. Yuan, Q. Huang, F. Long, A. Ma, J. Pan, Handy cloud point extraction coupled with inductively coupled plasma mass spectrometry for analysis of trace zirconium in complex biological samples, Microchem. J. 138 (2018) 190–196.
[78] D. Snigur, A. Chebotarev, V. Dubovyiy, D. Barbalat, K. Bevziuk, Salicylic acid assisted cloud point extraction at room temperature: Application for preconcentration and spectrophotometric determination of molybdenum(VI), Microchem. J. 142 (2018) 273–278.
[79] J. Xu, Y. Li, C. Li, R. Zhang, Y. Xiao, Hexafluoroisopropanol-mediated cloud point extraction of organic pollutants in water with analysis by high-performance liquid chromatography, Anal. Bioanal. Chem. 409 (2017) 4559–4569.
[80] N. Pourreza, R. Mirzajani, J. Burromandpiroze, Fluorescence detection of vitamin B12 in human plasma and urine samples using silver nanoparticles embedded in chitosan in micellar media, Anal. Methods 9 (2017) 4052–4059.
[81] S. Tiwari, M.K. Deb, B.K. Sen, Cloud point extraction and diffuse reflectance-Fourier transform infrared spectroscopic determination of chromium(VI): A probe to adulteration in food stuffs, Food Chem. 221 (2017) 47–53.
[82] M. Aswathi, S. Mathai, S.C. Joseph, V.M. Biju, Room Temperature Ionic Liquid, cetyl pyridinium naphthenate supported cloud point extractive separation and ultra trace determination of copper in blood and environmental samples, Sep. Sci. Technol. 52 (2017) 2540–2546.
[83] R. Gürkan, N. Altunay, N. Gürkan, Extraction, preconcentration and spectrophotometric determination of trace levels of thiosulfate in environmental waters, J. Iran Chem. Soc. 14 (2017) 1033–1049.
[84] D. Yıldız, M. Demir, Flame Atomic Absorption Determination of Copper in Environmental Water with Cloud Point Extraction Using Isonitrosoacetophenone 2-Aminobenzoylhydrazone, J. Anal. Chem. 74 (2019) 437–443.
[85] Y. Sürme, A.T. Bişgin, M. Uçan, İ. Narin, Cloud Point Extraction and Flame Atomic Absorption Spectrometric Determination of Cd(II) in Industrial and Environmental Samples, J. Anal. Chem. 73 (2018) 140–144.
[86] X. Luo, H. Zheng, Z. Zhang, M. Wang. B. Yang, L. Huang, M. Wang, Cloud point extraction for simultaneous determination of 12 phenolic compounds by high performance liquid chromatography with fluorescence detection, Microchem. J. 137 (2018) 148–154.
[87] K. Saridal, H.İ. Ulusoy, A simple methodology based on cloud point extraction prior to HPLC-PDA analysis for tetracycline residues in food samples, Microchem. J. 150 (2019) 104170.
[88] X. Luo, J. Hong, H. Zheng, J. Qin, M. Wang, B. Yang, A rapid synergistic cloud point extraction for nine alkylphenols in water using high performance liquid chromatography and fluorescence detection, J. Chromatogr. A 1611 (2020) 460606.
[89] N. Altunay, R. Gürkan, U. Orhan, Indirect determination of the flavor enhancer maltol in foods and beverages through flame atomic absorption spectrometry after ultrasound assisted-cloud point extraction, Food Chem. 235 (2017) 308–317.

[90] Y. Serfor-Armah, D. Carboo, R.K. Akuamoah, A. Chatt, Micelle-mediated extraction and neutron activation determination of nanogram levels of vanadium in seaweeds, J. Radioanal. Nucl. Chem. 318 (2018) 2039–2047.
[91] G. Blanchet-Chouinard, D. Larivière, Determination of Pb in environmental samples after cloud point extraction using crown ether, Talanta 179 (2018) 300–306.
[92] A.P. Nambiar, M. Sanyal, P.S. Shrivastav, Performance Evaluation and Thermodynamic Studies for the Simultaneous Cloud Point Extraction of Erythrosine and Tartrazine Using Mixed Micelles in Food Samples, Food Anal. Meth. 10 (2017) 3471–3480.
[93] Z.F. Akl, Sensitive quantification of uranium using cloud point extraction coupled with inductively coupled plasma-optical emission spectrometry, J. Radioanal. Nucl. Chem. 315 (2018) 21–28.
[94] N. Altunay, Utility of ultrasound assisted-cloud point extraction and spectrophotometry as a preconcentration and determination tool for the sensitive quantification of mercury species in fish samples, Spectroc. Acta Pt. A-Molec. Biomolec. Spectr. 189 (2018) 167–175.
[95] W. Wei, X-B. Yin, X-W. He, pH-mediated dual-cloud point extraction as a preconcentration and clean-up technique for capillary electrophoresis determination of phenol and m-nitrophenol, J. Chromatogr. A 1202 (2008) 212–215.
[96] A. Melnyk, J. Namieśnik, L. Wolska, Theory and recent applications of coacervate-based extraction techniques, Trac-Trends Anal. Chem. 71 (2015) 282–292.
[97] N. Gissawong, S. Boonchiangma, S. Mukdasai, S. Srijaranai, Vesicular supramolecular solvent-based microextraction followed by high performance liquid chromatographic analysis of tetracyclines, Talanta 200 (2019) 203–211.
[98] Q. Salamat, Y. Yamini, M. Moradi, M. Karimi, M. Nazraz, Novel generation of nano-structured supramolecular solvents based on an ionic liquid as a green solvent for microextraction of some synthetic food dyes, New J. Chem. 42 (2018) 19252–19259.
[99] S.B. Mammana, P. Berton, A.B. Camargo, G.E. Lascalea, J.C. Altamirano, Coprecipitation-assisted coacervative extraction coupled to high performance liquid chromatography: An approach for determining organophosphorus pesticides in water samples, Electrophoresis 38 (2017) 1334–1343.
[100] J. Xu, M. Niu, Y. Xiao, Hexafluoroisopropanol-induced catanionic-surfactants-based coacervate extraction for analysis of lysozyme, Anal. Bioanal. Chem. 409 (2017) 1281–1289.
[101] J. Xu, X. Li, C. Li, J. Chen, Y. Xiao, Hexafluoroisopropanol-induced salt-free catanionic surfactant coacervate extraction method for determination of fluoroquinolones in milk samples, Food Chem. 242 (2018) 122–130.
[102] K. Seebunrueng, C. Dejchaiwatana, Y. Santaladchaiyakit, S. Srijaranai, Development of supramolecular solvent based microextraction prior to high performance liquid chromatography for simultaneous determination of phenols in environmental water, RSC Adv. 7 (2017) 50143–50149.
[103] N. Feizi, Y. Yamini, M. Moradi, M. Karimi, Q. Salamat, H. Amanzadeh, A new generation of nano-structured supramolecular solvents based on propanol/gemini surfactant for liquid phase microextraction, Anal. Chim. Acta 953 (2017) 1–9.
[104] C.-W. Chen, F.-Y. Liao, Y.-C. Lin, T.-J. Hsieh, J.-R. Weng, C.-H. Feng, Microwave-assisted derivatization combined with coacervative extraction for

determining glutathione in biomatrix samples, followed by capillary liquid chromatography, Talanta 199 (2019) 464–471.
[105] W. Ahmad, A.A. Al-Sibaai, A.S. Bashammakh, H. Alwael, M.S. El-Shahawi, Recent advances in dispersive liquid-liquid microextraction for pesticide analysis, Trac-Trends Anal. Chem. 72 (2015) 181–192.
[106] A.B. Lara, C. Caballo, M.D. Sicilia, S. Rubio, Halogen bonding for increasing efficiency in liquid-liquid microextraction: Application to the extraction of hexabromocyclododecane enantiomers in river water, J. Chromatogr. A 1600 (2019) 95–104.
[107] M. Martinefski, N. Feizi, M.L. Lunar, S. Rubio, Supramolecular solvent-based high-throughput sample treatment platform for the biomonitoring of PAH metabolites in urine by liquid chromatography-tandem mass spectrometry, Chemosphere 237 (2019) 124525.
[108] F. Accioni, D. García-Gómez, E. Girela, S. Rubio, SUPRAS extraction approach for matrix-independent determination of amphetamine-type stimulants by LC-MS/MS, Talanta 182 (2018) 574–582.
[109] A.N. Anthemidis, K.G. Ioannou, Recent developments in homogeneous and dispersive liquid-liquid extraction for inorganic elements determination. A review, Talanta 80 (2009) 413–421.
[110] S.C. Cunha, J.O. Fernandes, Extraction techniques with deep eutectic solvents, Trac-Trends Anal. Chem. 105 (2018) 225–239.
[111] G. Li, K.H. Row, Utilization of deep eutectic solvents in dispersive liquid-liquid microextraction, Trac-Trends Anal. Chem. 120 (2019) 115651.
[112] A.K. Dwamena, Recent Advances in Hydrophobic Deep Eutectic Solvents for Extraction, Separations 6 (2019) 9.
[113] A. Shishov, A. Pochivalov, L. Nugbienyo, V. Andruch, A. Bulatov, Deep. Eutectic solvents are not only effective extractants, Trac-Trends Anal. Chem. 129 (2020) 115956.
[114] T. Khezeli, A. Daneshfar, R. Sahraei, Emulsification liquid–liquid microextraction based on deep eutectic solvent: An extraction method for the determination of benzene, toluene, ethylbenzene and seven polycyclic aromatic hydrocarbons from water samples, J. Chromatogr. A 1425 (2015) 25–33.
[115] A. Shishov, A. Gorbunov, L. Moskvin, A. Bulatov, Decomposition of deep eutectic solvents based on choline chloride and phenol in aqueous phase, J. Mol. Liq. 301 (2020) 112380.
[116] A. Shishov, A. Gerasimov, D. Nechaeva, N. Volodina, E. Bessonova, A. Bulatov, An effervescence-assisted dispersive liquid–liquid microextraction based on deep eutectic solvent decomposition: Determination of ketoprofen and diclofenac in liver, Microchem. J. 156 (2020) 104837.
[117] A. Thongsaw, Y. Udnan, G.M. Ross, W.C. Chaiyasith, Speciation of mercury in water and biological samples by eco-friendly ultrasound-assisted deep eutectic solvent based on liquid phase microextraction with electrothermal atomic absorption spectrometry, Talanta 197 (2019) 310–318.
[118] P. Menghwar, E. Yilmaz, S.T.H. Sherazi, M. Soylak, A sensitive and selective deep eutectic solvent-based ultrasound-assisted liquid phase microextraction procedure for separation-preconcentration and determination of copper in olive oil and water samples, Sep. Sci. Technol. 54 (2019) 2431–2439.
[119] T. Unutkan, B. Tışlı, Z. Tekin, G. Çetin, S. Bakırdere, Ultrasound assisted deep eutectic solvent based microextraction-slotted quartz tube-flame atomic

absorption spectrometry for the determination of cadmium, Spectroc. Acta Pt. B-Atom. Spectr. 155 (2019) 1–3.
[120] A. Shishov, N. Volodina, D. Nechaeva, S. Gagarinova, A. Bulatov, An automated homogeneous liquid-liquid microextraction based on deep eutectic solvent for the HPLC-UV determination of caffeine in beverages, Microchem. J. 144 (2019) 469–473.
[121] X. Li, M. Wang, J. Zhao, H. Guo, X. Gao, Z. Xiong, L. Zhao, Ultrasound-assisted emulsification liquid phase microextractionmethod based on deep eutectic solvent as extraction solvent fordetermination of five pesticides in traditional Chinese medicine, J. Pharm. Biomed. Anal. 166 (2019) 213–221.
[122] A.H. Panhwar, M. Tuzen, T.G. Kazi, Deep eutectic solvent based advance microextraction method for determination of aluminum in water and food samples: Multivariate study, Talanta 178 (2018) 588–593.
[123] P. Li, J. Ye, Y. Zhang, Z. Wang, S. Ren, X. Li, Y. Jin, Centrifugation free and air-assisted liquid-liquid microextraction based on deep eutectic solvent for determination of rare ginsenosides in *Kang'ai* injection, Microchem. J. 142 (2018) 313–320.
[124] R.A. Zounr, M. Tuzen, M.Y. Khuhawar, A simple and green deep eutectic solvent based air assisted liquid phase microextraction for separation, preconcentration and determination of lead in water and food samples by graphite furnace atomic absorption spectrometry, J. Mol. Liq. 259 (2018) 220–226.
[125] A.G. Moghadam, M. Rajabi, A. Asghari, Efficient and relatively safe emulsification microextraction using a deep eutectic solvent for influential enrichment of trace main anti-depressant drugs from complicated samples, J. Chromatogr. B 1072 (2018) 50–59.
[126] F. Aydin, E. Yilmaz, M. Soylak, Vortex assisted deep eutectic solvent (DES)-emulsification liquid-liquid microextraction of trace curcumin in food and herbal tea samples, Food Chem. 243 (2018) 442–447.
[127] R.A. Zounr, M. Tuzen, N. Deligonul, M.Y. Khuhawar, A highly selective and sensitive ultrasonic assisted dispersive liquid phase microextraction based on deep eutectic solvent for determination of cadmium in food and water samples prior to electrothermal atomic absorption spectrometry, Food Chem. 253 (2018) 277–283.
[128] R.A. Zounr, M. Tuzen, M.Y. Khuhawar, Novel ultrasonic□assisted deep eutectic solvent□based dispersive liquid–liquid microextraction for determination of vanadium in food samples by electrothermal atomic absorption spectrometry: A multivariate study, Appl. Organomet. Chem. 32 (2018) e4144.
[129] A.H. Panhwar, M. Tuzen, T.G. Kazi, Ultrasonic assisted dispersive liquid-liquid microextraction method based on deep eutectic solvent for speciation, preconcentration and determination of selenium species (IV) and (VI) in water and food samples, Talanta 175 (2017) 352–358.
[130] F. Aydin, E. Yilmaz, M. Soylak, A simple and novel deep eutectic solvent based ultrasound-assisted emulsification liquid phase microextraction method for malachite green in farmed and ornamental aquarium fish water samples, Microchem. J. 132 (2017) 280–285.
[131] L. Liu, T. Zhu, Emulsification liquid–liquid microextraction based on deep eutectic solvents: an extraction method for the determination of sulfonamides in water samples, Anal. Methods 9 (2017) 4747–4753.
[132] C. Karadaş, D. Kara, Emulsification liquid–liquid microextraction method based on a deep eutectic solvent for separation and preconcentration of lead from

environmental water samples, Water Sci. Technol.-Water Supply 19 (2019) 864–870.

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

[134] S. Babaee, A. Daneshfar, R. Sahraei, Deep eutectic solvent-based emulsification liquid–liquid microextraction coupled with gas chromatography for the determination of thiophenols in water samples, Anal. Methods 11 (2019) 1663–1670.

[135] L. Nugbienyo, A. Shishov, S. Garmonov, L. Moskvin, V. Andruch, A. Bulatov, Flow method based on liquid-liquid extraction using deep eutectic solvent for the spectrofluorimetric determination of procainamide in human saliva, Talanta 168 (2017) 307–312.

[136] N. Lamei, M. Ezoddin, K. Abdi, Air assisted emulsification liquid-liquid microextraction based on deep eutectic solvent for preconcentration of methadone in water and biological samples, Talanta 165 (2017) 176–181.

[137] Z.M. Memon, E. Yilmaz, A.M. Shah, T.G. Kazi, B.R. Devrajanl, M. Soylak, A green ultrasonic-assisted liquid–liquid microextraction technique based on deep eutectic solvents for flame atomic absorption spectrometer determination of trace level of lead in tobacco and food samples, J. Iran Chem. Soc. 16 (2019) 687–694.

[138] M. Soylak, S. Deryol, F. Uzcan, A new green microextraction method for traces Brown HT (E155) by using deep eutectic solvents prior to its spectrophotometric determination, Int. J. Environ. Anal. Chem. (2019) *in press*.

[139] E. Yilmaz, M. Soylak, A novel and simple deep eutectic solvent based liquid phase microextraction method for rhodamine B in cosmetic products and water samples prior to its spectrophotometric determination, Spectroc. Acta Pt. A-Molec. Biomolec. Spectr. 202 (2018) 81–86.

[140] I. Pacheco-Fernández, D.W. Allgaier-Díaz, G. Mastellone, C. Cagliero, D.D. Díaz, V. Pino, Biopolymers in sorbent-based microextraction methods, Trac-Trends Anal. Chem. 125 (2020) 115839.

[141] N. Altunay, A. Elik, R. Gürkan, Monitoring of some trace metals in honeys by flame atomic absorption spectrometry after ultrasound assisted-dispersive liquid liquid microextraction using natural deep eutectic solvent, Microchem. J. 147 (2019) 49–59.

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

[143] A. Elik, A. Demirbas, N. Altunay, Developing a new and simple natural deep eutectic solvent based ultrasonic-assisted microextraction procedure for determination and preconcentration of As and Se from rice samples, Anal. Methods 11 (2019) 3429–3438.

[144] M. Pourmohammad, M. Faraji, S. Jafarinejad, Extraction of chromium (VI) in water samples by dispersive liquid–liquid microextraction based on deep eutectic solvent and determination by UV–Vis spectrophotometry, Int. J. Environ. Anal. Chem. 100 (2020) 1146–1159.

[145] J.M. Kokosa, Selecting an extraction solvent for a greener liquid phase microextraction (LPME) mode-based analytical method, Trac-Trends Anal. Chem. 118 (2019) 238–247.
[146] R. Marcinkowska, K. Konieczna, Ł. Marcinkowski, J. Namieśnik, A. Kloskowski, Application of ionic liquids in microextraction techniques: Current trends and future perspectives, Trac-Trends Anal. Chem. 119 (2019) 115614.
[147] Z. Lei, B. Chen, Y.-M. Koo, D.R. MacFarlane, Introduction: Ionic Liquids, Chem. Rev. 117 (2017) 6633–6635.
[148] M.J. Trujillo-Rodríguez, P. Rocío-Bautista, V. Pino, A.M. Afonso, Ionic liquids in dispersive liquid-liquid microextraction, Trac-Trends Anal. Chem. 51 (2013) 87–106.
[149] I. Rykowska, J. Ziemblińska, I. Nowak, Modern approaches in dispersive liquid-liquidmicroextraction (DLLME) based on ionic liquids: A review, J. Mol. Liq. 259 (2018) 319–339.
[150] M. Baghdadi, F. Shemirani, In situ solvent formation microextraction based on ionic liquids: A novel sample preparation technique for determination of inorganic species in saline solutions, Anal. Chim. Acta 634 (2009) 186–191.
[151] C. Yao, J.L. Anderson, Dispersive liquid–liquid microextraction using an in situ metathesis reaction to form an ionic liquid extraction phase for the preconcentration of aromatic compounds from water, Anal. Bioanal. Chem. 395 (2009) 1491–1502.
[152] F.T. Tarhan, M. Antep, M. Merdivan, Vortex assisted in situ ionic liquid dispersive liquid–liquid microextraction for preconcentration of uranyl ion in water samples before spectrophotometric detection, J. Radioanal. Nucl. Chem. 320 (2019) 1–7.
[153] H. Piao, Y. Jiang, Z. Qin, S. Tao, P. Ma, Y. Sun, X. Wang, D. Song, Development of a novel acidic task-specific ionic liquid-based effervescence assisted microextraction method for determination of triazine herbicides in tea beverage, Talanta 208 (2020) 120414.
[154] J. Wu, Z. Xu, X. Pan, Y. Shi, X. Bao, J. Li, Y. Tong, H. Tang, S. Ma, X. Wang, J. Lyu, Combination of in situ metathesis reaction with a novel “magnetic effervescent tablet-assisted ionic liquid dispersive microextraction” for the determination of endogenous steroids in human fluids, Anal. Bioanal. Chem. 410 (2018) 2921–2935.
[155] J. Yang, C. Fan, D. Kong, G. Tang, W. Zhang, H. Dong, Y. Liang, D. Wang, Y. Cao, Synthesis and application of imidazolium-based ionic liquids as extraction solvent for pretreatment of triazole fungicides in water samples, Anal. Bioanal. Chem. 410 (2018) 1647–1656.
[156] M. Zeeb, H. Farahani, Trace Determination of Duloxetine in Human Plasma by a Novel Ionic Liquid-Based Ultrasound-Assisted In Situ Solvent Formation Microextraction and High-Performance Liquid Chromatography, Anal. Bioanal. Chem. Res. 5 (2018) 183–193.
[157] M. Khiat, I. Pacheco-Fernández, V. Pino, T. Benabdallah, J.H. Ayala, A.M. Afonso, A guanidinium ionic liquid-based surfactant as an adequate solvent to separate and preconcentrate cadmium and copper in water using in situ dispersive liquid–liquid microextraction, Anal. Methods 10 (2018) 1529–1537.
[158] M. Kaynaker, M. Antep, M. Merdivan, Determination of Tetracyclines in Milk, Eggs and Honey Using in-situ Ionic Liquid Based Dispersive Liquid–Liquid Microextraction, J. Anal. Chem. 73 (2018) 23–29.

[159] J.I. Cacho, N. Campillo, P. Viñas, M. Hernández-Córdoba, In situ ionic liquid dispersive liquid-liquid microextraction coupled to gas chromatography-mass spectrometry for the determination of organophosphorus pesticides, J. Chromatogr. A 1559 (2018) 95–101.
[160] S. Sadeghi. N. Sarrafi, A dispersive liquid–liquid microextraction based on a task-specific ionic liquid for enrichment of trace quantity of cadmium in water and food samples, J. Iran Chem. Soc. 15 (2018) 1913–1920.
[161] S.A. Pierson, M.J. Trujillo-Rodríguez, J.L. Anderson, Rapid analysis of ultraviolet filters using dispersive liquid–liquid microextraction coupled to headspace gas chromatography and mass spectrometry, J. Sep. Sci. 41 (2018) 3081–3088.
[162] F. Abbasi-Daronjoughi, A. Tamaddon, H.A. Panahi, In situ solvent formation microextraction based on a new ionic liquid for green preconcentration of trace amount of Cu (II) ions in water samples, Sep. Sci. Technol. 53 (2018) 2401–2408.
[163] K. Wang, J. Jiang, M. Kang, D. Li, S. Zang, S. Tian, H. Zhang, A. Yu, Z. Zhang, Magnetical hollow fiber bar collection of extract in homogenous ionic liquid microextraction of triazine herbicides in water samples, Anal. Bioanal. Chem. 409 (2017) 2569–2579.
[164] M.R. Jamali, B. Soleimani, R. Rahnama, S.H.A. Rahimi, Development of an in situ solvent formation microextraction and preconcentration method based on ionic liquids for the determination of trace cobalt (II) in water samples by flame atomic absorption spectrometry, Arab. J. Chem. 10 (2017) 321–327.
[165] S. Molaei, S. Seidi, A. Saleh, V. Ghoulipour, Ionic liquid based in situ solvent formation microextraction followed by on-line phase separation coupled with cold vapor-atomic absorption spectrometry for mercury determination in seafood samples, Anal. Methods 9 (2017) 5189–5197.
[166] V. Zare-Shahabadi, P. Asaadi, F. Abbasitabar, A. Shirmardi, Determination of Traces of Ni, Cu, and Zn in Wastewater and Alloy Samples by Flame-AAS after Ionic Liquid-Based Dispersive Liquid Phase Microextraction, J. Braz. Chem. Soc. 28 (2017) 887–894.
[167] C. Zhang, C. Cagliero, S.A. Pierson, J.L. Anderson, Rapid and sensitive analysis of polychlorinated biphenyls and acrylamide in food samples using ionic liquid-based in situ dispersive liquid-liquid microextraction coupled to headspace gas chromatography, J. Chromatogr. A 1481 (2017) 1–11.
[168] L. Li, M. Huang, J. Shao, B. Lin, Q. Shen, Rapid determination of alkaloids in *Macleaya cordata* using ionic liquid extraction followed by multiple reaction monitoring UPLC–MS/MS analysis, J. Pharm. Biomed. Anal. 135 (2017) 61–66.
[169] Y. Zhang, X. Yang, J. Wang, W. Zhou, R. Lu, H. Gao, S. Zhang, In situ solvent formation microextraction combined with magnetic dispersive micro-solid-phase extraction for the determination of benzoylurea insecticides in water samples, J. Sep. Sci. 40 (2017) 442–448.
[170] R. Su, D. Li, L. Wu, J. Han, W. Lian, H. Yang, Determination of triazine herbicides in juice samples by microwave-assisted ionic liquid/ionic liquid dispersive liquid–liquid microextraction coupled with high-performance liquid chromatography, J. Sep. Sci. 40 (2017) 2950–2958.
[171] I. Pacheco-Fernández, V. Pino, J.H. Ayala, A.M. Afonso, Guanidinium ionic liquid-based surfactants as low cytotoxic extractants: Analytical performance in an in-situ dispersive liquid–liquid microextraction method for determining personal care products, J. Chromatogr. A 1559 (2018) 102–111.
[172] I. Pacheco-Fernández, V. Pino, J. Lorenzo-Morales, J.H. Ayala, A.M. Afonso, Salt-induced ionic liquid-based microextraction using a low cytotoxic

guanidinium ionic liquid and liquid chromatography with fluorescence detection to determine monohydroxylated polycyclic aromatic hydrocarbons in urine, Anal. Bioanal. Chem. 410 (2018) 4701–4713.

[173] J. Ziemblińska□Bernart, I. Nowak, I. Rykowska, Fast dispersive liquid–liquid microextraction based on magnetic retrieval of in situ formed an ionic liquid for the preconcentration and determination of benzophenone-type UV filters from environmental water samples, J. Iran Chem. Soc. 16 (2019) 661–671.

[174] H. Wang, L. Hu, W. Li, X. Yang, R. Lu, S. Zhang, W. Zhou, H. Gao, J. Li, In-syringe dispersive liquid-liquid microextraction based on the solidification of ionic liquids for the determination of benzoylurea insecticides in water and tea beverage samples, Talanta 162 (2017) 625–633.

[175] C. Fan, Y. Liang, H. Dong, G. Ding, W. Zhang, G. Tang, J. Yang, D. Kong, D. Wang, Y. Cao, In-situ ionic liquid dispersive liquid-liquid microextraction using a new anion-exchange reagent combined Fe_3O_4 magnetic nanoparticles for determination of pyrethroid pesticides in water samples, Anal. Chim. Acta 975 (2017) 20–29.

[176] Y. Lv, H. Bai, J. Yang, Y. He, Q. Ma, Direct Mass Spectrometry Analysis Using In-Capillary Dicationic Ionic Liquid-Based in Situ Dispersive Liquid−Liquid Microextraction and Sonic-Spray Ionization, Anal. Chem. 91 (2019) 6661–6668.

[177] M.J. Trujillo-Rodríguez, J.L. Anderson, In situ formation of hydrophobic magnetic ionic liquids for dispersive liquid-liquid microextraction, J. Chromatogr. A 1588 (2019) 8–16.

[178] M.J. Trujillo-Rodríguez, J.L. Anderson, In situ generation of hydrophobic magnetic ionic liquids in stir bar dispersive liquid-liquid microextraction coupled with headspace gas chromatography, Talanta 196 (2019) 420–428.

[179] A.N. Bowers, M.J. Trujillo-Rodríguez, M.Q. Farooq, J.L. Anderson, Extraction of DNA with magnetic ionic liquids using in situ dispersive liquid–liquid microextraction, Anal. Bioanal. Chem. 411 (2019) 7375–7385.

[180] M.J. Trujillo-Rodríguez, H. Nan, M. Varona, M.N. Emaus, I.D. Souza, J.L. Anderson, Advances of Ionic Liquids in Analytical Chemistry, Anal. Chem. 91 (2019) 505–531.

[181] P.A. Albertsson, Partition of Proteins in Liquid Polymer–Polymer Two-Phase Systems, Nature 182 (1958) 709–711.

[182] M. Iqbal, Y. Tao, S. Xie, Y. Zhu, D. Chen, X. Wang, L. Huang, D. Peng, A. Sattar, M.A. Shabbir, H.I. Hussain, S. Ahmed and Z. Yuan, Aqueous two-phase system (ATPS): an overview and advances in its applications, Biological procedures online, 18 (2016) 18.

[183] Y.K. Yau, C.W. Ooi, E.-P. Ng, J.C.-W. Lan, T.C. Ling and P.L. Show, Current applications of different type of aqueous two-phase systems, Bioresour. Bioprocess. 2 (2015) 49.

[184] R.R.G. Soares, A.M. Azevedo, P. Fernandes, V. Chu, J.P. Conde, M.R. Aires-Barros, A simple method for point-of-need extraction, concentration and rapid multi-mycotoxin immunodetection in feeds using aqueous two-phase systems, J. Chromatogr. A 1511 (2017) 15-24.

[185] S. Ghaffari, J.R. Shahrouzi, F. Towfighi, A.B. Khoshfetrat, Partitioning of cefazolin in aqueous two-phase systems containing poly (ethylene glycol) and sodium salts (citrate, tartrate, and sulphate), Fluid Phase Equilibr. 488 (2019) 54-61.

[186] A.W. Vieira, G. Molina, A.B. Mageste, G. D. Rodrigues, L.R. de Lemos, Partitioning of salicylic and acetylsalicylic acids by aqueous two-phase systems: Mechanism aspects and optimization study, J. Mol. Liq. 296 (2019) 111775.
[187] R.C. Assis, B.A. de Araújo Faria, C.L. Caldeira, A.B. Mageste, L.R. de Lemos, G.D. Rodrigues, Extraction of arsenic(III) in aqueous two-phase systems: A new methodology for determination and speciation analysis of inorganic arsenic, Microchem. J. 147 (2019) 429-436.
[188] Z. Sun, Y. Lu, L. Zhu, W. Liu, Y. Qu, N. Lin, P. Yu, Simultaneous separation, concentration and determination of trace fluoroquinolone antibiotics in environmental samples using a polymer aqueous two□phase system coupled with HPLC, J. Chem. Technol. Biotechnol. 94 (2019) 2917-2927.
[189] X. Xie, D. Zhu, W. Zhang, W. Huai, K. Wang, X. Huang, L. Zhou, H. Fan, Microwave-assisted aqueous two-phase extraction coupled with high performance liquid chromatography for simultaneous extraction and determination of four flavonoids in Crotalaria sessiliflora L, Ind. Crops Prod. 95 (2017) 632–642.
[190] D. Guo, L. Ni, L. Wang, L. Shao, Separation/Extraction/Detection of Chloramphenicol Using Binary Small Molecule Alcohol-Salt Aqueous Two-phase System Coupled with High-performance Liquid Chromatography, Chem. Res. Chinese Universities 35 (2019) 209–215.
[191] D. Guo, L. Ni, L. Wang, L. Shao, Separation and determination of tetracycline hydrochloride in real water samples using binary small molecule alcohol□salt aqueous two□phase system coupled with high□performance liquid chromatography, Chirality 31 (2019) 658–668.
[192] L. Ma, W. Tong, L. Du, S. Huang, J. Wei, D. Xiao, Optimization of an Aqueous Two-Phase System for the Determination of Trace Ethyl Carbamate in Red Wine, J. Food Prot. 82 (2019) 1377–1383.
[193] L. Zhu, Y. Lu, Z. Sun, J. Han, Z. Tan, The application of an aqueous two-phase system combined with ultrasonic cell disruption extraction and HPLC in the simultaneous separation and analysis of solanine and Solanum nigrum polysaccharide from Solanum nigrum unripe fruit, Food Chem. 304 (2020) 125383.
[194] H. Zeng, X. Xi, Y. Huang, J. Chen, Y. Liu, Y. Zhang, X. Mai, J. Deng, H. Fan, W. Zhang, Enantioseparation and determination of triazole fungicides in vegetables and fruits by aqueous two-phase extraction coupled with online heartcutting two-dimensional liquid chromatography, Food Chemistry 301 (2019) 125265.
[195] W. Praikaew, W. Kiatkittipong, K. Kiatkittipong, S. Assabumrungrat, F. Aiouache,V. Najdanovic-Visak, Liquid−Liquid Phase Equilibria of Aqueous Biphasic Systems Based on Glycerol Formal: Application on Tetracycline Recovery from Water, J. Chem. Eng. Data 64 (2019) 4856−4862.
[196] F.S. Buarque, C.M.F. Soares, M.N. Marques, R.C.M. Miranda, E.B. Cavalcanti, R.L. Souza, Á.S. Lima, Simultaneous concentration and chromatographic detection of water pesticides traces using aqueous two-phase system composed of tetrahydrofuran and fructose, Microchem. J. 147 (2019) 303–310.
[197] H.F.D. Almeida, M.G. Freire, I.M. Marrucho, Improved monitoring of aqueous samples by the preconcentration of active pharmaceutical ingredients using ionic-liquid-based systems, Green Chem. 19 (2017) 4651-4659.
[198] A. Dimitrijević, L. Ignjatović, A. Tot, M. Vraneš, N. Zec, S. Gadžurić, T. Trtić-Petrović, Simultaneous extraction of pesticides of different polarity applying

aqueous biphasic systems based on ionic liquids, J. Mol. Liq. 243 (2017) 646–653.

[199] T. Yao, S. Yao, Magnetic ionic liquid aqueous two-phase system coupled with high-performance liquid chromatography: A rapid approach for determination of chloramphenicol in water environment, J. Chromatogr. A, 1481 (2017) 12–22.

[200] M.G. Bogdanov, I. Svinyarov, Analysis of acetylcholinesterase inhibitors by extraction in choline saccharinate aqueous biphasic systems, J. Chromatogr. A 1559 (2018) 62–68.

[201] T.B.V. Dinis, H. Passos, D.L.D. Lima, A.C.A. Sousa, J.A.P. Coutinho, V.I. Esteves, M.G. Freire, Simultaneous extraction and concentration of water pollution tracers using ionic-liquid-based systems, J. Chromatogr. A 1559 (2018) 69–77.

[202] J. Ren, Z. Li, J. Liu, Y. Pei, H. Wang, J. Wang, Choline derivative ionic liquids-based aqueous two-phase systems: Phase diagrams and partition of purine alkaloids, J. Chem. Thermodynamics 118 (2018) 51–57.

[203] O. Sha, Y. Wang, X.-B. Chen, J. Chen, L. Chen, Determination of Paraquat in Environmental Water by Ionic Liquid-Based Liquid Phase Extraction with Direct Injection for HPLC, J. Anal. Chem 73 (2018) 862–868.

[204] T. Trtić-Petrović, A. Dimitrijević, N. Zdolšek, J. Đorđević, A. Tot, M. Vraneš, S. Gadžurić, New sample preparation method based on task-specific ionic liquids for extraction and determination of copper in urine and wastewater, Anal. Bioanal. Chem. 410 (2018) 155–166.

[205] M.F. Yee, G.N. Emmel, E.J. Yang, E. Lee, J.H. Paek, B.M. Wu, D.T. Kamei, Ionic Liquid Aqueous Two-Phase Systems for the Enhanced Paper-Based Detection of Transferrin and Escherichia coli, Front. Chem. 6 (2018) 486.

[206] R. González-Martín, I. Pacheco-Fernández, J.H. Ayala, A.M. Afonso, V. Pino, Ionic liquid-based miniaturized aqueous biphasic system to develop an environmental-friendly analytical preconcentration method, Talanta 203 (2019) 305–313.

[207] Q. Li, W. Liu, X. Zhu, Green Choline Amino Acid Ionic Liquid Aqueous Two-Phase Extraction Coupled with HPLC for Analysis Sunset Yellow in Beverages, Food Anal. Methods 12 (2019) 2527–2534.

[208] H. Tian, H. Fu, C. Xu, C. Xu, Simultaneous Determination of Three Herbicides in Honey Samples Using an Aqueous Biphasic System Coupled with HPLC–MS/MS, Chromatographia 82 (2019) 1571–1577.

[209] X. Zhu, S. Chen, H. Fu, Separation/Analysis Safranine T in Food Samples Using Surfactant/Ionic Liquid Aqueous Two-Phase Systems, Food Anal. Methods 10 (2017) 2764–2771.

[210] H. Tian, C. Xu, J. Cai, J. Xu, The aqueous biphasic system based on cholinium ionic liquids and nonionic surfactant and its application for triazine-based herbicides extraction, J. Chem. Thermodynamics 125 (2018) 41–49.

[211] H.M. Antep, T. Mumcu, K. Bostanci, S.S. Bozkurt, M. Merdivan, Ultrasound-assisted surfactant/ionic liquid aqueous two-phase system extraction prior to high performance liquid chromatography for the determination of tetracyclines in milk and honey samples, Turk J Chem 41 (2017) 955-966.

[212] Y. Wei, L. Kai, L. Zhongling, Z. Hanqi, J. Xiangqun, Novelty aqueous two-phase extraction system based on ionic liquid for determination of sulfonamides in blood coupled with high-performance liquid chromatography, Microchem. J. 136 (2018) 263–269.

[213] P. Li, P. Zhao, W. Liu, Y. Jiang, W. Wang, L. Bao, Y. Jin, X. Li, Determination of common ginsenosides in Kang'ai injection by aqueous two-phase extraction with deep eutectic solvents and HPLC-UV/DAD, Microchem. J. 137 (2018) 302–308.
[214] Y. Ma, Q. Wang, T. Zhu, Comparison of hydrophilic and hydrophobic deep eutectic solvents for pretreatment determination of sulfonamides from aqueous environments, Anal. Methods 11 (2019) 5901-5909.
[215] H. Zhang, Y. Wang, Y. Zhou, J. Chen, X. Wei, P. Xu, Aqueous Biphasic Systems Formed by Deep Eutectic Solvent and New-type salts for the High-performance Extraction of Pigments, Talanta 181 (2018) 210-216.
[216] J. Meng, Y. Wang, Y. Zhou, J. Chen, X. Wei, R. Ni, Z. Liu, F. Xu, Development of different deep eutectic solvent aqueous biphasic systems for the separation of proteins, RSC Adv. 9 (2019) 14116-14125.
[217] P. Xu, Y. Wang, J. Chen, X. Wei, W. Xu, R. Ni, J. Meng, Y. Zhou, Development of deep eutectic solvent-based aqueous biphasic system for the extraction of lysozyme, Talanta 202 (2019) 1-10.
[218] A. Chakraborty, K. Sen, Impact of pH and temperature on phase diagrams of different aqueous biphasic systems, J. Chromatogr. A 1433 (2016) 41–55.
[219] M.G. Freire, A.F.M. Cláudio, J.M.M. Araújo, J.A.P. Coutinho, I.M. Marrucho, J.N. Canongia Lopes, L.P.N. Rebelo, Aqueous Biphasic Systems: a Boost Brought About by Using Ionic Liquids, Chem. Soc. Rev. 41 (2012) 4966-4995.
[220] K.E. Gutowski, G.A. Broker, H.D. Willauer, J.G. Huddleston, R.P. Swatloski, J.D. Holbrey, R.D. Rogers, J. Am. Chem. Soc. 125 (2003) 6632–6633.
[221] M. Freemantle, Designer solvents - Ionic liquids may boost clean technology development, Chem. Eng. News 76 (1998) 32–37.
[222] Q. Zeng, Y. Wang, Y. Huang, X. Ding, J. Chen, K. Xu, Deep eutectic solvents as novel extraction media for protein partitioning, Analyst 139 (2014) 2565-2573.
[223] E.L. Smith, A.P. Abbott, K.S. Ryder, Deep Eutectic Solvents (DESs) and Their Applications, Chem. Rev. 114 (2014) 11060−11082.
[224] I. Wazeer, M. Hayyan, M.K. Hadj-Kalia, Deep Eutectic Solvents: Designer Fluids for Chemical Processes, J. Chem. Technol. Biotechnol 93 (2018) 945-958.
[225] H. Passos, D.J.P. Tavares, A.M. Ferreira, M.G. Freire, J.A.P. Coutinho, Are Aqueous Biphasic Systems Composed of Deep Eutectic Solvents Ternary or Quaternary Systems?, ACS Sustainable Chem. Eng. 4 (2016) 2881–2886.
[226] F.O. Farias, H. Passos, Á.S. Lima, M.R. Mafra, J.A.P. Coutinho, Is it Possible to Create Ternary-Like ABS with Deep Eutectic Solvents?, ACS Sustainable Chem. Eng. 5 (2017) 9402–9411.
[227] J.R. Vanderveen, J. Durelle, P.G. Jessop, Design and evaluation of switchable-hydrophilicity solvents, Green Chem. 16 (2014) 1187–1197.
[228] P.G. Jessop, D.J. Heldebrant, X. Li, C.A. Eckert, C.L. Liotta, Reversible nonpolar-to-polar solvent, Nature 436 (2005) 1102.
[229] P.G. Jessop, L. Phan, A. Carrier, S. Robinson, C.J. Dürr, J.R. Harjani, A solvent having switchable hydrophilicity, Green Chem. 12 (2010) 809–814.
[230] H.-K. Shih, T.-Y. Shu, V.K. Ponnusamy, J.-F. Jen, A novel fatty-acid-based in-tube dispersive liquid–liquid microextraction technique for the rapid determination of nonylphenol and 4-tert-octylphenol in aqueous samples using high-performance liquid chromatography–ultraviolet detection, Anal. Chim. Acta 854 (2015) 70–77.
[231] G. Lasarte-Aragonés, R. Lucena, S. Cárdenas, M. Valcárcel, Use of switchable solvents in the microextraction context, Talanta 131 (2015) 645–649.

[232] M.S. Arain, T.G. Kazi, H.I. Afridi, N. Khan, J. Ali, A innovative switchable polarity solvent, based on 1,8□diazabicyclo□[5.4.0]□ undec□7□ene and decanol was prepared for enrichment of aluminum in biological sample prior to analysis by flame atomic absorption spectrometry, Appl. Organomet. Chem. 32 (2018) e4157.

[233] F. Zare, M. Ghaedi, R. Jannesar, L. Tayebi, Switchable polarity solvents for preconcentration and simultaneous determination of amino acids in human plasma samples, New J. Chem. 42 (2018) 10007–10015.

[234] T.G. Kazi, S. Samejo, H.I. Afridi, A. Akhtar, J.A. Baig, A switchable ionic liquid with polarity swing□assisted regeneration properties used for the preconcentration of cadmium in biological samples, Appl. Organomet. Chem. 34 (2020) e5263.

[235] H. Wang, M. Xia, Y. Ling, F. Qian, J. Xu, Z. Wang, J. Li, X. Wang, Switchable hydrophilicity solvent based and solidification-assisted liquid-phase microextraction combined with GFAAS for quantification of trace soluble lead in raw bovine and derivative milk products, Food Addit. Contam. Part A-Chem. 36 (2019) 1654–1666.

[236] S. Erarpat, A. Cağlak, S. Bodur, S.D. Chormey, Ö.G. Engin, S. Bakirdere, Simultaneous Determination of Fluoxetine, Estrone, Pesticides, and Endocrine Disruptors in Wastewater by Gas Chromatography–Mass Spectrometry (GC–MS) Following Switchable Solvent–Liquid Phase Microextraction (SS–LPME), Anal. Lett. 52 (2019) 869–878.

[237] X. Di, X. Wang, Y. Liu, X. Guo, X. Di, Solid-phase extraction coupled with switchable hydrophilicity solvent-based homogeneous liquid–liquid microextraction for chloramphenicol enrichment in environmental water samples: a novel alternative to classical extraction techniques, Anal. Bioanal. Chem. 411 (2019) 803–812.

[238] F. Kapukıran, M. Fırat, D.S. Chormey, S. Bakırdere, N. Özdoğan, Accurate and Sensitive Determination Method for Procymidone and Chlorflurenol in Municipal Wastewater, Medical Wastewater and Irrigation Canal Water by GC–MS After Vortex Assisted Switchable Solvent Liquid Phase Microextraction, Bull. Environ. Contam. Toxicol. 102 (2019) 848–853.

[239] S. Karayaka, D.S. Chormey, M. Fırat, S. Bakırdere, Determination of endocrine disruptive phenolic compounds by gas chromatography mass spectrometry after multivariate optimization of switchable liquid-liquid microextraction and assessment of green profile, Chemosphere 235 (2019) 205–210.

[240] M. Fırat, D.S. Chormey, S. Bakırdere, F. Turak, Experimental design of switchable solvent–based liquid phase microextraction for the accurate determination of etrimfos from water and food samples at trace levels by GC-MS, Environ. Monit. Assess. 191 (2019) 619.

[241] M. Fırat, E.G. Bakırdere, An accurate and sensitive analytical strategy for the determination of palladium in aqueous samples: slotted quartz tube flame atomic absorption spectrometry with switchable liquid–liquid microextraction after preconcentration using a Schiff base ligand, Environ. Monit. Assess. 191 (2019) 129.

[242] Z. Tekin, S. Erarpat, A. Şahin, D.S. Chormey, S. Bakırdere, Determination of Vitamin B12 and cobalt in egg yolk using vortex assisted switchable solvent based liquid phase microextraction prior to slotted quartz tube flame atomic absorption spectrometry, Food Chem. 286 (2019) 500–505.

[243] H. Ahmar, M. Nejati-Yazdinejad, M. Najafi, K.S. Sadat Hasheminasab, Switchable Hydrophilicity Solvent-Based Homogenous Liquid–Liquid Microextraction (SHS-HLLME) Combined with GC-FID for the Quantification of Methadone and Tramadol, Chromatographia 81 (2018) 1063–1070.

[244] N. Lamei, M. Ezoddin, N.R. Kakavandi, K. Abdi, M. Ghazi-khansari, Ultrasound□Assisted Switchable Solvent in Determination of Quaternary Ammonium Herbicide Paraquat in Biological, Environmental Water, and Apple Juice Samples Using Chemical Reduction Process Coupled to GC–MS Detection, Chromatographia 81 (2018) 923–930.

[245] M. Fırat, S. Bodur, B. Tışlı, C. Özlü, D.S. Chormey, F. Turak, S. Bakırdere, Vortex-assisted switchable liquid-liquid microextraction for the preconcentration of cadmium in environmental samples prior to its determination with flame atomic absorption spectrometry, Environ. Monit. Assess. 190 (2018) 393.

[246] X. Wang, M. Gao, Z. Zhang, H. Gu, T. Liu, N. Yu, X. Wang, H. Wang, Development of CO_2-Mediated Switchable Hydrophilicity Solvent-Based Microextraction Combined with HPLC-UV for the Determination of Bisphenols in Foods and Drinks, Food Anal. Meth. 11 (2018) 2093–2104.

[247] Y. Hamid, M.R. Fat'hi, A Novel Cationic Surfactant-Assisted Switchable Solvent-Based Dispersive Liquid–Liquid Microextraction for Determination for Orange II in Food Samples, Food Anal. Meth. 11 (2018) 2131–2140.

[248] E. Vessally, E. Ghorbani-Kalhor, R. Hosseinzadeh□Khanmiri, M. Babazadeh, A. Hosseinian, F. Omidi, M.H. Ebrahimi, Application of switchable solvent□based liquid phase microextraction for preconcentration and trace detection of cadmium ions in baby food samples, J. Iran Chem. Soc. 15 (2018) 491–498.

[249] Y. Hamid, M.R. Fat'hi, A fast and green preconcentration method based on surfactant ion pair-switchable solvent dispersive liquid–liquid microextraction for determination of phenazopyridine in pharmaceutical and biological samples, J. Iran Chem. Soc. 15 (2018) 1813–1820.

[250] S. Hu, J. Xue, X. Yang, X. Chen, R.-q. Wang, X.-h. Bai, Sodium dodecyl sulfate sensitized switchable solvent liquid-phase microextraction for the preconcentration of protoberberine alkaloids in *Rhizoma coptidis*, J. Sep. Sci. 41 (2018) 3614–3621.

[251] D.S. Chormey, S. Bodur, D. Baskın, M. Fırat, S. Bakırdere, Accurate and sensitive determination of selected hormones, endocrine disruptors, and pesticides by gas chromatography–mass spectrometry after the multivariate optimization of switchable solvent liquid-phase microextraction, J. Sep. Sci. 41 (2018) 2895–2902.

[252] M. Reclo, E. Yilmaz, Y. Bazel, M. Soylak, Switchable solvent based liquid phase microextraction of palladium coupled with determination by flame atomic absorption spectrometry, Int. J. Environ. Anal. Chem. 97 (2017) 1315–1327.

[253] Z.M. Memon, E. Yilmaz, M. Soylak, Switchable solvent based green liquid phase microextraction method for cobalt in tobacco and food samples prior to flame atomic absorption spectrometric determination, J. Mol. Liq. 229 (2017) 459–464.

[254] M. Reclo, E. Yilmaz, M. Soylak, V. Andruch, Y. Bazel, Ligandless switchable solvent based liquid phase microextraction of nickel from food and cigarette samples prior to its micro-sampling flame atomic absorption spectrometric determination, J. Mol. Liq. 237 (2017) 236–241.

[255] Y. Bazel, M. Reclo, J. Šandrejová, Using a Switchable-Hydrophilicity Solvent for the Extraction−Spectrophotometric Determination of Nickel, J. Anal. Chem. 72 (2017) 1018–1023.

[256] J. Rameshgar, K.S. Hasheminasab, L. Adlnasab, H. Ahmar, Switchable-hydrophilicity solvent-based microextraction combined with gas chromatography for the determination of nitroaromatic compounds in water samples, J. Sep. Sci. 40 (2017) 3114–3119.
[257] A. Habibiyan, M. Ezoddin, N. Lamei, K. Abdi, M. Amini, M. Ghazi-khansari, Ultrasonic assisted switchable solvent based on liquid phase microextraction combined with micro sample injection flame atomic absorption spectrometry for determination of some heavy metals in water, urine and tea infusion samples, J. Mol. Liq. 242 (2017) 492–496.
[258] M. Hassan, U. Alshana, Switchable-hydrophilicity solvent liquid–liquid microextraction of non-steroidal anti-inflammatory drugs from biological fluids prior to HPLC-DAD determination, J. Pharm. Biomed. Anal. 174 (2019) 509–517.
[259] E. Yazıcı, M. Fırat, D.S. Chormey, E.G. Bakırdere, S. Bakırdere, An accurate determination method for cobalt in sage tea and cobalamin: Slotted quartz tube-flame atomic absorption spectrometry after preconcentration with switchable liquid-liquid microextraction using a Schiff base, Food Chem. 302 (2020) 125336.
[260] B.Y. Durak, D.S. Chormey, M. Firat, S. Bakirdere, Validation of ultrasonic-assisted switchable solvent liquid phase microextraction for trace determination of hormones and organochlorine pesticides by GC–MS and combination with QuEChERS, Food Chem. 305 (2020) 125487.
[261] F. Heydari, M. Ramezani, Application of Response Surface Methodology for Optimization of Conditions for Nickel Determination in Water and Vegetables by Switchable Solvent Based Liquid Phase Microextraction, J. Anal. Chem. 74 (2019) 1081–1088.
[262] H. Ahmar, S.K. Shahvandi, Determination of 4-Nitrobenzaldehyde in Water Samples by Combination of Switchable Solvent Based Microextraction and Electrochemical Detection on MWCNTs Modified Electrode, Electroanalysis 31 (2019) 1238–1244.
[263] S.K. Shahvandi, M.H. Banitaba, H. Ahmar, Development of a new pH assisted homogeneous liquid-liquid microextraction by a solvent with switchable hydrophilicity: Application for GC-MS determination of methamphetamine, Talanta 184 (2018) 103–108.
[264] S. Shahraki, H. Ahmar, M. Nejati-Yazdinejad, Electrochemical determination of nitrazepam by switchable solvent based liquid-liquid microextraction combined with differential pulse voltammetry, Microchem. J. 142 (2018) 229–235.
[265] F. Xu, Q. Li, W. Wei, L. Liu, H. Li, Development of a Liquid–Liquid Microextraction Method Based on a Switchable Hydrophilicity Solvent for the Simultaneous Determination of 11 Drugs in Urine by GC–MS, Chromatographia 81 (2018) 1695–1703.
[266] S.K. Shahvandi, M.H. Banitaba, H. Ahmar, P. Karimi, A novel temperature controlled switchable solvent based microextraction method: Application for the determination of phthalic acid esters in water samples, Microchem. J. 152 (2020) 104300.
[267] S. Lebedinets, C. Vakh, K. Cherkashina, A. Pochivalov, L. Moskvin, A. Bulatov, Stir membrane liquid phase microextraction of tetracyclines using switchable hydrophilicity solvents followed by high-performance liquid chromatography, J. Chromatogr. A 1615 (2020) 460743.
[268] M. Hemmati, M. Rajabi, Switchable fatty acid based CO_2-effervescence ameliorated emulsification microextraction prior to high performance liquid

chromatography for efficient analyses of toxic azo dyes in foodstuffs, Food Chem. 286 (2019) 185–190.

[269] A. Pochivalov, P. Davletbaeva, K. Cherkashina, A. Lezov, C. Vakh, A. Bulatov, Surfactant-mediated microextraction approach using switchable hydrophilicity solvent: HPLC-UV determination of Sudan dyes in solid food samples, J. Mol. Liq. 271 (2018) 807–814.

[270] M. Gao, J. Wang, X. Song, X. He, R.A. Dahlgren, Z. Zhang, S. Ru, X. Wang, An effervescence-assisted switchable fatty acid-based microextraction with solidification of floating organic droplet for determination of fluoroquinolones and tetracyclines in seawater, sediment, and seafood, Anal. Bioanal. Chem. 410 (2018) 2671–2687.

[271] A. Shishov, I. Sviridov, I. Timofeeva, N. Chibisova, L. Moskvin, A. Bulatov, An effervescence tablet-assisted switchable solvent-based microextraction: On-site preconcentration of steroid hormones in water samples followed by HPLC-UV determination, J. Mol. Liq. 247 (2017) 246–253.

[272] Naeemullah, M. Tuzen, A new portable switchable hydrophilicity microextraction method for determination of vanadium in microsampling micropipette tip syringe system couple with ETAAS, Talanta 194 (2019) 991–996.

[273] M.S. Hosseininejad, H. Faraji, A. Jamshidi, A green dispersive liquid phase microextraction technique based on the solidification of switchable hydrophilic fatty acid for determination of polynuclear aromatic hydrocarbons in aqueous samples, Water Sci. Technol. 79 (2019) 93–103.

[274] A. Pochivalov, C. Vakh, S. Garmonov, L. Moskvin, A. Bulatov, An automated in-syringe switchable hydrophilicity solvent-based microextraction, Talanta 209 (2020) 120587.

[275] C. Mukhopadhyay, M. Suba, D. Sivakumar, K. Dhamodharan, R.V.S. Rao, Cloud point extractive spectrophotometric method for determination of uranium in raffinate streams during spent nuclear fuel reprocessing, J. Radioanal. Nucl. Chem. 322 (2019) 743–750.

[276] A. Boukhelkhal, O. Benkortbi, M. Hamadache, Use of an Anionic Surfactant for the Sorption of a Binary Mixture of Antibiotics from Aqueous Solutions, Environ. Technol. 40 (2019) 3328–3336.

[277] J. Ali, M. Tuzen, T.G. Kazi, Developed of a Green Water Switchable Liquid–Liquid Microextraction Method for Assessment of Selenium in Food and Soft Drink Samples by Using Hydride Generation Atomic Absorption Spectrometry, 12 (2019) 1298–1307.

2235 **Figure Captions**

2236 **Figure 1.** General scheme of the DLLME procedure and main variations to improve
2237 the most conventional mode.

2238 **Figure 2.** Classification of different LPME methods using hydrophilic media as
2239 extraction-phase depending on the driving force used for the phase
2240 separation.

2241 **Figure 3.** General scheme of the coacervation phenomena-based LPME methods: A)
2242 CPE, B) Conventional CAE and C) SUPRASs; and LPME strategies using
2243 other hydrophilic media: D) DES-DLLME, E) in situ IL-DLLME, F) ABSs,
2244 and G) SS-DLLME.

2245 **Figure 4.** Ternary phase diagram (in an orthogonal representation) for a hypothetical
2246 ABS.

2247 **Figure 5.** Summary of the analytical applications reported in the period 2017-2019
2248 involving LPME strategies using hydrophilic media as extraction phase.

2249

Table 1. Representative analytical applications of different hydrophilic media-based LPME methods, from 2017 to 2019.

Extraction medium (amount)	**Additive**	**Driving force**	**Assistance**	**Analytes (number)**	**Sample (amount, pretreatment)**	**Analytical technique**	**LOD**	**RSD_{max} (%, concentration)**	**Maximum E_F**	**Ref.**
CPE										
Triton X-114 (400 µL)	-	temperature (45 ºC / 15 min)	centrifugation	As(III) and As(V)	snow water (10 mL, dilution with water)	ICP-OES	720 $ng \cdot L^{-1}$	3.5 (10 $\mu g \cdot L^{-1}$)	n.r.	[36]
Triton X-114 (105 µL)	-	temperature (40 ºC / 20 min & 60 ºC / 10 min)	centrifugation	sulfonamides (3)	urine and water (10 mL)	LC-UV	3.0–6.2 $\mu g \cdot L^{-1}$	10.35 (5–10 $mg \cdot L^{-1}$)	n.r.	[39]
Triton X-114 (1 mL)	-	temperature (50 ºC / 15 min)	centrifugation	Sb(III) and Sb(V)	water (10 mL)	ETAAS	60 $ng \cdot L^{-1}$	5.9 (10 $\mu g \cdot L^{-1}$)	12	[73]

Triton X-100 (400 µL)	-	temperature (70 ºC / 10 min)	vortex / centrifugation	Bi(III)	water and roadside soil (10 mL, dilution with water)	UV-Vis	2.86 $\mu g \cdot L^{-1}$	2.42 (60 $\mu g \cdot L^{-1}$)	40	[28]
Triton X-114 (1 mL)	Na_2SO_4	temperature (40 ºC / 10 min)	centrifugation	quercetin	onion, tomato, apple and orange juice (10 mL, food was digested by MW)	UV-Vis	2.2 $\mu g \cdot L^{-1}$	2.8 (30 $\mu g \cdot L^{-1}$)	n.r.	[45]
Triton X-100 (1 mL)	salicylic acid	temperature (25 ºC / n.r.)	centrifugation	Mo(IV)	water, rose hip and pharmaceuticals (10 mL, dilution with water)	UV-Vis	50 $\mu g \cdot L^{-1}$	3.8 (0.24 and 0.72 $\mu g \cdot L^{-1}$)	n.r.	[78]
Triton X-114 + SDS (250 µL)	-	temperature (55 ºC / 17.5 min)	US / centrifugation	Sb, Sn, Tl species	carrot, potatoes, beetroot,	ICP-OES	7–10 $ng \cdot L^{-1}$	5.5 (5 and 50	160	[20]

					canned beans, spinach and water (10 mL, food was digested)			µg·L^{-1})		
Tergitol 15-S-7 (2 mL)	Na_2SO_4	temperature (50 ºC / 10 min)	centrifugation	phenols (12)	water (10 mL)	LC-FD	0.03 – 8.5 µg·L^{-1}	4.2 (2–450 µg·L^{-1})	n.r.	[86]
PEG 6000 (2 mL)	ACN / Na_2SO_4	temperature (25 ºC / 5 min)	centrifugation	alkylphenols (9)	water (10 mL)	LC-FD	170–390 ng·L^{-1}	4.98 (50 and 150 µg·L^{-1})	5.0	[88]
Brij-35 (300 µL)	HFIP	temperature (25 ºC / n.r.)	vortex / centrifugation	parabens (6)	water and pharmaceuticals (10 mL, dilution with	LC-DAD	42–167 ng·L^{-1}	7.9 (0.3–200 µg·L^{-}	193	[47]

					water)			^{1})		
Conventional CAE										
SDS (700 µL)	-	coprecipitation agent: $Al_2(SO_4)_3$ (80 µL)	vortex	organophosphorus pesticides (5)	water (9 mL)	LC-UV	0.7 – 2.5 µg·L^{-1}	8 (50–250 µg·L^{-1})	n.r.	[99]
DTAB + diDDAB (50 µL)	-	ionic strength: NaCl (2.5 g)	vortex / centrifugation	tetracyclines (5)	milks, eggs and honeys (10 mL, milk was deproteinized)	LC-UV	0.7 – 3.4 µg·L^{-1}	7.85 (5–30 µg·L^{-1})	198	[97]
SDS + DTAB (n.r.)	-	coacervate-inducing agent: HFIP (5 mL)	centrifugation	lysozyme	water (5 mL)	CE-UV	2.2 µg·L^{-1}	n.r.	n.r.	[100]
DES-DLLME										
Cholinium chloride:phenol (193 µL, 1:2)	-	THF (100 µL)	US / centrifugation	sulfonamides (4)	river water (1.5 mL)	LC-UV	1.2–2.3 µg·L^{-}	4.26 (0.1, 1 and	n.r.	[131]

							^{1}	10 mg·L^{-1})		
Cholinium chloride:TNO (100 µL, 1:2)	-	THF (100 µL)	air-assisted / centrifugation	methadone	water, urine and plasma (10 mL, dilution with water)	GC-FID	0.7 µg·L^{-1}	9.1 (100 and 200 µg·L^{-1})	270	[136]
TBAB:decanoic acid (200 µL, 1:2)	-	THF (200 µL)	US / centrifugation	E155 dye	water,artificial urine and cake (10 mL, dilution with water)	UV-Vis	0.23 mg·L^{-1}	n.r.	37.5	[138]
Cholinium chloride:phenol (600 µL, 1:4)	-	THF (800 µL)	air-assisted / centrifugation	Pb(II)	lake, river, sea and wastewater, and mushroom (30 mL, food was	GFAAS	0.6 ng·L^{-1}	2.9 (1, 2, 3, and 5 µg·L^{-1})	60	[124]

					digested by MW)					
Sucrose:citric acid (400 µL, 3:2)	-	THF (350 µL)	US / centrifugation	Cu(II), Cd(II), Pb(II)	honey (150 mL, dilution with acidic water)	FAAS	0.23–0.87 µg·kg^{-1}	5.2 (10–250 µg·kg^{-1})	80–105	[141]
In situ IL-DLLME										
[C_4MIm^+][Cl^-] (35 mg)	-	anion-exchange: Li-NTf_2 (240 µL, 1 M)	centrifugation	pesticides (9)	water (10 mL)	TD-GC-MS	5–16 ng·L^{-1}	9.7 (1 µg·L^{-1})	n.r.	[159]
[C_5MIm^+][Br^-] (100 mg)	-	anion-exchange: NH_4PF_6 (50 mg)	vortex / centrifugation	Cu(II)	water (5 mL, dilution with acidic water)	FAAS	0.12 µg·L^{-1}	4.1 (50 µg·L^{-1})	70	[162]
[$C_{10}Gu^+$][Cl^-] (20 µL)	-	anion-exchange: $NaClO_4$ (500 µL, 100%	vortex / centrifugation	OH-PAHs	urine (10 mL, dilution with water)	LC-FD	1–2 ng·L^{-1}	17 (0.08, 0.5 and	47.4	[172]

		w/v)						0.8 µg·L^{-1})		
[$C_4C_4Im^+$][Cl^-] (~26 mg)	MNPs	anion-exchange: Li-NTf_2 (500 µL, 0.2 M)	vortex / magnetic separation	fungicides (4)	water (10 mL)	LC-UV	0.74–1.44 µg·L^{-1}	11.32 (10, 50 and 100 µg·L^{-1})	247	[155]
[$Ni(C_4Im)_4^{2+}$]2[Cl^-] (20 mg)	acetone (dispersant)	anion-exchange: Li-NTf_2 (42.8 µL, 0.4 g·L^{-1})	vortex / magnetic separation	disrupting compounds (10)	tap, lake and pool water (5 mL)	LC-DAD	0.13–5.2 µg·L^{-1}	14 (81 and 300 µg·L^{-1})	44.3	[177]
[$Ni(BeIm)_4^{2+}$]2[Cl^-] (30 mg)	acetonitrile (dispersant)	anion-exchange: Li-NTf_2 (53.5 µL, 0.4	vortex / magnetic separation	disrupting compounds (10)	tap, lake and pool water (5 mL)	LC-DAD	0.012–1.6 µg·L^{-1}	16 (81 and 300	55.1	[177]

		$g \cdot L^{-1}$)						$\mu g \cdot L^{-1}$)		
ABSs										
PEG 8000 (75 µL, at 50 wt%)	-	$C_6H_5Na_3O_7$ (1200 µL, at15 wt%)	vortex / centrifugation	mycotoxins (3)	corn, soy, chickpea and sunflower (spiked, 400 mg, finely powdered)	microfluidic immunoassays	4.6–129.7 ng g^{-1}	53.1 (LOD)	10.4	[184]
THF (2.24 wt%)	-	fructose (83.7 wt%)	mixing / centrifugation	diuron and its degradation products (2)	river water (14.06 wt%, filtration)	LC-TOF	25 g L^{-1}	n.r.	200	[196]
$[Chol^+][Sac^-]$ (0.6 g, at 50 wt%)	-	Na_2CO_3 (4.0 g)	vortex / centrifugation	galantamine	tablets (10 mg, finely powdered and dissolved in 9.0 g of water) and urine (spiked with	LC-UV	0.005 $\mu g \cdot L^{-1}$	1.3 (spiked urine, 0.98 $\mu g \cdot L^{-1}$)	153	[200]

					0.98 µg·L^{-1}, 9.0 g)					
[N_{4444}^+][Cl^-] (1.18 wt%)	-	$C_6H_5K_3O_7$ (49.85 wt %)	mixing	caffeine and carbamazepine	WWTP e□uent (spiked with 1·10^3 g·L^{-1}, 48.98 wt%, filtration)	LC-UV	0.1 – 1.0 g·L^{-1}	n.r	50	[201]
[C_4Gu^+][Cl^-] (0.75 wt%, 73.1 µL)	-	K_3PO_4 (37.7 wt%)	vortex / centrifugation	PAHs (5)	Wastewater, sea water and tap water (non-spiked and/or spiked with 12 ng·L^{-1}, 61.55 wt%, filtration)	LC-FD	0.03–2 ng L^{-1}	14 (12 ng·L^{-1})	97.3	[206]
[C_4MIm^+][Sal^-] (0.06 mL)	-	K_3PO_4 (27.1 wt%)	vortex / centrifugation	Cu(II)	Tap water, wastewater and urine (2 mL)	DPASV	8 ng L^{-1}	7.8 (analysis of real	54	[204]

								samples)		
Cholinium chloride:phenol (200 µL, 2:1)	-	K_2HPO_4 (0.2 g mL^{-1})	vortex / centrifugation	sulfonamides (4)	Lake and river water (spiked with 2 µg mL^{-1}, 200 µL, filtration)	LC-UV	0.003 – 0.006 µg mL^{-1}	3.1 (0.2, 2, and 20 µg mL^{-1})	n.r.	[214]
SS-DLLME										
N,N-dimethylbenzylamine + dry ice (1 mL)	-	pH: concentrated NaOH (1.8 mL)	-	Co(II)	tea and vitamin B12 (8 mL, extraction with water)	FAAS	3.1 $µg·L^{-1}$	15.6 (250, 500 and 1000 $µg·L^{-1}$)	107	[259]
N,N-dimethylbenzylamine + dry ice (1.5 mL)	-	pH: concentrated NaOH (1 mL)	vortex / centrifugation	phenols (4)	tap and wastewater and migration from plastics containers to	GC-MS	0.13–0.54 $µg·L^{-1}$	13 (5, 50 and 100 $µg·L^{-}$	n.r.	[239]

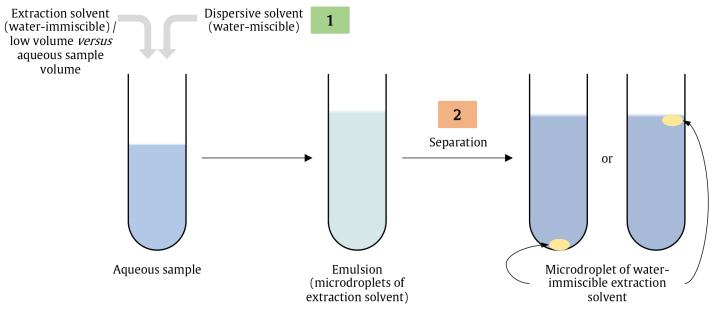
					water (8 mL)			^{1})		
N,N-dimethylbenzylamine + dry ice (1 mL)	-	pH: concentrated NaOH (2 mL)	centrifugation	Cd(II)	lake and wastewater (8 mL)	FAAS	0.7 µg·L^{-1}	12.7 (10, 20 and 30 µg·L^{-1})	n.r.	[245]
triethylamine + dry ice (900 µL)	-	pH: concentrated NaOH (1.8 mL)	vortex / centrifugation	Ni(II)	water and vegetables (15 mL, food was digested)	FAAS	3 µg·L^{-1}	1.1 (200 µg·L^{-1})	70	[261]
N,N-dimethylcyclohexylamine + HCl (400 µL)	-	pH: concentrated NaOH (400 µL)	centrifugation	drugs (11)	urine (2 mL, n.r.)	GC-MS	0.35–12.5 µg·L^{-1}	13.5 (20–50 µg·L^{-1})	n.r.	[265]
sodium hexanoate (100 µL, 3.2 M)	-	pH: concentrated HCl (20 µL)	magnetic stir-membrane	tetracyclines (3)	urine (1 mL, dilution with water)	LC-UV	30 µg·L^{-1}	8 (0.1 and 100	n.r.	[267]

								mg·L^{-1})		
hexanoic acid + Na_2CO_3 (130 µL + 500 µL, 2 M)	-	pH: concentrated H_2SO_4 (620 µL)	effervescency	azo dyes (3)	spices (6 mL, dilution with acidic water and methanol)	LC-UV	1–5 µg·L^{-1}	7.8 (15 and 30 µg·g^{-1})	65	[268]

For the definition of the abbreviations, please refer to the list of abbreviations.

n.r.: not reported.

Conventional DLLME



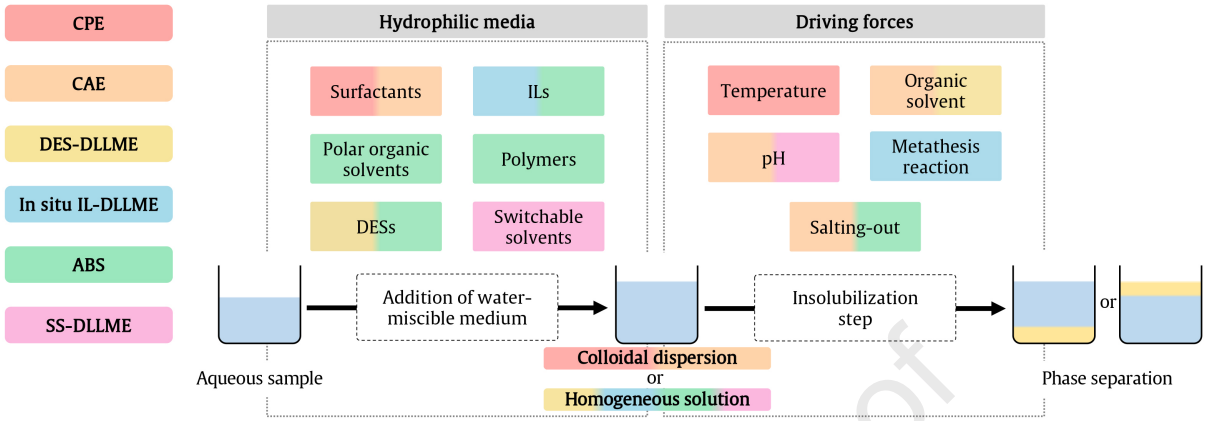
Main variations in the operational mode of DLLME

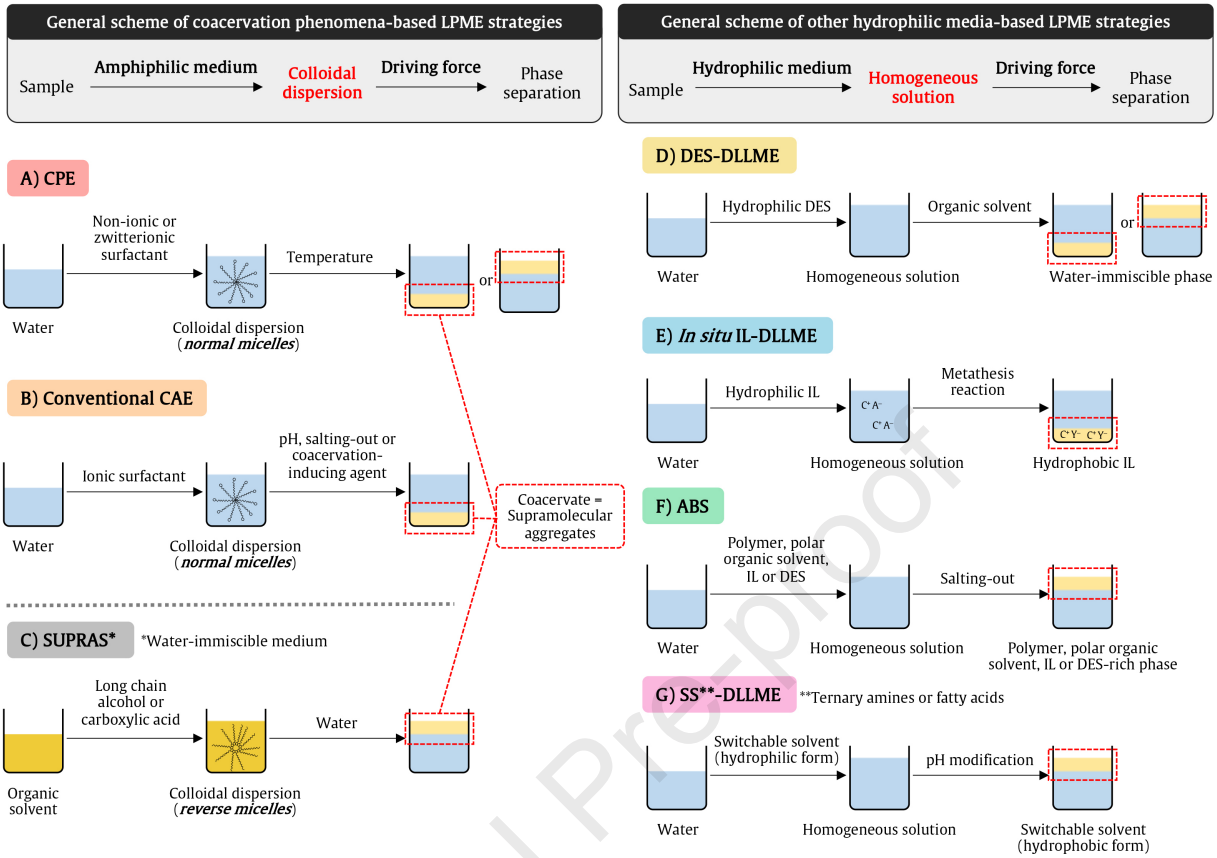
1. Alternative dispersion modes

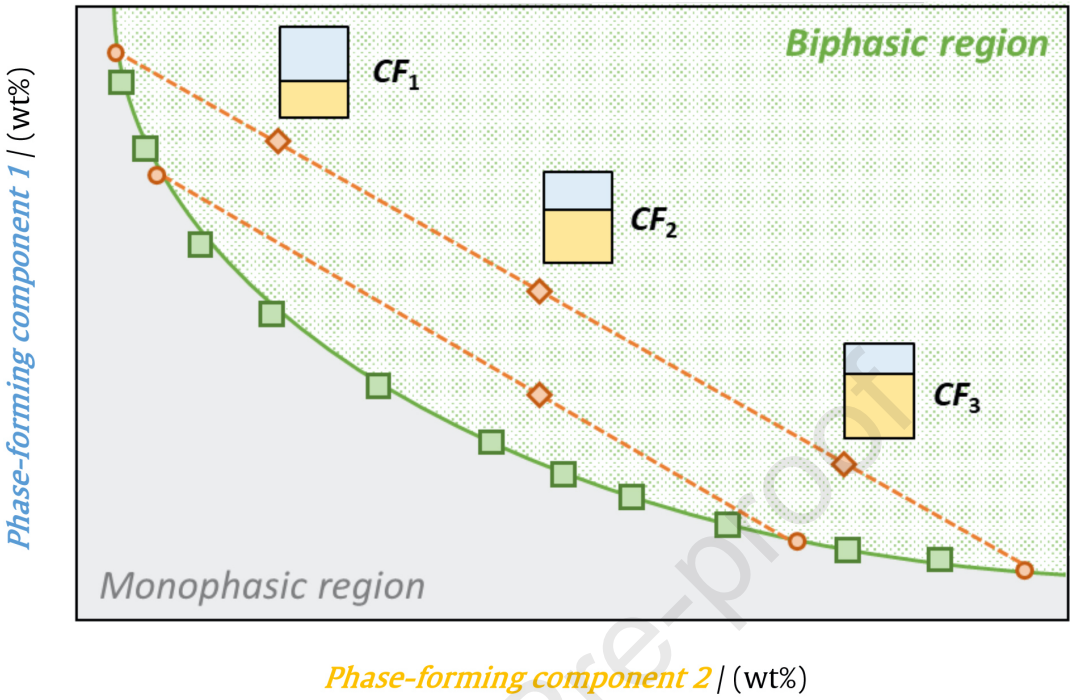
- Vortex-assisted DLLME
- Ultrasound-assisted DLLME
- Effervescence-assisted DLLME
- Air-assisted DLLME
- Surfactant-assisted DLLME
- Heating-assisted DLLME

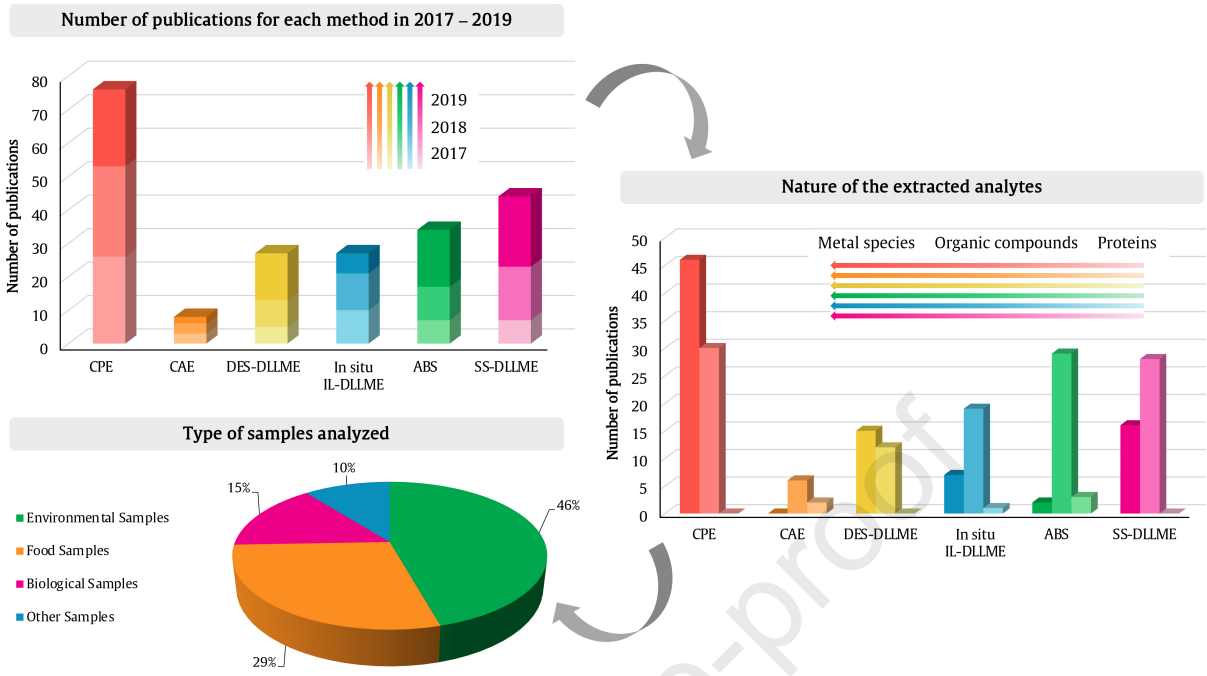
2. Modes of separation

- Simple decantation
- Centrifugation
- Freezing
- Magnetic separation (magnetic solvents or adding magnetic materials)









Highlights

- Dispersive LPME methods with hydrophilic media as extraction phase are classified
- Hydrophilic medium & driving force for separation are criteria for classification
- Physicochemical mechanisms of phase separation are critically discussed
- Main advances within each LPME method in the last three years are described
- Analytical applications of each LPME method in the last three years are reviewed

Francisca A. e Silva is a Researcher at CICECO-Aveiro Institute of Materials, Chemistry Department, University of Aveiro, Portugal. In 2018, she completed her PhD in Chemical Engineering with honor at the same institution, also receiving the "Best PhD thesis in Chemical Engineering" awarded by the Iberoamerican Congress in Chemical Engineering. She has published 21 articles and 1 encyclopedia entry. Her research interests entail the development of ionic-liquid-based technologies for the extraction and purification of disease biomarkers, pharmaceuticals, chiral compounds, and environmental contaminants.

Idaira Pacheco-Fernández is a PhD student under the supervision of V. Pino and J.H. Ayala, with a PhD defense set at December 2020. She completed her Degree in Chemistry in 2014, and Master's Degree in Chemistry in 2015 at Universidad de La Laguna. She has written 11 research articles, 5 review articles, 8 book chapters, presented 15 communications in international meetings, and granted with different fellowships and awards. She has also performed a four-month stay in Iowa State University (USA) supervised by J.L. Anderson. Her research project includes the use of ionic liquids and metal-organic frameworks in sample preparation methods.

Mara G. Freire graduated in Chemistry (2003) and holds a PhD in Chemical Engineering (2007). Currently she is a Coordinator Researcher at CICECO-Aveiro Institute of Materials, Chemistry Department, University of Aveiro, Coordinator of Group 5 - Biomedical and Biomimetic Materials - within CICECO, Deputy Chair of the Scientific Council of University of Aveiro and member of the Young Scientists Seminar of the Lisbon Academy of Sciences. In addition to other projects and awards, Freire was awarded with two European Research Council (ERC) Grants. Her main research interests comprise the development of sustainable separation platforms for value-added compounds with therapeutic properties.

Raúl González-Martín completed his Degree in Chemistry at Universidad de La Laguna (ULL) in 2018, granted by the Spanish Ministry of Education with a Research Collaboration Fellowship. He completed his Master's Degree in Chemistry in 2019, being awarded with the Best Final Master Project of Sciences at ULL. He is currently a PhD student granted with a FPU fellowship under the supervision of V. Pino and D. Díaz Díaz. He has written 2 research articles and presented 2 communications in international meetings. His research project includes the design, synthesis and use of polymers and other materials in sample preparation schemes.

Verónica Pino is a Professor at Universidad de La Laguna (Spain) since July 2018. She has been a postdoctoral fellow at Iowa State University (USA) in 2003, at Université Claude-Bernard (France) in 2005, and at The University of Toledo (USA) in 2006 and 2008. She has written around 98 publications, 22 book chapters, and has co-edited a book series published by Wiley. She is chief editor of Journal of Analytical Methods in Chemistry. She has supervised 5 PhD Thesis and currently has 4 PhD students. Her research interests mainly include the design and use of new materials in sample preparation.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: