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Review

Evolution of dispersive liquid–liquid microextraction method

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ABSTRACT

Dispersive liquid–liquid microextraction (DLLME) has become a very popular environmentally benign sample-preparation technique, because it is fast, inexpensive, easy to operate with a high enrichment factor and consumes low volume of organic solvent. DLLME is a modified solvent extraction method in which acceptor-to-donor phase ratio is greatly reduced compared with other methods. In this review, in order to encourage further development of DLLME, its combination with different analytical techniques such as gas chromatography (GC), high-performance liquid chromatography (HPLC), inductively coupled plasma-optical emission spectrometry (ICP-OES) and electrothermal atomic absorption spectrometry (ET AAS) will be discussed. Also, its applications in conjunction with different extraction techniques such as solid-phase extraction (SPE), solidification of floating organic drop (SFO) and supercritical fluid extraction (SFE) are summarized. This review focuses on the extra steps in sample preparation for application of DLLME in different matrixes such as food, biological fluids and solid samples. Further, the recent developments in DLLME are presented. DLLME does have some limitations, which will also be discussed in detail. Finally, an outlook on the future of the technique will be given.

Contents

Abbreviations: DLLME, dispersive liquid-liquid microextraction; SFO, solidification of floating organic drop; GC, gas chromatography; HPLC, high-performance liquid chromatography; ET-AAS, electrothermal atomic absorption spectrometry; SPE, solid phase extraction; SFE, supercritical fluid extraction; LLE, liquid-liquid extraction; SPME, solid-phase microextraction; LPME, liquid-phase microextraction; SDME, single-drop microextraction; HF-LPME, hollow fiber liquid-phase microextraction; CPE, cloud point extraction; HLLE, homogeneous liquid-liquid extraction; USAEME, ultrasound-assisted emulsification-microextraction; US, ultrasound; PF, preconcentration factor; ER, extraction recovery; PAHs, polycyclic aromatic hydrocarbons; OPPs, organophosphorus pesticides; ECD, electron capture detection; FPD, flame photometric detection; CBs, chlorobenzenes; THMs, trihalomethanes; MS, mass spectrometric detection; LODs, limits of detections; PFBAY, pentafluorobenzaldehyde; CPs, chlorophenols; OSPs, organosulphur pesticides; NPD, nitrogen-phosphorus detection; FID, flame ionization detection; $NaBEt_4$, sodium tetraethylborate; TCS, triclosan; MTCS, methyltriclosan; MTBSTFA, N-methyl-N(tert-butyldimethylsilyl) trifluoroacetamide; DAD, diode array detection; VWD, variable wavelength detection; UHPLC, ultra-high pressure liquid chromatography; TUV, tunable ultraviolet detection; TCC, triclocarban; M-TCS, methyl-triclosan; OAD, orthogonal array design; CCD, central composite design; EDTA, ethylendiaminetetraacetic acid; DMF, N, N-dimethyl formamide; FAAS, flame atomic absorption spectrometry; FO-LADS, fiber optic–linear array detection spectrophotometer; PAN, 1-(2-pyridylazol)-2-naphthol; ICP-OES, inductively coupled plasma-optical emission spectrometry; Sm, samarium; Eu, europium; Gd, gadolinium; Dy, dysprosium; LC-ES-MS/MS, liquid chromatography–electrospray-tandem mass spectrometry; 7-amino FM2, 7-aminoflunitrazepam; LOQs, limits of quantification; LC-APCI-MS-MS, liquid chromatography–atmospheric-pressure chemical ionization tandem mass spectrometry; CAP, chloramphenicol; THA, thiamphenicol; FLD, fluorescence detection; PCBs, polychlorinated biphenyls; MUSE, miniaturized ultrasonic solvent extraction; RTILS, room temperature ionic liquids; IL-DLLME, ionic liquid based dispersive liquid-liquid microextraction; PDLLME, partitioned dispersive liquid–liquid micro extraction; TCE, tetrachloroethylene; THF, tetrahydrofuran; PUHs, phenylurea herbicides; IBMK, isobutyl methyl ketone; IL-based USA-DLLME, ionic liquid-based ultrasound-assisted dispersive liquid-liquid microextraction; DLLME-LSC, DLLME technique with little solvent consumption; TBME, tert-butyl methyl ether; OCPs, organchlorine pesticides; PBDEs, polybrominated diphenyl ethers; DSPE, dispersive solid–phase extraction; HOCs, halogenated organic compounds; CE, capillary electrophoresis.

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1. Introduction

In spite of substantial technological advances in analytical field, most instruments cannot directly handle complex sample matrixes yet. As a result, a sample-preparation step is commonly involved before instrumental analysis. The main aim of sample preparation is to clean up and concentrate the analytes of interest, while rendering them in a form that is compatible with the analytical system. Liquid–liquid extraction (LLE), based on the transfer of analyte from the aqueous sample to a water-immiscible solvent, is widely employed for sample preparation. Nevertheless, some shortcomings such as emulsion formation, use of large sample volumes and toxic organic solvents and hence, generation of large amounts of pollutants make LLE labour to be intensive, expensive, time-consuming and environmentally unfriendly. Another popular sample-preparation approach is solid-phase extraction (SPE). Although it uses much less solvent than LLE, the usage can still be considered significant, and normally an extra step of concentrating the extract down to a small volume is needed. SPE can be automated but this entails complexity and additional cost [1,2]. There have been substantial efforts in the past two decades to adapt the existing sample-preparation methods and develop new approaches to save time, labour and materials. Miniaturization has been a key factor in the pursuit of these objectives.

Introduction of solid-phase microextraction (SPME) by Pawliszyn and co-worker [3] basically initiated the interest for microextraction techniques in analytical chemistry. With the SPME technique, target analytes of low or medium polarity are extracted from aqueous or gaseous samples onto a solid polymeric fiber. Extraction occurs by passive diffusion and the extraction yield is essentially determined by the fiber to sample partition coefficient. It is a portable, simple to use, relatively fast method and can be automated and coupled on-line to analytical instrumentation. However, the coated fibers are generally expensive, and for some applications, have limited lifetimes.

Liquid-phase microextraction (LPME) as an alternative miniaturized sample-preparation approach, emerged in the mid-to-late 1990s [4,5]. As its name suggests, in LPME, only a microliter volume of the solvent is needed to extract analytes from the aqueous samples. It overcomes many disadvantages of LLE as well as some of those of SPME (e.g. independence of a commercial supplier and sample carryover or cross-contamination) [6,7]. Single drop microextraction (SDME) was developed as a solvent-minimized sample pretreatment procedure. It is inexpensive, and since very little solvent is used, there is minimal exposure to toxic organic solvents [8,9]. However, some disadvantages of this method are as follows: fast stirring would tend to break up the organic drop; air bubble formation [10]; extraction is time-consuming and equilibrium could not be attained after a long time in most cases [9]. As a solution to improve the stability and reliability of LPME, Pedersen-Bjergaard and Rasmussen introduced hollow fiber based LPME in 1999. Hollow fiber liquid-phase microextraction (HF-LPME) allows extraction and preconcentration of analytes from complex samples in a simple and inexpensive way. In general, the extraction efficiency achieved by HF-LPME is higher than direct-SDME, since hydrophobic hollow fibers allow the use of vigorous stirring rates to accelerate the extraction kinetics. Moreover, the use of hollow fibers provides protection of the extractant phase and hence, the analysis of dirty samples is feasible. Further, the small pore size of hollow fibers allows microfiltration of the samples, thus yielding very clean extracts [11].

Recent research has focused on the development of efficient, economical and miniaturized sample-preparation methods. Cloud point extraction (CPE) is based on phase separation, which occurs in aqueous solutions of non-ionic surfactants, when heated above the so-called cloud point temperature [12]. Besides of the many benefits of CPE, the choice of surfactants often brings the nuisance to the analysis of analytes by analytical instruments such as GC and HPLC [13,14]. In addition, the use of anionic surfactants as effective extractants in CPE often requires salts and adjustment of pH [15,16]. Homogeneous liquid–liquid extraction (HLLE) utilizes the phase separation phenomenon from a homogeneous solution, and the target solutes are extracted into a sedimented phase. Ternary component solvent system and perfluorinated surfactant system are the two usual modes of HLLE [17–19].

Recently, a new mode of LPME based on solidification of floating organic droplet (LPME-SFO) was developed [20,21]. In this method, specific holders such as the needle tip of microsyringe, the hollow fiber and polychloroprene rubber (PCR) tube are not required for supporting the organic microdrop due to the use of organic solvents with low density and proper melting point. Combination of microextracting systems and ultrasound (US) radiation provides an efficient preconcentration technique such as ultrasound-assisted emulsification-microextraction (USAEME) for determining of analytes at trace levels. This preconcentration technique was first developed by Regueiro et al. [22]. The US radiation is an efficient tool to facilitate the emulsification phenomenon and accelerates the mass-transfer process between two immiscible phases, leading to an increment in the extraction efficiency of the technique in a minimum amount of time [23,24].

Dispersive liquid–liquid microextraction (DLLME) was introduced by Assadi and co-workers in 2006 [25]. It is based on the ternary component solvent systems such as HLLE and CPE. It is a simple and fast microextraction technique based on the use of an appropriate extractant, i.e., a few microliters of an organic solvent such as chlorobenzene, chloroform or carbon disulfide with high density and a disperser solvent such as methanol, acetonitrile or acetone with high miscibility in both extractant and aqueous phases. When the mixture of extractant phase and disperser is rapidly injected into the sample, a high turbulence is produced. This turbulent regimen gives rise to the formation of small droplets, which are dispersed throughout the aqueous sample. Emulsified droplets have interfacial area. After the formation of cloudy solution, the surface area between the extracting solvent and the aqueous sample becomes very large, so the equilibrium state is achieved quickly and, therefore, the extraction time is very short. In fact, this is the principal advantage of DLLME. After centrifugation of the cloudy solution, a sedimented phase is settled in the

bottom of a conical tube and used with the most appropriate analytical technique. Other advantages of DLLME include simplicity of operation, rapidity, low cost, high recovery, high enrichment factor and environmental benignity [25,26]. The present review focuses on the updated developments and applications of DLLME. It covers almost all the publications related to the procedure from the beginning. In addition, some limitations and an outlook on further developments will be discussed.

2. Principles of DLLME

DLLME consists of two steps: (1) Injection of an appropriate mixture of extracting and disperser solvents into aqueous sample, containing the analytes. In this step, the extracting solvent is dispersed into the aqueous sample as very fine droplets and the analytes are enriched into it. Owing to the large surface area between the extracting solvent and the aqueous sample, equilibrium state is achieved quickly and the extraction is independent of time. This is the most important advantage of this method. (2) Centrifugation of cloudy solution. After centrifugation, analytes in the sedimented phase can be determined by analytical instruments. The extraction steps of DLLME are illustrated in Fig. 1.

In DLLME, the factors that affect extraction efficiency are as follows: (1) suitable extracting solvent, (2) suitable disperser solvent, (3) volume of extracting solvent and (4) volume of disperser solvent. Selection of an appropriate extracting solvent is the major parameter for DLLME process. Organic solvents are selected on the basis of their higher density rather than water, extraction capability of interested compounds and good chromatographic behavior. Halogenated hydrocarbons such as chlorobenzene, chloroform, carbon tetrachloride and tetrachloroethylene are usually selected as extracting solvents because of their high density.

Miscibility of disperser solvent in both extracting solvent and aqueous phase is essential in selection of it. Acetone, methanol and acetonitrile are usually selected as disperser solvents. The extracting solvent volume has important effect on the preconcentration factor (*PF*). By increasing of the extracting solvent volume, the volume of sedimented phase obtained by centrifugation increases, resulting in a decrease on PF. Therefore, the optimal extracting solvent volume should ensure both high PFs and enough volume of the sedimented phase for the subsequent analysis after centrifugation. The disperser solvent volume directly affects the formation of cloudy solution (water/disperser solvent/extracting solvent), the dispersion degree of the extracting solvent in aqueous phase and, subsequently, the extraction efficiency. Variation of disperser solvent volume changes the volume of sedimented phase. Hence, it is necessary to change the volumes of disperser solvent and extracting solvent simultaneously to achieve a constant volume of sedimented phase. The suitable volume of disperser solvent for well cloudy solution depends on the volume of both aqueous phase and extracting solvent. In DLLME, the important factors affecting the volume of sedimented phase are: (1) solubility of extracting solvent in water, (2) sample solution volume, (3) disperser solvent volume and (4) extracting solvent volume. In experimental views, to obtain desired sedimented phase volume, some experimental tests should be done before the beginning of the main experiment. At first, solubility of extracting solvent in aqueous phase is calculated. Then, due to increase the solubility of extracting solvent in the presence of disperser solvent, some trial and errors should be done to calculate the exact volume of the sedimented phase that will be obtained using a desired volume of extracting and disperser solvents.

In DLLME, extraction time is defined as an interval between the injection of mixture of a disperser solvent and extraction solvent, before centrifugation. The surface area between extraction solvent and aqueous phase is infinitely large. Thereby, transfer of analytes from aqueous phase to extraction phase is fast. Subsequently, equilibrium state is achieved quickly.

In DLLME, *PF* is defined as the ratio of the analyte concentration in the sedimented phase (C_{sed}) and the initial concentration of analyte (C_0) in the sample:

$$PF = \frac{C_{sed}}{C_0} \quad (1)$$

C_{sed} is obtained from a suitable calibration graph. The extraction recovery (*ER*) is defined as the percentage of total analyte amount (n_0), extracted to the sedimented phase (n_{sed}):

$$ER = \frac{n_{sed}}{n_0} \times 100 = \frac{C_{sed} \times V_{sed}}{C_0 \times V_{aq}} \times 100 \quad (2)$$

$$ER = \left(\frac{V_{sed}}{V_{aq}}\right) PF \times 100 \quad (3)$$

where V_{sed} and V_{aq} are the volumes of sedimented phase and sample solution, respectively.

3. Applications of DLLME

3.1. DLLME combined with GC

Since water-immiscible solvents are generally used in DLLME, the preferred technique for the analysis of extracts is GC. The versatility of DLLME-GC is seen in relation to the variety of applications in many areas, as depicted in Table 1.

The application of DLLME was developed for extraction and determination of polycyclic aromatic hydrocarbons (PAHs) in water samples by Rezaee et al. [25]. One mL of acetone (as disperser solvent) containing 8.0 μL of C_2Cl_4 (as extracting solvent) was rapidly injected into a 5.00 mL of the sample solution by a 1.00-mL syringe, and the mixture was gently shaken. Then, the mixture was centrifuged and 2.00 μL of the sedimented phase was injected into the GC for analysis. Under the optimum conditions, the obtained *PFs* ranged from 603 to 1113. The linear range was 0.02–200 $\mu g\,L^{-1}$ and the detection limit (DL) was 0.007–0.030 $\mu g\,L^{-1}$ for most of the analytes. Berijani et al. [26] developed a new method for the extraction of organophosphorus pesticides (OPPs) from water samples by DLLME-GC-FPD. In this method, a mixture of 12.0 μL chlorobenzene and 1.00 mL acetone was rapidly injected into the 5.00 mL water sample by syringe. After centrifugation, 0.5 μL of sedimented phase was injected into the GC. Under the optimum conditions, the *PFs* and extraction recoveries were obtained as 789–1070% and 78.9–107%, respectively. Comparison of DLLME with SPME and SDME for the extraction of OPPs from water samples showed that DLLME is a very simple and rapid method (extraction time is less than 3 min) and has high *PF* and extraction recoveries. In 2007, Kozani et al. [27] described DLLME combined with GC-ECD for determining chlorobenzenes (CBs) in water samples. The results indicated that DLLME is a sensitive, rapid and reproducible technique that can be used for preconcentration of CBs from water samples. DLLME-GC-ECD has also been used for determination of trihalomethanes (THMs) in drinking water [28]. Relative recoveries from the samples of drinking water spiked at the levels of 2.00 and 5.00 $\mu g\,L^{-1}$ were 95.0–107.8% and 92.2–100.9%, respectively. Huang and co-worker [29] used DLLME in combination with gas chromatography–ion trap mass spectrometric detection (GC–MS) to preconcentrate triazine herbicides in water and the DLs in the range of 0.021–0.12 $\mu g\,L^{-1}$ were obtained.

For the strong polar and nonvolatile samples, which are unsuitable for analysis by GC, derivatization is necessary to increase the analytes volatility. Application of DLLME coupled with derivati-

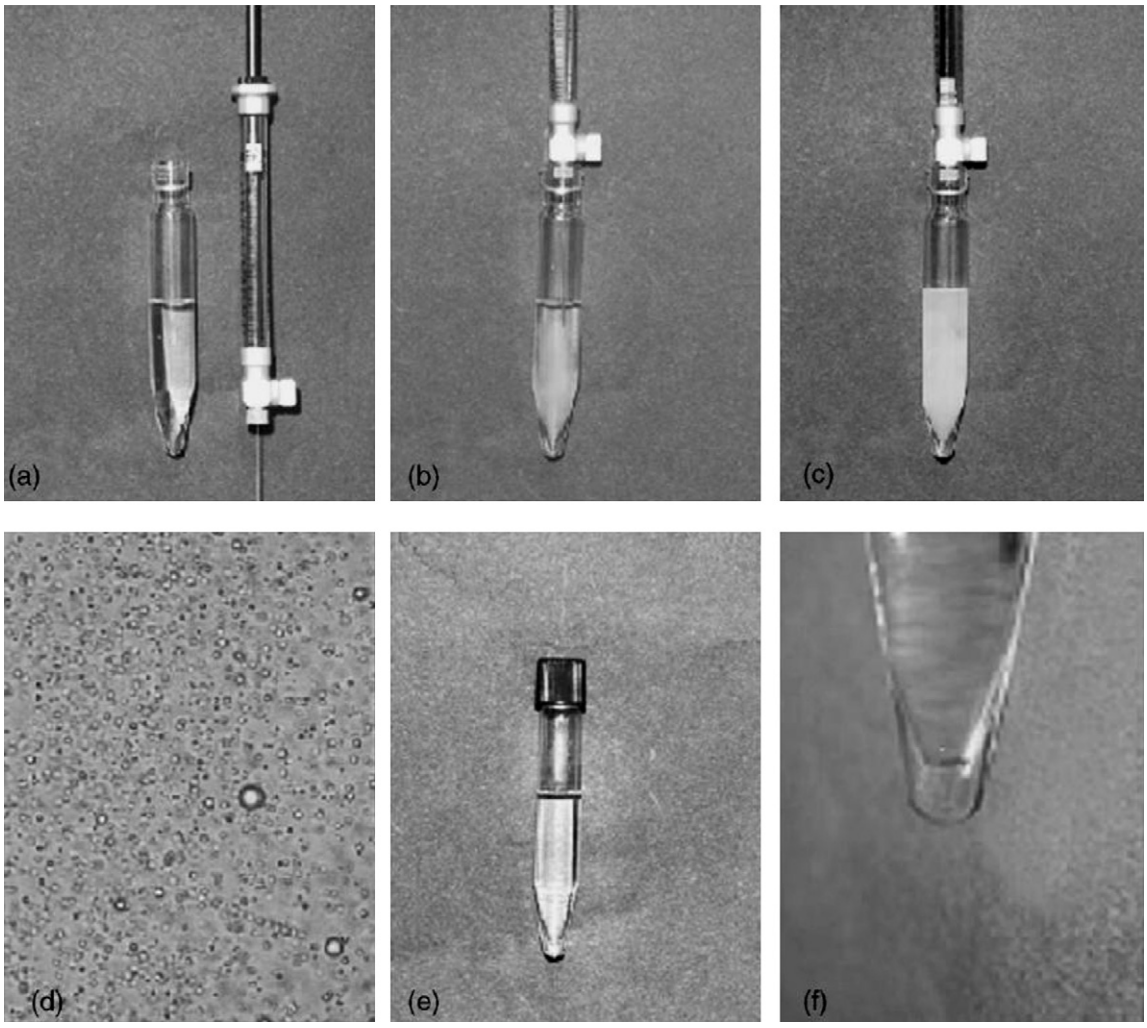

Fig. 1. Photography of different steps of DLLME: (a) before injection of mixture of disperser solvent (acetone) and extraction solvent (C_2Cl_4) into sample solution, (b) starting of injection, (c) end of injection, (d) optical microscopic photography, magnitude 1000 (that shows fine particles of C_2Cl_4 in cloudy state), (e) after centrifuging and (f) enlarged view of sedimented phase (5.0 0.2 μL). Reprinted with permission from [25].

zation reaction provides a one-step derivatization and extraction technique, greatly simplifying the operation steps and shortening the analysis time. Huang et al. have also combined GC–MS with DLLME to determine the anilines in wastewater samples [30]. In this method, the anilines are extracted by DLLME and derivatized using pentafluorobenzaldehyde (PFBAY) in aqueous solution simultaneously. Simultaneous derivatization and extraction by DLLME combined with GC-ECD was developed to determine chlorophenols (CPs) in water samples [31]. In this derivatization/extraction method, 500 μL of acetone containing 10.0 μL chlorobenzene and 50 μL of acetic anhydride (derivatization reagent) was rapidly injected by syringe into 5.00 mL of aqueous sample containing CPs (analyte) and K_2CO_3 (0.5%, w/v). Within few seconds, the analytes were derivatized and extracted into the extracting solvent. Two methods based on HF-LPME and DLLME have been critically compared for the analysis of organosulfur pesticides (OSPs) in environmental and beverage samples by GC-FPD [32]. Compared with HF-LPME, the advantages of DLLME were short extraction time and suitability for simultaneous treatment of batches of samples. In addition, a higher extraction recovery was obtained by DLLME in comparison with HF-LPME [32]. However, when dealing with more complicated matrixes such as soil and beverage samples, HF-LPME was demonstrated to be more robust and sensitive than DLLME without sample filtration and dilution. Also, the repeatability of HF-LPME was better than that of DLLME. Besides, DLLME-GC combined with various detectors was applied to determine phthalate esters in water samples (MS) [33], organophosphorus flame retardants and plasticizers in water samples (NPD) [34], volatile phenols in red wines (MS) [35], speciation of butyl and phenyltin compounds in water samples after derivatization with sodium tetraethylborate ($NaBEt_4$) (FPD) [36], amide herbicides in environmental water samples (MS) [37], amitriptyline and nortriptyline in environmental sample solutions (FID) [38], polychlorinated biphenyls in water samples (ECD) [39], fatty acids in water samples after derivatization with ethyl chloroformate (FID) [40], Rose extract constituents (MS) [41], phorate in water samples (FID) [42], pyrethroid pesticide residues in water samples (ECD) [43], nitroaromatic compounds in water samples (FID) [44], methyl tert-butyl ether in water samples (FID) [45], personal care products in natural water samples (MS) [46], organochlorine pesticides in water samples (MS) [47] and calcium stearate after its conversion to stearic acid in a polymeric matrix [48]. A solution of hydrochloric acid in 2-propanol was used to extract calcium stearate from its matrix. DLLME was applied to preconcentrate stearic acid before its injection into GC instrument. DLLME-GC–MS/MS was used to determine triclosan (TCS) and methyltriclosan (MTCS) after derivatization by N-methyl-N(tert-butyldimethylsilyl) trifluoroacetamide (MTBSTFA) [49].

Table 1
Application of DLLME combined with GC[a].

Analyte	Matrix	Extraction solvent volume	Disperser solvent volume	Detector	EF	LOD	Reference
PAHs	Water	8 μL tetrachloroethylene	1 mL acetone	FID	603–1113	0.007–0.030 μg L^{-1}	[25]
OPPs	Water	12 μL chlorobenzene	1 mL acetone	FPD	789–1070	0.003–0.020 μg L^{-1}	[26]
Chlorobenzenes	Water	9.5 μL chlorobenzene	0.50 mL acetone	ECD	711–813	0.0005–0.050 μg L^{-1}	[27]
OPPs	Watermelon and cucumber	27 μL chlorobenzene	1 mL acetonitrile	FPD	41–50	0.010–0.190 μg kg^{-1}	[95]
Trihalomethanes	Drinking water	20.0 μL carbon disulfide	0.50 mL acetone	ECD	116–355	0.005–0.040 μg L^{-1}	[28]
Triazine herbicides	Water	12 μL chlorobenzene	1.0 mL acetone	MS	151–722	0.021–0.12 μg L^{-1}	[29]
Chlorophenols	Water	10 μL chlorobenzene	0.50 mL acetone	ECD	287–906	0.010–2.0 μg L^{-1}	[31]
Phthalate esters	Water	9.5 μL chlorobenzene	0.50 mL acetone	MS	681–889	0.002–0.008 μg L^{-1}	[33]
Organophosphorus flame retardants and plastizicers	Water	20 μL 1,1,1-trichloroethane	1 mL acetone	NPD	190–830	LOQ: 0.01–0.08 ng mL^{-1}	[34]
Volatile phenols	Red wines	50 μL carbon tetrachloride	1 mL acetone	MS	–	28–95 μg L^{-1}	[35]
Chlorophenols (SPE-DLLME)	Water	13 μL chlorobenzene	1.0 mL acetone	ECD	4390–17,870	0.0005–0.1 μg L^{-1}	[121]
PCBs	Water	10 μL chlorobenzene	0.50 mL acetone	ECD	378–540	0.0010–0.0020 μg L^{-1}	[39]
Amide herbicides	Water	25 μL carbon tetrachloride	0.50 mL acetone	MS	437.1–460.7	0.003–0.04 μg L^{-1}	[37]
Butyl and phenyltin compounds	Water	11.5 μL carbon tetrachloride	0.50 mL ethanol	FPD	825–1036	0.0002–0.001 μg L^{-1}	[36]
Anilines	Water	10 μL chlorobenzene	0.50 mL acetone	MS	212–645	0.04–0.09 μg L^{-1}	[30]
Organosulfur pesticides	Environmental and beverage samples	10.0 μL carbon tetrachloride	0.80 mL methanol	FPD	176–946	0.21–3.05 μg L^{-1}	[32]
Selenium	Water	11 μL chlorobenzene	0.50 mL ethanol	ECD	122	0.005 μg L^{-1}	[71]
Amitriptyline and nortriptyline	Water	18 μL carbon tetrachloride	1.0 mL methanol	FID	740.04–1000.25	5–10 μg L^{-1}	[38]
Captan, folpet and captafol	Apples	9 μL chlorobenzene	1 mL acetone	ECD	824–912	3.0–8.0 μg kg^{-1}	[99]
Halogenated organic compounds (SFO-DLLME)	Water	10 μL 2-dodecanol	0.50 mL acetone	MS	228–322	0.005–0.047 μg L^{-1}	[126]
Phorate	Water	–	–	FID	300	0.001 μg L^{-1}	[42]
Pyrethroid pesticides	Water	10 μL chlorobenzene	1 mL acetone	ECD	708–1087	0.04–0.10 μg L^{-1}	[43]
Calcium stearate	Polyolefin samples	40 μL carbon tetrachloride	2 mL HCl 2 M in 2-propanol	FID	–	15 mg L^{-1}	[48]
PCBs	Fish	30 μL chlorobenzene	1 mL acetone	ECD	87–123	0.12–0.35 μg kg^{-1}	[100]
Organochlorine pesticides (DLLME-LSC)	Water	Tetrachloroethylene (TCE) 5.2 μL	Tert-butyl methyl ethers (TBME) 7.8 μL	MS	1885–2648	0.0008–0.0025 μg L^{-1}	[120]
Amide herbicides (SPE-DLLME)	Water	25.0 μL carbon tetrachloride	1 mL acetone	MS	6593–7873	0.002–0.006 μg L^{-1}	[123]
PBDEs (SPE-DLLME)	Water and plant samples	22.0 μL 1,1,2,2-tetrachloroethane	1 mL acetonitrile	ECD	6838–9405	0.00003–0.00015 μg L^{-1}	[122]
PCBs	Soil	30 μL chlorobenzene	1 mL acetone	ECD	–	0.20–0.50 μg kg^{-1}	[101]
OPPs	Tea	n-Hexane	acetonitrile	FPD	–	0.030–1 μg kg^{-1}	[104]
Fatty acid	Water	10 μL carbon tetrachloride	0.96 mL acetone	FID	–	0.67–14.5 μg L^{-1}	[40]
Triclosan and methyltriclosan	Water	40 μL CH_3CCl_3	1.0 mL methanol	MS/MS	–	LOQ: 2–5 ng L^{-1}	[49]
Water-soluble constituents	Rosa damascena Mill. essential oil	37 μL chloroform	0.50 mL ethanol	MS	231–378	0.001–1.121 mg L^{-1}	[41]
Chlorothalonil, captan and folpet	Grape samples	9 μL chlorobenzene	1 mL acetone	ECD	788–876	6.0–8.0 μg kg^{-1}	[107]
Nitroaromatic	Water	20 μL carbon tetrachloride	0.75 mL methanol	FID	202–314	0.09–0.5 μg L^{-1}	[44]
Organochlorine pesticides	Water	10 μL tetrachloroethylene	1 mL acetone	MS	46–316	1–25 ng L^{-1}	[47]
Personal care products	Natural waters	250 μL carbon tetrachloride	0.62 mL methanol	MS	–	8–63 ng L^{-1}	[46]
Methyl tert-butyl ether	Water	–	–	FID	–	0.1 μg L^{-1}	[45]
Seven fungicides (SPE-DLLME)	Wine	0.1 mL CH_3CCl_3	1 mL acetone	ECD and MS	200	–	[124]
PCBs	Soil	30 μL chlorobenzene	1 mL acetone	ECD	–	0.20–0.50 μg kg^{-1}	[101]
OPPs	Tea	n-Hexane	Acetonitrile	FPD	–	0.030–1 μg kg^{-1}	[104]
Fatty acid	Water	10 μL carbon tetrachloride	0.96 mL acetone	FID	–	0.67–14.5 μg L^{-1}	[40]
Triclosan and methyltriclosan	Water	40 μL CH_3CCl_3	1.0 mL methanol	MS/MS	–	LOQ: 2–5 ng L^{-1}	[49]
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Nitroaromatic	Water	20 μL carbon tetrachloride	0.75 mL methanol	FID	202–314	0.09–0.5 μg L^{-1}	[44]
Organochlorine pesticides	Water	10 μL tetrachloroethylene	1 mL acetone	MS	46–316	1–25 ng L^{-1}	[47]
Personal care products	Natural waters	250 μL carbon tetrachloride	0.62 mL methanol	MS	–	8–63 ng L^{-1}	[46]
Methyl tert-butyl ether	Water	–	–	FID	–	0.1 μg L^{-1}	[45]

[a] It is updated to 1 September 2009.

3.2. DLLME combined with HPLC

In general, HPLC is a widely used versatile separation and quantification instrument. It is important that the selected extracting organic solvent for DLLME method be compatible with the HPLC mobile phase. However, halogenated hydrocarbons such as chlorobenzene, carbon tetrachloride, chloroform and tetrachloroethylene, usually selected as extracting solvents in DLLME, are not compatible with the reverse-phase-HPLC mobile phase, because of their high density and an extra step is needed to evaporate them before final analysis. In 2007, Farajzadeh et al. [50] reported a preliminary study on a combination of DLLME with high-performance liquid chromatography-diode array detection (HPLC-DAD) for the analysis of antioxidants in aqueous samples. The reported method was very efficient, rapid and repeatable. Further, nearly 100% recovery and *PFs* about 200 times were attained. DLs of the method were between 3 and 7 ng mL^{-1}. The versatility of DLLME-HPLC is seen in relation to the variety of applications in many areas, as depicted in Table 2. Wei et al. [51] applied DLLME in combination with HPLC-variable wavelength detection (VWD) for determination of methomyl in water samples. Comparison of this method with SPE, SPME and SDME indicates that DLLME combined with HPLC-VWD is a simple, fast and low cost method thus it has tremendous potential in trace analysis of methomyl in natural waters.

Guo et al. [52] employed DLLME combined with ultra-high pressure liquid chromatography (UHPLC)-tunable ultraviolet detection (TUV) for preconcentration and determination of triclosan (TCS), triclocarban (TCC) and methyltriclosan (M-TCS) in aqueous samples. Under the optimum conditions, linearity of the method was in the range of 0.05–100 μg L^{-1} for TCS, 0.025–50.0 μg L^{-1} for TCC and 0.500–100 μg L^{-1} for M-TCS. DLs were in the range of 45.1–236 ng L^{-1}. Recently, a novel method has been developed [53] for determining of bisphenol A in water samples by DLLME-HPLC-UV. The method showed an acceptable DL (0.07 μg L^{-1}) and good linear range (0.5–100 μg L^{-1}) without using any derivatization reagent or applying very sensitive determination methods as GC–MS and HPLC–MS. In 2008, Xia et al. [54] described DLLME-HPLC-UV–vis detection for determination of metacrate in water samples. Firstly, an orthogonal array design (OAD) was used to choose the significant factors. Secondly, the significant factors were optimized by a central composite design (CCD). Then, the quadratic model between the dependent and independent variables was built. The method showed a good agreement between the experimental data and predictive value. Farajzadeh et al. [55] proposed DLLME combined with HPLC-UV for determining of Irganox 1010 and Irgafos 168 from polyolefins. Then, acetonitrile (2 mL) and carbon tetrachloride (200 μL) were added. The tube was capped and the mixture was heated at 100 °C in a water bath for 3 h. After cooling and filtering, water (5.00 mL) was injected rapidly into the solution by a 5-mL syringe. The cloudy solution produced was centrifuged for 5 min at 1000 rpm. The sedimented phase was quantitatively transferred into another test tube and left to evaporate at room temperature. Finally, the residue was dissolved in 0.5 mL LC-grade methanol and 20 μL of the obtained solution was then injected into HPLC for analysis. DLLME-HPLC-DAD detection was used for extraction and preconcentration of phenoxyacetic acid herbicides in water samples [56]. A 5.00-mL water sample (pH = 1.5) containing 10% (w/v) sodium chloride was placed in a 10-mL glass tube with a conical bottom. Acetone (1 mL) as disperse solvent, containing 25 μL chlorobenzene as extracting solvent was injected rapidly into the sample. The mixture was then centrifuged for 5 min at 5000 rpm. The method had good linearity and a wide linear dynamic range (0.5–750 μg L^{-1}). Further, its DL was 0.16 μg L^{-1} for both analytes. In 2009, Maleki et al. [57] applied DLLME-HPLC-DAD for extraction and determination of ethylenediaminetetraacetic acid (EDTA) in sediments and water samples. A 7.00-mL working standard solution containing 30 ng mL^{-1} EDTA (pH 2.0) was placed in a 12-mL glass tube with conical bottom. Acetone (500 μL) containing 50 μL carbon tetrachloride was injected rapidly into the sample solution. After centrifuging, the sediment phase was completely transferred into another test tube with conical bottom using a 100-μL HPLC syringe. After evaporation of the solvent in a water bath, the residue was dissolved in 50 μL acetate buffer and injected into the separation system. Under the optimal conditions, the analytical range was 3.0–50.0 μg L^{-1} and DL of 1.7 μg L^{-1} was obtained for EDTA. In 2009, Farhadi et al. [58] reported DLLME combined with HPLC for determining benomyl in water samples. The method is based on the extraction of benomyl from acidified sample solution and its conversion into carbendazim via solvolysis reaction with N,N-dimethyl formamide (DMF) as organic solvent. It showed a good linearity (0.998) with wide linear dynamic range (0.01–25 mg L^{-1}) and low DL (0.0033 mg L^{-1}). In addition, DLLME-HPLC in combination with different detectors was applied for determination of pentachlorophenol (DAD) [59], polybrominated biphenyl ethers at trace levels in landfill leachate (VWD) [60], four aromatic amines (VWD) [61], decabrominated diphenyl ether (VWD) [62], atrazine (UV) [63], three phthalate esters (VWD) [64], carbamate pesticides (DAD) [65], atrazine and simazine [66], trace amounts of dichlorodiphenyltrichloroethane and its main metabolites (UV) [67] and trace level bisphenol A in water samples [68].

3.3. Metal ions

3.3.1. DLLME combined with AAS

The majority of work on DLLME mentioned here has so far been focused on organic compounds, but there have been attempts to extend the procedure to inorganic analytes as well. Electrothermal atomic absorption spectrometry (ET-AAS) needs microamounts of the sample for analysis. Therefore, by combination of DLLME and ET-AAS, a unique analysis system can be obtained. In this method, a chelating agent is added to the sample solution. Then, DLLME is conducted by using appropriate extracting and disperser solvents. The versatility of DLLME for extraction of metal ions from various matrixes is tabulated in Table 3.

Zeini Jahromi et al. reported some early studies in this area. The application of this approach has been demonstrated for determination of cadmium in water samples [69]. Five hundred μL of methanol containing 34 μL carbon tetrachloride and 0.00010 g of ammonium pyrrolidine dithiocarbamate was rapidly injected by a syringe into the water sample containing cadmium ions. After centrifugation (2 min at 5000 rpm), the droplets were sedimented at the bottom of the conical test tube (25 ± 1 μL). Then, 20 μL of the sedimented phase containing enriched analyte was determined by ET-AAS. Under the optimum conditions, the *PF* was obtained for Cd 25 using only 5.00 mL of the water sample. The calibration graph was linear in the range of 2–20 ng L^{-1} with the DL of 0.6 ng L^{-1}.

The same authors also proposed DLLME combined with iridium-modified tube ET-AAS for determination of selenium (Se) in water samples [70]. The calibration graph was linear in the range of 0.1–3 μg L^{-1} with the DL of 0.05 μg L^{-1}.

Later, the same authors established an optimal derivatization reaction for Se(IV) followed by DLLME for microextraction and analysis of the piazselenol complex formed by GC-ECD [71]. The results showed that to obtain a low DL value (0.005 μg L^{-1}, which was similar to that of the mass spectrometry detectors), DLLME requires the lower sample-preparation time and sample consumption (5.00 mL). Liang and Sang employed DLLME to determine the trace amount of lead in biological and water samples using ET-AAS. The DL of the proposed method for lead was obtained as 39 ng L^{-1}. The method was also applied for determination of Pb ions in human

Table 2
Application of DLLME combined with HPLC[a].

Analytes	Matrix	Extraction solvent volume	Disperser solvent volume	Detector	EF	LOD	Reference
Antioxidants	Water	40 μL carbon tetrachloride	2 mL acetonitrile	Photo diode array detector	168–220	3–7 ng mL^{-1}	[50]
Methomyl	Water	20 μL tetrachloroethane	0.50 mL methanol	VWD	70.7	1.0 ng mL^{-1}	[51]
Chloramphenicol	Honey	30 μL 1,1,2,2-tetrachloroethane	1.0 mL acetonitrile	VWD	68.2	0.6 μg kg^{-1}	[105]
Clenbuterol	Water	25 μL tetrachloroethylene	0.50 mL acetone	UV	175	4.9 ng mL^{-1}	[114]
Chlorophen oxyacetic acids	Water	Tetrachloroethylene	THF	UV	131–156	2.3–3.3 ng mL^{-1}	[112]
Aromatic amines	Water	50 μL [Bmim][PF_6]	–	VWD	31–269	0.45–2.6 μg L^{-1}	[108]
Pentachlorophenol	Water	15 μL tetrachloroethylene	1 mL acetone	DAD	–	0.03 μg L^{-1}	[59]
PBDEs	Water	20 μL tetrachloroethane	1.0 mL acetonitrile	VWD	268–305	12.4–55.6 pg mL^{-1}	[60]
Aromatic amines	Water	25.0 μL tetrachloroethane	0.50 mL methanol	VWD	41.3–94.5	0.8–1.8 ng mL^{-1}	[61]
Phthalate esters	Water	41 μL carbon tetrachloride	0.75 mL acetonitrile	VWD	45–196	0.64–1.8 ng mL^{-1}	[64]
Atrazine	Water	60 μL carbon tetrachloride	550 μL methanol	UV	–	0.601 ng mL^{-1}	[63]
Decabrominated diphenyl ether	Water	22.0 μL tetrachloroethane	1.0 mL THF	VWD	153	0.2 ng mL^{-1}	[62]
Carbamate pesticides	Water	70 μL chloroform	1 mL acetone	DAD	101–145	0.4–1.0 ng mL^{-1}	[65]
Benomyl	Water	25 μL chlorobenzene	0.5 mL N,N-dimethyl formamide (DMF)	Fluorescence	–	0.0033 mg L^{-1}	[58]
Carbendazim and thiabendazole	Water and soil	80.0 μL chloroform	0.75 mL THF	Fluorescence	149–210	0.5–1.0 ng mL^{-1}(water), 1.0–1.6 ng g^{-1}(soil)	[106]
PAHs (DLLME-SFO)	Water	100 μL 1-dodecanol	200 μL methanol	VWD	88–118	0.045–1.1 ng mL^{-1}	[127]
Heterocyclic insecticides	Water	0.052 g [C_6MIM][PF_6] as ionic liquid	0.50 mL methanol	DAD	209–276	0.53–1.28 μg L^{-1}	[109]
Chloramphenicol and thiamphenicol	Honey	30 μL 1,1,2,2-tetrachloroethane	1.0 mL acetonitrile	VWD	68.2–87.9	0.1–0.6 μg kg^{-1}	[97]
Cholesterol	Food	35 μL carbon tetrachloride	0.8 mL ethanol	UV	–	0.01 μg L^{-1}	[96]
Triazophos and carbaryl pesticides	Water and fruit juice	15.0 μL tetrachloroethane	1.0 mL acetonitrile	Fluorescence	87.3–275.6	12.3–16.0 pg mL^{-1}	[98]
7-Aminoflunitrazepam	Urine	250 μL dichloromethane	500 μL isopropyl alcohol	Electrospray-tandem mass spectrometry (ES-MS/MS)	20	0.025 ng mL^{-1}	[91]
Psychotropic drugs	Urine	20 μL carbon tetrachloride	0.5 mL acetonitrile	UV	23.5–24.1	3–8 ng mL^{-1}	[92]
PAHs	Water and fruit juice	16.0 μL $C_2H_2Cl_4$	1.0 mL acetonitrile	Fluorescence	296–462	0.001–0.01 μg L^{-1}	[103]
Carbamate pesticides	Water	40.0 μL trichloromethane	1.0 mL acetonitrile	DAD	80–177	0.1–0.5 ng mL^{-1}	[65]
Triclosan, triclocarban, methyltriclosan	Water	15.0 μL $C_6H_4Cl_2$	1.0 mL THF	Tunable ultraviolet detection (TUV)	–	45.1–236 ng L^{-1}	[52]
Irganox 1010 and Irgafos 168	Polyolefins	200 μL carbon tetrachloride	2 mL acetonitrile	UV	–	–	[55]
Bisphenol A	Water	142.0 μL chloroform	2.0 mL acetone	UV	150	0.07 μg L^{-1}	[53]
Phenoxyacetic acid herbicides	Water	25 μL chlorobenzene	1 mL acetone	DAD	–	0.16 μg L^{-1}	[56]
EDTA	Water	50 μL carbon tetrachloride	0.5 mL acetone	DAD	–	1.7 μg L^{-1}	[57]
Hexanal and heptanal	Human blood	50 μL tetrachloromethane	85 μL acetonitrile	Atmospheric-pressure chemical ionization tandem mass spectrometry (APCI-MS–MS)	63–73	0.17–0.076 nmol L^{-1}	[93]
Atrazine and simazine	Water	Carbon tetrachloride	Methanol	–	–	0.04–0.1 μg L^{-1}	[66]
Bisphenol A	Water	22.5 μL chlorobenzene	0.5 mL acetone	–	1905–2527	0.1 μg L^{-1}	[68]
Sulfonylurea herbicides (DSPE-DLLME)	Soil	60 μL chlorobenzene	Acetone	DAD	102–216	0.5–1.2 ng g^{-1}	[125]
Biogenic amines (USA-DLLME)	Rice wine samples	50 μL 1-octanol	–	Fluorescence	–	0.02–5 ng mL^{-1}	[117]
Non-steroidal anti-inflammatory drugs	Urine	280 μL [Bmim][PF_6]	720 μL methanol	Single wavelength photometer	73.7–84.6	8.3–32 ng mL^{-1}	[118]
PAHs	Water	50 μL [C_8MiM][PF_6]	1 mL acetone	Fluorescence	–	LOQ: 0.1–7.0 ng L^{-1}	[111]
Phenylurea herbicides	Aqueous samples	Dichloromethane	THF	DAD	68–126	0.10–0.28 ng mL^{-1}	[113]
Eight pesticides	Bananas	88 mg [C_6MIM][PF_6]	714 μL methanol	DAD	–	0.320–4.66 μg kg^{-1}	[102]
Dichlorodiphenyl trichloroethane	Water	50 μL carbon tetrachloride	600 μL acetonitrile	UV	–	0.32–0.51 μg L^{-1}	[67]
Metacrate	Water	116 μL CH_2Cl_2	565 μL methanol	UV	118	1 ng mL^{-1}	[54]

[a] It is updated to 1 September 2009.

Table 3
Application of DLLME combined with other instruments[a].

Analytes	Matrix	Extraction solvent volume	Disperser solvent volume	Instrument	Chelating agent	LOD	Reference
Cadmium	Water	34 μL carbon tetrachloride	0.50 mL methanol	GF AAS	Ammonium pyrrolidine dithiocarbamate (APDC)	0.6 ng L^{-1}	[69]
Selenium	Water	35 μL carbon tetrachloride	0.50 mL ethanol	GF AAS	APDC	0.05 μg L^{-1}	[70]
Palladium and cobalt	Water	70 μL 1,2-dichlorobenzene	0.40 mL ethanol	Fiber optic-linear array detection spectrophotometry (FO-LADS)	1-(2-Pyridylazo)-2-naphthol (PAN)	0.2–0.25 μg L^{-1}	[87]
Lead	Water	35 μL carbon tetrachloride	0.50 mL acetone	ET AAS	Diethyl dithiophosphoric acid (DDTP)	0.02 μg L^{-1-}	[80]
Lead	Biological and water	40 μL carbon tetrachloride	0.50 mL ethanol	GF AAS	1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP)	39 ng L^{-1}	[72]
Gold	Water and silica ore	40 μL chlorobenzene	1 mL acetone	GF AAS	Victoria blue R (VBR)	0.005 ng mL^{-1}	[74]
Lead	Water	52 μL carbon tetrachloride	2.5 mL methanol	F AAS	DDTP	0.5 μg L^{-1}	[75]
Samarium, europium, gadolinium and dysprosium	Water	400 μL chloroform	10 mL methanol	ICP-OES	PAN	–	[89]
Copper(II)	Water	250 μL chloroform	1.5 mL methanol	F AAS	8-Hydroxy quinoline	3 μg L^{-1}	[73]
Arsenic and antimony	Water	50 μL carbon tetrachloride	0.4 mL methanol	ET AAS	APDC	0.01–0.05 μg L^{-1}	[76]
As(III) and As(V)	Water	35 μL carbon tetrachloride	0.5 mL methanol	GF AAS	APDC	36 ng L^{-1}	[77]
Palladium	Water	40 μL carbon tetrachloride	0.50 mL ethanol	GF AAS	Diethyl dithiocarbamate (DDTC)	2.4 ng L^{-1}	[78]
Chromium	Water	60 μL carbon tetrachloride	2.0 mL ethanol	F AAS	APDC	0.07 μg L^{-1}	[81]
Copper and lead	Water	Xylene	Methanol	F AAS	Ammonium diethyldithiophosphate	0.04 (cu(II))–0.54 (pb(II)) μg L^{-1}	[115]
Palladium	Water	150 μL chloroform	1.5 mL ethanol	F AAS	Thioridazine HCl (TRH)	90 μg L^{-1}	[79]
Samarium, europium, gadolinium and dysprosium	Uranium dioxide powder	600 μL ionic liquid	8.0 mL methanol	ICP-OES	1-Hydroxy-2,5-pyrrolidinedione (HYD)	0.34–1.29 μg L^{-1}	[110]
Nitrite	Environmental and biological	Carbon tetrachloride	Ethanol	Digital colorimetry	P-Nitro-aniline and diphenyl amine	0.22 μg L^{-1}	[90]
Cd(II)	Water	34 μL carbon tetrachloride	0.5 mL methanol	GF AAS	Salen(N,N-bis salicylidene)-ethylene diamine	0.5 ng L^{-1}	[86]
Cobalt	Water	Chloroform	Ethanol	Spectrophotometer	PAN	0.5 μg L^{-1}	[88]
Co and Ni	Environmental water and rice samples	15 μL carbon tetrachloride	1 mL acetone	GF AAS	PAN	21 (Co)–33(Ni) pg mL^{-1}	[82]
Cadmium (IL-based USA-DLLME)	Water	1-Hexyl-3-methylimidazolium hexafluorophosphate ($HMIMPF_6$)	–	ET AAS	DDTC	7.4 ng L^{-1}	[116]
Cobalt	Water	50 μL carbon tetrachloride	2.0 mL methanol	F AAS	Br-TAO	0.9 μg L^{-1}	[83]
Lead and cadmium	Water	50 μL carbon tetrachloride	0.4 mL methanol	ET AAS	APDC	Lead (10) and cadmium (4) ng L^{-1}	[85]
Silver	Water	15.0 μL carbon tetrachloride	0.5 mL ethanol	FAAS	–	1.2 ng mL^{-1}	[84]

[a] It is updated to 1 September 2009.

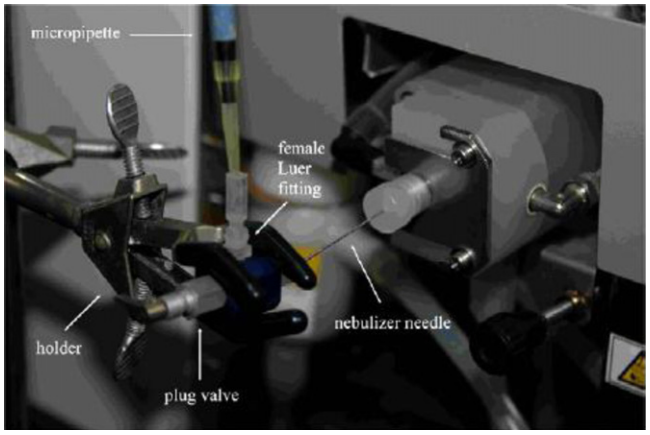

Fig. 2. Photography of the microsample introduction system in the FAAS. Reprinted with permission from [75].

urine and tap water samples [72]. Extraction and preconcentration of Cu^{2+} ions by DLLME were optimized using one variable at a time as well as a simultaneous optimization method [73]. The optimization procedure was a chemometric method using a central composite design for obtaining the optimal conditions. The application of DLLME has been extended to the selective determination of ultra trace amounts of gold in different samples [74]. The preconentration procedure resulted in quantitative extraction of gold by Victoria Blue R from a 10-mL sample into fine droplets of chlorobenzene with a sedimented volume of 25 μL. The DL and relative standard deviation were 0.005 ng mL^{-1} and 4.2%, respectively.

For the first time DLLME was combined with flame atomic absorption spectrometry (FAAS) using a microsample introduction system [75]. A new FAAS sample introduction system was employed for the micro volume nebulization of non-flammable chlorinated organic extracts. Injection of 20 μL volume of the organic extract into an air-acetylene flame provided very sensitive spike-like and reproducible signals (Fig. 2). The results demonstrated that DLLME-FAAS by microsample introduction is a sensitive, fast and reproducible technique for preconcentration and determination of lead in water samples. In 2009, Rivas et al. [76] by combining DLLME with ET-AAS developed a new method for speciation of very low amounts of arsenic and antimony in water samples. The DLs of 0.01 and 0.05 μg L^{-1} were obtained for As(III) and Sb(III), respectively, with the *PF* of 115. Besides, DLLME in combination with ET-AAS and FAAS were applied for speciation of As(III) and As(V) in water samples (ET-AAS) [77], preconcentration of palladium in water samples (ET-AAS) [78], selective determination of the trace amounts of palladium (FAAS) [79], rapid determination of lead in water samples (ET-AAS) [80], speciation of chromium in water samples (FAAS) [81], determination of trace amounts of Co and Ni in environmental water and rice samples (ET-AAS) [82], determination of cobalt in water samples (FAAS) [83], separation of trace amounts of silver ions in water samples (FAAS) [84], determination of traces of lead and cadmium (ET-AAS) [85] and preconcentration of ultra trace amounts of Cd(II) [86].

3.3.2. DLLME combined with other instruments

DLLME can also be combined with spectrophotometric instruments for quantitative determination of metal ions. Shemirani and co-workers [87] proposed DLLME combined with fiber optic-linear array detection spectrophotometer (FO-LADS) by using a cylindrical micro-cell for simultaneous preconcentration and determination of palladium and cobalt in real and synthetic samples. Under the optimum conditions, the calibration graphs were linear in the range of 2–100 and 1–70 μg L^{-1} with the DLs of 0.25 μg L^{-1} and 0.2 μg L^{-1} for palladium and cobalt, respectively. Ghrehbaghi et al. [88] applied DLLME for extraction and determination of trace levels of cobalt in tap and river water samples by spectrophotometer method. They used 1-(2-pyridylazol)-2-naphthol (PAN) as suitable chelating agent for cobalt ions. The PF and DL were 150 and 0.5 μg L^{-1}, respectively. Considering the compatibility of the extracting organic solvents of DLLME with inductively coupled plasma-optical emission spectrometry (ICP-OES), the extract is not directly analyzable by this technique. Mallah et al. [89] reported DLLME for simultaneous preconcentration of lanthanides such as samarium (Sm), europium (Eu), gadolinium (Gd) and dysprosium (Dy). The settled phase was dried in oven at 80 °C. Then, 0.5 mL of 1 mol L^{-1} solution of HNO_3 was added. The obtained solution was introduced into ICP-OES by peristaltic pump. Under the best operating conditions, the PFs of 80, 100, 103 and 78 were obtained for Sm, Eu, Gd and Dy, respectively. In 2009, Ding and Liu [90] reported DLLME combined with digital colorimetry for determination of trace nitrite in water samples. The settled organic phase was spotted into the silica gel TLC plate and then directly imaged by a digital camera. The spot's gray scale integral value was proportional to nitrite concentration. The calibration curve was linear in a concentration range of 2.0–80 μg L^{-1} and DL was 0.22 μg L^{-1}.

3.4. Applications of DLLME for other matrixes such as food and biological samples

DLLME is widely applied for environmental water samples but rarely applied for the analysis of drugs in complex matrixes such as biological fluids. In spite of several advantages of DLLME, it is not well compatible for extraction of analytes from biological samples. Due to the interaction of matrix components in these kinds of samples with organic solvents, it is not possible to produce suitable sediment phase for injection into analytical instruments such as GC. To obtain suitable sediment phase, dilutions of the samples are needed. Also, dilution of real samples causes changes in the inherent property of the matrix, but under this condition, the method is applicable only for the samples containing high concentrations of the analytes.

A few papers have reported the application of DLLME in urine samples. For the first time, Fuh and co-workers [91] developed DLLME combined with liquid chromatography–electrospray-tandem mass spectrometry (LC–ES-MS/MS) for the extraction and determination of 7-aminoflunitrazepam (7-amino FM2), a biomarker of hypnotic flunitrazepam (FM2), in urine sample. To demonstrate the potentiality of the technique in various urine samples, each sample was basified using ammonia so that the overall concentration of ammonia was 0.2 M. Then, 5% of NaCl was added to the sample. The resulted precipitate was filtered off and 5 mL of an aliquot of the clear supernatant urine sample solution was placed in a test tube and extracted using DLLME. 7-Amino FM2 was extracted from the basified urine sample into the dispersed dichloromethane (DCM) droplets. The PF for the extraction process was about 20. A good linearity (0.05–2.5 ng mL^{-1}) with the DL of 0.025 ng mL^{-1} was obtained. In a subsequent study, Xiong et al. [92] proposed DLLME combined with HPLC-UV for determining of three psychotropic drugs in urine samples. For aqueous standards, a small droplet of carbon tetrachloride was sedimented in the bottom of the conical test tube. But for urine sample, white lipidic solid was sedimented in the bottom of the conical test tube, probably due to the co-sedimentation of the matrixes (such as carbamide and uric acid) in urine at high pH values. After slowly discarding the aqueous solution, the resulting droplets and lipidic solid were dissolved in 200 μL of acetonitrile and the solution was filtrated through a 0.45-μm membrane to discard the white floccule from the extract solution. Finally, an appropriate volume of the extract was with-

drawn into a micro syringe and then injected into the HPLC for analysis. The DLs and limits of quantification (LOQs) of the method were 3 and 10 ng mL^{-1} for amitryptiline, 7 and 21 ng mL^{-1} for clomipramine, and 8 and 25 ng mL^{-1} for thioridazine, respectively. Under the optimal DLLME conditions, the absolute recoveries of amitryptiline, clomipramine and thioridazine were 96%, 97% and 101%, respectively.

In 2009, Xu et al. [93] developed a method for simultaneous derivatization and DLLME combined with liquid chromatography–atmospheric-pressure chemical ionization tandem mass spectrometry (LC–APCI-MS–MS) for the analysis of hexanal and heptanal in human blood samples. The DLs of the method for hexanal and heptanal were 0.17 and 0.076 nmol L^{-1}, respectively. The PFs for one mL sample were 63 and 73 for hexanal and heptanal, respectively. Rezaee et al. [94] proposed a DLLME combined with HPLC-UV for the extraction and determination of letrozole in biological fluids. To develop DLLME for plasma sample and to obtain relatively clean sedimented phase and suitable results, some extra process is needed. At first, the plasma sample was dissolved in a suitable amount of acetonitrile such as 1:1 (v/v) for reducing the effect of matrix and then the mixtures were centrifuged. Then, they were filtered to obtain clear solution. Finally, the solution was diluted as 1:10 for DLLME procedure.

Some applications of DLLME have been reported for food and soil analysis. For the first time, DLLME combined with GC-flame photometric detection (FPD) was developed for determination of organophosphorus pesticides (OPPs) in cucumber and watermelon samples [95]. Two hundred fifty grams of the sample was homogenized by a food processor. Ten grams of the previously homogenized sample was weighed in 50 mL PTFE centrifuge tube. Ten mL of acetonitrile, 4 g of anhydrous $MgSO_4$ and l g of NaCl were added and the mixture was shaken vigorously on a vortex mixer for 1 min. The mixed samples were centrifuged for 3 min at 4000 rpm. For DLLME, an aliquot of 5 mL purified water was placed in a 10-mL screw cap glass centrifuge tube with conical bottom. Twenty-seven μL of chlorobenzene was added to 1 mL of acetonitrile extract, which was used as the extracting solvent. The mixture was gently shaken by hand for several seconds. After centrifugation, 1 μL of the sedimented phase was injected into the GC. Daneshfar et al. [96] proposed DLLME combined with HPLC-UV for analyzing cholesterol in milk, egg yolk and olive oil. Egg yolk samples were manually separated from the albumen and placed on the absorbing paper to remove albumen. Then, they were homogenized by a food processor. 0.1 g of the yolk was added to l0 mL of doubly distilled water and shaken for 1 min. The obtained yolk suspension was centrifuged at 2000 rpm for 2 min. A 100-μL aliquot of the upper aqueous phase was spiked with the standard solution of cholesterol, treated with acetonitrile (0.4 mL) and centrifuged at 1000 rpm for 1 min. The upper aqueous layer was then transferred into another test tube for the extraction of cholesterol using DLLME. Sample preparation for milk was done as follows: An aliquot (100 μL) of the milk sample, preciously centrifuged at 2000 rpm for 10 min, was spiked with the standard solution of cholesterol. The solution was then treated with acetonitrile (0.4 mL) and centrifuged at 1000 rpm for 1 min. The upper aqueous layer was transferred into another test tube for the extraction of cholesterol using DLLME. Under the optimized conditions, the linear range, the DLs and LOQs were 0.03–10 μg L^{-1}, and 0.01 and 0.03 μg L^{-1}, respectively.

In 2009, Chen et al. [97] developed DLLME combined with HPLC-VWD for determination of chloramphenicol (CAP) and thiamphenicol (THA) in honey samples. One gram of honey was weighed into a 10-mL centrifuge tube with conical bottom, and 5.0 mL water was added. Then, the mixture was vortexed until a homogeneous sample was obtained. The obtained homogeneous sample was used for DLLME-HPLC analysis. Under the optimum extraction conditions, the linear range of 3–2000 μg kg^{-1} was obtained for target analytes. The *PFs* for CAP and THA were 68.2 and 87.9, and the DLs (S/N = 3) were 0.6 and 0.1 μg kg^{-1}, respectively.

Fu et al. [98] combined DLLME with HPLC-fluorescence detection (FLD) for determination of carbamate (carbaryl) and organophosphorus (triazoshos) pesticides in water and fruit juice samples. In order to reduce the matrix effect, the fruit juice was diluted at 1:1 ratio with deionized water. No dilution was needed for the water samples. In comparison with HF-LPME, DLLME showed lower RSDs (1.36–2.74%) and DLs (12.3–16.0 pg mL^{-1}) and much broad linear range (0.1–1000 ng mL^{-1}) for the analysis of carbaryl and triazophos. A novel method was developed for determination of captan, folpet and captafol in apples by DLLME combined with GC-ECD [99]. A 20.0-g apple sample was accurately weighed into a 50-mL centrifuge tube, to which 5.0 mL of 0.1 mol L^{-1} zinc acetate dihydrate solution (to prevent the degradation of captan and folpet) and 20.0 μL of internal standard α-hexachlorobenzene (20.0 mg L^{-1}) were added. The mixture was then homogenized using a food homogenizer and subsequently centrifuged at 5000 rpm for 10 min. The supernatant was transferred into Buchner funnel for filtration under reduced pressure. The filtrate was diluted to 25.0 mL with doubly distilled water. A 5.00-mL aliquot of the filtrate solution was placed in a 10-mL screw cap glass tube with conic bottom and centrifuged at 5000 rpm for 10 min. The supernatant was then transferred into another similar tube and 1 mL acetone was added. After the mixture was gently shaken, it was centrifuged at 5000 rpm for 10 min again. The supernatant was transferred into a third similar type of tube, into which 9 μL of chlorobenzene was injected. As a result, a cloudy solution was formed. After centrifugation at 5000 rpm for 5 min, the chlorobenzene phase was sedimented in the bottom of the centrifuge tube. The recoveries of fungicides in the apple samples at the spiking levels of 20.0 and 70.0 μg kg^{-1} were 93.0–109.5% and 95.4–107.7%, respectively.

In 2009, Hu et al. [100] proposed DLLME combined with GC-ECD for extraction and determination of four polychlorinated biphenyls (PCBs) in fish samples. The extraction procedure of PCBs for fish samples was as follows: About 1.0 g of each fish muscle homogenate was mixed with 3.0 g of anhydrous sodium sulfate to form a flowing powder. Then, the mixture was extracted using 10 mL of acetone by vigorously shaking for 30 min at 250 rpm on a mechanical shaker. The upper solution was transferred into a 10-mL glass test tube. Then, the solution was stored at −80 °C in a refrigerator overnight to deposit the lipids. For DLLME, an aliquot of 5.00 mL purified water was placed in a 10-mL screw cap glass test tube with conical bottom. After rapidly injecting 1.0 mL of acetone extract containing 30.0 μL of chlorobenzene into the water sample, a cloudy solution was formed in the test tube. After centrifugation, the sedimented phase was injected into GC-ECD for further analysis.

In 2009, Dai and co-workers [101] proposed DLLME combined with GC-ECD for determination of polychlorinated biphenyls (PCBs) in soil. Aliquots (1.0 g) of soil samples were loaded into a 50-mL conical flask. The samples were extracted with 10 mL of acetone for 30 min at 250 rpm on a mechanical shaker. The upper solution was transferred into a 10-mL glass test tube. For DLLME, 5.0 mL of ultra pure water was placed in a 10-mL screw cap glass test tube with conical bottom. Then 30.0 μL of chlorobenzene was dissolved into 1.0 mL of acetone extract, which was then rapidly added into the aqueous solution by a 1.0-mL syringe. The PCBs were extracted into fine droplets of chlorobenzene. The mixture was centrifuged and the sedimented phase was completely transferred into another test tube with conical bottom. After evaporation of the extracting solvent by a gentle nitrogen flow, the residue was dissolved in 20.0 μL *n*-hexane. The comparison of DLLME with liquid–liquid extraction (LLE) and miniaturized ultrasonic solvent extraction (MUSE) demonstrated that DLLME has comparable DLs (0.2–0.5 μg kg^{-1}) with those of LLE and MUSE. Besides, DLLME

has the advantage of lower consumption of organic solvent (about 10 mL) compared with the other methods. In 2009, Ravelo-Perez et al. proposed ionic liquid-based DLLME for the extraction of pesticides from bananas [102]. The fruit samples were first homogenized and extracted (1 g) with acetonitrile. After suitable evaporation and reconstitution of the extract in 10 mL of water, DLLME was performed using 1-hexyl-3-methylimidazolium hexafluorophosphate ($[C_6MIM][PF_6]$) as extracting solvent. Mean recovery values of the extraction of pesticides from the banana samples were in the range of 69–97% (except for thiophanate-methyl and carbofuran, which were 53–63%). Further, the DLs (0.320–4.66 $\mu g\,kg^{-1}$) obtained by DLLME were below the harmonized maximum residue limits established by the European Union (Eu).

In addition, the application of DLLME-HPLC-fluorescence detection for determination of PAHs in the water and fruit juice samples [103], DLLME-GC-FPD for determination of organophosphorus pesticides (OPPs) in tea [104], DLLME-HPLC-VWD for determination of chloramphenicol in honey [105], DLLME-HPLC-fluorescence detection for determination of carbendazim and thiabendazole in water and soil samples [106] and DLLME-GC-ECD for determination of chlorothalonil, captan and folpet residues in grape samples [107] has been reported as well.

4. Recent developments in DLLME

Room temperature ionic liquids (RTILS) are an interesting alternative to organic solvents because of their unique physicochemical properties, which depend on the nature and size of their cationic and anionic constituents. The main advantages of RTILS include negligible vapor pressure, good thermal stability, tunable viscosity and miscibility with water and organic solvents and thus an environmentally friendly extraction phase. Therefore, they are useful as extraction solvents for DLLME technique. For the first time, Zhu and co-workers [108] developed ionic liquid-based dispersive liquid–liquid microextraction (IL-DLLME) combined with HPLC-VWD for the extraction of 2-methylaniline, 4-chloroaniline, 1-naphthylamine and 4-aminobiphenyl from water samples. Unlike DLLME, the IL-DLLME method is a binary component solvent system (i.e. no disperser solvent is required). A 1.8-mL portion of the sample solution and 50 μL of 1-butyl-3-methylimidazolium hexafluorophosphate ($[Bmim][PF_6]$), as extracting solvent, were placed in a 2.2-mL glass test tube with conical bottom. One mL of the above mixture was withdrawn into a 1-mL syringe. Then the syringe plunger was pushed rapidly to inject the contents into the remaining solution. The cloudy mixture was centrifuged. The ionic liquid (IL) phase was injected directly into the HPLC. The DLs (S/N = 3) were in the range of 0.45–2.6 $\mu g\,L^{-1}$. The spiked recoveries, determined by spiking the samples with 40 $\mu g\,L^{-1}$ of aromatic amines, were in the range of 43.4–106.4%. In 2009, Liu et al. [109] proposed IL-DLLME combined with HPLC-DAD for determination of four heterocyclic insecticides in water samples. A mixture of 0.052 g of 1-hexyl-3-methylimidazolium hexafluorophosphate $[C_6MIM][PF_6]$ (extracting solvent) and 0.5 mL of methanol (disperser solvent) was quickly injected into a sample solution by a 1-mL syringe ($[C_6MIM][PF_6]$ is too viscose to be transferred by syringe). After centrifugation, the IL phase (about 19 μL) was dissolved in 50 μL of methanol, 10 μL of which was injected into the HPLC for analysis.

Under the optimized conditions, good *PFs* (209–276) were obtained. The calibration curves were linear in the range of 2–100 $\mu g\,L^{-1}$ and the DLs for the four insecticides were in the range of 0.53–1.28 $\mu g\,L^{-1}$ at a signal-to-noise ratio (S/N) of 3. Shemirani and co-workers [110] developed IL-DLLME-ICP-OES for determination of lanthanoids such as samarium, europium, gadolinium and dysprosium in uranium dioxide powder. Therefore, the ionic liquids

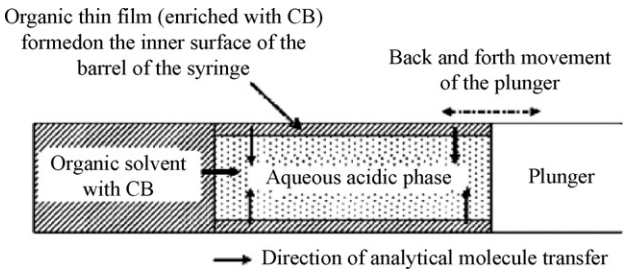

Fig. 3. Basic principle of extraction of CB into FA in the in-syringe back extraction step. Reprinted with permission from [114].

such as 1-butyl-3-methylimidazolium hexafluorophosphate and 1-hexyl-3-methylimidazolium hexafluorophosphate were used instead of an organic solvent. A significant increase in the *PFs* of Sm, Gd and Dy ions (but not Eu) were obtained in comparison with the organic solvents. Recently, Cela and co-workers [111] developed IL-DLLME method for the extraction of PAHs from water samples. The extraction yields for the different compounds obtained by IL-DLLME ranged from 90.3% to 103.8%. Furthermore, high PFs (301–346) were achieved.

In order to improve the extraction efficiency of polar organic compounds, Fuh and co-worker [112] developed partitioned dispersive liquid–liquid microextraction (PDLLME) combined with HPLC-UV for the extraction of chlorophenoxyacetic acids from river water samples. Based on their reported partition coefficients, the polar compounds were extracted into the dispersed tetrachloroethylene (TCE) droplets containing tetrahydrofuran (THF). Under the optimized conditions, the linear range was from 5 to 1000 $ng\,mL^{-1}$, DLs were in the range of 2.3–3.3 $ng\,mL^{-1}$ and *PFs* were in the range of 131–156. The same research group [113] proposed PDLLME method for determination of phenylurea herbicides (PUHs) in aqueous samples. The *PFs* of PUHs ranged from 68 to 126 under the optimal conditions. The linear range for each analyte was 0.5–100 $ng\,mL^{-1}$.

One limitation of DLLME is its unsuitability for the extraction of ionizable organic compounds. To solve this problem, Melwanki and Fuh [114] employed DLLME-HPLC-UV combined with semi-automated in-syringe back extraction for determination of ionizable organic compounds. Clenbuterol (CB), a basic organic

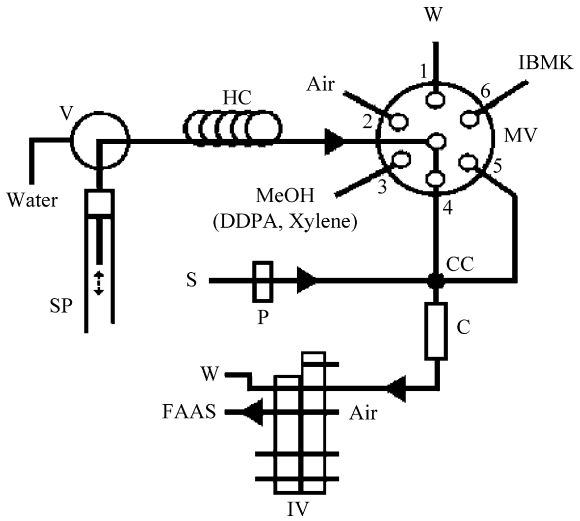

Fig. 4. Schematic manifold for SI-DLLME metal determination by FAAS. S, sample; MeOH, solution containing 2.0% (v/v) xylene and 0.3% (m/v) DDPA; W, waste; P, peristalic pump; SP, syringe pump; MV, multiposition valve; IV, injection valve in "load" position; V, valve in "out" position; HC, holding coil; C, microcolumn; CC, confluence connector. Reprinted with permission from [115].

compound, was extracted from a basified aqueous sample using 25 μL of TCE dissolved in 500 μL acetone. After centrifugation, the CB, already enriched in TCE phase, was back extracted into 10 μL of 1% (w/v) aqueous solution of formic acid (FA) within the syringe. Back extraction was facilitated by repeatedly moving the plunger back and forth within the barrel of the syringe, assisted by a syringe pump (Fig. 3). Due to the plunger movement, a thin organic film was formed on the inner layer of the syringe that came in contact with the acidic aqueous phase. Here, CB was protonated and back extracted into FA. Under the optimum conditions, the linear ranges were within 10–1000 ng mL^{-1}, DL was 4.9 ng mL^{-1} and *PF* was obtained as175.

Automatic on-line hydrodynamic analytical system could be exploited with a view to enhancing the inherent properties of conventional measurement procedures. Unlike SPME, automation and on-line combining of DLLME to analytical instruments seems to be difficult. For the first time, Anthemidis' group developed an on-line sequential injection DLLME system to FAAS for determination of copper and lead in water samples [115]. The manifold and its operation for on-line sequential injection dispersive liquid–liquid microextraction (SI-DLLME) metal determination by FAAS are presented schematically in Fig. 4. The xylene droplets, containing the metal complexes, were retained on the PTFE-turnings into the microcolumn. Then, a segment of 300 μL isobutyl methyl ketone (IBMK) was pumped through C eluting the analyte. The eluent was forwarded to the nebulizer for atomization and measuring. Unlike the conventional DLLME systems, in the present method no extracting solvent is necessary to have higher density than water, due to the fact the formation of cloudy solution takes place in a moving system and the retention of the extracting fine droplets is based on the hydrophobicity of the sorbent material. From commercial, economical and environmental points of view, SI-DLLME offers several important advantages: faster operation in micro-scale analysis, extremely low analysis time, low cost, low consumption of organic solvent, simple manifold (no need of separation unit), high recovery and high enhancement factor. In 2009, Li et al. [116] developed ionic liquid-based ultrasound-assisted dispersive liquid–liquid microextraction (IL-based USA-DLLME) followed by ET-AAS for determination of cadmium in water samples. The IL-based USA-DLLME is free of volatile organic solvents, and in contrast to conventional DLLME, there is no need for a dispersive solvent. The ionic liquid was quickly disrupted by an ultrasonic probe for 1 min and dispersed in the water sample like a cloud. The *PF* of the method was 67 and the DL was 7.4 ng L^{-1}. In another research by Huang et al. [117], USA-DLLME was used for determination of biogenic amines in rice wine samples. Fluorescence probe 2,6-dimethyl-4-quinoline carboxylic acid N-hydroxysuccinimide ester was applied for derivatization of biogenic amines. The calibration graph of the proposed method was linear in the range of 5–500 μg mL^{-1} (for octopamine and tyramine) and 0.025–2.5 μg mL^{-1} (for phenethylamine).

Recently, Valcarcel and co-workers [118] developed a one-step in-syringe ionic liquid-based DLLME. This novel approach avoids the centrifugation step. Further, it is typically off-line and time-consuming, opening up a new horizon on DLLME automation. Essentially, phase separation can be automated using a typical syringe pump. In addition, the centrifugation step restricts the use of solvents in DLLME, since only the solvents denser than water

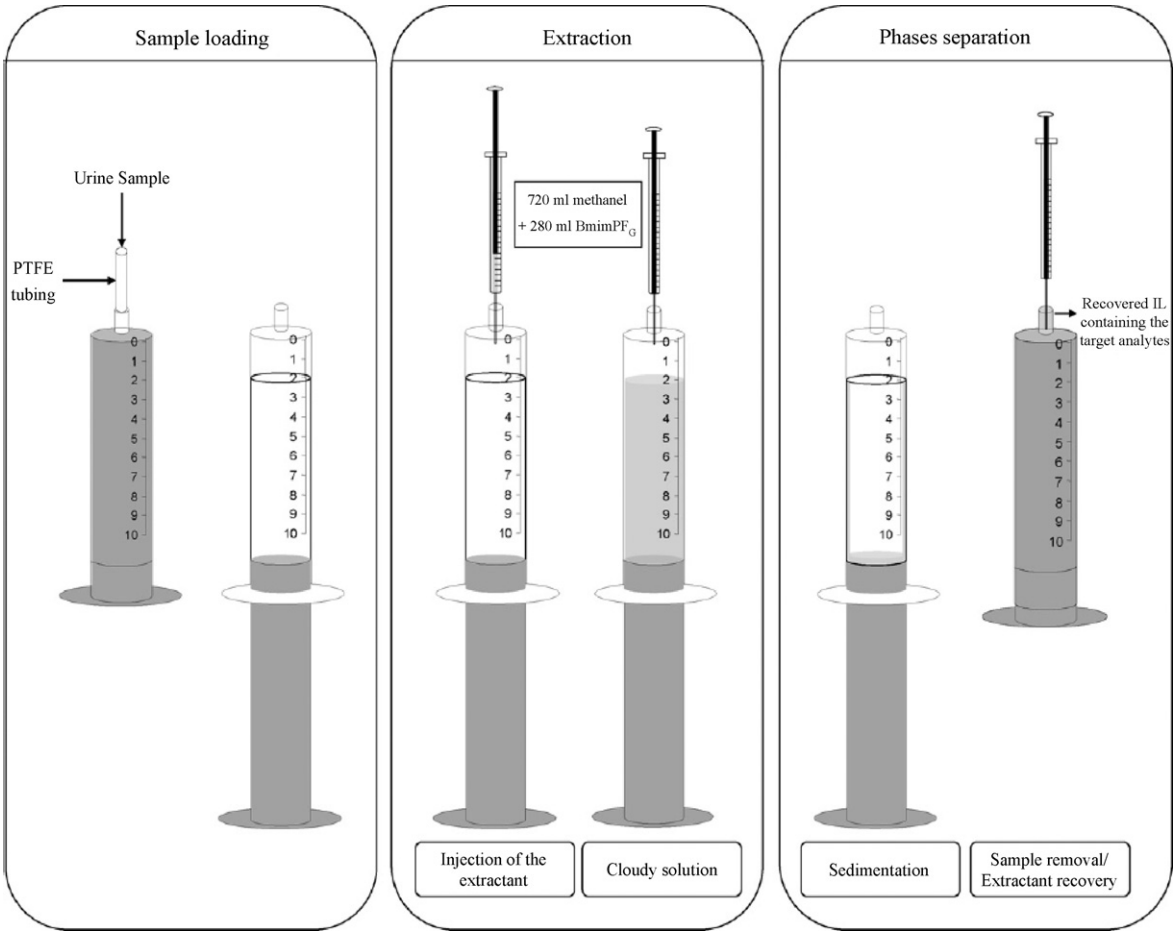

Fig. 5. Experimental set-up proposed for in-syringe ionic liquid-based dispersive liquid–liquid microextraction. Reprinted with permission from [118].

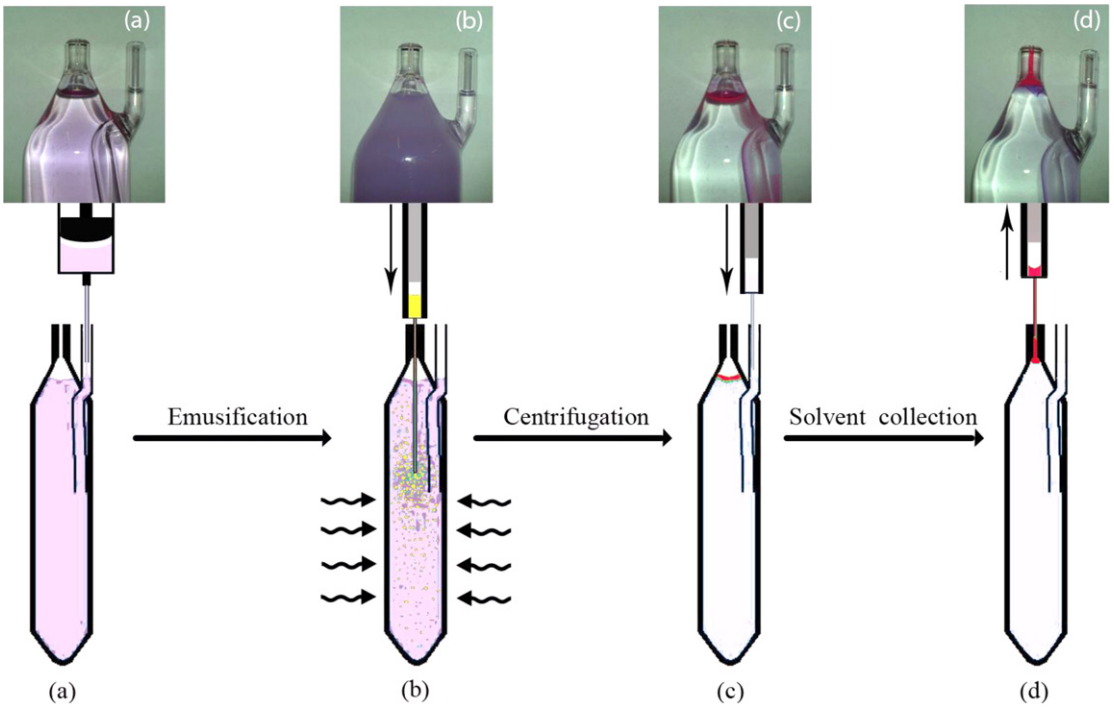

Fig. 6. Schematic representation of USAEME applying low density organic solvent. (a) Aqueous sample solution in the home-designed emulsification glass vial, (b) simultaneous injection and emulsification of 14 μL toluene into aqueous sample, (c) addition of a few μL of doubly distilled water into the vial and (d) collection of toluene transferred into the capillary tube at the top of the vial (4 μL) (a hydrophobe-red reagent was added to aqueous sample to distinguish colored toluene after centrifugation in the pictures). Reprinted with permission from [119].

can be employed. This new approach can overcome this restriction by changing the direction of the syringe during the phase separation step. The general scheme of the extraction process is depicted in Fig. 5. The procedure consists of three well-defined steps, namely: sample loading, extraction and phase separation. At the beginning, a specific volume of standard solution or urine sample (typically 10 mL) was aspirated into a 10-mL syringe by means of a PTFE tabbing adapted to the tip of the syringe. Then, 1000 μL of the extracting mixture, containing 720 μL of methanol and 280 μL of the extractant ([Bmim][PF_6]), were sprayed by a 1000-μL glass syringe, resulting in the immediate formation of a cloudy solution. Finally, the IL phase was easily removed from the syringe tip.

Yamini's research group [119] proposed ultrasound-assisted emulsification-microextration method based on applying low density organic solvents. Home-designed centrifuge glass vials containing an aqueous sample were immersed into an ultrasonic water bath. Micro volumes of the organic solvents were withdrawn into a microsyringe and injected slowly into the sample through the capillary tube at the top of the centrifuge vial. The conic top of the centrifuge vial attached to a capillary tube makes it suitable for easy collection of micro volumes of the floated organic solvents on the surface of the aqueous sample (Fig. 6). The proposed method is an efficient, rapid, simple and cheep microextration technique that can be a complement for DLLME and USAEME that have been used for organic solvents denser than water.

The usage of a disperser solvent in DLLME results in lower extraction efficiencies. In 2009, Tsai and Huang [120] proposed a novel DLLME technique with little solvent consumption (DLLME-LSC). Thirteen μL of a binary mixture of disperser solvent (tert-butyl methyl ether (TBME)) and extracting solvent (TCE) was used in a ratio of 6:4. DLLME-LSC-GC–MS was developed for the extraction of organochlorine pesticides (OCPs) in water samples. This new technique is less harmful to the environment and yields a higher *PF* (1885–2648). The linear calibration for the targeted OCPs was in the range of 2–2000 ng L^{-1}, except for endosulfan-II (EDS-II) which was 5–2000 ng L^{-1}. It is also a rapid, easy and convenient procedure for the quantitative and qualitative analysis of OCPs.

5. Combination of DLLME with other extraction techniques

5.1. DLLME combined with SPE

Solid-phase extraction (SPE) is a widely used sample-preparation technique for isolation of selected analytes, usually from a gas, fluid or liquid phases. The principal goals of SPE are trace enrichment (preconcentration), matrix simplification (sample clean-up) and medium exchange. However, DLLME is not suitable for complex matrixes (such as highly saline solution). Assadi and co-workers [121] introduced combination of SPE and DLLME for extraction and determination of chlorophenols (CPs) in complex matrixes (such as highly saline solution) using GC-ECD. This combination leads to a very high *PF* (up to about 18,000, ultra preconcentration). In SPE-DLLME, CPs were adsorbed from a large volume of the aqueous samples (100 mL) into 100 mg functionalized styrene–divinelybenzene polymer sorbent. After elution of the desired compounds from the sorbent by acetone, the DLLME technique was performed on the obtained solution. The calibration graphs were linear in the range of 0.001–20 μg L^{-1} and the DLs ranged from 0.0005 to 0.1 μg L^{-1}. In 2009, Liu et al. [122] developed SPE-DLLME-GC-ECD for determination of polybrominated diphenyl ethers (PBDEs) in water and plant samples. After preconcentration and purification of the samples in C18 cartridge, 1.0 mL of the elution sample, containing 22.0 μL 1,1,2,2-tetrachloroethane, was injected rapidly into 5.0 mL of pure water. After centrifugation, the sediment phase was injected into the GC-ECD. Under the optimum conditions, the *PFs* obtained were in the range of 6838–9405 for water samples. The calibration curves were linear in the range of 0.1–100 ng L^{-1} (BDES 28 and 47) and 0.5–500 ng L^{-1} (BDES 100, 99, 85, 154 and 153) and the DLs were in the range of 0.03–0.15 ng L^{-1}. For plant samples, the DLs were in the range of 0.04–0.16 μg kg^{-1}.

In addition, SPE-DLLME-GC–MS was developed for the sensitive determination of amide herbicides in the environmental water samples [123]. In this method, amide herbicides were adsorbed quantitatively from a large volume of the aqueous sample (100 mL) onto a multi-walled carbon nanotube adsorbent (100 mg). After elution of the target compounds from the adsorbent by acetone, the DLLME technique was performed on the resulting solution. There was linearity over the range of 0.01–10 $\mu g\,L^{-1}$ with the DLs ranging from 0.002 to 0.006 $\mu g\,L^{-1}$. Rodriguez and co-workers [124] developed SPE-DLLME for determination of seven fungicides in wine samples. Under optimized conditions, 20 mL of wine was first concentrated using a reversed-phase sorbent. Then, the target compounds were eluted with 1 mL of acetone. This extract was mixed with 0.1 mL of CH_3CCl_3 and the obtained blend was added to 10 mL of ultra pure water. The method resulted in the *PFs* around 200 and an improved selectivity was obtained in comparison with the single SPE.

In 2009, Wu et al. [125] proposed dispersive solid-phase extraction (DSPE) combined with DLLME for the extraction of four sulfonylurea herbicides in soil. DSPE is based on the SPE methodology, but the sorbent is directly added into the extract without conditioning. The clean-up is easily carried out by just shaking and centrifugation. The soil samples were air-dried at room temperature, pulverized and passed through a 250-μm sieve. Ten grams of the soil sample was accurately weighed and put into a 50-mL centrifuge tube and 20.0 mL of acetone:0.15 mol L^{-1} $NaHCO_3$ (2:8, v/v) was added. The resultant sample mixture was first vigorously shaken on a vibrator for 30 min and then filtrated under reduced pressure. For DSPE, 0.15 g of C18 per 10 mL of filtrate was added and shaken for 5 min. After filtration through 0.45 μm filter, the filtrate pH was adjusted to 2.0 by dropwise addition of 1 mol L^{-1} HCl. Then, the filtrate was transferred into a 25-mL volumetric flask. The solution was diluted with a solution of acetone–water (2:8, v/v) at pH 2.0. For DLLME, a 5.0-mL aliquot of the above sample solution was placed in a 10-mL screw cap glass tube with conical bottom. Then 60 μL of chlorobenzene was added. After centrifugation, the sediment phase was injected into the HPLC.

5.2. DLLME combined with SFO

DLLME consumes extracting solvents such as chlorobenzene, chloroform, tetrachloromethane and carbon disulfide, which have higher density than water, and are toxic and environmentaly unfriendly. In 2007, our research group introduced a new mode of liquid-phase microextraction based on solidification of floating organic droplet (LPME-SFO) [20,21]. In this method, no specific holders such as the needle tip of microsyringe, hollow fiber or polychloroprene rubber (PCR) tube is required for supporting the organic microdrop due to the using organic solvents with low density and proper melting point. Furthermore, the extractant droplet can be collected easily by solidifying it at low temperature. However, the extraction time was somewhat long, thus it cannot satisfy the demand of fast analysis. Huang's researcher group [126] proposed a new method, based on DLLME and LPME-SFO, which overcomes the aforementioned problems. The large contact surface between the sample and the droplets of the extractant speeds up mass transfer, as fast as DLLME, and shorter extraction time than that of LPME-SFO. In DLLME-SFO, lower toxicity extracting solvents can be used. The floated extractant is solidified and easily collected from the top of the solution for analysis. For the first time, DLLME-SFO-GC–MS was developed for determination of halogenated organic compounds (HOCs) in water samples [126]. A diagrammatic sketch of DLLME-SFO is shown in Fig. 7. A mixture of 0.5 mL acetone, containing 10 μL of 2-dodecanol (2-DD-OH) was rapidly injected by syringe into a 5-mL water sample. After centrifugation, the fine 2-DD-OH droplets (8 ± 0.5 μL) were floated at the top of the screw cap test tube. The test tube was then cooled down in an ice bath. After 5 min, the 2-DD-OH solvent was solidified, then transferred into a conical vial and melted quickly at room temperature. Finally, 2 μL of the solvent was injected into GC–MS. The DLs were in the range of 0.005–0.047 $\mu g\,L^{-1}$ and the linear range was from 0.02 to 500 $\mu g\,L^{-1}$. In a subsequent study, DLLME-SFO-HPLC-VWD was developed for determination of PAHs in aqueous samples [127]. Under the optimized conditions, the PFs for PAHs were obtained in the range of 88–118. The DLs for naphthalene, diphenyl, acenaphthene, anthracene and fluoranthene were 0.045, 0.86, 0.071, 1.1 and 0.66 ng mL^{-1}, respectively.

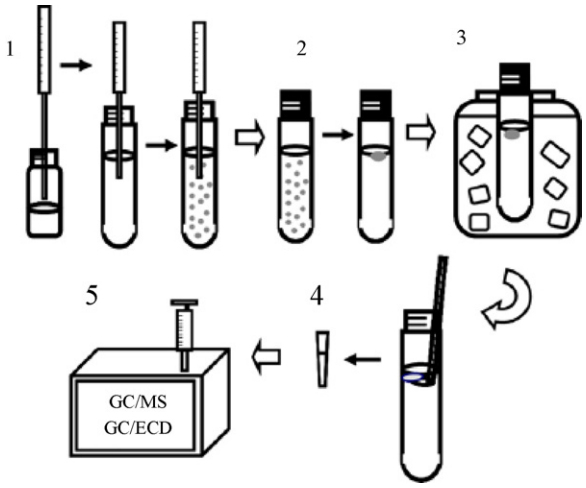

Fig. 7. Schematic diagram of the proposed DLLME-SFO apparatus. Reprinted with permission from [126].

There are only a few papers in the literature reporting the use of ICP-OES to analyze the sedimented phase resulted from DLLME. In DLLME, solvents with the densities higher than water are required, most of which are not often compatible with ICP-OES. For the first time, our research group [128] developed DLLME-SFO for determination of aluminium in water samples. In DLLME-SFO, extracting solvents with lower toxicity than suitable solvents for DLLME can be used. An appropriate mixture of 1-undecanol and disperser solvent was injected rapidly into the aqueous sample by syringe. Thereby, a cloudy solution was formed and centrifuged. The extraction solvent after DLLME was solidified by inserting it into an ice bath for 5 min. The solidified 1-undecanol on the top of solution was transferred into a suitable vial and immediately melted. Then it was dissolved in 1-propanol to decrease its viscosity and increase nebulization efficiency in the ICP-OES. The solution of extracting phase in 1-propanol was injected into the ICP-OES by an injection valve for subsequent analysis. Under the optimized conditions, the linear dynamic range of 1.0–250.0 $\mu g\,L^{-1}$ and the DL of 0.8 $\mu g\,L^{-1}$ for Al^{3+} was obtained. In comparison with SPE and CPE, DLLME-SFO demonstrated lower DL, very short extraction time and ease of operation. Also, in comparison with DLLME, DLLME-SFO used lower toxicity solvents and has higher extraction recovery for determination of Al^{3+} in water sample. Further, it is cheap and has higher PF (128) for trace analysis of Al^{3+} in water sample.

5.3. DLLME combined with SFE

In spite of several advantages of DLLME, it is not suitable for extraction of compounds from solid samples and extra steps in sample preparation before DLLME are needed, leading to the consumption of high volumes of toxic organic solvent before DLLME. Sometimes, drying and filtering processes are needed, which are time-consuming. Also, sometimes it is impossible to do DLLME for the extraction of analytes from complex matrixes. Supercritical

fluid extraction (SFE) has been adopted as an extraction media to extract different substances from solid matrixes for three decades ago. For the first time, our research group [129] developed a combination of SFE and DLLME, as a sample-preparation method for determination of ten PAHs in marine sediment samples. In SFE-DLLME, the collecting solvents such as methanol and acetonitrile in SFE can be used as disperser solvent in DLLME. After performing SFE and collecting the extracted analytes in the disperser solvent, a suitable volume of the extracting solvent was added into the collecting solvent. Finally, the mixture was injected to the aqueous sample. The other steps were similar to DLLME method. SFE-DLLME leads to high *PF* for determining organic compounds in solid samples and can eliminate the need to evaporate the collecting solvent at the end of SFE. The vaporization of organic solvent is a time-consuming process and emission of the solvent into atmosphere is environmentally unfriendly. The performance of SFE-DLLME in the extraction of PAHs from different marine sediment samples with various matrixes was excellent. This method possesses a great potential in the analysis of trace organic compounds in real solid samples. Under the optimum conditions, the calibration plots were linear in the range of 0.41–41.6 mg kg^{-1} and the DLs were 0.15 mg kg^{-1}. Application of SFE-DLLME in the extraction of OPPs pesticides from marine sediments is in progress by our research group.

6. Limitations and future trends

The present review has focused on the recent developments in DLLME and its applications in conjunction with different analytical techniques and also, when used in combination with different extraction techniques. DLLME enjoys the advantages of simplicity of operation, rapidity, low cost, high recovery, high preconcentration factor and environment benignity. DLLME has emerged as a viable sample-preparation approach, by which one could obtain generally acceptable analytical data. Due to its simplicity, ease of implementation and insignificant startup cost, DLLME is accessible to most of laboratories. The fundamental theory of DLLME needs further improvement. There is no equation in DLLME for calculating the volume of sedimented phase without further experimental test. Development of equations that show the relationship between the four important factors in DLLME (types and volumes of the extracting and disperser solvents) needs some progress.

The performance of DLLME in aqueous samples is excellent; however, it is not yet suitable in complex matrixes such as biological samples. Therefore, it needs further improvement. The main drawback of DLLME is the consumption of higher volumes (i.e. mL) of disperser solvent. Some progress has been made to use ultrasonic energy to disperse the extraction solvent in the absence of disperser solvent. Although the use of disperser solvent in DLLME helps us to combine SFE with DLLME, research in SFE-DLLME process is still in progress, and hopefully in the near future, the application of this method will be developed for different solid samples.

DLLME is not yet suitable as a routine applicable on-line preconcentration procedure. Although some progress has been made to automate DLLME, but further research is still needed to complete the experiences in this area.

In DLLME, the extracting solvents should have higher density than water. It creates some problem such as incompatibility of the extracting solvents with some instruments such as ICP-OES and reverse-phase HPLC. Sometimes, very low extraction recoveries are obtained with the general organic solvent in DLLME. Combination of SFO with DLLME solves some of these problems. However, a specially design needs to collect lighter organic solvents. DLLME may be used in combination with capillary electrophoresis (CE) in future. Also, the general extracting solvents are compatible with the normal phase HPLC system and hopefully the near future will show the application of DLLME combined with this system without any further treatment of the extracting solvents. Finally, other efforts can be made to further develop the application of DLLME for the extraction of polar and ionizable compounds from different matrixes.

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References

[1] L. Xu, C. Basheer, H.K. Lee, J. Chromatogr. A 1152 (2007) 184.
[2] F. Pena-Pereira, I. Lavilla, C. Bendicho, Spectrochim. Acta, Part B 64 (2009) 1.
[3] C.L. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145.
[4] H. Liu, P.K. Dasgupta, Anal. Chem. 68 (1996) 1817.
[5] M.A. Jeannot, F.F. Cantwell, Anal. Chem. 68 (1996) 2236.
[6] K.E. Rasmussen, S. Pederson-Bjergaard, Trends Anal. Chem. 23 (2004) 1.
[7] E. Psillakis, N. Kalogerakis, Trends Anal. Chem. 21 (2002) 53.
[8] M.A. Jeannot, F.F. Cantwell, Anal. Chem. 69 (1997) 235.
[9] F. Ahmadi, Y. Assadi, S.M.R. Milani Hosseini, M. Rezaee, J. Chromatogr. A 1101 (2006) 307.
[10] G. Shen, H.K. Lee, Anal. Chem. 74 (2002) 648.
[11] S. Pedersen-Bjergaard, K.E. Rasmussen, Anal. Chem. 71 (1999) 2650.
[12] M.F. Silva, E.S. Cerutti, L.D. Martinez, Microchim. Acta 155 (2006) 349.
[13] R. Carabias-Martinez, E. Rodriguez-Gonzalo, B. Moreno-Cordero, J.L. Perez-Pavon, C.C. Garcia-pinto, E. Fernandez-Laespada, J. Chromatogr. A 902 (2000) 251.
[14] R. Ferrer, J.L. Beltran, J. Guiteras, Anal. Chim. Acta 330 (1996) 199.
[15] I. Casero, D. Sicilia, S. Rubio, D. Perez-Bendito, Anal. Chem. 17 (1999) 4519.
[16] D. Sicilia, S. Rubio, D. Perez-Bendito, N. Maniasso, E.A.G. Zagatto, Anal. Chim. Acta 392 (1999) 29.
[17] Y. Takagai, S. Igarashi, Am. Lab. 34 (2002) 30.
[18] S. Oshite, M. Furukawa, S. Igarashi, Analyst 126 (2001) 703.
[19] S. Igarashi, A. Takahashi, Y. Ueki, H. Yamaguchi, Analyst 125 (2000) 797.
[20] M.R. Khalili-Zanjani, Y. Yamini, S. Shariati, J.A. Jonsson, Anal. Chim. Acta 585 (2007) 286.
[21] M.R. Khalili-Zanjani, Y. Yamini, N. Yazdanfar, S. Shariati, Anal. Chim. Acta 606 (2008) 202.
[22] J. Regueiro, M. LIompart, C. Garcia-Jares, J.C. Garcia-Monteagudo, R. Cela, J. Chromatogr. A 1190 (2008) 27.
[23] M.D. Luque de Castro, F. Priego-Capote, Analytical Applications of Ultrasound, Elsevier, Amsterdam, 2006.
[24] M.D. Luque de Castro, F. Priego-Capote, Talanta 72 (2007) 321.
[25] M. Rezaee, Y. Assadi, M.R. Milani Hosseini, E. Aghaee, F. Ahmadi, S. Berijani, J. Chromatogr. A 1116 (2006) 1.
[26] S. Berijani, Y. Assadi, M. Anbia, M.R. Milani Hosseini, E. Aghaee, J. Chromatogr. A 1123 (2006) 1.
[27] R.R. Kozani, Y. Assadi, F. Shemirani, M.R. Milani Hosseini, M.R. Jamali, Talanta 72 (2007) 387.
[28] R.R. Kozani, Y. Assadi, F. Shemirani, M.R. Milani Hosseini, M.R. Jamali, Chromatographia 66 (2007) 81.
[29] D. Nagaraju, S.D. Huang, J. Chromatogr. A 1161 (2007) 89.
[30] J.S. Chiang, S.D. Huang, Talanta 75 (2008) 70.
[31] N. Fattahi, Y. Assadi, M.R. Milani Hosseini, E.Z. Jahromi, J. Chromatogr. A 1157 (2007) 23.
[32] J. Xiong, B. Hu, J. Chromatogr. A 1193 (2008) 7.
[33] H. Farahani, P. Noruzi, R. Dinarvand, M.R. Ganjali, J. Chromatogr. A 1172 (2007) 105.
[34] M. Garcia-Lopez, I. Rodriguez, R. Cela, J. Chromatogr. A 1166 (2007) 9.
[35] L. Farina, E. Boido, F. Carrau, E. Dellacassa, J. Chromatogr. A 1157 (2007) 46.
[36] A. Pajand Birjandi, A. Bidari, F. Rezaei, M.R. Milani Hosseini, Y. Assadi, J. Chromatogr. A 1193 (2008) 19.
[37] R.S. Zhao, C.P. Diao, X. Wang, T. Jiang, J.P. Yuan, Anal. Bioanal. Chem. 391 (2008) 2915.
[38] A. Sarafraz-Yazdi, N. Razavi, S. Raouf Yazdinejad, Talanta 75 (2008) 1293.
[39] F. Rezaei, A. Bidari, A. Pajand Birjandi, M.R. Milani Hosseini, Y. Assadi, J. Hazard. Mater. 158 (2008) 621.
[40] E. Pusvaskiene, B. Januskevic, A. Prichodko, V. Vickackaite, Chromatographia 69 (2009) 271.
[41] H. Sereshti, M. Karimi, S. Samadi, J. Chromatogr. A 1216 (2009) 198.
[42] X. Hong-Xue, H. Li-Jun, W. Xiu-Ling, F. Lu, L. Kui, W. Mei-Mei, M. Da-Wei, Chin. J. Anal. Chem. 36 (2008) 1543.
[43] Z. Xiao-Huan, W. Chun, G. Shu-Tao, Z. Xin, W. Zhi, Chin. J. Anal. Chem. 36 (2008) 765.
[44] H. Ebrahimzadeh, Y. Yamini, F. Kamarei, Talanta 79 (2009) 1472.
[45] K. Farhadi, R. Maleki, N. Mohammad Nezhad, J. Chin. Chem. Soc. 56 (2009) 575.
[46] A.N. Panagiotou, V.A. Sakkas, T.A. Albanis, Anal. Chim. Acta 649 (2009) 135.

[47] C. Cortada, L. Vidal, R. Pastor, N. Santiago, A. Canals, Anal. Chim. Acta 649 (2009) 218.
[48] A. Ranji, M.G. Ravandi, M.A. Farajzaded, Anal. Sci. 24 (2008) 623.
[49] R. Montes, I. Rodriguez, E. Rubi, R. Cela, J. Chromatogr. A 1216 (2009) 205.
[50] M.A. Farajzadeh, M. Bahram, J.A. Jonsson, Anal. Chim. Acta 591 (2007) 69.
[51] G. Wei, Y. Li, X. Wang, J. Sep. Sci. 30 (2007) 3262.
[52] J.H. Guo, X.H. Li, X.L. Cao, Y. Li, X.Z. Wang, X.B. Xu, J. Chromatogr. A 1216 (2009) 3038.
[53] M. Rezaee, Y. Yamini, S. Shariati, A. Esrafili, M. Shamsipur, J. Chromatogr. A 1216 (2009) 1511.
[54] J. Xia, B. Xiang, W. Zhang, Anal. Chim. Acta 625 (2008) 28.
[55] M.A. Farajzadeh, M.R. Vardast, M. Bahram, Chromatographia 69 (2009) 409.
[56] K. Farhadi, A.A. Matin, P. Hashemi, Chromatographia 69 (2009) 45.
[57] R. Maleki, N. Mohammad Nezhad, N. Samadi, K. Farhadi, Microchim. Acta 165 (2009) 97.
[58] K. Farhadi, M.A. Farajzadeh, A.A. Matin, J. Sep. Sci. 32 (2009) 2442.
[59] K. Farhadi, M.A. Farajzadeh, A.A. Matin, P. Hashemi, Cent. Eur. J. Chem. 7 (2009) 369.
[60] Y. Li, G. Wei, J. Hu, X. Liu, X. Zhao, X. Wang, Anal. Chim. Acta 615 (2008) 96.
[61] X. Wang, L. Fu, G. Wei, J. Hu, X. Zhao, X. Liu, Y. Li, J. Sep. Sci. 31 (2008) 2932.
[62] Y. Li, J. Hu, X. Liu, L. Fu, X. Zhang, X. Wang, J. Sep. Sci. 31 (2008) 2371.
[63] Q.X. Zhou, G.H. Xie, L. Pang, Chin. Chem. Lett. 19 (2008) 89.
[64] P. Ling, J. Xu, Q. Li, Anal. Chim. Acta 609 (2008) 53.
[65] Q. Wu, X. Zhou, Y. Li, X. Zang, C. Wang, Z. Wang, Anal. Bioanal. Chem. 393 (2009) 1755.
[66] Q. Zhou, L. Pang, G. Xie, J. Xiao, H. Bai, Anal. Sci. 25 (2009) 73.
[67] Q. Zhou, L. Pang, J. Xiao, J. Chromatogr. A 1216 (2009) 6680.
[68] Y. Li, J.L. Liu, X.L. Wang, Y.H. Jian, D.M. Dong, N. Li, Chem. J. Chin. Univ. Chin. 29 (2008) 2142.
[69] E. Zeini Jahromi, A. Bidari, Y. Assadi, M.R. Milani Hosseini, M.R. Jamali, Anal. Chim. Acta 585 (2007) 305.
[70] A. Bidari, E. Zeini Jahromi, Y. Assadi, M.R. Milani Hosseini, Microchem. J. 87 (2007) 6.
[71] A. Bidari, P. Hemmatkhah, S. Jafarvand, M.R. Milani Hosseini, Y. Assadi, Microchim. Acta 163 (2008) 243.
[72] P. Liang, H. Sang, Anal. Biochem. 380 (2008) 21.
[73] M.A. Farajzadeh, M. Bahram, B. Ghorbani Mehr, J.A. Jonsson, Talanta 75 (2008) 832.
[74] M. Shamsipur, M. Ramezani, Talanta 75 (2008) 294.
[75] M.T. Naseri, P. Hemmatkhah, M.R. Milani Hosseini, Y. Assadi, Anal. Chim. Acta 610 (2008) 135.
[76] R.E. Rivas, I. Lopez-Garcia, M. Hernandez-Cordoba, Spectrochim. Acta, Part B 64 (2009) 329.
[77] P. Liang, L. Peng, P. Yan, Microchim. Acta 166 (2009) 47.
[78] P. Liang, E. Zhao, F. Li, Talanta 77 (2009) 1854.
[79] T. Ahmadzadeh Koky, K. Farhadi, J. Hazard. Mater. 169 (2009) 726.
[80] M.T. Naseri, M.R. Milani Hosseini, Y. Assadi, A. Kiani, Talanta 75 (2008) 56.
[81] P. Hemmatkhah, A. Bidari, S. Jafarvand, M.R. Milani Hosseini, Y. Assadi, Microchim. Acta 166 (2009) 69.
[82] H. Jiang, Y. Qin, B. Hu, Talanta 74 (2008) 1160.
[83] P.X. Baliza, L.S.G. Teixeira, V.A. Lemos, Microchem. J. 93 (2009) 220.
[84] S.Z. Mohammadi, D. Afzali, M.A. Taher, Y.M. Baghelani, Talanta 80 (2009) 875.
[85] R.E. Rivas, I. Lopez-Garcia, M. Hernandez-Cordoba, Microchim. Acta 166 (2009) 355.
[86] A. Moghimi, J. Chin. Chem. Soc. 55 (2008) 369.
[87] N. Shokoufi, F. Shemirani, Y. Assadi, Anal. Chim. Acta 597 (2007) 349.
[88] M. Ghrehbaghi, F. Shemirani, M. Baghdadi, Int. J. Environ. Anal. Chem. 88 (2008) 513.
[89] M.H. Mallah, F. Shemirani, M. Ghannadi Maragheh, J. Radioanal. Nucl. Chem. 278 (2008) 97.
[90] Z.Q. Ding, G.D. Liu, Chin. J. Anal. Chem. 37 (2009) 119.
[91] M.B. Melwanki, W.S. Chen, H.Y. Bai, T.Y. Lin, M.R. Fuh, Talanta 78 (2009) 618.
[92] C. Xiong, J. Ruan, Y. Cai, Y. Tang, J. Pharm. Biomed. Anal. 49 (2009) 572.
[93] H. Xu, D. Song, Y. Cui, S. Hu, Q.W. Yu, Y.Q. Feng, Chromatographia 70 (2009) 775.
[94] M. Rezaee, Y. Yamini, M. Hojjati, M. Faraji, J. Pharm. Biomed. Anal., submitted for publication.
[95] E. Zhao, W. Zhao, L. Han, S. Jiang, Z. Zhou, J. Chromatogr. A 1175 (2007) 137.
[96] A. Daneshfar, T. Khezeli, H.J. Lotfi, J. Chromatogr. B 877 (2009) 456.
[97] H. Chen, H. Chen, J. Ying, J. Huang, L. Liao, Anal. Chim. Acta 632 (2009) 80.
[98] L. Fu, X. Liu, J. Hu, X. Zhao, H. Wang, X. Wang, Anal. Chim. Acta 632 (2009) 289.
[99] X. Zang, J. Wang, O. Wang, M. Wang, J. Ma, G. Xi, Z. Wang, Anal. Bioanal. Chem. 392 (2008) 749.
[100] J. Hu, Y. Li, W. Zhang, H. Wang, C. Huang, M. Zhang, X. Wang, J. Sep. Sci. 32 (2009) 2103.
[101] J. Hu, L. Fu, X. Zhao, X. Liu, H. Wang, X. Wang, L. Dai, Anal. Chim. Acta 640 (2009) 100.
[102] L.M. Ravelo-Perez, J. Hernandez-Borges, M. Asensio-Ramos, M.A. Rodriguez-Delgado, J. Chromatogr. A 1216 (2009) 7336.
[103] X. Zhao, L. Fu, J. Hu, J. Li, H. Wang, C. Huang, X. Wang, Chromatographia 69 (2009) 1.
[104] S. Moinfar, M.R. Milani Hosseini, J. Hazard. Mater. 169 (2009) 907.
[105] H. Chen, J. Ying, H. Chen, J. Huang, L. Liao, Chromatographia 68 (2008) 629.
[106] Q. Wu, Y. Li, C. Wang, Z. Liu, X. Zang, X. Zhou, Z. Wang, Anal. Chim. Acta 638 (2009) 139.
[107] X. Zhou, X.H. Zang, D.Y. Wang, P.L. Cui, Z. Wang, Chin. J. Anal. Chem. 37 (2009) 41.
[108] Y.C. Fan, Z.L. Hu, M.L. Chen, C.S. Tu, Y. Zhu, Chin. Chem. Lett. 19 (2008) 985.
[109] Y. Liu, E. Zhao, W. Zhu, H. Gao, Z. Zhou, J. Chromatogr. A 1216 (2009) 885.
[110] M.H. Mallah, F. Shemirani, M.G. Maragheh, Environ. Sci. Technol. 43 (2009) 1947.
[111] M.T. Pena, M.C. Casais, M.C. Mejuto, R. Cela, J. Chromatogr. A 1216 (2009) 6356.
[112] M.B. Melwanki, M.R. Fuh, J. Chromatogr. A 1207 (2008) 24.
[113] T.Y. Chou, S.L. Lin, M.R. Fuh, Talanta 80 (2009) 493.
[114] M.B. Melwanki, M.R. Fuh, J. Chromatogr. A 1198 (2008) 1.
[115] A.N. Anthemidis, K.I.G. Ioannou, Talanta 79 (2009) 86.
[116] S. Li, S. Cai, W. Hu, H. Chen, H. Liu, Spectrochim. Acta, Part B 64 (2009) 666.
[117] K.J. Huang, C.Y. Wei, W.L. Liu, W.Z. Xie, J.F. Zhang, W. Wang, J. Chromatogr. A 1216 (2009) 6636.
[118] M. Craz-Vera, R. Lucena, S. Cardenas, M. Valcarcel, J. Chromatogr. A 1216 (2009) 6459.
[119] A. Saleh, Y. Yamini, M. Faraji, M. Rezaee, M. Ghambarian, J. Chromatogr. A 1216 (2009) 6673.
[120] W.C. Tsai, S.D. Huang, J. Chromatogr. A 1216 (2009) 5171.
[121] N. Fattahi, S. Samadi, Y. Assadi, M.R. Milani Hosseini, J. Chromatogr. A 1169 (2007) 63.
[122] X. Liu, J. Li, Z. Zhao, W. Zhang, K. Lin, C. Huang, X. Wang, J. Chromatogr. A 1216 (2009) 2220.
[123] R.S. Zhao, C.P. Diao, Q.F. Chen, X. Wang, J. Sep. Sci. 32 (2009) 1069.
[124] R. Montes, I. Rodriguez, M. Ramil, E. Rubi, R. Cela, J. Chromatogr. A 1216 (2009) 5459.
[125] Q. Wu, C. Wang, Z. Liu, C. Wu, X. Zeng, J. Wen, Z. Wang, J. Chromatogr. A 1216 (2009) 5504.
[126] M.I. Leong, S.D. Huang, J. Chromatogr. A 1211 (2008) 8.
[127] H. Xu, Z. Ding, L. Lv, D. Song, Y.Q. Feng, Anal. Chim. Acta 636 (2009) 28.
[128] M. Rezaee, Y. Yamini, A. Khanchi, M. Faraji, A. Saleh, J. Hazard. Mater., submitted for publication.
[129] M. Rezaee, Y. Yamini, M. Moradi, A. Saleh, M. Faraji, unsubmitted results.