Recent Advances in Dispersive Liquid–Liquid Microextraction for Organic Compounds Analysis in Environmental Water: A Review

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Abstract: Dispersive liquid-liquid microextraction (DLLME) is a novel microextraction technique with a great potential in sample pretreatment, which has been increasingly used for preconcentration of diverse analytes. This review updates the state of the art and discusses promising prospects of DLLME, especially focuses on its combined use with chromatographic techniques for organic compounds analysis in environmental water samples. General and specific concepts of the fundamental theory of DLLME are described, and examples of recent innovations and applications are provided to demonstrate its potential for the determination of a wide range of organic compounds in various water matrices. Moreover, some limitations related to DLLME are also discussed in detail, and an outlook on the future of the technique, specifically its coupling with other pretreatment approaches, separation and detection techniques, is also given.

Keywords: Dispersive liquid-liquid microextraction, Organic compounds, Environmental water samples.

1. INTRODUCTION

Sample pretreatment is usually used to extract, isolate and concentrate the target analytes in complex matrices which is hardly directly determined by the analytical instruments. Traditional methods for sample pretreatment including liquid-liquid extraction (LLE), soxhlet extraction, chromatography, distillation and absorption [1], have been widely used in all kinds of fields. However, these techniques are usually time-consuming, difficult to automation and require large amounts of toxic organic solvents. The current trend is to develop simple, miniature, automatic, high selectivity and recovery sample pretreatment techniques in order to achieve the trace level pollutant analysis. Solid phase extraction (SPE) [2-4], solid phase microextraction (SPME) [5-7], liquid-phase microextraction (LPME) [8-10], stir bar sorptive extraction (SBSE) [11, 12] and cloud point extraction (CPE) [13, 14] are new methods which have been used for the separation and preconcentration of diverse analytes and have solved some of the problems mentioned above of conventional techniques. Nevertheless, some drawbacks still exist for these techniques. Although SPE uses less organic solvent than LLE, the extra step of concentrating the extractant down to a small volume is needed, such as nitrogen blow. For SPME, it is simple, rapid, portable, solvent free, sensitive for the extraction of the analytes and can be automated and coupled on-line to analytical instrumentation. However, the special desorption apparatus is needed when SPME is used to determine analytes coupling with high performance liquid chromatography (HPLC) and the coated fiber is expensive and fragile, with limited lifetime. LPME often requires careful manual

operation, and the extraction is time-consuming and equilibrium can not be attained even after a long time in most cases. SBSE as well as SPME is a solvent-free technique based on sorptive extraction. At present, only PDMS-coated stir bars are commercially available, so that polar compounds can not be well extracted. In the case of CPE, it involves complex steps which can cause poor reproducibility, low preconcentration factor and time consuming.

Dispersive liquid-liquid microextraction (DLLME), a new mode of LPME, was introduced by Assadi and co-workers in 2006 [15]. This method is based on the ternary component solvent systems involving extraction solvent, disperser solvent and an aqueous phase. In DLLME, the mixture of extraction solvent and disperser solvent is rapidly injected by syringe into the sample solution containing the analytes. Then the mixture is gently shaken and a cloudy solution (water/disperser solvent/extraction solvent) is formed in the conical tube, resulting from the formation of small droplets of extraction slovent which is dispersed in the sample solution. After the formation of the cloudy solution, the surface area between the extraction solvent and the sample solution is very large and transition of analytes from sample solution to extraction solvent is very fast [16, 17]. So, an equilibrium state can be reached immediately even within a few seconds. Also, because of the rapidity (immediate equilibrium), the presence of a chelating agent in the solution can not change the equilibrium [15]. After centrifugation, the small droplets of extraction solvent are sedimented at the bottom of the test tube. Finally, the sediment phase is collected and determined with the appropriate analytical techniques. The extraction steps of DLLME are illustrated in Fig. (**1**).

DLLME has become a very popular environmentally benign sample pretreatment technique [16-22] since its initial introduction, because of its remarkable advantages, such as simplicity of operation, rapidity, high recovery and high enrichment factor, and low consumption of solvents and

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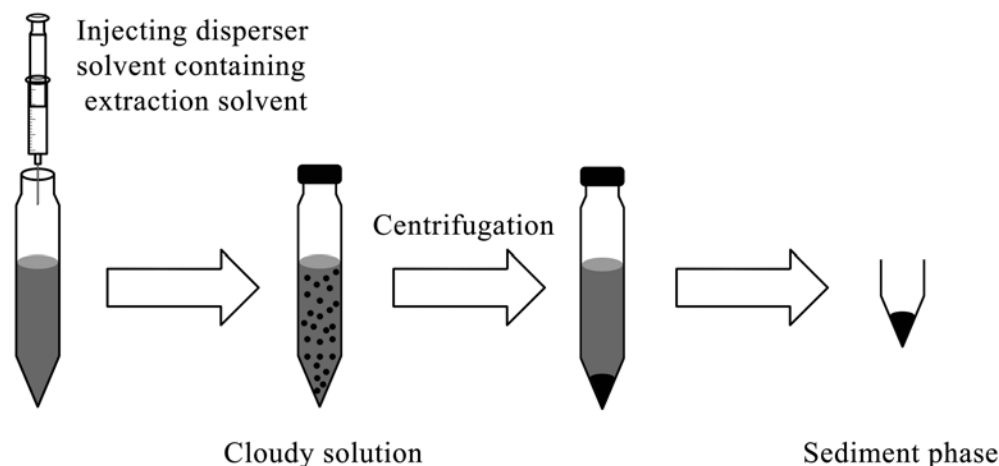
Fig. (1). Scheme of DLLME procedure.

sample [18, 19]. Several very recent reviews have excellently summarized a good number of works on rapid development and wide applications of DLLME [17-20, 22]. Ojeda and Rojas reviewed the related works on separation and preconcentration of trace organic pollutants and metal ions in environmental samples by DLLME [18], Rezaee *et al.* comprehensively summarized the evolution of DLLME especially on its combination with different analytical techniques and the extra steps in sample preparation [17]. Anthemidis and Ioannou concerned recent developments in DLLME for inorganic elements determination [20], Herrera-Herrera *et al.* summarized DLLME applications for determination of organic analytes [19], and Nuhu *et al.* paid more attentions to recent applications in bioanalysis of DLLME with derivatization [22]. However, to the best of our knowledge, there is no specific publication to review the different applications of DLLME to environmental water samples for organic compounds analysis.

In this review, we briefly discuss various influence factors of DLLME efficiency, summarize the current status of DLLME, especially focus on the latest advances of DLLME and its coupling with various chromatographic techniques for the preconcentration and determination of organic compounds in environmental water samples. Finally, we also make some attempts to explore the future development trend of DLLME.

2. PARAMETERS AFFECTING EXTRACTION EFFICIENCY OF DLLME

In DLLME, the factors that can affect the extraction efficiency include types and volumes of extraction and disperser solvent as well as the extraction time. The suitable disperser solvent can make the extraction solvent form fine droplets in aqueous solution, the volume of extraction solvent can affect the enrichment factor (EF) and the volume of the disperser solvent can directly affect the formation of the cloudy solution. Therefore, it is important to optimize all the factors in order to obtain good performance.

Selection of an appropriate extraction solvent as the major parameter is crucial for DLLME performance.

Firstly, organic solvents should have higher density than water, which could easily enable to separate the extraction solvent from the water phase by centrifugation. Then, it should have high extraction efficiency, selectivity, good chromatographic behavior and low solubility in water. Halogenated hydrocarbons such as chlorobenzene, chloroform, tetrachloromethane, tetrachloroethylene or carbon disulfide are usually selected as extraction solvents because of their high density.

In addition, the volume of extraction solvent has an important effect on the enrichment factor. With the increase of the extraction solvent volume, the volume of small droplets of the extraction solvent obtained by centrifugation is increased, resulting in a decrease on EF. Therefore, the optimal extraction solvent volume should allow achieving minimum but enough volume of the sediment phase after centrifugation for the subsequent determination, and therefore lead to as high as possible EF.

Disperser solvent plays a key role in helping the extraction solvent forming fine droplets in aqueous samples. The high miscibility in both the extraction solvent and the aqueous phase is the essential point for the selection of disperser solvent. For low toxic and cost, methanol, ethanol, acetone and acetonitrile are usually used as disperser solvents.

Disperser solvent volume can directly affect the formation of cloudy solution (water/disperser solvent/extraction solvent), the dispersion degree of the extraction solvent in aqueous phase, and subsequently, the extraction efficiency. Variation of disperser solvent volume changes the volume of sediment phase, through the salting-out effect. At too low volume, the dispersion of the extraction solvent is not proper and the cloudy solution is not formed completely, while at too high volume, the solubility of analytes in water increases and the extraction efficiency decreases. Hence, it is necessary to change the volumes of disperser solvent and extraction solvent simultaneously to achieve an optimal constant volume of sediment phase.

In DLLME, extraction time is defined as the interval between the injection of the mixture of disperser solvent and extraction solvent, and before start to centrifuge. It is revealed to have little effect on the extraction efficiency. The large

surface contact between fine extraction solvent droplets and the sample solution speeds up the mass transfer process of analytes from aqueous phase to organic phase, so that the equilibrium is reached quickly. Short extraction time is the principal advantage of DLLME, i.e. rapidity.

3. APPLICATIONS OF TRADITIONAL DLLME

As a novel sample pretreatment technique, DLLME coupling with gas chromatography (GC) or high performance liquid chromatography (HPLC) for the determination of organic compounds in environmental water samples has received greate concerns [15, 17-22, 23-59]. For the studies, BTEX, polycyclic aromatic hydrocarbons (PAHs), organophosphorous pesticides (OPPs), organochlorine pesticides (OCPs), organosulphur pesticides (OSPs), nitromatic compounds, polychlorinated biphenyls (PCBs), triazine herbicides, phthalate esters (PAEs), decabrominated diphenyl ether, aromatic amines, phenoxyacetic acid herbicides, bisphenol A, and endocrine-disrupting phenols, for examples, are depicted [15, 23-59] in Table **1**. Several typical applications are sampled as follows.

DLLME was firstly developed by Assadi and co-workers and used to determine PAHs in water samples coupling with GC-flame ionization detection (GC-FID) [15]. In this method, the appropriate mixture of extraction solvent (8.0 μL tetrachloroethylene) and disperser solvent (1.00 mL acetone) were injected into the aqueous sample (5.00 mL) by syringe, rapidly. Therefore, cloudy solution was formed. After centrifugation, the fine particles of extraction solvent were precipitated in the bottom of the conical test tube (5.0 ± 0.2 μL) and the sediment phase was injected for GC-FID analysis. Under the optimum conditions, the EF ranged from 603 to 1113, the linear range was 0.02-200 μg L^{-1} (four orders of magnitude) and limits of detection (LODs) were 0.007-0.030 μg L^{-1} for most of analytes. The ability of DLLME technique in the extraction of other organic compounds such as OCPs, OPPs and substituted benzene compounds (benzene, toluene, ethyl benzene, and xylenes) from water samples were also studied.

DLLME coupled with HPLC-variable wavelength detector (HPLC-VWD) for determination of three phthalate esters (dimethyl phthalate (DMP), diethyl phthalate (DEP), di-*n*-butyl phthalate (DnBP)) in water samples was developed by Liang *et al.* [46]. A mixture of extraction solvent (41 μL carbon tetrachloride) and disperser solvent (0.75 mL acetonitrile) were rapidly injected into 5.0 mL aqueous sample for the formation of cloudy solution, and the analytes in the sample were extracted into the fine droplets of CCl$_4$. The method yielded a linear calibration curve in the concentration range from 5 to 5,000 ng mL^{-1} for the target analytes, the EFs for DMP, DEP, DnBP were 45, 92 and 196, and the limits of detection were 1.8, 0.88 and 0.64 ng mL^{-1}, respectively.

Two methods based on hollow fiber liquid phase microextraction (HF-LPME) and DLLME had been critically compared for the analysis of organosulfur pesticides (OSPs) in environmental samples by GC-flame photometric detection (GC-FPD) [29]. Experimental conditions including extraction solvent, solvent volume, extraction time, temperature and ionic strength had been investigated for both HF-LPME and DLLME. The LODs for six OSPs (malathion, chlorpyrifos, buprofezin, triazophos, carbosulfan and pyridaben) obtained by HF-LPMA-GC-FPD and DLLME-GC-FPD were ranged from 1.16 to 48.48 μg L^{-1} and 0.21 to 3.05 μg L^{-1}, and the EFs were 27-530 and 176-946, respectively. Compared with HF-LPME, the advantages of DLLME technique were less

Table 1. DLLME Coupling with Chromatography Techniques to the Determination of Organic Compounds in Environmental Water Samples

Analyte	Extraction Solvent and Volume	Disperser Solvent and Volume	Water Sample Volume	Analytical Method	EF	LOD (μg L^{-1})	Ref.
PAHs (16 kinds)	8 μL tetrachloroethylene	1 mL acetone	5 mL	GC-FID	603-1113	0.007-0.030	[15]
Parabens	20 μL octanol	0.5 mL acetone	10 mL	GC-FID	100-276	5-15	[23]
BTEX	25 μL carbon disulfide	1 mL acetonitrile	5 mL	GC-FID	122-311	0.1-0.2	[24]
Nitromatic compounds	20 μL carbon tetrachloride	0.75 mL methanol	9 mL	GC-FID	202-314	0.09-0.5	[25]
Mononitrotoluenes	10 μL chlorobenzene	0.5 mL acetonitrile	5 mL	GC-FID	351-357	0.5	[26]
Amitriptyline, norteiptyline	18 μL Carbon tetrachloride	1 mL methanol	5 mL	GC-FID	740.04-1000.25	5-10	[27]
OPPs (13 kinds)	12 μL chlorobenzene	1 mL acetone	5 mL	GC-FPD	789-1070	0.003-0.020	[28]
OSPs (6 kinds)	10 μL Carbon tetrachloride	0.8 mL methanol	5 mL	GC-FPD	176-946	0.21-3.05	[29]
Butyl-, pehenyltin	11.5 μL carbon tetrachloride	0.5 mL ethanol	5 mL	GC-FPD	825-1036	0.2-1 ng L^{-1}	[30]
PCBs (10 kinds)	10 μL chlorobenzene	0.5 mL acetone	5 mL	GC-ECD	540	0.002	[31]
Chlorophenols	10 μL chlorobenzene	0.5 mL acetone	5 mL	GC-ECD	287-906	0.010-2.0	[32]
Trihalomethanes	20 μL Carbon disulfide	0.5 mL acetone	5 mL	GC-ECD	116-355	0.005-0.040	[33]
Chlorobenzenes	9.5 μL chlorobenzene	0.5 mL acetone	5 mL	GC-ECD	711-813	0.0005-0.05	[34]
UV-filter	60 μL chlorobenzene	1 mL acetone	10 mL	GC-MS	170-200	0.002-0.014	[35]
Anilines	10 μL chlorobenzene	0.5 mL acetone	5 mL	GC-MS	212-645	0.04-0.09	[36]

Table 1. contd…..

Analyte	Extraction Solvent and Volume	Disperser Solvent and Volume	Water Sample Volume	Analytical Method	EF	LOD (µg L^{-1})	Ref.
Methyl *tert*-butyl ether	42 µL trichloroethylene	0.3 mL methanol	2 mL	GC-MS	—	0.3 ng L^{-1}	[37]
Triazine herbicides (8 kinds)	12 µL chlorobenzene	1 mL acetone	5 mL	GC-MS	151-722	0.021-0.12	[38]
Endosulfan	40 µL chloroform	0.5 mL methanol	2 mL	GC-MS	163.4	0.020	[39]
PAEs (6 kinds)	9.5 µL chlorobenzene	0.5 mL acetone	5 mL	GC-MS	681-889	0.002-0.008	[40]
Nonylphenol, octylohenol	50 µL chloroform	0.5 mL methanol:pyridine (4:1, v/v)	5 mL	GC-MS	—	0.002-0.03	[41]
Estrone,17β-estradiol	25 µL tetrachloroethane	0.5 mL methanol	5 mL	HPLC-VWD	203-347	0.1-0.2	[42]
Decabrominated diphenyl ether	22 µL tetrachloroethane	1 mL tetrahydrofuran	5 mL	HPLC-VWD	153	0.2	[43]
Aromatic amines (4 kinds)	25 µL tetrachloroethane	0.5 mL methanol	5 mL	HPLC-VWD	41.3-94.5	0.8-1.8	[44]
Methomyl	20 µL tetrachloroethane	0.5 mL methanol	5 mL	HPLC-VWD	70.7	1	[45]
PAEs (3 kinds)	41 µL carbon tetrachloride	0.75 mL acetonitrile	5 mL	HPLC-VWD	45-196	0.64-1.8	[46]
Polybrominated diphenyl ethers	20 µL tetrachloroethane	1 mL acetonitrile	5 mL	HPLC-DAD	268-305	0.0124-0.0556	[47]
Phenoxyacetic acid herbicides	25 µL chlorobenzene	1 mL acetone	5 mL	HPLC-DAD	—	0.16	[48]
Carbamate pesticides (5 kinds)	40 µL trichloromethane	1 mL acetonitrile	5 mL	HPLC-DAD	80-177	0.1-0.5	[49]
Benomyl	25 µL chlorobenzene	0.5 mL N,N-dimethylformamide	5 mL	HPLC-FLD	—	3.3	[50]
Triazophos, carbaryl pesticides	15 µL tetrachloroethane	1 mL acetonitrile	5 mL	HPLC-FLD	87.3-275.6	0.0123-0.0160	[51]
Carbendazim, thiabendazole	80 µL chloroform	0.75 mL tetrahydrofuran	5 mL	HPLC-FLD	149-210	0.5-1.0	[52]
Alkylphenols and their short-chained ethoxylates	50 µL trichloroethylene	1.5 mL acetone	5 mL	HPLC-FLD	—	0.1 -0.3	[53]
Metacrate	116 µL dichloromethane	565 µL methanol	6 mL	HPLC-UV	—	1	[54]
Bisphenol A	142 µL chloroform	2 mL acetone	10 mL	HPLC-UV	—	0.07	[55]
Endocrine-disrupting phenols	9 µL decanol	141 µL acetonitrile	5 mL	HPLC-UV	123-275	0.2-1.6	[56]
Trislosan, triclocarban, methyl-triclosan	15 µL 1,3-dichlorobenzene	1 mL tetrahydrofuran	5 mL	UHPLC-TUV	—	0.0451-0.236	[57]
Carbofuran, clomzaone, tebuconazole	60 µL carbon tetrachloride	2 mL acetonitrile	5 mL	LC-MS/MS	50	0.02	[58]
Rhamnolipids	70 µL chloroform	1 mL acetone	6 mL	LC-MS/MS	118-154	0.003-0.004	[59]

extraction time, suitable for batches of samples pretreatments simultaneously, a higher extraction capacity when analyzing simple samples such as water samples. Both methods were applied to the analysis of six OSPs in different water samples.

4. ADVANCES OF DLLME AND THEIR APPLICATIONS

Since the initial introduction of DLLME, several modifications of this technique have also been developed and successfully applied to determine organic compounds in environmental water samples [60-107], such as solidification of floating organic drop-DLLME (SFO-DLLME), ionic liquid-DLLME (IL-DLLME), SPE and SBSE combined with DLLME, ultrasound-assisted DLLME (UA-DLLME), surfactant assisted-DLLME (SA-DLLME), molecular-imprinted polymer extraction-DLLME (MIP-DLLME), solvent terminated DLLME (ST-DLLME), low toxic DLLME (LT-DLLME) and magnetic stirring-assisted DLLME. In SFO-DLLME, the extraction solvents had low density and proper
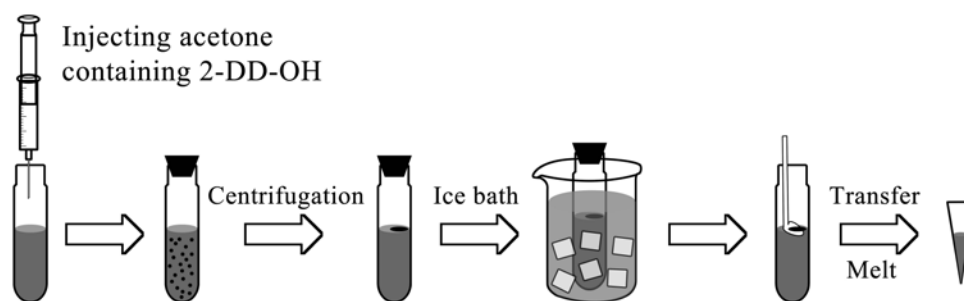
Fig. (2). Schematic diagram of the DLLME-SFO apparatus.

melting point that can solidify at low temperature. IL-DLLME used IL as extraction solvent which had high thermal and chemical stability, negligible vapor pressure, tunable viscosity and miscibility with water and organic solvents. MIP-DLLME, SPE and SBSE combined with DLLME were suitable for the analysis of ultra trace analytes. UA-DLLME used ultrasound-assisted process to accelerate the formation of the fine cloudy solution based on the conventional DLLME. Surfactant was used as disperser solvent in SA-DLLME. ST-DLLME and LT-DLLME were used as low density and low toxic extraction solvent for the DLLME procedure.

4.1. Solidification of Floating Organic Drop-DLLME (SFO-DLLME)

The conventional extraction solvent of DLLME such as chlorobenzene, chloroform, carbon disulfide and tetrachloromethane have higher density than water, but they are high toxic and environmental unfriendly. In 2007, Rezaee *et al.* [60, 61] introduced a new mode of liquid phase microextraction based on solidification of floating organic solvent (LPME-SFO). In this method, the specific holder was not required for supporting the organic microdrop, and stirring of the solution at very high speed was possible because of using organic solvent with low density and proper melting point. However, the extraction time was somewhat long and the efficient of extraction was slower. To meet the demand of fast analysis, Huang *et al.* [62] proposed a new method based on the principle of DLLME and LPME-SFO called DLLME-SFO. The diagrammatic sketch was shown in Fig. (2). Large contact surface between the sample solution and the extraction solvent speeded up mass transfer, as far as DLLME, and shorter extraction time than LPME-SFO. The floated extractant was easy to collect from the top of the sample solution by solidifying it at low temperature. DLLME-SFO combined with GC-MS was developed for the determination of halogenated organic compounds (HOCs) in water samples. A mixture of acetone (as disperser solvent) containing 2-dodecanol (2-DD-OH, as extraction solvent) was rapidly injected into the sample solution by syringe. After centrifugation, the 2-DD-OH droplet was floated at the top of the tube which was then cooled in an ice bath. Then, the solidify droplet was transferred into a conical vial and melted quickly at room temperature and it was injected into GC-MS for analysis. The limit of detection for this technique was 0.005-0.047 µg L^{-1} and the linear range was from 0.02 to 500 µg L^{-1}.

DLLME-SFO combined with HPLC was developed by Cheng *et al.* [63] for the determination of fungicides (diethofencarb and pyrimethanil) in aqueous samples. 1-dodecanol with its much lower toxicity was used as extraction solvent. Under the optimized conditions, the enrichment factors for a 5 mL water samples were between 145 and 161, the limits of detection for diethofencarb and pyrimethanil were 0.24 and 0.09 µg L^{-1}, respectively.

Besides, DLLME-SFO has also been applied to the determination of organochlorine pesticides [64], dinitrobenzenes [65], pyrethroids [66] and volatile aromatic hydrocarbons [67] combined with GC-ECD or FID, PAHs [68], diphenyl ether [69], steroid hormone [70] combined with HPLC-VWD or UV.

4.2. Ionic liquid-DLLME (IL-DLLME)

Ionic liquids (ILs) are organic salts with melting points near room temperature (or by convention below 100 °C), resulting from combinations of organic cations and various anions [71]. ILs had also been widely used in different fields (e.g., chromatography, electrochemistry or extraction) because of their unique properties, such as high thermal and chemical stability, negligible vapor pressure, tunable viscosity and miscibility with water and organic solvents [72, 73]. ILs have been proposed as extractants in DLLME (IL-DLLME) which applied widely as preconcentration technique for the determination of organic compounds in environmental water samples . Several kinds of IL-DLLME have been developed in recently years, such as conventional IL-DLLME, temperature-controlled IL-DLLME (TC-IL-DLLME), IL cold-induced aggregation DLLME (IL-CIA-DLLME) and ultrasound-assisted IL-DLLME.

4.2.1. Conventional IL-DLLME

Conventional IL-DLLME used IL as the extraction solvent of DLLME and it was a biphasic process, since the aqueous samples and the extractant were immiscible during extraction. The selection of IL depended on the good performance of the disperser solvent. He *et al.* [74] proposed a new technique of preconcentration of OPPs (parathion, phoxim, phorate and chlorpyifos) from water samples by using DLLME with 1-octyl-3-methylimidazolium hexafluorophosphate ([C$_8$MIM][PF$_6$]) ionic liquid as extraction solvent. The extraction procedure was induced by the formation of cloudy solution, which was composed of fine drops of [C$_8$MIM][PF$_6$] dispersed entire into sample solution with the help of disperser solvent (methanol). After centrifugation, the sediment phase was withdrawn using a microsyringe and then injected into HPLC

for determine. The method showed that up to 200-fold enrichment factor of analytes and linear in the range of 10.5-1045.0 µg L^{-1} for parathion, 10.2-1020.0 µg L^{-1} for phoxim, 54.5-1089.0 µg L^{-1} for phorate and 27.2-1089.0 µg L^{-1} for chlorpyifos, respectively. The limits of detection were in the range of 0.1-5.0 µg L^{-1}. Comparison of this method with HS-SPME, CPE-MABE, LPME and SBSE indicated that IL-DLLME combined with HPLC is a fast, reproducible and simple technique that can be used for the preconcentration of OPPs from water samples. Pena *et al.* [75] had also used [C$_8$MIM][PF$_6$] as extraction solvent in DLLME to preconcentrate 18 PAHs in water samples. The preconcentration and microextraction of the analytes into one step by using [C$_8$MIM][PF$_6$] and offered significant saving of reagents and time. Analysis of extracts was performed by HPLC coupled with fluorescence detection (Flu). The optimized method exhibited a good precision for all the analytes and high enrichment factors (301-346) were also achieved.

Liu *et al.* [76] provided a new method based on DLLME and used the room temperature ionic liquid 1-hexyl-3-methylimidazolium hexafluorophosphate ([C$_6$MIM][PF$_6$]) as extraction solvent combining HPLC with diode array detection (HPLC-DAD) to determine heterocyclic insecticides in water samples. Under the optimal conditions, the EFs were from 209 to 276 for the extraction of fipronil, chlrofenapyr, buprofezin and hexythiazox in water samples and the LODs were 0.53-1.28 µg L^{-1}. The calibration curves were linear with correlation coefficient ranged from 0.9947 to 0.9973 in the concentration range of 2-100 µg L^{-1}. The proposed method was compared with the other extraction techniques, such as SPE, SPME and LPME, indicated that IL-DLLME presented a simple, fast, low sample consumption and environmental friendly technique that can be used for the preconcentration of some pesticide from liquid samples.

Fan *et al.* [77] used 1-butyl-3-methylimidazolium hexafluorophosphate ([B$_{min}$][PF$_6$]) as the extraction solvent of DLLME and after extraction the IL phase was injected into the HPLC system to determine aromatic amines in water samples. The main advantages of the method were simple, high recovery, good repeatability and environmental friendly. The IL-DLLME was also used to the extraction of phenols [78] in water samples, and the IL phase obtained after the extraction was analysis by HPLC system.

4.2.2. Temperature-controlled IL-DLLME (TC-IL-DLLME)

Temperature-controlled IL-DLLME (TC-IL-DLLME) was firstly proposed by Zhou and co-workers [79]. In this technique, dispersive solvent was not required and the extraction procedure was accomplished by rise and fall of the temperature. One function of temperature is to promote the dispersing of IL into the solution and forming the fine drops and increasing the chance of the analytes extracted into ionic liquid phase, and the other is to perform the phase separation. 1-Hexyl-3-methylimidazolium hexa-fluorophosphate ([C$_6$MIM][PF$_6$]) used as extraction solvent was added into the sample solution (containing the analytes, methylparathion and phoxim) and heated. The IL was dissolved and mixed entirely in the sample and the

solution was thereafter cooled with icewater to form cloudy phenomenon. After centrifugation, the sediment phase was dissolved in methanol and injected into HPLC for analysis. Under the optimal extraction conditions, methylparathion and phoxim exhibited good linear relationship in the range of 1-100 ng mL^{-1} and the LODs were 0.17 ng mL^{-1} and 0.29 ng mL^{-1}, respectively. This proposed method was successfully applied in the environmental water samples and good spiked recoveries over the range of 88.2 %-103.6 % were obtained.

Kamarei *et al.* [80] used TC-IL-DLLME combined with HPLC-DAD to preconcentrate and determine chlorobenzenes (CBs) in water samples. In order to obtain the optimal conditions of TC-IL-DLLME, the Plackett-Burman design was used for screening the variables. Then, the significant factors were optimized by using a central composite design (CCD) and the response surface equations were developed. The proposed method was evaluated for extraction and determination of CBs in well water samples in µg L^{-1} and satisfactory results were obtained (RSD < 9.2%). This technique was also applied to extract dichlorodiphenyltrichlo-roethane (DDT) and its metabolites [81], triclosan (TCS) and triclocarban (TCC) [82, 83] in water samples combining with HPLC, UHPLC-TUV or HPLC-ESI-MS/MS. Besides HPLC, the TC-IL-DLLME was also coupled with GC, e.g. the TC-IL-DLLME for determination of dicofol and DDT in environmental water samples prior to GC-MS [84].

4.2.3. IL Cold-induced Aggregation DLLME (IL-CIA-DLLME)

Similar to TC-IL-DLLME, ionic liquid cold-induced aggregation dispersive liquid-liquid microextraction (IL-CIA-DLLME) was proposed by Zhang and co-workers coupled with LC for the determination of benzoic acid in water samples [85]. In this procedure, the sample solution was firstly heated and the mixture of acetonitrile (as disperser solvent) and 1-butyl-3-methylimidazolium hexafluorophosphate ([C$_4$MIM][PF$_6$], as extraction solvent) was rapidly injected into the solution, then the solution was cooled and the cloudy medium was formed. After centrifugation, the IL phase was dissolved in methanol and injected into the LC for analysis. Compared with SPE, HS-SPME and conventional IL-DLLME, IL-CIA-DLLME presented a simple, fast, low sample consumption and environmental friendly technique for the determination of benzoic acid in water samples. A similar extraction procedure was also employed by Zhang *et al.* [86] for the determination of three phthalate esters (dimethylphthalate ester (DMP), diethyl phthalate ester (DEP) and benzyl-n-butyl phthalate ester (BBP)) in water samples. The method had a wide linear range (2-100 ng mL^{-1}), good repeatability (RSD 2.2-3.7 %) for the determination of PAEs.

4.2.4. Ultrasound-assisted IL-DLLME

In recent study, Zhou *et al.* [87] established a new and environmental friendly preconcentration method with 1-Hexyl-3-methylimidazolium hexafluorophosphate ([C$_6$MIM][PF$_6$]) termed as ultrasound-assisted ionic liquid dispersive liquid-phase microextraction for the determination of four aromatic amines in water samples. In the extraction procedure, [C$_6$MIM][PF$_6$] was added into the sample and sonicated for 5 min to make the IL dispersed into the solution to achieve homogenous solution that was subsequently cooled to form the cloudy solution. After centrifugation, the IL phase was

dissolved in mobile phase and injected into the HPLC system for analysis. The LODs of aromatic amines were in the range of 0.17-0.49 ng mL^{-1} and the proposed method was applied to analyze the real water samples. A similar procedure was proposed by Mao *et al*. [88] for the analysis of lovastatin and simvastatin in aqueous samples combined with HPLC-UV using [B$_{min}$][PF$_6$] as extraction solvent. However, high-energy ultrasound was used instead of normal ultrasound in this study.

4.3. Combination of DLLME with Other Extraction Techniques

The enrichment factors using DLLME was often in the range of 50-1000, which still can not be satisfied for the requirement of the ultra trace level analysis. Assadi and co-workers [89] introduced SPE joined with DLLME as an ultra preconcentration for the extraction and determination of chlorophenols (CPs) using GC-ECD. This combination provided an ultra enrichment factor (4390-17,870) for 19 CPs. In SPE-DLLME, CPs were adsorbed from a large volume of aqueous samples (100 mL) into 100 mg functionalized styene-divinylbenzene polymer (PPL) sorbent. After the elution of the desired compounds from the sorbent by using acetone, DLLME procedure was performed on the obtained solution. The linear ranges and the LODs were 0.001-20 μg L^{-1} and 0.005-0.1 μg L^{-1}, respectively. The proposed method was applied to the analysis of the well, tap and river water samples and the relative recoveries, spiked with different levels of CPs, were 71-110 %, 73-115 % and 88-121 %. This combination technique was not only lead to a high enrichment factor, but also it can be used in complex matrices (such as highly saline solution). Zhao *et al*. [90] used multiwalled carbon nanotube adsorbent for SPE combined with DLLME to preconcentrate amide herbicides in environmental water samples. The analytes in the extraction solvent were determined by GC/MS. In 2009, Liu *et al*. [91] used commercial LC-C$_{18}$ SPE columns combined with DLLME to the determination of polybrominated diphenyl ethers (PBDEs) in water and plant samples by GC-ECD. For water samples, EFs were in the range of 6838-9405 under the optimum conditions. The calibration curves were linear in the range of 0.1-100 ng L^{-1} (BDEs 28, 47) and 0.5-500 ng L^{-1} (BDEs 100, 99, 85, 154, 153). The relative standard deviations (RSDs) and the LODs were in the range of 4.2-7.9 % (n=5) and 0.03-0.15 ng L^{-1}, respectively.

Stir bar sorptive extraction (SBSE)-DLLME was proposed by Farajzadeh *et al*. [92] coupled with GC-FID to determine six triazole pesticides (penconazole, hexaconazole, diniconazole, tebuconazole, triticonazole and difenconazole) in aqueous samples. The sample solution was stirred using a stir bar coated with octadecylsilane (ODS) and then the analytes on the sorbent (stir bar) were desorbed with methanol. A mixture of methanol containing 1,1,2,2-tetrachlorothane was rapidly injected into sodium chloride solution 30 % w/v. After centrifugation, the sedimented organic phase was injected into GC system for analysis. The methodology showed broad linear range for the six triazole pesticides studied, with correlation coefficients higher than 0.993, lower LODs and LOQs between 0.53-24.0 and 1.08-80.0 ng mL^{-1}

, respectively, and suitable precision (RSD < 5.2 %). This method showed higher EFs (282-1792) when compared with conventional methods of sample preparation to screen pesticides in aqueous samples.

4.4. DLLME-Back Extraction

Halogenated hydrocarbons were usually selected as extraction solvent in DLLME. Because of their high density, they were not compatible with the reverse phase HPLC mobile phase. The incompatibility of the final drop conductivity with the capillary electrophoresis (CE) system resulted in electrical current break-downs. Therefore, an extra step was required to evaporate them before the HPLC and CE analysis. In 2007, Farajzaded *et al*. [93] proposed a new method of DLLME combined with HPLC-DAD to the determination of anti-oxidants in aqueous samples. Before the injection of HPLC, the sediment phase obtained from DLLME was transferred to another tube and evaporated on a water bath and the residue was re-dissolved in HPLC mobile phase. This method was effective but laborious approach and prone to loss of analytes during evaporation. DLLME followed by a newly designed semi-automated in-syringe back extraction technique combined with RP-HPLC for the determination of clenbuterol (CB) was reported by Melwanki and Fuh [94]. After centrifugation, CB enriched in the sediment phase was withdrawn into a syringe and back extracted into 10 μL of 1 % aqueous formic acid (FA) within the syringe. Back extraction was facilitated by repeatedly moving the plunger back and forth within the barrel of syringe, assisted by a syringe pump. Due to the plunger movement, a thin organic film was formed on the inner layer of syringe that came in contact with the acidic aqueous phase. CB was protonated and back extracted into FA. This newly designed approach shared the advantages of DLLME and easy back extraction method and was applied to the analysis of CB in river, lake and stream water samples.

DLLME combined for the first time with nonaqueous CE for the determination of eight fluoroquinolone antibiotics (lomefloxacin, levofloxacin, marbofloxacin, ciprofloxacin, sarafloxacin, enrofloxacin, danofloxacin and difloxacin) in mineral and run-off waters by Herrera-Herrera *et al*. [95]. Field-enhanced sample injection was carried out in order to improve the sensitivity, whereas pipemidic acid was used as internal standard. The background electrolytes (BGE) that provided complete separation of the eight analytes and the internal standard was composed of 3 M acetic acid, 49 mM ammonium acetate in 45:55 v/v methanol:ACN. In DLLME, a mixture of 685 μL CHCl$_3$ as extraction solvent and 1250 μL ACN as disperser solvent was rapidly injected into the aqueous solution. After centrifugation, the sediment phase was transferred to a vial using a microsyring and evaporated to dryness. The residue was dissolved in 200 μL 1.5 M acetic acid in 25:75 v/v methanol:ACN and injected into the CE system. Optimum DLLME conditions were achieved by means of experimental design methodology. Calibration curves of the whole method were obtained with correlation coefficients (R) higher than 0.994 in all cases. LODs of the method ranged between 1.6 and 15.2 μg L^{-1} for mineral water and between 6.6 and 155 μg L^{-1} for run-off water.

4.5. Other Modality of DLLME

Recently, other modality of DLLME was developed and applied to the analysis of organic compounds in water

samples, such as ultrasound-assisted DLLME (UA-DLLME), surfactant assisted DLLME (SA-DLLME), molecular-imprinted polymer-DLLME (MIP-DLLME), solvent terminated DLLME (ST-DLLME), low toxic DLLME (LT-DLLME) and solvent-based de-emulsification-DLLME (SD-DLLME).

A simple and rapid ultrasound-assisted DLLME (UA-DLLME) technique has been developed for diverse organic pollutants [96-99]. Compared to the conventional DLLME, an ultrasound-assisted process was applied to accelerate the formation of the fine cloudy solution. UA-DLLME combined with capillary GC-FID [96] and HPLC-UV [97] was used to the determination of pyrethroids in domestic wastewater and river water samples. For the analysis of four fluoquinolones (ofloxacin, norfloxacin, enrofloxacin and lomefloxacin) in pharmaceutical wastewater samples coupled with HPLC-UV, UA-DLLME was improved by Yan and co-workers [98]. The sediment phase obtained from DLLME was evaporated to dryness and re-dissolved in the mobile phase for the further HPLC analysis. The linear ranges obtained for all analytes were 0.01-2.0 μg mL^{-1} with LODs ranged from 0.14 to 0.81 μg L^{-1}. Lately, the UA-DLLME was also further developed by Chen and co-workers [99, 100]. Sixteen PAHs in seawater samples were excellently separated and determined by UA-DLLME combined with little solvent consumption by GC-MS [99], and five sulfonamides were successfully detected in several environmental water samples by UA-DLLME coupled with capillary electrophoresis (CE) with the aid of experimental design [100].

Surfactant assisted DLLME (SA-DLLME) couple with HPLC-UV for extraction and determination of chlorophenols in environmental water samples was developed by Yamini *et al.* [101]. In this procedure, cethyltrimethyl ammonium brimide (CTAB) was used as a disperser agent. 1-octanol as an extraction solvent was injected into the sample solution containing CTAB. The mixture was then shaken to disperse the organic phase. After centrifugation, the dispersed fine droplets of the extraction phase were collected on the top of the vial and the collected phase was directly injected into HPLC for analysis. The EFs in a range of 187-353 were obtained under the optimum conditions. The linear range, LODs and precision (n=5) were 0.2-200 μg L^{-1}, 0.1 μg L^{-1}, and 4.7-6.9 %, respectively.

Ebrahimzadeh *et al.* [102] developed molecular-imprinted polymer (MIP) combined with DLLME for ultra-preconcentration and determination of mononitrito-luenes in wastewater samples using GC-FID. MIP was synthesized by copolymerization of methacrylic acid (MAA)-ethylene glycole dimethacrylate (EGDMA)-2, 2-azobisisobutyronitrile (AIBN) as the initiator that imprinted with 3-nitrotoluene (3-NT) as the template molecule. In MIP-DLLME procedure, dried polymer beads were suspended in the sample solution containing 3-NT which was subsequently stirred for 1 h. Then, the mixture was filter and the solid phase was rinsed with water to remove the matrix interferences. After filtration, it was transferred into a glass bottle and 7 % (v/v) acetic acid in methanol solution was added and the mixture was stirred for 12 h. Then the solution was filter and transferred into a

conical tube for preconcentration by DLLME [103]. CCl$_4$ was added into the final solution obtained at the last step and the resulted solution was rapidly injected into the aqueous sample solution. A cloudy solution was formed and the sediment phase obtained after centrifugation was diluted with internal standard solution (NB) and injected into GC for analysis. Preconcentration factor (PF) of MIP-DLLME method was about 2800 under the optimum conditions. The LOD and linear range were 0.02 μg L^{-1} and 0.04-20 μg L^{-1}, respectively. Compared with other techniques, such as SPME, SDME, DLLME, HSME, HLLE and HF-LPME, MIP-DLLME showed the LODs and RSDs were similar to these methods and the PF was 10 times higher than the other methods. Simultaneous preconcentration of many samples with trace concentration can be performed by the MIP-DLLME method, which can solve the problem of longer time of the proposed method.

Extraction solvents often used in DLLME were high density than water and environmental unfriendly. Low density and low toxic extraction solvent of DLLME was necessary to apply. Chen *et al.* [104] used low density extraction solvent based solvent terminated DLLME (ST-DLLME) to determine carbamate pesticide in water samples coupled with gas chromatography-tandem mass spectrometry (GC-MS/MS). After dispersing, the obtained emulsion cleared into two phase quickly when another aliquot of disperser solvent (served as the demulsifier) was added into the aqueous solution. Therefore, the ST-DLLME procedure did not need centrifugation to achieve phase separation. It was convenient for the usage of low density extraction solvents such as toluene, cyclohexane and octanol in DLLME. The LODs and the precisions for all carbamate pesticides were 0.001-0.50 ng mL^{-1}, 2.3-6.8 % (RSDs, 2 ng mL^{-1}, n=5), respectively. The proposed method was successfully applied to determine real water samples and good spiked recoveries were in the range of 94.5-104 %. Leong *et al.* [105] proposed to use low toxic bromosolvent (1-bromo-3-methylbutane) as extraction solvent in DLLME called low toxic DLLME (LT-DLLME) combined with GC-MS to extraction and determination of 16 PAHs in water samples. A mixture of 50.0 μL propionic acid (as disperser solvent) containing 10.0 μL 1-bromo-3-methylbutane (as extraction solvent) was injected into the sample solution. A cloudy solution resulted from the dispersion of fine 1-bromo-3-methylbutane droplets in the solution was formed and 88.0 μL 40 % (w/v) KOH was added to decrease the emulsion of the extraction solvent after centrifugation. The sediment phase was collected to inject into GC for analysis. The range of EFs and extraction recoveries of tap water samples were ranging 372-1308 and 87-105 % under the optimum conditions. The linear range was wide (0.01-10.00 μg L^{-1}) and the LODs were between 0.0003 and 0.0078 μg L^{-1} for most of the analytes. The performance of the method was gauged by analyzing samples of tap water, sea water and lake water samples. Compared to the other pretreatment techniques, such as SPE, SPME, HS-SPME, IL-SPME, HSME, HF-LPME, DLLME, LPME-SFO, DLLME-SFO, HLLE and USAEME, the extraction time was shorter than most of the above methods and the LODs were the best of the list methods.

Solvent-based de-emulsification-DLLME (SD-DLLME) was proposed by Zacharis *et al.* combined with GC-MS to the preconcentration and determination of OCPs from environmental water samples [106]. The sample solution was
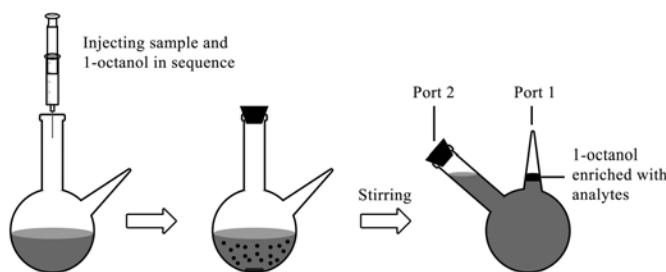
Fig. (3). Schematic of the extraction process.

transferred in a 10 mL volumetric flask and kept under continuous stirring at 200 rpm. A mixture of ACN (as disperser solvent) containing m-xylene (as extraction solvent) was injected into the solution and an emulsion was formed. After 2 min a second 750 μL acetonitrile (as de-emulsifier) was injected into the solution to break down the emulsion. The phase separation was achieved in less than 1 min without centrifugation. The organic phase was collected and injected into GC for analysis. Under the optimum conditions, the LODs were in the range of 2-50 ng L^{-1} using selective ion monitoring (SIM).

A new device for magnetic stirring-assisted DLLME was developed by Zhang *et al.* coupled with HPLC for the analysis of UV-filter (4-hydroxybenzophnone (HB), benzo-phenone (BP), 2,4-dihydrozybenzophenone (DB) and 2-hydroxy-4-methoxybenzophenone(HMB)) in water samples [107]. The schematic extraction procedures were depicted in Fig. (**3**). A specially designed flask, which had two narrow open necks with one of them having a capillary tip, was employed to facilitate the DLLME process. The extraction was carried out in a binary system of the extractant (1-octanol) and the aqueous sample solution without disperser solvent. Magnetic stirring was involved to accelerate the mass transfer from the aqueous sample to the extraction solvent. After extraction, phase separation was easily achieved by leaving the extraction system statically for a while. No centrifugation step was necessary. The analyte-enriched phase, floating above the sample solution, was elevated and concentrated into the narrow open tip of the flask by adding pure water into it via the other port, which was withdrawn with a microsyringe and diluted with mobile phase for the subsequent HPLC analysis. The LODs for the analytes were in range of 0.2-0.8 ng mL^{-1} under the optimum conditions. The linear ranges were 8-20,000 ng mL^{-1} for HB, 7-20,000 ng mL^{-1} for DB, 8-10,000 ng mL^{-1} for BP and 5-20,000 ng mL^{-1} for HMB, respectively. The relative standard deviations (n=3) at a spiked level of 80 ng mL^{-1} were in the range of 1.4-4.8 %. The proposed magnetic stirring-assisted DLLME method was successfully applied to the analysis of lake water samples.

5. CONCLUSIONS AND OUTLOOK

The present review has focused on the recent advances in DLLME and its applications for analysis of organic compounds in water samples of environmental interest in conjunction with various chromatographic techniques as well as other extraction techniques. DLLME enjoys the advantages of simplicity, rapidity, low cost, high recovery and enrichment factor, and environmental benignity. As a

viable sample-preparation approach, DLLME is receiving rising concern and achieving greater importance. With the rapid development of DLLME as a research hotspot, however, it involves a number of limitations that should be taken into serious account. Take major examples as follows. There is no equation in DLLME for calculating the volume of sediment phase without further experimental test. DLLME is not yet suitable as a routine applicable on-line pretreatment technique. Automation and on-line combining of DLLME to analytical instruments is very difficult to be achieved since most of the process of DLLME is genuinely manual. Up to date, only one publication relevant to its automatic operation is found, in which a novel on-line sequential injection (SI) DLLME system was constructed [108] for the determination of trace copper and lead in water samples using flame atomic absorption spectrometry (FAAS). In addition, one of the main disadvantages of DLLME is that its efficiency is restricted by solvent selection to systems capable of forming a dispersive phase, somewhat limiting its range of application by sample. Since DLLME need small volume of water sample, EF is usually in the range of 50-1000, and for most applications the LODs are μg L^{-1} level. However, there are many ng L^{-1} or lower levels of organic pollutants in environmental water, which still can endanger human and other organisms even at much lower the regulated safe dose levels [109, 110].

To address the proposed problems means to exploit greater development potential and opportunities of DLLME. We attempt to take some important exploration initiatives as follows: **1) To further enrich fundamental theories of DLLME.** The relationship between the several important parameters in DLLME needs more developments. The current status, challenges, and technology improvement and wider applications of DLLME need systematic studies. **2) To expand the combination ranges of DLLME.** The coupling with other analytical instruments, such as inductively coupled plasma-optical emission spectrometry (ICP-OES) and capillary electrophoresis (CE), need some progress, which has not been widely applied [100]. The conjunction with other pretreatment methods, such as solid-liquid extraction, SBSE and SPE, can provide high EF, consistent recovery values as well as highly selective extractions. **3) To broaden the applicability of DLLME.** More complex matrices should be employed for sampling, such as pharmaceuticals and biological samples, in order to allow DLLME a truly practical approach for sample cleanup and enrichment. We strongly encourage further works studying these possible applications for a wider variety of analytes to fully demonstrate the potential of DLLME. **4) To investigate more new solvents of extraction and dispersion.** It creates some problems such as incompatibility of the extracting solvents. New solvents may provide new insight

such as its application for reversing solvent polarity. **5) To fully utilize chemometrics for the optimization of influence factors of DLLME.** The use of chemometrics, in particular, experimental design methodology, can enable to achieve the best extraction conditions quickly in a relatively small number of experiments [100]. **6) To motivate the automation and instrumentation of DLLME.** Automatic on-line hydrodynamic analytical systems can be exploited with a view to enhancing the inherent properties of conventional measurement procedures [17, 20, 108]. In spite of few studies on the automation of DLLME [108], further research has a promising potential and is coveted to complete the experiences in this area. We strongly encourage that new developments of automation and instrumentation of DLLME are conducted.

6. ACKNOWLEDGEMENTS

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