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RESEARCH ARTICLE

RECENT DEVELOPMENTS AND APPLICATIONS OF DISPERSIVE LIQUID–LIQUID MICROEXTRACTION (DLLME)

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ABSTRACT

Many DLLME methods have been developed in recent years. DLLME is a novel microextraction technique with great potential in sample pretreatment. In most works, the intensive research on DLLME is concerned with the broadening of the range of used extraction solvents to increase the extraction capability of the method. In response, some interesting solutions based on viable substitutes have been published; these solutions involve the adoption of ionic liquids, methods based on the solidification of a floating organic drop, procedures utilizing special devices, the adjustment of the mixture density of the solvents with the use of an auxiliary solvent, and methods based on supramolecules, all of which are widely applicable to analytes and demonstrate economical or environmental benefits. In this review paper, DLLME with lower and higher density extraction solvents and its combination with other extraction techniques with exemplified applications is discussed.

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INTRODUCTION

Despite the significant advances in analytical instruments and approaches that have been made in recent years, sample pretreatment procedures must still be considered prior to an instrumental determination of analytes, especially for trace analytes in a sample with a large amount of potential interferences. In this sense, the pretreatment step generally plays the combined roles of extraction, cleanup, and concentration while rendering the analytes into a form that is compatible with the analytical system; therefore, pretreatment is an essential step in the analytical process. Thus, current efforts are being focused on the improvement of this procedure, following the current trends toward miniaturization, simplification, automation, economization, and solvent-free or environmentally friendly alternatives. In the effort to achieve this objective, several pretreatment techniques have been introduced that have been successful in certain aspects. In particular, the most traditional and classical technique is liquid–liquid extraction (LLE) (Moore, *et al*., 1956), which remains the most frequently used technique in separation and analytical chemistry. However, this technique's shortcomings of time consumption, tedium, and extensive consumption of hazardous organic solvents and samples seem to be unavoidable. Therefore, LLE has been overshadowed by the broad application of solid-phase extraction (SPE) (Asafu-Adjaye, *et al*. 1986) which lessens the disadvantages of time, labour and organic solvents reduction but not sufficiently; in addition, SPE introduces the waste and contamination of disposable SPE cartridges, as well as high costs. Thus, modern trends in the analytical field include the miniaturisation and simplification of sample preparation procedures, such as liquid-phase microextraction (LPME) (He, *et al*., 1997) and solid-phase microextraction (SPME) (Helena, *et al*., 1999) which retain the advantages of SPE and LLE. Various other modifications have since been introduced; these modifications involve single drop microextraction (SDME) (Jeannot, *et al*., 1996) solvent bar microextraction (SBME) (Jiang, *et al*., 2004), and hollow-fibre LPME (HF-LPME) among others. These techniques have received favorable responses in different fields and have gained their place in modern analytical laboratories. Nevertheless, these techniques face their own restrictions, which make the development of sample preparation techniques a continuing process.

The dispersive liquid–liquid microextraction (DLLME) method was proposed by Assadi and co-workers in 2006 (Cruz-Vera, *et al*., 2011; Khalili-Zanjani, *et al*., 2007) and immediately garnered considerable attention from researchers. As the name suggests, DLLME is equivalent to a miniaturized type of LLE that is generally established on a ternary

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component solvent system, in which an appropriate disperser solvent is introduced to help the dispersion of an organic extraction solvent into an aqueous sample and further achieve a highly efficient extraction. Briefly, a DLLME procedure can be outlined as follows: (a) the injection of extraction and disperser solvents into samples; (b) the formation of a cloudy solution due to the cosolvency of the disperser solvent with two other solvents; (c) the accomplishment of extraction equilibrium in a short time based on the extensive surface contact between the droplets of the extraction solvent and the sample; (d) centrifugation to obtain the sedimented extraction phase, which is abundant with analytes for instrument analysis. Obviously, the advantages of DLLME are mainly the following: (a) the negligible consumption of extraction solvents (only microliter volumes); (b) the short extraction time due to the rapid achievement of an equilibrium state; (c) the high enrichment factor (EF) due to the high phase ratio of the donor (aqueous sample) and the acceptor (extraction solvent). Accordingly, the DLLME technique is simple, quick, efficient, and simultaneously meets the development requirement of green chemistry. Nevertheless, this technique also possesses certain limitations, which primarily result from requirements related to the extraction and disperser solvents, namely (a) the extraction solvent must have a good extraction capability of the target analyte, a low solubility in the aqueous phase, and a greater density than water; (b) the disperser solvent must be miscible with both the extraction solvent and the aqueous phase. For this reason, the selection of the extraction solvent becomes the most restrictive part because few organic solvents meet such requirements, and of those solvents, halogenated hydrocarbons are in the majority. In addition, other parameters affecting DLLME, such as pH value and salt addition, may crucially influence the extraction results and must also be optimized.

In light of the obvious merits of DLLME, such as simplicity and rapidity of operation, low cost, high enrichment factor and lack of negative environmental impact, the DLLME technique seems to be accessible to most laboratories and compatible with various analytical techniques such as gas chromatography (GC), high-performance liquid chromatography (HPLC), electrothermal atomic absorption spectrometry (ETAAS) and flame atomic absorption spectrometry (FAAS). Therefore, DLLME has attracted considerable attention and been widely accepted, as evidenced by its appearance in a continually increasing number of original articles and reviews since the technique's introduction.

DLLME with lower-density extraction solvent

DLLME based on solidification of floating organic droplet (DLLME-SFO)

Liquid–liquid microextraction based on solidification of floating organic droplet (LLME-SFO) was introduced by Khalili-Zanjani *et al*. (Khalili-Zanjani, *et al*., 2007; Khalili-Zanjani, *et al*., 2008). It is simple, inexpensive, and it involves minimal consumption of organic solvent. However, its extraction rate is lower than that of DLLME. DLLME-SFO (Lv *et al*., 2010) was developed to combine the benefits of DLLME and LLME-SFO. Unlike LLME-SFO, DLLME-SFO does not involve stirring during extraction, and unlike traditional DLLME, it does not use chlorinated solvents and conical bottom glass tubes. Instead, a mixture of low-toxicity extraction solvent (which is also less dense than water) and disperser solvent are rapidly injected into the sample solution to form a cloudy dispersion in the glass test tube.

DLLME with special extraction devices

Recently, many researchers have attempted to use lower-toxicity solvents with density lower than that of water in DLLME. One possible way of enabling the application of such solvents in DLLME is the use of special extraction devices, such as specially designed centrifugation tubes and pipette collection tubes. In 2009, Farajzadeh *et al*. designed a special vessel (Asadollahi, *et al*., 2010) for use in DLLME to extract organophosphorus pesticides (OPPs). In this extraction method, a mixture of cyclohexane (extraction solvent) and acetone (disperser solvent) is rapidly injected by syringe into an aqueous sample in a special vessel. After centrifugation, fine droplets of cyclohexane accumulate in the upper layer of aqueous solution. The upper phase is injected into a gas chromatograph for separation. This method is rapid and easily recovers the extractant; however, it is not suitable for extracting volatile compounds. Hashemi *et al*. developed a DLLME method that uses a special device to enrich glycyrrhizic acid from aqueous extracts of licorice (Hashemi, *et al*., 2009). The device consists of a narrow-necked glass tube (NNGT) inserted into a centrifuge tube. Hexanol and acetone are used as the extraction solvent and disperser solvent, respectively. A uniformly distributed cloudy suspension is produced by further aspiration and expulsion of about 2 mL of the cloudy sample by syringe. The mixture is then centrifuged for phase separation. Since hexanol is lighter than water, the extraction phase accumulates on the surface of the aqueous solution. Additional water is added from the opening of NNGT; then, the extraction phase is raised and fills the narrow neck of NNGT. As a result, the extraction phase can easily be withdrawn by microsyringe.

Hu *et al*. developed (Hu, *et al*., 2010) a DLLME method based on a molecular complex for analysis of polar compounds in aqueous solution. The principle of this method is the hydrogen bonding between the extractant and the analytes. In this approach, the Lewis base tri-n-butylphosphate (TBP) instead of conventional water-immiscible organic solventsis directly used as extractant for DLLME. The sample containing the analytes is placed in a disposable polyethylene pipette. A mixture of the extractant TBP and the disperser solvent methanol is rapidly injected into the sample solution by syringe. Subsequently, the pipette is placed in a 10 mL Eppendorf tube and is agitated by a vortex mixer. After centrifugation, the organic phase floating on theaqueous solution is concentrated in the narrow neck of the pipette, and is easily withdrawn by a 10.0 μL microsyringe. This technique expands the application of classical DLLME for various organic analytes, and enables extraction in a disposable polyethylene pipette.

Su and Jen developed an in-syringe USAEME for the extraction of OPPs from water samples by using GC with micro electron capture detection (Su, *et al*., 2010). Ultrasound radiation is applied to accelerate the emulsification of microliter volumes of low-density organic solvent in aqueous solutions to enhance the efficiency of OPPs microextraction from the sample. Initially, the sample solution is drawn into a 5 mL syringe. After removal of the plunger and sealing of the syringe with a silicone-plug, the barrel is held upside down and the needle is removed.

Table 1. Examples of DLLME-SFO applications

Analyte	Matrix	Technique	Extraction solvent	Disperser solvent	EF	LOD	Ref.
HOCs	Water	GC-ECD	2-Dodecanol	Acetone	174–246	0.005–0.05 µg/L	Leong, *et al*., 2008
PAHs	Water	HPLC-VWD	1-Dodecanol	Methanol	88–118	0.045–1.1 ng/mL	Xu, *et al*., 2009
Al	Water	ICP-OES	1-Undecanol	Acetone	128	0.8 µg/L	Rezaee, *et al*., 2010
OCPs	Water	GC-ECD	Hexadecane	Acetonitrile	37–872	0.011–0.11 µg/L	Leong, *et al*., 2009
Decabrominateddiphenyl ether	Surficial sediments	HPLC-UV	Dodecanol	Methanol	-	2.3 pg/g	Jian, *et al*., 2010
Hexanal, heptanal	Human blood	HPLC-VWD	1-Dodecanol	Methanol		7.90, 2.34 nmol/L	Lv, *et al*., 2010
Steroid hormone	River, tap water	HPLC-DAD	1-Undecanol	Methanol	121–329	0.8–2.7, 1.4–3.1 µg/L	Chang, *et al*., 2010
carbamates	Fruit juices	LC-MS/MS	1-Dodecanol	Acetonitrile	-	0.002–0.02 µg/L	Vichapong, *et al*., 2015
Aliphatic amines	Water	HPL-DAD	1-Undecanol	Acetonitrile	210–290	0.005–0.02 µg/L	Kamarei, *et al*., 2011
Triazines	Water, sugarcane sample	GC-MS	1-Undecanol	Acetonitrile	195–322	0.037–0.008 ppb	Sanagi, *et al*., 2012
Amphetamines and metha mphetamine	Urine	HPLC-UV	1-Undecanol	SDS	56, 48	2, 3 µg/L	Saber-Tehrani, et al., 2012
V	Water,	ETAAS	1-Undecanol	Acetone	184	7 ng/L	Asadollahi, *et al*., 2010
Ni, Co, Pb, Cr	Water, waste water	GFAAS	1-Undecanol	Ethanol	800	0.2–1.3 ng/L	Mirzaei, *et al*., 2011
Fe, Fe	Water	UV-Vis	1-Undecanol	Ethanol	125, 162	25, 8 µg/L	Samadi, *et al*., 2016
Ag	Water	GFAAS	1-Undecanol	Methanol	250	0.056 ng/mL	Demirhan, *et al*., 2016

Table 2. Combination of DLLME with other extraction techniques

Analyte	Matrix	Technique	Extraction Solvent	Disperser Solvent	Feature	EF	LOD	Ref.
OPPs	Water	GC-MS	Carbon tetrachloride	acetone	SPE-DLLME		38-230 pg/L	Rezaee, *et al*., 2010
fungicides	Wine	GC-ECD	1,1,1-Trichloethane	Acetone	SPE-DLLME	156-254	30-120, 40-250 ng/L	Shi, *et al*., 2010
PCB,PBDEs	wine	HPLC	Chlorobenzene	Acetone	SPE-DLLME	150-600	0.01-0.4µg/L	Ping, *et al*., 2017
Sulfonyl urea herbicides	Soil	HPLC-DAD	Chlorobenzene	Acetone	DSPE-DLLME	102-216	0.5-1.2 ng/g	Montes, *et al*., 2009
Flavoring compounds	Tobacco aditives	GC-MS	Chloroform	Methanol	UAE-DLLME	140-208	0.04-0.24 ng/mL	Liu, *et al*., 2011
Chlorophenols	Soil and marine sediments	HPLC-UV	Chlorobenzene	Acetone	MAE-DLLME	25-30	0.0005-0.002 mg/Kg	Li, *et al*., 2012
PAHs	Environmental water	GC-MS	1-Octanol		DLLME-D-µ-SPE	110-186	11.7-61.4 pg/mL	Rezaee, *et al*., 2010

Table 3. Applications of DLLME

Analyte	Matrix	Technique	Extraction solvent	Disperser solvent	EF	LOD	Ref.
PAHs	Water samples	GCIFID	Dichoromethane	Acetone	603-1113	0.007-0.03 µg/L	Cruz-Vera, *et al*., 2011
Triazine herbicides	Water samples	GC-MS	Chlorobenzene	Acetone	150-722	0.021-0.12 µg/L	Shi, *et al*.,2010
PBDEs	Environmental water	HPLC-VWD	Tetrachloroethane	THF	153	0.2ng/L	Nagaraju, *et al*., 2007
Cd	Water samples	GFAAS	Carbontetrachloride	Methanol	125	0.6ng/L	Li, *et al*., 2007
Carbamates	Rain, surface and ground water	HPLC-DAD	Trichloromethane	Acetonitrile	80-117	0.1-0.5ng/mL	Jahromi, *et al*., 2007
Pyrethroids	River water	HPL-UV	Tetrachloromethane	Acetone	767-1033	0.11-0.3 µg/L	Sergiane, *et al*., 2010
Multiclass pesticides	Natural waters	LC-MS	Carbontetrachloride	Acetonitrile	50	0.02µg/L (LOQ)	Yan, *et al*., 2010
Nitrobenzenes and nitrochlorobenzenes	Water samples	GC-MS	Trichloromethane	Acetonitrile	243-525	24.1-107.4 pg/mL	Caldas, *et al*., 2010
Pd	River water	FAAS	Chloroform	Ethanol	45.1	90µg/L	Zhaoxiong, *et al*., 2012
MeHg+, Hg2+	Tap,snow and lake water	HPLC-ICP-MS	Carbontetrachloride	Methanol	138,350	0.0076, 0.0014 ng/mL	Kokya, *et al*., 2009
PCBs	Soil samples	GC-ECD	Chlorobenzene	Acetone		0.2-0.5 µg/Kg	Jia, *et al*., 2011
Hg , Ag	Environmental and geological samples	Electrophoresis, GFAAS	Carbon tetrachloride	Methanol	72	20ng/L	Liang, *et al*., 2010; Hu, *et al*., 2009
Pyrethroids	Fruit juices	HPLC–UV	Chloroform	Methanol	62–84	2–5 µg/L	Boonchiangma, *et al*., 2012
Opium alkaloids	Urine samples	HPLC–UV	Chloroform	Acetone	63.0–104.5	0.2–10 µg/L	Shamsipur, *et al*., 2011

The extraction solvent (toluene) is then injected into the sample solution by using a 100 µL glass syringe. After ultrasonication and centrifugation, the plunger of the 5 mL syringe is slowly pushed to transfer the recovered extractant into a graduated capillary tube. Finally, the extracting phase containing the target OPPs is easily recovered by syringe. One microliter of the separated extractant is injected into GC for analysis. This method uses a 5 mL syringe as the sample vial instead of a centrifuge tube, and a 100 µL glass syringe is used to inject the extraction solvent and to recover the extractant. This device is easy to operate, and the extractant volume is easily read from the scale on the capillary tube. This method does not require a narrow-necked port to collect the extractants and the device is very easy to clean.

Low-density-solvent based solvent demulsification DLLME (LDS-SD-DLLME)

All of the aforementioned extraction devices possess advantages and drawbacks in terms of ease of operation and manifold complexity. Guo and Lee (2011) reported a LDS-SD-DLLME method for the determination of 16 priority PAHs in environmental samples. No centrifugation is required in this procedure. A 5 mL sample solution is placed in a 5 mL polyethylene Pasteur pipette by using a 5 mL syringe. A mixture of the extraction solventn-hexane (50 µL) and the dispersive solvent acetone (500 µL) is injected rapidly into the sample solution by a 1.0 mL syringe to form an emulsion. The demulsification solvent acetone (500 µL) is then injected into the aqueous solution to break up the emulsion and separate it into two layers. The upper layer (about 35 µL n-hexane) is collected and analyzed by gas chromatography–mass spectrometry (GC–MS). Notably, the extraction requires only 2–3 min, and is therefore faster than conventional DLLME or similar techniques. This method permits a solvent that is less dense than water to be used as extraction solvent, and expands the applicability of DLLME to a wider range of solvents.

Chang *et al*. (2011) used DLLME combined with an improved solvent collection system to separate water and organic solvent in the collected extractant drop. This method uses very small volumes of low-toxicity solvents (11 µL of 1-nonanol and 400 µL of methanol) to extract organochlorine pesticides (OCPs) from 10 mL water samples prior to analysis by GC. After centrifugation, a liquid organic drop accumulates between the water surface and the glass wall of the centrifuge tube. The liquid organic drop is transferred along with some of the water into a microtube (3 mm × 15 mm) by syringe. The organic and aqueous phases then immediately separate in the microtube. The organic solvent is easily collected by syringe and then injected into the GC instrument for analysis. Moreover, it is better to centrifuge the collected phases in the microtube for about 1 min before injection, because it further removes water; in this manner, two clear phases are obtained. This improved sol-vent collection system can protect the instrument from damage by the injected water and increase the reproducibility of the results.

DLLME with higher-density extraction solvent

DLLME with low-toxicity solvent

In addition to the many DLLME methods that have been developed to use low-density organic solvents, other methods using higher-density extraction solvent have been introduced to overcome the drawbacks of normal DLLME. In 2010, LT-DLLME was developed by Leong *et al.* (2010). This method uses lower-toxicity brominated, iodinated and other halogenated solvents such as 1-bromo-3-methylbutane (1-bromo-3-methylbutane,the median lethal dose (LD50) 6150 mg kg−1) instead of the highly toxic solvents normally used in DLLME. This method also demonstrates that propionic acid is suitable as a disperser solvent; as little as 50 µL of the acid is sufficient for extraction. A 7 mL sample of water is spiked with PAHs. The disperser solvent propionicacid and the extraction solvent 1-bromo-3-methylbutane (10.0 µL) are rapidly injected into the sample solution and the resulting mixture is shaken by hand for a few seconds. Potassium hydroxide (88 µL, 40% (w/v)) is added to the sample to minimize emulsion formation by the extraction solvent before centrifugation. After centrifugation, the organic solvent is sedimented at the bottom of the conical test tube, and then a microsyringe is used to collect and inject it into a gas chromatograph for further analysis. The selected extraction solvent is less toxic than chlorinated solvents in normal DLLME. In particular, some brominated solvents are less toxic than the conventional low-density solvents in DLLME or dispersion LPME.

Auxiliary solvent to adjust the density of DLLME

Kocúrová *et al.* (2010) developed an adjusting-density DLLME (AS-DLLME) technique. A quaternary system consisting of an aqueous sample, an extraction solvent, an auxiliary solvent, and a disperser solvent is employed in this method. The auxiliary solvent (a chlorinated solvent), which is denser than water, is used to adjust the density of the extraction solvent–auxiliary solvent mixture to facilitate its separation from the aqueous sample by centrifugation. This method does not require the use of special devices. A 5 mL sample solution containing Au (III) is prepared in conical microcentrifuge tubes. A 0.5 mL mixture of the disperser solvent methanol, the extraction solvent toluene (145 µL), and the auxiliary solvent carbon tetrachloride (CCl_4; 145 µL) is vigorously injected by using a 0.5 mL glass syringe. The mixture is gently shaken and centrifuged. A layer of sediment containing a mixture of toluene and CCl_4 accumulates at the bottom of the tube. The extractant is removed by syringe and then analyzed by UV–visible spectrometer. Alternatively, the extractant may be transferred to a graphite atomizer for atomic absorption spectroscopy. This novel method combines the advantages of conventional DLLME and the use of lower-density solvent and lower volumes of toxic solvents.

DLLME with automated online sequential injection

Anthemidis and Ioannou (2011) developed an automated on-line sequential injection dispersive liquid–liquid microextraction SI-DLLME system for metal preconcentration. The mixture of disperser solvent, extraction solvent, and chelating agent is mixed with a stream of aqueous sample through an online system. After extraction, droplets of the organic phase are retained in a microcolumn. The eluent is then transferred by a nebulizer for analysis by flame atomic absorption spectrometry (FAAS) analysis, or injected into a graphite tube for electrothermal atomic absorption spectrometry (ETAAS) measurement (Anthemidis, *et al.*, 2010). This method does not require centrifugation and an extraction solvent that is denser than water, and the process is fully automated. However, this method requires a microcolumn for retention of the analytes and several hundred microliters of solvents for elution of the analytes. Andruch *et al.* (2012) reported a novel SI-DLLME. In the method, sample and all reagents are drawn into the holding coil of the sequential injection analysis (SIA) manifold, and the resulting mixture is delivered into a conical tube. A mixture of the extraction solvent is then added at a high flow rate to form a cloudy suspension and to extract the analytes. The extraction phase consequently separates rapidly at the bottom of the conical tube. Afterward, the extraction phase is transferred to a microvolume Z-flow cell for spectrophotometric detection. The online DLLME methods achieved a major breakthrough in DLLME and overcame the difficulties of rapidly extracting analytes and collecting the organic solvent in online analysis.

Combination of DLLME with other Extraction techniques

Solid-phase extraction (SPE)

SPE and DLLME coupled with GC were used for determination of 13 OPPs in aqueous samples (Samadi, *et al*., 2012). The analytes were collected from large volumes of aqueous solutions (100 mL) into the sorbent SPE C18 (100 mg). The C18 SPE cartridge was used in separation of the desired compounds by elution with 1 mL of acetone. Eluates were collected into a 10 mL screw-cap glass test tube. Chlorobenzene (12 µL) was added to the test tube and the resulting mixture was drawn into a syringe and rapidly injected into double distilled water in a screw-cap glass test tube with conical bottom. The mixture was then centrifuged and the extractant was injected into the GC for analysis. This method is fast and simple, and affords very high EFs and short analysis time.

Stir bar sorptive extraction (SBSE)

SBSE combined with DLLME (Farajzadeh, *et al*., 2010) has been developed for the extraction of six triazole pesticides in aqueous samples. In this method, 100 mL of standard or sample solution is stirred with astir bar coated with octadecyl silane for 30 min at 300 rpm. The stirbar is subsequently removed and placed in a 1.5 mL glass vial containing 1 mL of methanol for liquid desorption. After the stir bar is removed, 25 µL of the extraction solvent 1, 1, 2, 2-tetrachloroethane is added to the extracted analytes. The resulting solution is rapidly injected into 5 mL of sodium chloride solution by syringe and then centrifuged. The sedimented organic phase is removed and injected into GC for analysis. This method enables simple, selective, and sensitive determination of analytes in complex matrixes.

Molecularly imprinted matrix solid-phase dispersion

A MIM synthesized by aqueous suspension polymerization was applied as a selective sorbent for the simultaneous determination of four Sudan dyes in egg yolk samples (Yan, *et al*., 2011). The sorbent was a miniaturized matrix solid-phase dispersion used for MSPD–DLLME. The miniaturized MSPD procedure was performed by using small amounts of sample, support, and solvent. An aliquot of the egg yolk sample and MIM sorbent were placed in a small glass beaker and blended together. The homogenized mixture was transferred to an empty cartridge (5 cm × 8 mm i.d., prepacked with50 mg of MIM), rinsed with 4.0 mL of methanol–water solution, and then eluted with 3.0 mL of acetone–acetic acid solution. The eluate was collected in a 10 mL conical tube and then evaporated to 1.0 mL. It was then mixed with 100 µL of TCE and 5.0 mL of water for further purification and concentration of analytes by DLLME. This MIM–MSPD–DLLME method combined the advantages of MIM, MSPD, and DLLME.

Supercritical fluid extraction (SFE)

SFE followed by DLLME (Liu, *et al*., 2011) has been developed for extraction and determination of PAHs in marine sediments. SFE of PAHs was performed at 313 K and 253.2 bar, and the extracted PAHs were collected in 1 mL of acetonitrile. Subsequently, 16 µL of the extraction solvent chlorobenzene was added to the collecting solvent (1.0 mL of acetonitrile). The resulting mixture was rapidly injected into 5.0 mL of aqueous solution. After centrifugation, the PAHs in the sedimented phase were analyzed by GC. This procedure extends the application of DLLME to solid samples. In particular, it holds great potential in the analysis of trace organic compounds in solid samples.

Nanotechniques combined with DLLME

Dispersive micro-solid-phase extraction (D- µ-SPE) combined with DLLME (Li, 2012) was developed for GC–MS of PAHs in environmental samples. For the dispersion step, 1-octanol is injected rapidly into a vial containing sample solution and the vial is subsequently sealed and vortexed. For SPE step (absorption and elution), derivatized magnetic nanoparticles are then quickly added to the vial. In this approach, hydrophobic magnetic nanoparticles are used to recover the extractant 1-octanol in the DLLME step. A magnet is held next to the bottom of the vial to attract and isolate the nanoparticles, and the sample solution is discarded by decantation. The magnet is thereafter removed, and 100 µL of acetonitrile is introduced to the vial to desorb the 1-octanol from the nanoparticles by sonication. Finally, the magnet is again placed next to the vial, and the supernatant is collected into an Eppendorf tube by an automatic pipett or for analysis. This procedure does not require special apparatus such as conical-bottom test tubes as well as tedious procedures of centrifugation and refrigeration of the solvent. It also potentially lends itself to possible automation.

Applications of DLLME

DLLME is simple, rapid, and inexpensive, requires low volumes of sample, and affords high EF. It can be applied in the analysis of organic compounds (pesticides, pharmaceuticals, and phenols) and inorganic analytes (Cu, Pb, and Cd). DLLME methods have been used in the analysis of various samples such water samples, food, urine, animal tissue, soil, and leaves. DLLME is a popular sample pretreatment step in methods developed for analysis of food. The recent applications of DLLME are summarized in the following table.

Conclusion

It is notable that studies involving varying the disperser solvent also achieve great progress in extracting target analytes with strong polarities and in helping the dispersion of organic solvents into the aqueous phase by using a partitioned solvent and a surfactant as a substitute, respectively. In addition, from economic and environmental perspectives, the DLLME procedure could be performed smoothly in the absence of a disperser solvent by utilizing some mechanical methodologies (e.g., ultrasound, vortex), reducing the solvent consumption and the unavoidable loss of analytes in the disperser solvent.

Facing the challenge of the incompatibility of the DLLME pretreatment with complex matrices, connecting this method to other extraction techniques seems to be an alternative solution that emerged in many papers, providing consistent recovery values, as well as highly selective extractions. In this sense, researchers have exhibited wide combinations associating with SBSE, SPE, DSPE, SFE, MSPD, UAE, and MAE, showing an excellent compatibility and feasibility of DLLME with others. Finally, the current trend is moving toward simplification and miniaturization of sample preparation as well as reduction of the cost, labor, time and quantities of organic solvents used. DLLME and dispersion LPME have great prospects for these approaches in the future.

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