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Recent advances in liquid-phase microextraction techniques for the analysis of environmental pollutants

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ABSTRACT

The liquid-phase microextraction (LPME) method is a sample pretreatment technique that uses small volumes of organic solvents to extract a wide variety of analytes from different matrices prior to instrumental analysis. The development of these techniques focuses on providing simple, inexpensive, and environmentally friendly extraction procedures for sample preparation or pretreatment. In this review, the most recent developments in LPME techniques for the analysis of various environmental pollutants are summarized after being categorized into several groups such as dispersive liquid–liquid microextraction (DLLME), ferrofluid-based microextraction, supramolecular-based liquid phase microextraction, and vortex-assisted liquid–liquid microextraction. Moreover, the extraction principles, the solvent production mechanism, and the historical development of the LPME techniques are also discussed. Finally, recent reports on the applications of these methodologies are reviewed.

Abbreviations: AA-DLLME, Alcoholic-assisted dispersive liquid–liquid microextraction; AFS, Atomic fluorescence spectrometry; BPA, Bisphenol A; BTEXs, Benzene, toluene, ethylbenzene, and xylenes; CEC-UV, Capillary electro chromatography-ultraviolet detection; CPAs, Chlorophenoxyacetic acids; CPAHs, Carcinogenic polycyclic aromatic hydrocarbons; CTAB, Cetyltrimethyl ammonium bromide; DLLME, Dispersive liquid–liquid microextraction; DLLME-SFO, Dispersive liquid–liquid microextraction based on the solidification of floating organic drops; EF, Enrichment factor; ETAAS, Electrothermal atomic absorption spectrometry; ETV-ICP-MS, Electrothermal vaporization inductively coupled plasma mass spectrometry; FAAS, Flame atomic absorption spectrometry; FO-LADS, Fiber optic-linear array detection spectrophotometry; GC–ECD, Gas chromatography–electron capture detection; GC–μECD, Gas chromatography–micro electron-capture detector; GC–FID, Gas chromatography–flame ionization detector; GC–MS, Gas chromatography–mass spectrometry; GFAAS, Graphite furnace atomic absorption spectrometry; HF-LPME, Hollow fiber liquid-phase microextraction; HOCs, Halogenated organic compounds; HPLC–DAD, High-performance liquid chromatography–diode array detection; HPLC–ESI-MS/MS, High-performance liquid chromatography–electrospray ionization tandem mass spectrometry; HPLC–FLD, High-performance liquid chromatograph–fluorescence detection; HPLC–UV, High-performance liquid chromatography–ultraviolet detector; LQ–UV, Liquid chromatography–ultraviolet detector; HPLC–VWD, High-performance liquid chromatography–variable wavelength detector; ICP-MS, Inductively coupled plasma mass spectrometry; ICP-OES, Inductively coupled plasma-optical emission spectrometry; ISD-DLLME, In-syringe demulsified dispersive liquid–liquid microextraction; LLE, Liquid–liquid extraction; LLME, Liquid–liquid microextraction; LLME-SFO, Liquid–liquid microextraction based on the solidification of organic droplets; LOD, Limit of detection; LPME, Liquid-phase microextraction; MF, Magnetic fluid; MNPs, Magnetic nanoparticles; MSA-DLLME, Magnetic stirring-assisted DLLME; NP, Nonylphenol; OP, Octylphenol; OPPs, Organophosphorus pesticides; PCBs, Polychlorinated biphenyls; PFOS, Perfluorooctane sulfonate; SA-DLLME, Surfactant-assisted dispersive liquid–liquid microextraction; SDME, Single-drop microextraction; SPE, Solid-phase extraction; SPME, Solid-phase microextraction; ST-DLLME, Solvent-terminated dispersive liquid–liquid microextraction; UHPLC–MS/MS, Ultra-high-performance liquid chromatography–tandem mass spectrometry; UV–Vis, Ultraviolet–visible spectrophotometry; VALLME, Vortex-assisted liquid–liquid microextraction.

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1. Introduction

Enormous technological progresses have been achieved to analyze diverse harmful chemicals including herbicides and pesticides [1–3], phenolic compounds [4–6], polycyclic aromatic hydrocarbons [7–10], and heavy metals [11–13]. The demand on analytical methods that can enable the accurate and rapid determination of harmful compounds in the environment has nontheless been increasing dramatically in recent years. Due to their disruptive effects and toxicity, the analysis of environmental samples is of great importance. Despite recent advances in such field, sample pre-treatment steps are still invariably required for an accurate quantification of analytes in environmental samples. Therefore, it is crucial to develop efficient, low-cost, and simple procedures for the pre-treatment/pre-concentration/separation of the trace-level contaminants in various environmental samples. The use of such procedures is indispensable to separate the analytes from the matrix so that the treated samples should be analyzed in a form compatible with the measurement system.

The most widely used pretreatment techniques include liquid–liquid extraction (LLE) and solid phase extraction (SPE). LLE is a simple technique, but it is often time-consuming with the requirement of large volumes of sample and organic solvent. On the other hand, SPE is still considered a useful method for the facile extraction of environmental contaminants due to the availability of sorbents with various sorption characteristics. However, it is also time-consuming, while requiring several steps of treatment involving washing, conditioning, sample loading, eluting, and drying the solid cartridge [14]. The use of large volumes of toxic chemicals and organic solvents could also result in environmental pollution. Therefore, several alterations have been introduced to these procedures to reduce the amount of organic solvent and to decrease their negative impacts on the environment.

In 1990, solid-phase microextraction (SPME) was introduced by Pawliszyn's research group [15] as a new advancement in the field of sample preparation. SPME is a solvent-free method wherein the target analytes are adsorbed on a polymer-coated fiber. This technique is simple, rapid, and sensitive enough for the extraction of different analytes. Also, it is compatible with either GC or HPLC analysis. However, the coated-fibers exhibit relatively short lifetimes and their instability against organic solvents restricted their applications toward HPLC to a certain degree [16].

Liquid-phase microextraction (LPME) was proposed as an alternative solvent-minimized sample pretreatment technique to overcome the shortcomings of SPME [17]. In this method, only a few microliters of solvent are needed to extract analytes in comparison to the large amount of toxic organic solvent required in traditional LLE techniques. In addition, LPME is faster, more environmentally friendly, and simpler method. In LPME, the extraction process occurs between a small amount of water-immiscible solvent (acceptor phase) and an aqueous phase (donor phase) containing target compounds. The application of LPME has been developed into several subsets to be carried out under a number of different extraction modes: single-drop microextraction (SDME) [18], hollow fiber-LPME (HF-LPME) [19], and dispersive liquid–liquid microextraction (DLLME) [20].

In recent years, LPME has become one of the most common extraction procedures for the pretreatment and separation of environmental [6,21–23], food [24,25], and pharmaceutical [26–28] samples. In LPME, the distribution of analytes between the interface of the organic solvent (acceptor phase) and water facilitates the extraction and pre-concentration of the analytes into the organic phase. The highest enrichment factors are best obtained using a high sample volume to organic solvent ratio. This method is simple, rapid, and affordable to be used to extract a wide variety of analytes from complex matrices.

This review article provides useful information about different modes of LPME along with a comprehensive overview on the mechanism of screening different organic and inorganic chemicals based on these methods. In addition, we emphasize recent innovations in liquid–liquid microextraction techniques in terms of extraction (acceptor) phase preparation and reducing (or eliminating) time-consuming steps during analytical procedures. Finally, several liquid–liquid microextraction techniques and their applications for analysis of different environmental pollutants will be described to facilitate an evaluation of their performance. The basic information provided in this review is expected to help researchers make a suitable decision about the choice of a proper extraction phase before instrumental analysis, while promoting the development and expansion of greener separation methods.

2. Dispersive liquid–liquid microextraction (DLLME)

Over the last decade, advances in sample preparation techniques have been achieved to minimize the consumption of organic solvent and to simplify systems, leading to the widespread use of greener analytical procedures. Liquid–liquid microextraction (LLME), as one of the main groups of LPME categories, is a superior extraction method that can be divided into four main groups based on the type of extractant phase: dispersive liquid–liquid microextraction (DLLME), ferrofluid-based microextraction, supramolecular-based liquid-phase microextraction, and vortex-assisted liquid–liquid microextraction.

Dispersive liquid–liquid microextraction (DLLME) is well-known as a simple and rapid liquid phase microextraction method. It was first applied by Rezaee et al. [20]. Among other microextraction procedures, DLLME has attracted a great amount of interest for pre-concentration and analysis of different chemicals. In this technique, the cloudy state is formed due to the solvent droplets upon injection of the binary solvent mixture (extraction and disperser solvents) into an aqueous sample. The large surface area between the fine droplets and the aqueous phase facilitates the quick transfer of analytes from the sample solution into the extraction phase. Subsequent centrifugation of the mixture causes sedimentation of the fine droplets at the bottom of the conical tube. Finally, the sediment phase can be collected using a syringe and analyzed with the appropriate analytical equipment (Fig. 1a). Since its introduction, DLLME has become a very popular microextraction method due to several advantages (e.g., simplicity, rapidity, high enrichment factors, and low organic solvent consumption) [29,30]. Examples of approaches related to DLLME for the extraction and determination of different organic and inorganic pollutants from environmental samples are given in Tables 1 and 2.

The selection of key experimental variables (e.g., type of extraction, disperser solvents, and their volumes) can influence the DLLME extraction efficiency of target analytes. Thus, these factors should be optimized to obtain good recovery. First, selection of an appropriate extraction solvent is essential in the DLLME procedure. These solvents are selected based on density, extraction capability of the analytes, solubility in water, and proper chromatographic response. Chlorobenzene, carbon tetrachloride, and tetrachloroethylene are commonly used as extraction solvents because their density is higher than that of water. Moreover, the volume of extraction solvent and the octanol–water partition co-efficient (K_{ow}) can influence the efficiency of DLLME procedure because the enrichment factor decreases with increasing volume of the extraction solvent [7].

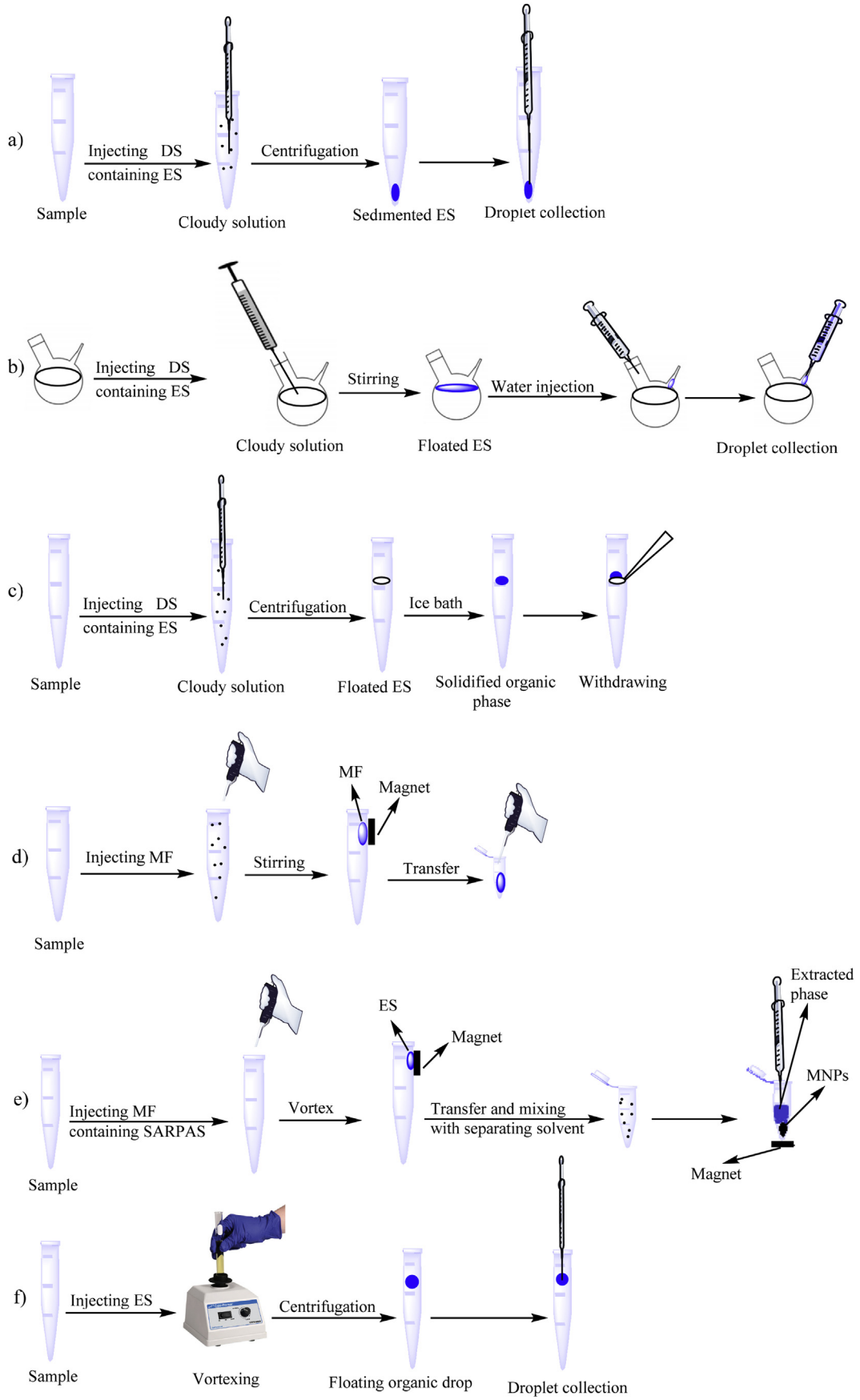

Fig. 1. Schematic of different LLME techniques: a) dispersive liquid–liquid microextraction, b) DLLME using special extraction devices, c) DLLME based on the solidification of floating organic drops, d) Ferrofluid-based liquid-phase microextraction, e) Supramolecular solvent-based microextraction, and f) Vortex-assisted liquid–liquid microextraction.

Table 1
Applications of conventional dispersive liquid–liquid microextraction (DLLME) methods for the analysis of organics.

Order	Analytes	Matrix	Detection system	Extraction solvent	Disperser solvent	EF	LOD (μg L^{-1})	Ref
A) LC and HPLC								
1	Methomyl	Natural water	HPLC–VWD	Tetrachloroethane	Methanol	70.7	1.0	[68]
2	Antioxidants	Tap and packed water	HPLC–DAD	Carbon tetrachloride	Acetonitrile	–	3.0–7.0	[69]
3	Clenbuterol	River, lake, and stream water	LC–UV	Trichloromethane	Acetone	175	4.90	[70]
4	Polybrominated diphenyl ethers	Environmental water	RP-HPLC	Tetrachloroethane	Acetonitrile	268–305	0.0124–0.0556	[71]
5	Phthalate esters	Water	HPLC–VWD	Carbon tetrachloride	Acetonitrile	45–196	0.64–1.80	[72]
6	Heterocyclic insecticides	Water	HPLC–DAD	$[C_6MIM][PF_6]$	Methanol	209–276	0.53–1.28	[73]
7	Pyrethroids	River water	HPLC–UV	Tetrachloroethane	Acetone	767–1033	0.11–0.3	[74]
8	Levonorgestrel	Tap, lake, and river water	HPLC–DAD	Trichloromethane	Methanol	428	0.30	[75]
9	Tetrabromobisphenol A	Water	HPLC–ESI-MS/MS	$[C_8MIM][PF_6]$	Acetonitrile	–	0.06	[76]
10	Fungicides	Water	HPLC–UV	[C8MIM][PF_6]	Methanol	–	0.32–0.79	[77]
11	Malachite green and crystal violet	Environmental water	HPLC–UV	$[C_8MIM][PF_6]$	Methanol	254–276	0.03–0.086	[78]
12	Benzoylurea pesticides	Environmental water	HPLC–UV	Chlorobenzene	Ethanol	–	0.24–0.82	[79]
13	Nitroimidazoles and amphenicol antibiotics	Water	UHPLC–MS/MS	Dichloromethane	Acetonitrile	–	0.00039–0.00138	[80]
14	Phthalate esters	Cosmetic products	LC–MS	Carbon tetrachloride	Acetonitrile	27–148	0.04–0.45	[81]
B) GC								
15	PAHs	Surface water samples	GC–FID	Tetrachloroethylene	Acetone	603–1113	0.007–0.03	[20]
16	Phthalate and polycyclic musks	Water	GC–MS	Carbon tetrachloride	Methanol	–	0.008–0.063	[82]
17	BTEXs	Tap, well, and lake water	GC–FID	Nitrobenzene	–	653–835	0.40–2.0	[83]
18	UV filters	Seawaters	GC–MS	Chloroform	Acetone	112–263	0.01–0.03	[84]
19	OPPs	River water and fruit juice	GC–FID	Dichloromethane	DMSO	1600–2075	0.82–2.72	[85]
20	Phthalate	Water samples	GC–MS	Trichloroethylene	Acetone	14.1–16.3	0.03–0.10	[86]
C) Other techniques								
21	Sulfonamides	Water	CE–UV	Chlorobenzene	DMSO	–	0.0002–0.00057	[87]
22	Benzimidazole	Fish farm, spring, and well water	CEC–UV	Chloroform	Ethanol	16.7	2.8	[88]
23	Dyes	Water samples	UV–Vis	Chloroform	Ethanol	79.82–115.54	1.72–2.043	[89]

Table 2
Analysis of inorganics using conventional DLLME methods.

Order	Analytes	Matrix	Detection system	Extraction solvent	Disperser solvent	EF	LOD (μg L^{-1})	Ref
A) FAAS								
1	Bi^{3+}	River water	FAAS	Dichlorobenzene	Acetone	28.6	3.0	[90]
2	Pd^{2+}	Water, soil, and food samples	FAAS	Chloroform	Acetone	20.7	8.0	[91]
3	Pb^{2+}	Tap, dam, and river water	FAAS	Chloroform	Ethanol	50	4.3	[92]
4	Cd^{2+}	Sediment and water samples	FAAS	Carbon tetrachloride	Ethanol	14	0.26	[93]
B) Other techniques								
5	Pb^{2+}	Environmental water	AFS	Carbon tetrachloride	Ethanol	–	0.00095	[94]
6	Mo (VI)	Water and plant leaves	FO-LADS	[HMIM][Tf_2N]	Acetone	72.6	1.43	[95]
7	Se (IV)	Environmental water	ETV-ICP-MS	Chloroform	Ethanol	64.8	0.047	[96]
8	Cr (III), (VI)	Tap and sea water	Fluorescence detection	Chloroform	Methanol	–	0.57	[97]
9	Zn^{2+}	Oil and water	GFAAS	Chloroform	Methanol	167	0.05	[98]

The miscibility of the disperser solvent in both the extraction solvent and the aqueous phase is an essential factor that should be considered. Acetone, ethanol, methanol, and acetonitrile are usually used as disperser solvents due to their low toxicity and cost. Also, the efficiency of the DLLME process can be influenced by the volume of disperser solvent. At low volumes of these solvents, the cloudy state cannot form properly, while increasing the volume of disperser solvent decreases the extraction efficiency due to the enhanced solubility of analytes in the aqueous phase [21].

2.1. DLLME using special extraction devices

The concerns related to the toxicity of chlorinated extraction solvents led to the use of less toxic solvents. Usually, such solvents are lighter than water and can be collected from the sample surface. A preferable route of collecting the organic phase has been demonstrated to use special centrifugation tubes and pipette collection tubes (Fig. 1b). In this method, the extraction phase is forced to move through the narrow part of the special vessel by the injection of water. Subsequently, the organic phase is removed by a micro-syringe for further analysis.

In 2009, Farajzadeh et al. [31] reported a custom-made device for dispersive liquid–liquid extraction of organophosphorus pesticides (OPPs) from water samples. In their study, a mixture of disperser (acetone) and extraction (cyclohexane) solvent was injected into the sample held in a custom-designed vessel. After centrifugation, 1 mL of distilled water was injected into the bottom of the glass tube. Then, the upper phase was collected in the narrow neck of the test tube and injected into the GC column for analysis. Similarly, a molecular complex-based DLLME was also proposed for the extraction of polar compounds in aqueous solution [32]. In this approach, a mixture of tri-*n*-butylphosphate (TBP) as the extraction solvent (a Lewis base) and methanol (as disperser solvent) was injected into the sample solution placed in a disposable polyethylene pipette. Afterward, the pipette was placed into a 10 mL Eppendorf tube. It was agitated and then centrifuged to concentrate the floating organic phase in the narrow part of the pipette which was then collected with a microsyringe.

For the pretreatment of chlorophenols in environmental water samples, surfactant assisted-DLLME (SA-DLLME) was proposed [33]. In this approach, a cationic surfactant cetyltrimethyl ammonium bromide (CTAB) was used as a disperser solvent. The extraction procedure was then carried out in a custom-designed centrifuge glass vial. The reported procedures were all based on the same principle: low-density organic solvent was accumulated on the top of the sample solution in the narrow neck of the custom-designed device. Thus, an aliquot from the extractant collected in the narrow neck was injected into an appropriate analytical instrument.

Centrifugation is considered to be the most time-consuming step in the DLLME procedure. To overcome this disadvantage, a simple method of solvent-terminated dispersive liquid–liquid microextraction (ST-DLLME) was reported for the highly sensitive determination of carbamate pesticides in water samples without centrifugation [34]. For this purpose, an emulsion of water, acetonitrile, and toluene was formed in a 5 mL volumetric flask. After 10 min, the separation of the extractant from the aqueous phase was achieved by injection of acetonitrile as a terminating solvent to break up the emulsion. Thus, the centrifugation step was omitted. The upper layer of the solution was subsequently collected in a single-use glass capillary for GC analysis. The proposed method is simple, easy to operate, and does not require a narrow part of the apparatus to collect the extraction phase. In addition, solvent demulsification DLLME was also proposed for GC–MS based fast and efficient analysis of 16 priority polycyclic aromatic hydrocarbons in environmental water samples [35]. In the extraction procedure, n-hexane (density of 0.655 g/mL) was injected as an extraction solvent into the sample solution containing the target analytes. Following which, acetone was used both as a disperser solvent and a demulsifier to disrupt the emulsion. This process avoided the centrifugation step; therefore, the whole extraction procedure could be performed within 2 min. The emulsion was rapidly cleared into phases and the upper extracted phase was collected for subsequent GC–MS analysis.

A special flask with two narrow open necks was used for the extraction and analysis of four UV filters (4-hydroxybenzophenone (HB), 2,4- dihydroxybenzophenone (DB), benzophenone (BP) and 2-hydroxy-4-methoxybenzophenone (HMB)) in environmental water samples [36]. In this method, there is no need for either disperser solvent or centrifugation step. This alternative technique employs the magnetic stirring in which the phases are self-separated. In the extraction procedure, 1-octanol was slowly injected as an extraction solvent into the flask containing sample solution. After magnetic stirring and static holding for several minutes, the extracted phase was floated in the narrow branch tip of the flask by adding pure water into the other port.

Then, the target was collected by a microsyringe for HPLC analysis. Although this method is simple, fast, and easy to automate, caution is needed due to the low efficiency in the mixing of binary phases (water sample and low-density solvent) relative to the disperser solvent in the ternary solvent system.

Another example of solvent demulsification DLLME was introduced by Xia et al. [37]. This technique was based on in-syringe demulsified DLLME (ISD-DLLME), followed by HPLC–MS for the analysis of trace fungicides in environmental water samples. In this extraction process, all the necessary extraction, dispersion, and phase separation procedures were carried out in a 5 mL syringe. As a first step, an emulsion containing water, toluene (extraction solvent), and methanol (disperser) was formed in the syringe. This emulsion was then disrupted by injecting 500 μL of methanol as a demulsifier agent. As a result, the organic phase floated which was then collected into a pipette tip fitted on the top of the syringe. This method offers a simple and convenient procedure for the preconcentration of fungicides.

A simple approach for the extraction of PAHs using alcoholic-assisted DLLME (AA-DLLME) was introduced by Fatemi et al. [38] who used alcoholic solvents as both extraction and disperser agents. A special glass container was used to hold the analyte sample. A cloudy solution formed as 2-ethyl-1-hexanol (extraction solvent) and methanol (disperser solvent) were injected in to the reaction vessel. Finally, the extracted layer was removed using a Hamilton syringe and analyzed with HPLC. Contrary to other general sample preparation methods, the above discussed technique is advantageous to avoid the commonly encountered problems of evaporation, refrigeration, and thawing of solvent.

Recently, a simple combining device has been introduced to perform magnetic stirring-assisted DLLME (MSA-DLLME) for the extraction and separation of several pesticides in tea beverages [39]. In this extraction procedure, the combining apparatus includes a 1 mL cut plastic dropper and a 10 mL sample vial. The open bulb end of the plastic dropper was inserted into the neck of the sample vial. Then, the open tip of the plastic dropper was cut to an appropriate length to obtain the extracted phase. In the experiment, 1-octanol was injected into the tea drink sample solution, and phase separation was accelerated by magnetic stirring. The agitation was followed with several minutes of settling down process which resulted in clear separation of the two layers. The organic phase (the upper layer) was collected from the sample vial by the cut plastic dropper. Finally, the extractant was withdrawn using a microsyringe and injected into the HPLC for analysis. The magnetic stirring increased the contact area between the organic phase and aqueous sample. Therefore, it facilitated mass transfer between two different phases. As a beneficial factor, this technique does not require the use of the disperser solvent and centrifugation step.

In recent years, the automation of DLLME procedure has attracted a great amount of attention. Such development helped improve the accuracy of the method while reducing the time-consuming stages of this procedure including manual handling of the extraction solvent and collection of the extracted phase [40]. Up to now, several approaches have been introduced for the automation of DLLME such as on-line sequential injection analysis (SIA), on-line flow injection analysis (FIA), flow-batch SIA, and the automated in-syringe DLLME [41–45]. In 2009, the automatic sequential injection-DLLME (SI-DLLME) was introduced for the extraction of two heavy metal ions (Pb^{2+} and Cu^{2+}) from water samples [46]. In this procedure, the cloudy solution was formed as a result of the on-line injection of the mixture of disperser solvent (methanol) and extraction solvent (xylene) into the aqueous sample. Then, the organic phase consisting of the metal complexes with chelating agent (ammonium diethyldithiophosphate) was maintained in the microcolumn in which the analytes were eluted using isobutylmethylketone and injected into the nebulizer of FAAS for subsequent analysis. Application of the automated DLLME system provided several advantages including simplicity, rapidity, and efficient recovery.

2.2. DLLME based on the solidification of a floating organic drop

The solidification of the organic phase is another interesting route of pre-concentrating the analytes in extraction solvents. In 2007, a novel liquid-phase microextraction method was proposed based on the solidification of organic droplets (LPME-SFO) [47]. In this method, the extraction phase, which had a low density, was collected at the top of the aqueous phase by solidification at low temperature. DLLME-SFO combines advantages of both DLLME and LPME-SFO [48]. Unlike DLLME, chlorinated solvents are not used in this method; the extraction time is also shorter than that of LPME-SFO because the stirring stage is not necessary. In this approach (Fig. 1c), 0.5 mL of acetone containing 10 μL 2-dodecanol was

injected into the sample solution which led to the formation of a cloudy solution containing fine droplets of 2-dodecanol. After centrifugation, the sample was transferred into an ice-bath, and the organic phase was solidified and removed from the sample tube. The solid drop melted at room temperature and subsequently was injected into the gas chromatograph for analysis. This novel technique is simple, rapid, and compatible with a variety of analytical instruments. The recent applications of DLLME-SFO in environmental analysis are summarized in Tables 3 and 4. This technique provides a simple approach for the pre-concentration of target compounds. However, the major limitations of this technique are related with the selection of the suitable solvent as it should possess a melting point near room temperature (in the range of 10–30°C), low solubility in water, and solidification in an ice bath.

3. Ferrofluid-based liquid-phase microextraction

In recent years, nanotechnology has become an important discipline for liquid–liquid microextraction techniques. Among different nanoparticles, magnetic iron oxide nanoparticles (MNPs) have attracted much attention due to their unique properties. These particles have been used for extraction and analysis of a variety of organic or inorganic chemicals from environmental samples [49–52].

The retrieval of organic solvents after the liquid-phase microextraction process is very important. Therefore, magnetic fluids (MFs), which are liquids consisting of magnetic nano-sized particles (ferri- or ferro-magnetic particles) and carrier liquids (such as oleic acid), have been recently reported as extractants for preconcentration of analytes from different matrices. The applications of magnetic fluids are still limited because the surface properties of the nanoparticles are sensitive to both pH changes and ionic strength. Therefore, MNPs are generally coated and stabilized using organic [53,54] and inorganic [51,55] materials to obtain different surface properties that can also avoid undesired defects (e.g., agglomeration).

In 2010, a new mode of liquid-phase microextraction based on a ferrofluid was proposed for the analysis of polycyclic aromatic hydrocarbon (PAHs) in environmental samples [56]. To prepare the ferrofluid, an appropriate amount of silica-coated magnetic particles and 1-octanol (as the extraction solvent) were mixed in a vial by sonication. In the presence of a magnet at the bottom of the vial, the excess amount of 1-octanol was recovered using a pipette. Then, 20 mL of the sample solution containing target analytes was added to this vial. The extraction efficiency was enhanced by a reciprocating external magnet. Subsequently, the ferrofluid settled at the bottom of the vial due to the magnet, and the supernatant was discarded simply by decanting. Thereafter, magnetic particles were eluted by 100 μL of acetonitrile to desorb the 1-octanol and

Table 3
Applications of DLLME-SFO for analysis of organics.

Order	Analytes	Matrix	Detection system	Extraction solvent	Disperser solvent	EF	LOD (μg L^{-1})	Ref
A) LC and HPLC								
1	Aliphatic amines	Water	HPLC–DAD	1-Undecanol	Acetonitrile	210–290	0.005–0.02	[99]
2	Chlorpyrifos	Water	HPLC–UV	1-Dodecanol	Methanol	96–114	0.10–0.12	[100]
3	Parabens	Water, mouth rinse solutions, and shampoo	HPLC–UV	1-Undecanol	Acetone	245–1886	0.3–1.7	[101]
4	Nitrophenols	Water	HPLC–UV	1-Undecanol	Methanol	100–116	1.70	[21]
5	PAHs	Water	HPLC–UV	1-Undecanol	Methanol	1630–2637	0.0067–0.010	[7]
6	Benzoylurea insecticides	Water and tea beverage samples	HPLC–UV	($[N_{8881}][PF_6]$)	–	81–86	0.29–0.59	[102]
7	Kanamycin	Wastewater and soils	HPLC–FLD	Decanol	Ethanol	270	0.012	[103]
8	Albendazole and triclabendazole	Tap and wastewater, milk, and urine samples	HPLC–FLD	1-Dodecanol	–	281–311	0.02–0.06	[104]
9	Thiamphenicol and florfenicol	Environmental water	HPLC–UV	1-Undecanol	Acetone	223–241	0.33–0.56	[105]
10	Steroid hormones	Tap and river water	HPLC–DAD	1-Undecanol	Methanol	121–329	0.80–2.70	[106]
B) GC								
11	HOCs	Tap and lake water	GC–ECD, GC–MS	2-Dodecanol	Acetone	174–322	0.005–0.05	[48]
12	Anilines	Tap and river water	GC–MS	Cyclohexane	Ethanol	–	0.07–0.29	[107]
13	BTEX	Tap, well, and river water	GC–FID	1-Undecanol	–	301–514	0.04–0.09	[108]
14	Methyl methacrylate	Wastewater	GC–FID	2-Dodecanol	–	862	8.0	[109]
C) Other techniques								
15	Boron	Tap and river water	Fluorescence detection	1-Undecanol	Ethanol	86	0.00011	[110]
16	Nitro-PAHs	Lake and drinking water	Fluorescence detection	1-Dodecanol	Methanol	380–400	1.7–23	[111]

Table 4
Applications of DLLME-SFO for analysis of inorganics.

Order	Analytes	Matrix	Detection system	Extraction solvent	Disperser solvent	EF	LOD (μg L^{-1})	Ref
A) ICP								
1	Al^{3+}	Water	ICP-OES	1-Undecanol	Acetone	128	0.80	[112]
2	Pb^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}	Wastewater	ICP-MS	1-Undecanol	Acetone	240–270	0.97–2.18	[113]
B) FAAS								
3	Cu^{2+}	Tap, river, and sea water	FAAS	1-Undecanol	Ethanol	20	0.93	[114]
4	Ni^{2+}	Water	FAAS	1-Dodecanol	Ethanol	158	1.27	[115]
C) Other techniques								
5	As (III), (V)	Water	ETAAS	1-Undecanol	–	1000	0.0092	[116]
6	Ni^{2+}, Co^{2+}, Pb^{2+}, Cr^{3+}	Industrial wastewater	GFAAS	1-Undecanol	Ethanol	800	0.0002–0.0013	[117]
7	V (V)	Water and parsley	ETAAS	1-Undecanol	Acetone	184	0.007	[118]

analytes. Finally, magnetic particles were retrieved using a magnet, and the clear solution containing the target compounds was injected into the GC for analysis (Fig. 1d).

The most significant research works on ferrofluid-based liquid-phase microextraction for the analysis of organics and inorganics are summarized in Tables 5 and 6, respectively.

4. Supramolecular solvent-based microextraction

Recently, water immiscible nano-structured liquids named as supramolecular solvents (SURPASs) were introduced to reduce the organic solvent usage in microextraction procedures [57]. SURPASs are produced via a self-assembly procedure by changing the pH [58], temperature [59], and ionic strength [60] of a solution while adding a non-solvent amphiphile [61]. Then, the generated nano-structures are separated from the bulk solution through coacervation [62–65]. The two fundamental properties of alkyl carboxylic acid-based coacervates make them very attractive in analytical extraction processes. First, the polar areas of SURPASs consist of carboxylic or ammonium groups. Thus, a variety of interactions including π-cation, electrostatics, and hydrogen bonds occur with the analytes. Also, the hydrocarbon chains of the ordered structures provide hydrophobic interactions for extraction of nonpolar compounds [66]. Second, the high concentration of aggregates in SURPAS (and the corresponding large number of binding sites they provide) enables solubilization of a large amount of both polar and nonpolar molecules in aggregates. These outstanding features of supramolecular solvents as the extraction phase enable simple, fast, and efficient pre-treatment of different analytes.

The first application of the tetrabutylammonium-induced liquid–liquid phase extraction in alkyl carboxylic acid vesicular solution was investigated for the pre-concentration of organic compounds in water samples prior to their chromatographic analysis [60]. As part of a typical extraction procedure, an appropriate amount of tetrabutylammonium hydroxide was added to 4-chlorophenol as a model compound in a 50 mL glass tube with a narrow neck. Afterward, predetermined amounts of sodium hydroxide and octanoic acid were added to this solution, and the mixture was centrifuged at 3000 rpm for 5 min. To accelerate the phase separation, the mixture was stirred for 5 min. Then, the coacervate was collected at the upper surface of the solution and was transferred to a sample vial for the LC analysis (Fig. 1e). The results showed that vesicular coacervates made up of alkyl carboxylic acids were valuable analytical structures for the extraction of target analytes in a wide polarity/charge range.

To conclude this section, Tables 7 and 8 are organized to present the recent environmental applications of supramolecular solvent-based microextraction in organic and inorganic analyses, respectively. The main features of LLME based on a supramolecular solvent (e.g., enrichment factor (EF), composition of the extraction phase, limit of detection (LOD), and instrumentation) are summarized in these tables.

5. Vortex-assisted liquid–liquid microextraction (VALLME)

A new microextraction procedure termed vortex-assisted liquid–liquid microextraction (VALLME) was presented in 2010 [67]. VALLME is a technique of sample preparation by dispersion of extraction solvent into an aqueous phase using vortex mixing, a mild emulsification procedure. The target molecules can be extracted from water into fine droplets of the extraction phase due to the very large surface area and short diffusion distance of these fine droplets. After centrifugation, the floating microdroplet can easily be collected by a microsyringe at the top of the aqueous phase and can be used for subsequent instrumental analysis (Fig. 1f). The simplicity, rapidness, and elimination of the disperser solvent make VALLME an efficient method for extraction and analysis of different organic and inorganic pollutants from environmental samples with high enrichment factors and low limits of detection.

VALLME was first used as a new and fast equilibrium-based solvent microextraction method for the trace analysis of octylphenol, nonylphenol, and bisphenol A in water and wastewater samples [67]. In this research work, 50 μL of octanol (as the extraction phase) was injected into 20 mL of a sample solution spiked with all target compounds. Vortex mixing (2500 rpm for 2 min) was then used to disperse fine droplets of low-density organic solvents into the aqueous phase. Target analytes were then rapidly extracted into the organic solvent. After centrifugation,

Table 5
Ferrofluid-based liquid-phase microextraction used for analysis of organics.

Order	Analytes	Matrix	Detection system	Extraction solvent	Desorption solvent	EF	LOD (μg L^{-1})	Ref
A) HPLC								
1	OPPs	Fruit juice, tap and spring water	HPLC–UV	Supramolecular	Methanol	108–135	0.1–0.35	[66]
B) GC								
2	Organochlorine pesticides	Water	GC–ECD	n-Octane	Methanol/Ethanol	153–214	0.0018–0.0084	[119]
3	PAHs	River water	GC–MS	1-Octanol	Acetonitrile	102–173	0.0168–0.0567	[56]
C) Other techniques								
4	Methylene blue	Shrimp and water samples	UV–Vis	[HMIM][BF_4]	Methanol	135	2.5	[120]
5	Crystal violet	Fish and environmental water samples	FO-LADS	1-Octanol	HNO_3	267	1.51	[121]

Table 6
Ferrofluid-based liquid-phase microextraction used for the analysis of inorganics.

Order	Analytes	Matrix	Detection system	Extraction solvent	Desorption solvent	EF	LOD (μg L^{-1})	Ref
1	Pd^{2+}	Well, river, and sea water	FAAS	1-Octanol	Acetylacetone	267	0.35	[122]
2	Pb^{2+}	Water, soil, and rice	FAAS	[HMIM][BF_4]	HNO_3	200	1.66	[123]
3	Cd^{2+}	Mineral, tap and sea water	FAAS	[BMIM][BF_4]	HNO_3	200	0.11	[124]
4	Cu^{2+}	Water, potato, broccoli, spinach, and green tea samples	FAAS	[HMIM][BF_4]	HCl	267	0.32	[125]
5	Tl (I)	Water, cabbage, nail, hair, and iron ore samples	FAAS	1-Octanol	HCl	298	0.85	[126]
6	Cd^{2+}	Environmental, vegetable, and tobacco samples	FAAS	[BMIM][BF_4]	HNO_3	250	0.12	[127]

Table 7
Applications of supramolecular solvent-based microextraction to extract organic compounds.

Order	Analytes	Matrix	Detection system	Component driving phase separation	EF	LOD (μg L^{-1})	Ref
A) LC and HPLC							
1	Organic compounds	Environmental water	LC–MS	Vesicles of octanoic acid in the presence of (Bu_4N^+)	–	0.6–1.5	[60]
2	Bisphenol A, bisphenol F, and their corresponding diglycidyl ethers	Wastewater and river water	LC–fluorescence detection	Reverse micelles of decanoic acid in THF	82–107	0.03–0.035	[128]
3	CPAHs	Environmental water	LC–fluorescence detection	Reverse micelles of decanoic acid in THF	–	0.0001–0.001	[129]
4	Benzimidazolic fungicides	River and underground water	LC–fluorescence detection	Vesicles of decanoic acid in the presence of (Bu_4N^+)	160–190	0.0001–0.032	[130]
5	Ochratoxin A	Raw water	LC–fluorescence detection	Reverse micelles of decanoic acid in THF	–	0.5 (μg kg^{-1})	[131]
6	PAHs	Smoked meat and fish	LC–fluorescence detection	Vesicles of octanoic acid in the presence of (Bu_4N^+)	–	0.1–0.5 (μg kg^{-1})	[132]
7	Mecoprop and Dichlorprop	Soil	LC–MS/MS	Reverse micelles of dodecanoic acid in THF	–	0.03 ng g^{-1}	[133]
8	Phenols	Wastewater, surface water, and ground water	LC–UV	Vesicles of decanoic acid in the presence of (Bu_4N^+)	–	0.1–0.3	[134]
9	Parabens	Natural water and cosmetic samples	HPLC–UV	Vesicles of decanoic acid in the presence of (Bu_4N^+)	81–174	0.2–0.5	[135]
10	CPAs	Tap water, river water, and sea water	HPLC–UV	Reverse micelles of dodecanoic acid in THF	148–157	0.5–0.8	[136]
11	Triazine herbicides	Tap, river, and spring waters	HPLC–UV	Vesicles of decanoic acid in the presence of (Bu_4N^+)	183–256	300–500	[137]
12	Parabens	Cosmetics, beverages, and water	HPLC–UV	Propanol/gemini surfactant	98–156	0.5–0.7	[138]
13	Glucocorticoids	Water samples	HPLC–DAD	[BMIM]BF_4/n-butanol	–	0.0992–2.428	[139]
B) Other techniques							
14	Malachite Green	Textile industry wastewater	FO-LADs	Reverse micelles of decanoic acid in THF	52	4	[140]

Table 8
Applications of supramolecular solvent-based microextraction for the extraction of inorganic analytes.

Order	Analytes	Matrix	Detection system	Component driving phase separation	EF	LOD (μg L^{-1})	Ref
A) FAAS							
1	Pb^{2+}	Food and water samples	GFAAS	Reverse micelles of decanoic acid in THF	52	0.027	[141]
2	Cu^{2+}	Food and water samples	FAAS	Reverse micelles of decanoic acid in THF	60	0.52	[142]
B) UV–Vis							
3	Cr (VI)	Water samples	UV–Vis spectrophotometry	Reverse micelles of decanoic acid in THF	50	0.23	[143]
4	Uranyl ion	Natural water samples	UV–Vis spectrophotometry	Reverse micelles of decanoic acid in THF	54.43	2.0	[144]

the octanol phase was separated and collected at the top of the sample surface using a microsyringe. The phase was then used for HPLC analysis.

Tables 9 and 10 present the summary of some of the recent research publications describing the application of VALLME towards the extraction and pre-concentration of different forms of organic and inorganic compounds, respectively. Related data have been selected to show the influence of several important factors on the efficiency of the VALLME procedure for the extraction of targets in environmental samples.

6. Comparison between different extraction approaches

In this review, we attempted to offer a comprehensive surevy on the recent advances in the liquid-phase microextraction techniques and their applications to the analysis of different organic and inorganic pollutants contained in a variety of matrices. The miniaturization of liquid-base extraction methods has led to a significant reduction not only in solvent consumption and sample workup time but also in liquid waste generation. Different liquid–liquid microextraction procedures such as DLLME, ferrofluids, supramolecular methods, and vortex-based extraction methods have been developed and employed for the extraction and pre-concentration of various environmental contaminants, as discussed in this paper. Although all of these techniques can be used to analyze target analytes, DLLME should be the method that has been explored most intensively. This technique is simple, inexpensive, and easy to operate. Also, it is compatible with many instruments for analysis of different analytes such as polycyclic aromatic hydrocarbons (PAHs), pesticides, insecticides, and heavy metals. However, this separation technique has some drawbacks such as restrictions related to the selection of extraction solvent, the centrifugation step, freezing, use of special devices, and demulsification. The VALLME is a simple, fast, and new extraction method that can provide a pretreatment procedure with both high enrichment factors and low detection limits. This technique can help resolve the main drawback of DLLME, i.e., the high consumption of disperser solvent. However, the main limitation of this extraction mode is the use of low-density extraction solvents such as 1-octanol, toluene, n-hexane, and octane; this disadvantage should not be ignored. Among these solvents, only 1-octanol can form a single droplet after centrifugation and can be collected easily, while the other solvents remain dispersed on the top of the sample surface.

Generally, for the selection of a proper sample preparation technique, it is very important to establish an acceptable extraction

Table 9
Applications of VALLME to the extraction of organic compounds in analytical processes.

Order	Analytes	Matrix	Detection system	Extraction solvent	Rotational speed (rpm)	EF	LOD (μg L^{-1})	Ref
A) LC and HPLC								
1	PFOS	Tap, river, and well water	LC–MS	Octanol	2500	250	0.0016	[145]
2	BPA, OP, NP	Tap, river, and effluent water	HPLC–FLD	Octanol	2500	150–690	0.01–0.07	[67]
3	PAHs	Real natural sediment	HPLC–FLD	Dichloromethane	2800	–	2.3–6.8 (ng g^{-1})	[146]
4	Fungicides	Tap, rain, and lake water	HPLC–DAD	Octanol	3000	144–183	0.73–1.33	[147]
5	OPPs	Water	HPLC–DAD	1-Dodecanol	1800	72–79	0.25–1	[148]
6	Pesticides	Pesticides, manufacturing wastewater	HPLC–DAD	$[C_6$ MIM$][(CF_3 SO_2)_2$ N]	2500	33–125	1.8–8.6	[149]
7	Aromatic amines	Environmental water	UFLC–UV	$[C_6$ MIM$][PF_6]$	2800	–	0.24–0.57	[150]
8	Tricyclic antidepressants	Water	HPLC–UV	[HMIM][FAP]	–	17–43	0.3–1	[151]
B) GC								
9	PCBs	Water and wastewater	GC–MS	Chloroform	3000	–	0.00036–0.00073	[152]
10	OPPs	Environmental water and wines	GC–MS	Toluene	2000	65–389	0.002–0.011	[153]
11	Benzophenone UV filters	Spiked and natural water	GC–MS	Tetrachloroethane	3200	310	0.008–0.045	[154]
12	Phthalate esters	Environmental water	GC–MS	*n*-Hexane	–	–	0.006	[155]
13	Phthalate esters	Distillates	GC–MS	Dichloromethane	–	–	0.003–0.3 (mg kg^{-1})	[156]
14	Pesticides	Tap and snow water	GC–μECD	Toluene	2800	835–1115	<0.010	[157]
15	Fungicides	Chrysanthemum	GC–ECD	Toluene	–	50–88	(0.005–0.05) × 10^{-3} mg kg^{-1}	[158]

Table 10
Applications of VALLME to the extraction of inorganic compounds in analytical processes.

Order	Analytes	Matrix	Detection system	Extraction solvent	Rotational speed (rpm)	EF	LOD (μg L^{-1})	Ref
A) FAAS								
1	Cd^{2+}	Water and spinach leaves	FAAS	[Hmim][PF 6]	4000	31	1.1	[159]
2	Cd^{2+}	Tap water, apple, and rice	FAAS	[Omim][PF_6]	2800	35	2.9	[160]
3	Co^{2+}	Water	FAAS	1-Undecanol	2800	18	5.4	[161]
4	Pb^{2+}	Water, plant, and hair	FAAS	$[C_4$ mim$][PF_6]$	2800	160	0.57	[162]
5	Cd^{2+}	Tap water and apple	GFAAS	[Hmim][PF6]	–	116.7	0.01	[163]
B) UV–Vis Spectrophotometry								
6	Hg^{2+}	Water samples	UV–Vis Spectrophotometry	Toluene	3000	–	0.8	[164]
7	Iodide	Mineral water	UV–Vis Spectrophotometry	Amyl acetate	3000	–	1.75	[165]
8	Inorganic iodine species	Water samples	UV–Vis Spectrophotometry	Amyl acetate	3000	57	1.1–2.3	[166]

time as a means to eliminate or reduce time consuming steps (such as centrifugation and freezing the floating drop). Liquid-phase microextraction using ferrofluids is a convenient pre-treatment mode for retrieval of organic solvent after extraction because there is no need to apply any other special apparatus except an external magnet. In addition, compared to other microextraction methods, no extra solvent is needed in the extraction and phase separation process.

Supramolecular solvents have been introduced recently as another alternative extraction solvent in LPME. The most important benefit of supramolecular solvents is their high solvation potential for a wide range of target compounds (both polar and non-polar ones), which makes them valuable for environmental analysis. These solvents provide several advantages during the sample pre-treatment process including simplicity, rapidity, and high extraction efficiency. In addition, these solvents are either compatible with different instruments for analysis or have minimal solvent consumption. Miniaturization of the extraction process should be indeed beneficial in many respects with convenience and economic/environmental advantages. Consequently, further innovations in extraction solvent preparation and materials are expected in the near future in order to address separation problems. Topics for future research studies include development of combined extraction methods to maximize their merits, presenting and using new extraction solvents with lower toxicity and greater compatibility with the analytical instruments, and increasing the selectivity of the extraction procedures.

7. Conclusions

Recently, monitoring of both organic and inorganic environmental pollutants has become an important objective for society due to the growing concerns on the hazardous effects of these harmful substances on humans, animals, and plants. Therefore, current trends have focused on the application of simple and fast separation techniques that enable analysts to extract these hazardous compounds from complex matrices. Over the past years, a variety of microextraction techniques based on SPME or LPME have been introduced for the analysis of both organic and inorganic contaminants in environmental samples. Among these techniques, diverse types of liquid–liquid microextraction are now being developed and used frequently as the subset sample preparation procedure of LPME. More specifically, LLME is a solvent-minimized extraction technique of LPME in which analytes can be extracted from various environmental samples using a few microliters of extraction solvent to achieve a high pre-concentration factor rather than the large volume of solvent required for conventional approaches. The major advantages of LLME methods are their low-cost operation, simplicity, rapidity, and compatibility with different analytical instruments. However, more breakthroughs are expected in terms of introducing more environmentally-friendly solvents and automation to develop highly selective LLME techniques. Moreover, future trends will move toward decreasing the number of tedious steps required for the procedures and eliminating organic solvents required for extraction.

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