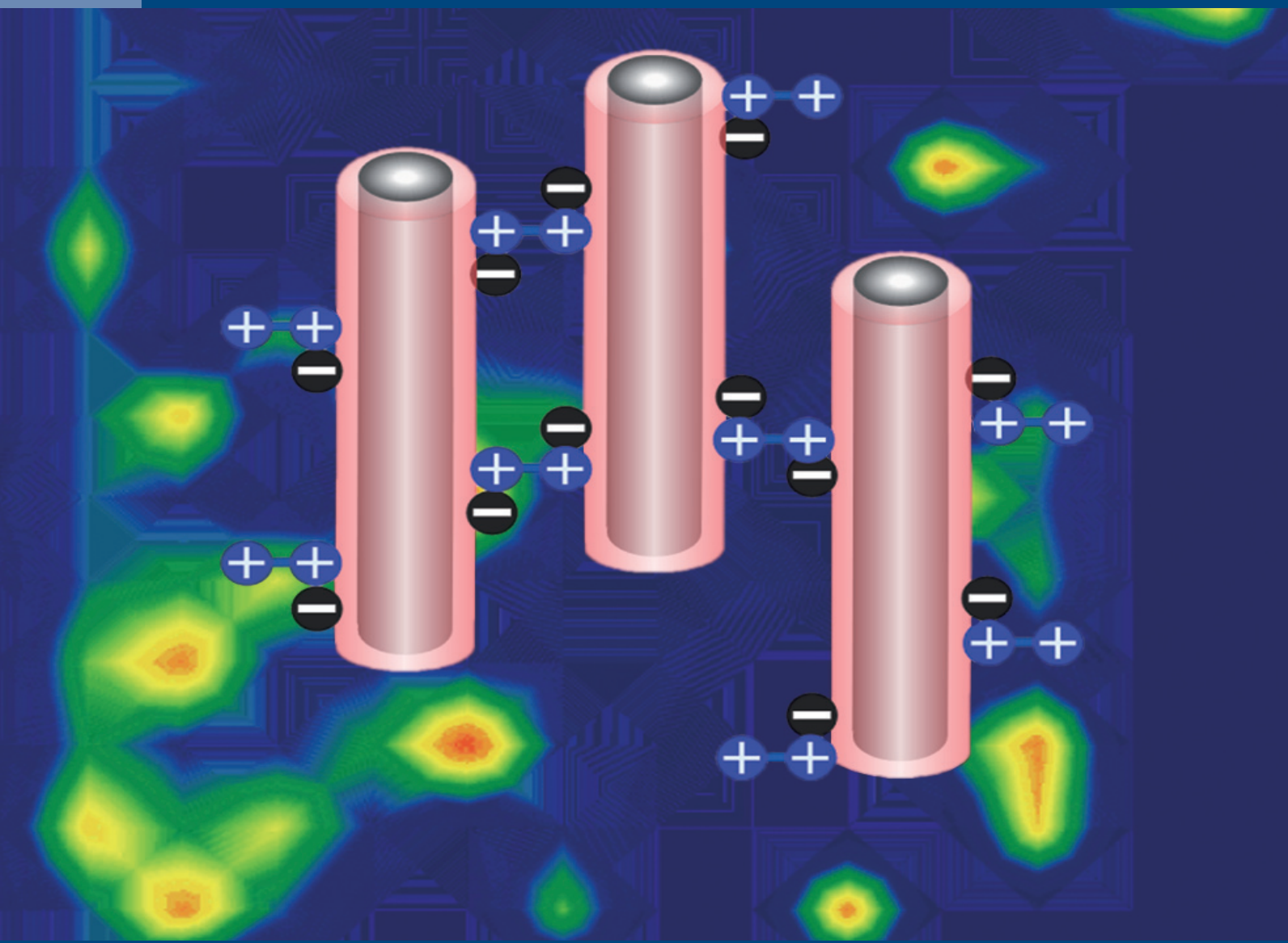
ISSN 1615-9306 · JSSCCJ 42 (1) 1–458 (2019) · Vol. 42 · No. 1 · January 2019 · D 10609

JSS

JOURNAL OF SEPARATION SCIENCE

1|19



Methods
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Received: 27 August 2018 | Revised: 8 October 2018 | Accepted: 9 October 2018

DOI: 10.1002/jssc.201800903

REVIEW ARTICLE

JOURNAL OF SEPARATION SCIENCE

Critical evaluation of microextraction pretreatment techniques—Part 2: Membrane-supported and homogenous phase based techniques

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This review follows up on Part 1, which focused on classification and evaluation of single drop and sorbent-based microextraction techniques. Membrane- and homogenous phase-based microextraction techniques are discussed and classified in Part 2. These techniques are more recent than those in Part 1 and considerable attention has been paid to their development. The new methodologies are more sensitive and, thanks to their miniaturization, they can be classified as "green", but no exhaustive classification is available. We hope that this review will contribute to better orientation in these methods.

KEYWORDS
hollow fibers, homogenous phase, membranes, microextraction

1 | MEMBRANE MICROEXTRACTION

Microextraction methods based on the use of membranes eliminate some of the disadvantages of single drop microextraction (SDME), especially drop instability. Their common principle is based on the application of polymeric membranes [1].

Membrane-based microextraction techniques can be divided into two main categories [2], which have widely different characteristics and fields of application:

(a) Porous membrane techniques

In these methods, the organic (often extraction) phase is soaked into the membrane pores, which allow analyte diffusion from the donor to the acceptor phase. The membrane does not play an active role in the separation but only provides a support for the extraction phase. Hollow fiber liquid phase microextraction (HF-LPME) [3] belongs to this group, utilizing the membrane in the form of short fiber sections. Other methods use a flat sheet of the porous membrane [1]. This is the simplest form of microporous solid support for the liquid membrane. [4–6]. Porous membranes are more universal than nonporous ones because it is possible to detect compounds that can pass through the membrane [6].

(b) Nonporous membrane techniques

These methods utilize nonporous membranes (polymer or liquid) to separate the donor and acceptor phases [1]. Membrane-assisted solvent extraction (MASE) [7] belongs in this group, where an aqueous-polymer-aqueous extraction

Article Related Abbreviations: DES, deep eutectic solvents; DLLME, dispersive liquid–liquid microextraction; EME, electro-membrane extraction; EMI, electro-membrane isolation; FS-MMLLE, flat sheet microporous membrane liquid–liquid extraction; HF, hollow fiber; HF-LLLME, hollow fiber liquid–liquid–liquid microextraction; HF-LPME, hollow fiber liquid phase microextraction; HF-SBME, hollow fiber solvent bar microextraction; IL, ionic liquid; IL-DLLME, ionic liquid dispersive liquid–liquid microextraction; LGLME, liquid–gas–liquid microextraction; LLSME, liquid–liquid–solid microextraction; LPME-BE, liquid phase microextraction with back extraction; MASE, membrane assisted solvent extraction; MIL, magnetic ionic liquid; MPMSME, microporous membrane/solvent microextraction; SD-DLLME, solvent demulsification dispersive liquid–liquid microextraction; SDME, single drop microextraction; SI-DLLME, sequential injection dispersive liquid–liquid microextraction; SLM, supported liquid membrane; SPE, solid phase extraction; SPME, solid phase microextraction; SUPRAS, supramolecular solvents; USAEME, ultrasound-assisted emulsification; VALLME, vortex-assisted emulsification

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setup is exploited. These nonporous membranes are more selective and specific for the analytes than porous ones, because they represent a more complex barrier during the extraction step [6].

1.1 | Hollow fiber liquid-phase microextraction

Hollow fiber liquid-phase microextraction (HF-LPME), which was first introduced in 1999 [3], is one of the most frequently used porous-membrane microextraction techniques. The extraction phase is placed in the body (lumen) of a hydrophobic porous hollow fiber, so that the solvent is not in direct contact with the sample solution. The organic phase forms a thin layer on the surface and within the pores of the hollow fiber, through which analytes are extracted from an aqueous sample [1]. Polypropylene is the preferred material of the hollow fibers. It is resistant to most organic solvents, which can be easily immobilized in the fiber pores [8]. Moreover, the low cost of this fiber allows a new one to be used for each analysis, so undesirable carry over errors are minimized. HF-LPME methods can further be classified into two sub-groups according to the type of sampling: the two-phase and three-phase modes [9] but a great many modifications now exist; this aspect will be discussed separately below.

1.2 | Two-phase hollow fiber liquid-phase microextraction

The principle of two-phase HF-LPME is based on the transport of analytes from the donor to the acceptor phase through the wall of a hollow fiber (HF), in which the acceptor solvent is immobilized. Usually the analyte is dissolved in an aqueous phase and the same organic phase is both in the fiber pores and in the fiber lumen. The mass transfer occurs by passive diffusion and is pH dependent. Therefore, it is important to adjust the pH of the sample solution to suppress the ionization of analytes. One approach is based on the use of a short section of tube-shaped hollow fiber immersed in the solution, which is attached to the tip of a syringe needle (Figure 1B) [10]. The syringe can perform several functions, such as introducing an acceptor phase or holding the fiber or can be used after the extraction as the injection syringe for introducing the sample into the GC instrument [11]. This attachment of the HF is also advantageous for the dynamic extraction [12]. Another setup uses a U-shaped fiber section filled with the acceptor solvent, where both its ends are attached to two syringe needles (Figure 1A). The syringes prevent solvent loss during the extraction. The bottom section of the U-shaped fiber is immersed in the sample solution for the extraction [13,14] or the ends of the U-shaped fiber are sealed, so no syringe is needed (Figure 1D). The method using shorter fibers sealed at both ends and free stirring in the sample solution (see Figure 1C) is called solvent bar microextraction

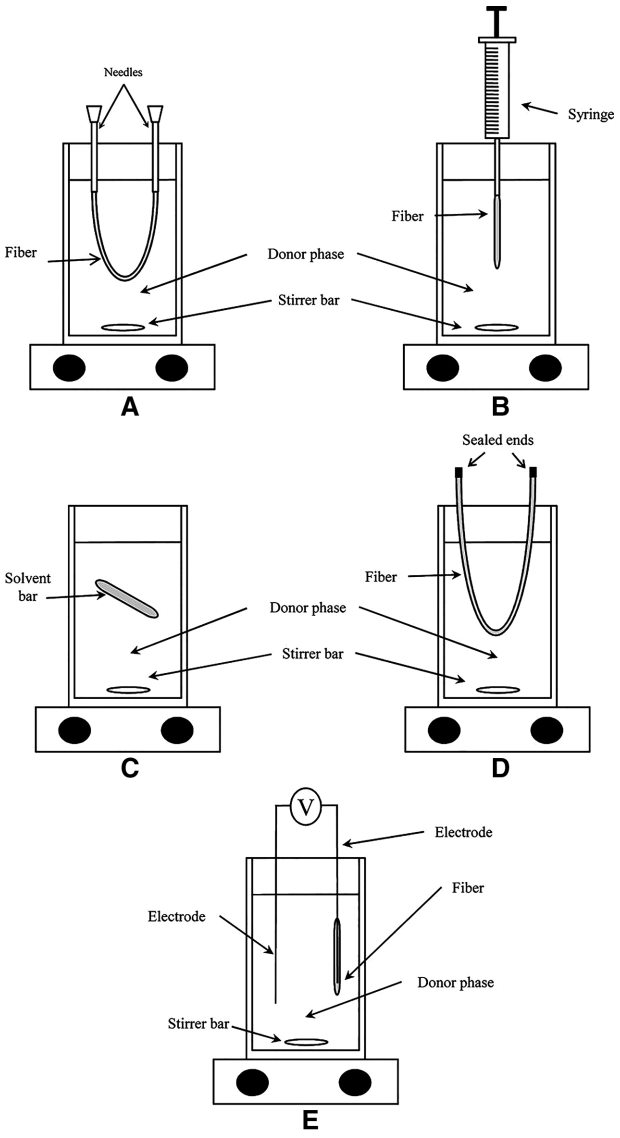


FIGURE 1 Some typical experimental setups used in HF-LPME. (A) Two needles inserted at both fiber ends; (B) one fiber end sealed and a chromatographic syringe placed at the other end; (C) both fiber ends sealed and free fiber stirring; (D) both fiber ends sealed; and (E) typical configuration used in electromigration [17]

(HF-SBME) [15,16]. The fiber is cut open after the extraction and its contents are analyzed. The contact surface area is larger during the extraction than for the U-shaped arrangement so the preconcentration yield is higher and faster [17,18]. An organic layer is easily formed on the surface and in the pores by dipping the hollow fiber into the organic solvent.

The most frequently utilized fiber material is polypropylene but exceptionally porous polyvinylidene difluoride tubing is used [12,19]. Polypropylene appears to be an excellent material thanks to its resistance to organic solvents, its flexibility and mechanical strength and the absence of sorption of analytes on its surface. The optimal parameters of the hollow fiber have been shown to be as follows: 600 μm internal

diameter (a microsyringe needle can be easily inserted into the lumen), 200 μm wall thickness (short diffusion distance but still mechanically stable), 0.2 μm pore size, and 70% porosity. Under these conditions, the organic solvent is strongly immobilized but the pore structure is still relatively open for analytes, the interfacial area between solvent and aqueous phase is large so that the extraction efficiency is relatively high [12].

Organic solvents for HF-LPME must fulfill several criteria. They should be immiscible with water, should have low volatility, should be strongly immobilized in the pores, and should dissolve easily the analytes. For the extraction of nonpolar compounds, the most commonly used solvents are 1-octanol, dihexyl ether, undecane, and toluene. Due to the nature of the acceptor solution, two-phase HF-LPME is mostly followed by GC or GC–MS analyses [8]. HPLC or CE can be used after evaporation of the solvent and reconstruction in an aqueous medium. Ionic liquids, [20,21] which can be directly injected in HPLC, can also be used [17]. Some applications were carried out with a derivatization step: directly in the sample [22], in the injection-port [23] or in-fiber (in the acceptor phase) [6,17,24]. This extra step is required for analysis of polar, semi-volatile, or thermally labile compounds to achieve better sensitivity in GC analyses [6].

HF-LPME methods are especially suitable for the analysis of "dirty" aqueous samples, because there is no danger of contamination of the acceptor phase and because of protection of the solvent from solid-matrix effects. Carryover effects are minimized by using a new hollow fiber for each extraction. The sample could be stirred or vibrated vigorously without losing the extraction phase. The method is robust and no expensive equipment is needed. [12,17] Another advantage is the possibility of online connection with chromatographic and other instrumental techniques and automation. However, HF-LPME requires larger extraction volumes (4–20 mL) and longer extraction times to reach extraction equilibrium, compared to SDME [1].

A less conventional technique consists in the connection of HF-LPME with headspace analysis. Tsai et al. [25] volatilized hexachlorocyclohexane present in water at a high temperature using microwaves and then extracted it into 1-octanol, present in the lumen and fiber pores located above in the cooled tube. Jiang et al. [26] used headspace HF-LPME for determination of PAHs in the dynamic mode.

Automation of this technique is mainly connected with the GC method but online hyphenation with HPLC has also been described. Esrafili et al. [27] automated the whole procedure with HPLC for the analysis of pyridine in cigarette smoke samples. The first attempt to automate this technique followed from the dynamic mode of the experiment. The organic solvent was repeatedly withdrawn from and discharged into the HF with the GC syringe, which was connected to a programmable pump [28]. This arrangement resulted in a higher enrichment factor. The easiest form of semi-automation is a setup where HF is connected with the vial septum, so the GC syringe could automatically take the organic phase from HF during classic injection and inject it into the GC system [29,30]. One of the possible means of automation with GC connection utilizes an HF-based extraction syringe, which is placed at the top of the GC. The syringe contains a stagnant organic phase and a sample solution is continuously delivered around HF. Norberg and Thordarson [31] used this arrangement for extraction of benzene, xylenes, etc. from human blood plasma.

Some typical experimental setups used in HF-LPME are depicted in Figure 1.

1.3 | Hollow fiber liquid–liquid–liquid microextraction

Liquid phase microextraction with back extraction, LPME-BE [32] or three phase hollow fiber liquid phase microextraction [33] are other names used for this procedure. This method is based on a supported liquid membrane (SLM) [4,5] formed by a thin layer of organic phase, which can be immobilized onto a suitable inert microporous support. Hollow fiber liquid–liquid–liquid microextraction (HF-LLLME) enables the preconcentration of analytes (polar and ionizable) from the donor phase through a hollow fiber with immobilized organic solvent (SLM) to the acceptor phase (in the lumen), which is immiscible with the organic solvent present in the hollow fiber pores [34]. This arrangement reduces the possibility of transmission of undesirable substances, because the small fiber pores prevent the transfer of large molecules and particles that may be present in the aqueous sample. HF-LLLME can be further divided into two main modes, depending on whether the acceptor phase in the lumen is an aqueous solution or an organic solvent. In the case of an aqueous solution, the analytes are extracted from an aqueous sample through the membrane organic layer into the other aqueous solution present in the body of the hollow fiber (lumen) [3]. The extraction phase in the HF pores has to satisfy the same criteria as for the two-phase system and also the configuration used has to be similar, e.g., a U-shape.

Reverse extraction from the acceptor solution back into the organic phase in the pores of the fiber is prevented by pH adjustment. The pH of donor phase must be set at a value at which the analyte ionization is suppressed, while the pH of the acceptor solution should induce effective analyte ionization. If an organic solvent is used as the acceptor phase, it has to be immiscible with the immobilized solvent. One of the published examples combines nonpolar *n*-dodecane immobilized in the pores of the fibers with acetonitrile or methanol as the acceptor phase in the lumen [35]. HF-LLLME methods are commonly combined with analytical methods, such as GC, HPLC, or CE [8]. A special case of HF-LLLME is a method where air replaces the organic liquid phase in the pores of

the hollow fiber. This setup is referred to as liquid–gas–liquid microextraction (LGLME) [36]. The use of IL as the acceptor phase in the lumen of the fiber [37] or water immiscible IL in the fiber wall [38] was also tested. But the results were not satisfactory, because of the high solubility of IL in aqueous solutions [20,21].

This extraction mode is limited to basic or acidic analytes with ionizable functionalities; therefore, a carrier-mediated HF-LPME was introduced for extraction of hydrophilic compounds. The function of the carrier is to facilitate the transfer of the ionized analyte from the donor to the acceptor phase and the transfer of counter-ions in the opposite direction [17]. One possibility is to dissolve the carriers in the impregnating solvent in the pores of HF [39,40]. The carrier forms a neutral ion-pair complex with the analyte in the organic phase. The complex can diffuse through the membrane and the analyte can be replaced on the interface with the acceptor phase by the corresponding counter-ion, which is in excess. The newly created ion-pair complex is re-extracted into the donor phase [17]. At the present time, it is more common to add the carrier to the sample solution [41,42]. The carrier charge depends only on the pH; therefore, the pH of the sample solution must be suitably adjusted for efficient carrier-analyte ion-pair generation. This hydrophobic ion-pair complex can be extracted into the organic phase. In the acceptor solution, the analyte is released from the complex into the acceptor solution. Because of the high excess of counter ions in the acceptor solution, a new complex (carrier and counter ion) can be formed and back-extracted into the donor phase. The optimum pH value of the acceptor solution causes that the analytes are in a form such that formation of new ion pairs and their back-extraction is prevented. Problems can also be encountered with achieving a neutral state of the analyte in the two-phase arrangement. There is no need for the counter ions. In this case, tetrabutylammonium [43] or ammonium salts of pyrrolidine dithiocarbamate [44] are used as the ion-pair carriers [17]. This two-phase technique is mostly utilized for the extraction of metal ions [4]. For the three-phase mode, trioctylphosphine, *N*-methyl-*N*,*N*,*N*-trioctylammonium chloride (Aliquat 336), or simply octanoic acid (for basic analytes) was used as carriers and dissolved in the liquid membrane. Most of the analyses performed using these carriers are used in the field of biomedical analysis [17]. Back extraction of the target analyte from the acceptor phase is usually prevented by proper pH adjustment of the solution. The analyte is ionized in the acceptor phase and therefore cannot pass through the organic phase but, for nonionized analytes, it is possible to add soluble antibodies to the acceptor phase that could prevent back-extraction [45].

HF-LLLME combined with SPME forms a popular subgroup of HF-LLLME and this technique also belongs among liquid–liquid–solid microextraction methods (LLSME). The transfer of analytes between the two liquid phases proceeds through the porous membrane, which moreover protects the SPME fiber [46]. HF-LPME is the first extraction step and the second one is performed in the fiber lumen, where the analyte is extracted onto the SPME fiber surface. This process could be also carried out in the electro-membrane extraction (EME) mode, where an SPME fiber is used as one of the electrodes [47] (details are described below).

1.4 | Electro-membrane extraction

In this special variant of HF-LLLME, the extraction is supported by an applied electric field generated by electrodes placed inside and outside the fiber (Figure 1E) [48]. Under these conditions, the ionized analytes are effectively and rapidly transferred from an aqueous sample through an organic solvent, which is immobilized in the wall of the polypropylene hollow fiber, into an aqueous solution present in the body of the fiber. To ensure an effective electrokinetic EME transmission system, the pH must be adjusted so that complete analyte ionization is achieved in both aqueous solutions and, therefore, the organic solvents usually differ from those used in other HF microextraction techniques. The membrane must be able to conduct the generated electric current, so apolar solvents must be avoided [17,49]. The use of 1-octanol or 2-nitrophenyl octyl ether has been described [12]. The ability to adjust the intensity of the electric field allows very rapid extraction from small sample volumes [48]. The configuration is the same as for HF-LLLME and one platinum electrode is placed inside the lumen of the hollow fiber in the acceptor phase (the fiber should be wider) and the second one in the sample solution. The extraction is controlled by a number of parameters like the applied voltage, the pH, the stirring rate or the type of SLM (organic solvent) [17]. Polypropylene is suitable, especially for the analysis of basic drugs [18] but acidic drugs [50] or peptides [51,52] and Pb^{2+} ions [53] have also been extracted by the optimized technique.

An increase in the extraction yield or reduction of the extraction time is facilitated by membrane modification. Silver nanoparticles (nanometallic silver) [54] were deposited or generated on the HF. Hidalgo et al. [55] synthesized a new support containing silver nanoparticles. They prepared agar films containing silver nanoparticles to assist EME and used dihexyl ether as SLM. In comparison with the polypropylene membrane, the extraction was more efficient because of the low system currents and the possibility of easy tuning of the membrane (thickness or type of metal nanoparticles).

EME seems to be a very suitable method for on-chip miniaturization. Sikanen et al. [56] developed a chip application with a microporous membrane, but the efficiency was poor. The construction was improved [57] and the equipment was also directly connected with a mass spectrometer [58]. For the extraction in such small volumes (units of μL of sample

solution), it is important that the analytes pass through the membrane with sufficient force. Li et al. [59] took advantage of the driving force caused by a pH gradient, but electromigration has proven to be the most efficient method. Payán et al. [60] described nano-EME with a membrane directly fixed on the CE capillary at a site where a crack was made.

1.5 | Flat sheet microporous membrane liquid–liquid extraction

Flat sheet microporous membrane liquid–liquid extraction (FS-MMLLE) and HF–LPME belong to the same class of techniques called microporous membrane liquid–liquid extraction. A great many microextraction techniques utilize a flat sheet of the porous membrane for the aqueous-organic extraction. They will be described separately here; this arrangement is older than HF-LPME [61]. First, the membrane pores are filled with the extraction solvent by immersing the sheet in the solvent. Then there are two possibilities:

(1) The piece of membrane sheet can be attached to the syringe needle and immersed in the sample for the extraction, followed by releasing of the analyte, mostly by a second extraction [62]. Xing et al. [63] call this technique microporous membrane/solvent microextraction (MPMSME) and it can have several arrangements. More than one sheet of membrane could be fixed on the needle for simultaneous extraction. Each sheet can contain a different solvent, so it is possible to extract more than one type of analyte in 1 s [64].

The headspace mode can be another arrangement, where the needle with the membrane is not immersed in the sample but is just above it in the headspace zone [65]. The membrane sheet can be placed between two drops of solvent or between two blocks with flow channels. Then the organic phase is partly in the pores of the membrane and partly in the acceptor channel [5]. The system can be dynamic or static, so the organic phase can be stagnant or can flow around the membrane. The static system is less effective because the only driving force is the concentration gradient, which deteriorates gradually. Therefore, an alternative electromigration extraction was developed (similar to EME but called electro membrane isolation–EMI in presented study). In this case, the sheet impregnated with organic solvent is formed into an envelope shape, inside which are placed a drop of aqueous acceptor phase and one electrode. This whole envelope is then immersed in the sample solution in which the second electrode is placed [66].

(2) In the second arrangement, the membrane is not self-supporting but one block has to hold the membrane and the second sandwiches membrane, which is placed between two micro-channels. This arrangement was miniaturized and automated with GC [6]. The automation was already employed for measurements of basic analytes in plasma in 1998 [61] and the system was miniaturized for determination of PCBs in river water samples [67].

1.6 | Membrane assisted solvent extraction

Membrane assisted solvent extraction (MASE) differs from other membrane techniques in the type of membrane because the aqueous and organic phases are separated by a nonporous polymer membrane (sometimes one or both liquid phases are replaced by a gaseous phase). The organic analytes present in the aqueous sample dissolve in the membrane material and pass through it. The membrane can be flat or bag-shaped and the acceptor phase is commonly nonpolar. Solvents like heptane, hexane, or cyclohexane are used [6]. The analyte is concentrated in a small volume of the acceptor phase and all the advantages of membrane extractions are preserved, such as prevention of emulsion formation or prevention of macromolecular compounds from passing through membrane [7]. Nonporous membranes can be used for more complex samples and are preferred in order to exclude traces of water from the organic phase, which could affect the final analysis. The extraction yield depends mainly on the analyte solubility and diffusivity into the membrane [6]. In 1990, Melcher and Morabito [68] devised an automated extraction analysis system, which extracted chlorinated aromatic compounds and pesticides from an aqueous sample (which was pumped above the exterior of the fiber) into the lumen of a tubular silicone rubber membrane filled with organic solvent. The internal content of the tubular membrane was automatically injected into the GC system. Garcia Sanchez et al. [69] used a flat silicone membrane for extraction of phenols and the extraction system was coupled online to a chromatographic system. Hauser and Popp [7] used a nonporous low-density polyethylene film to extract organochlorine compounds from water, urine, and milk and demonstrated that the membrane suppressed matrix interferences and decreased the baseline noise. Hauser´s experimental setup was not automatic but was performed in a glass vial, which was divided into two compartments. The sample solution at the bottom of the vial was separated by the membrane from the upper part filled with the acceptor solution. The vial is then horizontally shaken and the final solvent extract is analyzed by GC. The experimental setup of membrane-assisted solvent extraction is depicted in Figure 2.

The main disadvantage of this technique is the fact that the selection of membrane materials is limited (mainly low-density polyethylene, dense polypropylene, or silicone rubbers), so there are less possibilities for tuning the method (use of a carrier, etc.) and the analysis is slower than in other membrane techniques. On the other hand, the donor and acceptor solutions, which are miscible, can be combined without any risk of contamination [45]. Rodil et al. [70] showed that the membrane material can affect the analysis and should

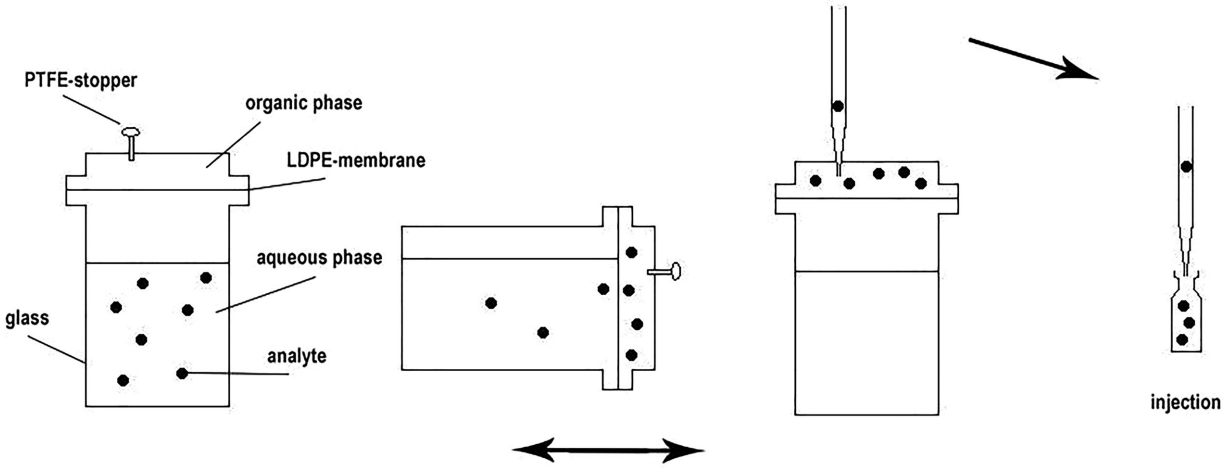


FIGURE 2 Experimental setup of membrane-assisted solvent extraction [7]

therefore be selected carefully. The same authors also speeded up the extraction by connecting the MASE with pressurized liquid extraction [71], where the solid sample with diluent was transferred into the membrane bag, which was placed in the acceptor solution and extracted at elevated temperature and high pressure.

This method can be easily miniaturized and automated. A commercial, fully automated MASE system connected to the GC is produced by Gerstel (Műhlheim, Germany). This device uses polypropylene bags filled with an organic phase connected to the vial cap; many applications were published using this instrument [72–75]. Schellin and Popp [76] employed the automated MASE device for extraction of seven volatile organic compounds with miniaturization of the extraction part. Usually the extraction takes place in the headspace vial, where a membrane bag filled with the extraction solvent is placed. The bag can be placed in a sample or simply be held upon the sample in the headspace area. Schellin and Popp shortened the length of the bag, so the preconcentration yield of the analyte was higher.

The main drawback of this technique is the requirement of membrane preconditioning and removal of interfering compounds from the membrane before the first sample extraction [6].

Membrane techniques are promising, especially for extraction of analytes from complex or dirty samples. Therefore, Shen and Lee [10] also called this technique HF-protected liquid phase microextraction. It is also favorable that a commercial instrument is available enabling automatic membrane extraction in combination with GC. On the other hand, the main disadvantage of these techniques is that they are mostly nonexhaustive. Each extraction must be carefully calibrated.

More information about membrane microextraction methods and their application in analytical chemistry is provided in several comprehensive articles [1,8,17,77,78] and the summary of the mentioned techniques is provided in Table 1.

2 | HOMOGENOUS PHASE BASED MICROEXTRACTION

The last group of microextraction techniques is based on the use of homogeneous or homogenous-like system. These methods employ rapid extraction of the analyte into the extraction solution, which forms an emulsion with the sample solution as a result of an appropriate composition of the solution or the use of ultrasound, a vortex etc. Dispersive liquid–liquid microextraction (DLLME) [79,80], ultrasound assisted emulsification microextraction (USAEME) [81], or vortex-assisted emulsification (VALLME) [82] belong to this class of techniques.

2.1 | Dispersive liquid–-liquid microextraction

DLLME was first published in 2006 as a preconcentration technique based on the ternary fluid system [79]. The microextraction procedure begins by adding a homogeneous mixture of extraction and dispersive solvents to an aqueous sample containing the analyte. According to the solvent used, the method can be divided into two categories: DLLME with lower or higher density extraction solvents [83]. A dispersive solvent is dissolved in excess water and the extracting organic phase, which is immiscible with water, forms microscopic droplets creating a cloudy solution. Because of the large surface area of the microscopic drops, the analytes are rapidly extracted into the organic phase and therefore the extraction is almost instantaneous and independent of time. After extraction, the cloudy solution is centrifuged and the organic solvent droplets are united. The organic phase can be easily removed by a microsyringe and the analyte can be determined by a suitable instrumental method, usually by GC or HPLC. This method is simple, rapid, and affords high enrichment factor but, on the other hand, larger volumes of organic solvents (in many cases toxic ones) have to be used.

TABLE 1 Summary of possible modifications of membrane microextraction techniques

Type of membrane	Modification	Commonly used abbreviations	Reviews including the methodology	First or significant application of the methodology
Porous	(Two-phase) Hollow fiber liquid phase microextraction	HF-LPME	Bello-Lopez et al. [17]	Rasmussen et al. [13]
	Hollow fiber solvent bar microextraction	HF-SBME	Barri and Jonsson [6]	Jiang and Lee [15]
	Hollow fiber liquid–liquid–liquid microextraction/Three phase hollow fiber liquid-phase microextraction	HF-LLLME	Ghambarian et al. [12]	Pedersen-Bjergaard and Rasmussen [3]
	Electro-membrane extraction	EME	Huang et al. [49] Ocana-Gonzalez et al. [18]	Pedersen-Bjergaard and Rasmussen [48]
	Flat sheet microporous membrane liquid–liquid extraction	FS-MMLLE	Yan et al. [65]	Shen et al. [61]
	Microporous membrane/solvent microextraction	MPMSME	Yan et al. [65]	Xing et al. [63]
Nonporous	Membrane assisted solvent extraction	MASE	Jonsson and Mathiasson [45] Barri and Jonsson [6]	Hauser and Popp [7] Melcher and Morabito [68]

The properties of the solvents play an important role. The extraction solvent must be able to extract analytes, be immiscible with water but miscible with the dispersive solvent and be compatible with the analytical instrumentation. The dispersive solvent must be miscible with water (sample) and also with the organic phase (extraction solvent). Methanol, acetonitrile, and acetone are often used. The volume ratios of the solvents are usually such that the sample is in excess (several milliliters), the dispersive solvent volume is about 1000 μL and the extraction solvent volume is about hundreds of ig microliters.

Rezaee´s DLLME method of 2006 [79] employs a high-density solvent (tetrachloroethylene) in combination with acetone for the preconcentration of PAHs in water samples. After centrifugation, the extraction solvent settles to the bottom of the tube, which is usually conical for easy collection of the solvent with the syringe. The most commonly used extraction solvents are halogenated compounds (chlorobenzene, chloroform, carbon tetrachloride, etc.), since they have a higher density than water and possess suitable properties for the following chromatographic measurements. They have the disadvantage of their high toxicity. Therefore, Leong et al. [84] developed and compared methods using more (chlorinated solvents) and less toxic solvents (halogenated solvents with bromine or iodine). 1-Bromo-3-methylbutane was used instead of the highly toxic solvents (normally used in DLLME also in other applications) [85]. Kocúrová et al. [86] described a DLLME technique using auxiliary solvent to adjust the density of the extraction solvent. Here, the toxic chlorinated solvent is the auxiliary one and its volume is smaller than in normal DLLME. The system is formed by a mixture of four solvents, namely aqueous sample, dispersive, extraction, and auxiliary solvents. As the extraction solvent, less toxic toluene was used and its density was modified by addition of the same volume of carbon tetrachloride. This arrangement preserves the advantages of normal DLLME (easy collection of the extraction solvent) but is less toxic.

An automated online sequential injection system (SI-DLLME) was developed. The older one used (after mixing the solvents) a microcolumn for retention of the analytes before transferring the eluent by a nebulizer to the atomic absorption spectrometer [87]. The newer SI-DLLME method utilizes a conical tube, where the solvents are mixed with the sample (mixture of amyl acetate as extraction solvent, tetrachloromethane as auxiliary solvent, and acetonitrile as disperser solvent); the extraction phase rapidly separates spontaneously without centrifugation and is transferred from the bottom of the tube for spectrophotometric detection [88].

As mentioned above, toxic solvents can be eliminated by using solvents with lower density. But the same problem arises in connection with collecting them from the sample solution, similar to methods utilizing only a drop of solvent for extraction [89]. Therefore, many of the methodologies for collecting a drop are similar. One approach involves solidification of a floating organic droplet. The method has all the advantages and disadvantages of SDME or solid drop liquid phase microextraction with the exception of the requirement to stir the sample solution (but this is possible) and the extraction is more rapid because of solution dispersion [90,91]. Mirparizi et al. [92] used the salting-out effect instead of centrifugation for separation of the extraction solvent layer. 1-Dodecanol was mixed with the sample solution, fine droplets

were created and the extraction was carried out. This mixture was poured into a barrel with a sodium chloride layer at the bottom. The salting-out phenomenon caused the fine droplets of the organic extraction solvent to pass through the solution and form a separate layer at the top. After letting out the aqueous part and blocking the bottom of the barrel, the organic layer was left inside and the whole barrel was immersed in ice water bath for 2 min. The extracting solvent was solidified and easily collected.

Special extraction devices for easy collection of the drop were described. Narrow parts (the neck, port, etc.) of the device are often used, where the solvent can be collected. The possible arrangements are summarized in specialized reviews [83,93,94]. After extraction and centrifugation, an excess of water is added and the organic phase is displaced into the narrow part [95,96]. The devices can be in the shape of a tube (narrow neck), flask, or syringe [97,98]. Li et al. [99] used the shape of a plastic Pasteur pipette and extracted chlorophenols from the sample with a mixture of toluene and methanol. The extraction step was rapid and, after separation of the two phases, the analyte was re-extracted from toluene into a drop of the basic aqueous solution. With a variation of the extraction solvent, this method was also used for determination of sulfonamides [100]. The great advantages of using Pasteur pipettes are easy cleaning [101] and transfer of the organic phase into the narrow part by just squeezing them. To improve the collection of a small drop of organic solvent from the sample solution, Chang et al. [102] suggested double centrifugation. After the first centrifugation, they collected a drop with part of the water sample in a small vial, then centrifuged it again and collected the clear organic phase. The main benefit is the very small consumption of toxic solvents.

For low density solvents, a system based on solvent demulsification (SD-DLLME or sometimes called solvent-terminated DLLME) was developed. There is no need to use a centrifuge because, after extraction, a demulsification solvent is injected into the aqueous solution to break up the emulsion, leading to separation into two layers [103,104]. The method is faster than classic DLLME and no expensive devices are required. The demulsification solvent is often the same solvent as the dispersive one. However, this step can increase the solubility of the extraction solvent and make its collection more difficult [93,94].

Hosseini et al. [105] suggested that nitrogen flotation can be used instead of centrifugation for breaking up the emulsion in the separation of two immiscible phases. Due to the different solubilities of the solvents, toluene as an extraction solvent is transferred to the surface of the mixture, where it can be collected by a microsyringe. They called this method flotation-assisted homogeneous liquid–liquid microextraction.

Another way how to avoid toxic solvents is by using ionic liquids (ILs) [106]. ILs can be employed instead of an organic (extraction) solvent with addition of dispersive solution. Their first application was for the DLLME of metal ions, where the dispersion was induced by cooling the solution in an ice bath so no dispersive solvent was required [107]. The temperature is generally important for these extractions mostly without dispersive solvent; high temperature is sometimes necessary for dissolution of the IL and low temperature is always required for the formation of a cloudy solution. The method is called temperature-controlled IL-DLLME. This method has high enrichment factors but problem are encountered with losing the analyte due to the high temperature during the extraction (e.g., for organophosphorus pesticides) [108]. ILs were also used for an automated SI-DLLME method with a column as described above [109]. When ILs are used with sonication (see below), a totally organic solvent-free emulsification microextraction system can be achieved and green chemistry can be discussed.

In situ solvent formation microextraction is often connected with IL. After addition of an ion-exchange reagent, a previously water-miscible IL becomes water immiscible. A similar effect can be achieved by addition of two salts that form the IL in the sample, creating immiscible drops/layer directly in the centrifuge tube [110,111]. ILs are now very popular and all the methods utilizing them are summarized in the review by Trujillo-Rodríguez et al. [112].

Quite a new type of ILs consists in magnetic ionic liquids (MILs). The molecules of these compounds contain a paramagnetic component, because of which, after extraction, they can be easily separated from the aqueous part by attaching an external magnet to the solution [113].

Creation of extraction solvent emulsion can be initiated also by change of pH (acid-induced, acid-assisted [114]) or change of ionic strength (salt-induced [115]). In the acid-induced procedures, organic acids are used employing dependence of their solubility on pH, where a large pH decrease drops their solubility and creates the emulsion. This microextraction procedure is than called homogenous liquid-liquid microextraction (HLLME). After the creation of the solvent emulsion, the sample pretreatment procedure is identical with DLLME.

DLLME is often used as a final extraction technique. The analyte is usually eluted during SPE employing acetone, methanol, etc. and the final solution with the analyte can be used further as a dispersive solution. Therefore, the final concentration of the analyte can be higher compared to the case when only one of these technique is used [116,117]. A very similar procedure was used by Farajzadeh et al. [118] but, instead of SPE, they utilized a stir bar sorptive extraction method (a large amount of extraction phase is coated on a stirrer bar and analyte is released from it by immersion of the stir bar into the organic solvent) [119]. Very promising supercritical fluid extraction, which is useful especially for extraction from solids, has a few disadvantages like co-extraction of compounds other than the analyte and the requirement of reduction of the collecting solvent (mostly

acetonitrile or methanol). This solvent could be used as a dispersive solvent for DLLME and the problem is elegantly overcome [120,121]. Better results can be achieved by combining several micro-extraction techniques like EME, where the final solution is polar, so it could be used as sample solution for DLLME or for emulsification microextraction enhanced by ultrasound [122,123].

The extracts are suitable for the subsequent measurements by GC, HPLC, or spectroscopic methods without additional steps. For the online connection of these extraction methods with CE, a system was developed where the sample is oil, the extraction solvent is a mixture of methanol and sodium hydroxide, and the dispersive solution is hexane [124]. The main advantage is the omission of the evaporation step, which would be normally required after DLLME because the final organic phase is not suitable for classical CE measurement.

2.2 | Assisted emulsification microextraction technique

Another way to reach or support emulsification is by using equipment like a vortex, microwave, or ultrasound [83]. The main advantages of these techniques are the shorter extraction times, lower volumes of extraction solvents, and sometimes omission of the dispersion solvents so the sample is less diluted [94]. However, automation of these assisted techniques is problematic [125].

The simplest arrangement is manual shaking of the solvent mixture. As next option the vortex-assisted emulsification (VALLME) can be used. It was first described by Yantzi et al. [82]. Here, a dispersive solvent is not required and the volume of the extraction solvent is very low (just 50 μL). For better compatibility of this technique with HPLC or CE, Makahleh et al. [126] employed VALLME with toluene as an extraction solvent. Then this toluene extract was used as a sample for the next micro VALLE step, where the analyte was re-extracted into the aqueous phase. This solution could be directly injected into HPLC or CE system and the step of evaporation of the organic phase could be omitted.

Air-assisted liquid-liquid microextraction lies at the borderline between SDME and DLLME methods [127]. In this technique, a dispersive solvent is not present but fine droplets are formed by repeatedly aspirating and expelling the sample and extraction solution mixture using a syringe. Then the centrifugation is performed and the drops of extraction solvent are collected.

Ultrasound-assisted emulsification (USAEME), which was first described by Regueiro at al. [81], is very popular. In comparison with VALLME, this method is faster because the formation of microdroplets as well as analyte transfer is faster [128]. Low- or high-density extraction solvents can be used in this method. For low-density solvents, specially designed vials [129] such as those for classic DLLME must be used. However, problems with uniformity in the energy distribution in the solution may cause repeatability problems. Temporary local increases in temperature or pressure in the sample solution can occur, which could lead in the worst case to decomposition of the thermally labile analyte [125]. Li et al. [130] demonstrated that a vortex dispersed the solution better compared to manual shaking and ultrasound. They used a supramolecular solvent and compared the size and shape of droplets under an optical microscope. They confirmed that ultrasound caused over-emulsification, resulting in an incomplete phase separation. It follows from their results that prolonged exposure to ultrasound does not contribute to better extraction but, to the contrary, causes problems like overheating of the sample, long emulsion droplet stability, and inhomogeneity of the emulsion. Lin and Fuh [131] solved this problem by occasional manual shaking during ultrasonic agitation of the sample, with good efficiency of the extraction. Some problems connected with ultrasound can be solved by using an ultrasound probe instead of a bath [132]. The probes can be used in the continuous or pulsed wave mode so the temperature of the sample can be controlled. Moreover, the size and ultrasound frequency of the probe can be chosen according to the sample so that a fine emulsion can be made. In 2011, an ultrasound probe was used for the first time with the DLLME technique.

Another way to improve the extraction by DLLME is the use of microwave-assisted emulsification. Xiao and Zhang [133] used IL as an extraction solvent to efficiently absorb the microwave energy. The comparison of several dispersion extraction techniques was demonstrated on analysis of phenolic compounds in food samples [134,135].

Another approach to support the formation of an emulsion in the presence of ultrasound and without using toxic solvents is to add a surfactant to the sample solution instead of a dispersion solution. This method was described in 2010 [136] and Tween 80, Triton X or Tween 20 were used as a surfactant for the first time. The surfactant caused that the dispersion of the organic phase in the inorganic phase increased so that the contact area between two solvents was larger [125]. This technique is also suitable for extraction of metal ions [137] because a suitably chosen surfactant can form an ion pair with the metal ion without using other ligands and a large volume of toxic solvents. A drawback lies in the possibility of surfactant transfer into the extraction solution together with the analyte, which limits the selection of subsequent detection methods.

Surfactant extractions can also be classified as coacervative microextractions, because fine droplets are formed in the aqueous solution. Coacervation is defined as a separation of a colloidal system into two liquid phases. Coacervate (colloid-rich or coacervative phase) is the phase more concentrated in the colloid component and the phase containing a low colloid concentration is called the equilibrium

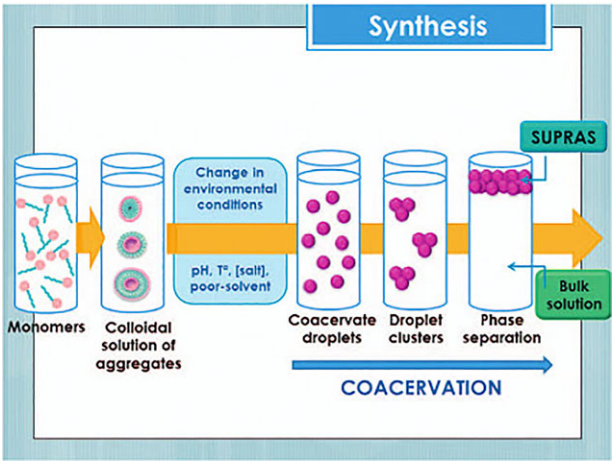


FIGURE 3 Schema of the processes of self-assembly and coacervation involved in the synthesis of supramolecular solvents from amphiphiles [139]

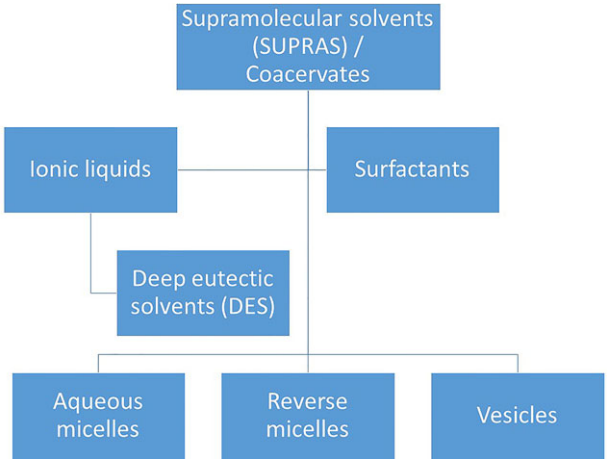


FIGURE 4 Classification overview of supramolecular solvents

solution (colloid-poor phase or aqueous bulk). Aqueous micelles, reverse micelles, or vesicles can be included among the coacervates [138,139]. The nanostructured liquids formed in a colloid-rich phase (phase formed of coacervate droplets) were also called supramolecular solvents (SUPRAS) because, in this case, they exhibit self-assembling ability (Figure 3). The aggregates in the solution created from ionic amphiphilic molecules are held together by non-covalent interactions. A coacervative phase can be formed by pH changes in the solution or by the addition of an electrolyte or water-miscible solvent in which the macromolecules have low solubility. If the monomer molecules are neutral (nonionic or zwitterionic), coacervates are formed by a change in the temperature. This process is called cloud point extraction (CPE) [138]. Recently, some techniques utilizing SUPRAS may rather be classified as deep eutectic solvents (DES), which are now very popular for extraction. This fact makes classification of the methods more complicated. DES are a new class of ILs with lower toxicity, composed of a hydrogen-bond acceptor (e.g., quaternary ammonium salt) and a hydrogen-bond donor (e.g., organic acid, amino acid, and sugar) [140]. The classification of DES with respect to ILs is still under rapid development and is sometimes unclear (Figure 4). An example of the method formerly classified as SUPRAS based on DLLME, but now probably referred to as a DES microextraction technique, could be the addition of ammonium pyrrolidinedithiocarbamate and decanoic acid in tetrahydrofuran to an aqueous sample. Fine droplets of water-immiscible reverse micelles are formed and the analytes can be extracted via them. The separation of the coacervate from the bulk solution is accelerated by centrifugation. The coacervative phase can be removed and subsequently analyzed [141]. Decanoic acid is a popular hydrogen bond donor and could form vesicles in the right solution composition [142]. DES or SUPRAS have great advantages in the possibility to tune them for a specific application with predetermined function similar to ILs [139]. The right combination of acceptor and donor molecules even allows the creation of either hydrophobic or hydrophilic DES [143]. The extraction of the analyte into the coacervate can be accelerated and improved by using manual shaking, a vortex, or ultrasound [130]. Coacervative DLLME using Triton X-114 was supported by ultrasound [144], which can also be used for supporting the DLLME when DES is used (decanoic acid and trioctylmethylammonium chloride) [145]. Vortex-assisted DES DLLME was successfully used for extraction of curcumin (a mixture of choline chloride and phenol was used as DES) [146]. Very popular seems to be air-assisted DES DLLME by which various analytes were extracted (drugs [147], aromatic amines [148], benzophenone-type UV filters [149], etc.) A number of another various combinations of DES and supported techniques have been described [150].

At the present time, the DLLME technique and various combinations of it are probably among the most popular microextraction techniques, especially due to efforts to use environmental friendly solvents like ILs and DES. More information and applications of the DLLME method are given in several papers [34,83] [151–154].

3 | CONCLUDING REMARKS

Microextraction techniques are very popular for preconcentration or purification of samples. Membrane-supported techniques are used especially for extraction of analytes from dirty and/or complex samples. The collection of the acceptor phase is easy and can be automated. The membranes/fibers are cheap so a new one is often used for each analysis to eliminate possible carryover and also the experimental conditions can be simply modified.

Homogenous phase-based microextraction is the most rapidly growing area of all the described techniques. A large number of modifications exist and now extractions using various ILs are very popular because their properties can be tuned. The use of modern solvents like DES can make the extraction step rapid and easy and, with the right component selection, it can be considered to be a "green" method.

The aim of this two-part review is not to provide an exhaustive summary of all the techniques and their combinations and modifications but an effort to classify the basic principles of microextraction techniques as clearly as possible and present some representative examples. This branch of pretreatment techniques is rapidly developing and is promising because of their potential to be rapid, cheap, automated, and/or environmental friendly.

ACKNOWLEDGMENTS

The study was financially supported by the Charles University, project GA UK no. 760216 and the project of the Specific University Research (SVV260440).

CONFLICT OF INTEREST

The authors have declared no conflict of interest.

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How to cite this article: Havlikova M, Cabala R, Pacakova V, Bosakova Z. Critical evaluation of microextraction pretreatment techniques – Part 2: Membrane-supported and homogenous phase based techniques. *J Sep Sci* 2019;42:303–318. https://doi.org/10.1002/jssc.201800903