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Review

An overview of liquid phase microextraction approaches combined with UV–Vis spectrophotometry

Malihe Dehghani Mohammad Abadi [a], Narges Ashraf [a,*], Mahmoud Chamsaz [a], Farzaneh Shemirani [b]

[a] Department of Chemistry, Faculty of sciences, Ferdowsi University of Mashhad, Mashhad, Iran
[b] School of Analytical Chemistry, University College of Science, University of Tehran, Tehran, Iran

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ABSTRACT

Ultraviolet and visible spectrophotometer has become a popular analytical instrument in the modern day laboratories. However, the low concentrations of many analytes in samples make it difficult to directly measure them by UV–Vis spectrophotometry.

This overview focuses on the combinations of microvolume UV–Vis spectrophotometry with miniaturized approaches to sample preparation, namely, single drop microextraction (SDME), dispersive liquid–liquid microextraction (DLLME), cold induced aggregation microextraction (CIAME), in situ solvent formation microextraction (ISSFME), ultrasound assisted emulsification microextraction (USAEME), solidified floating organic drop microextraction (SFODME), and hollow fiber based liquid phase microextraction (HF-LPME) to improve both the selectivity and sensitivity.

Integration of these techniques provides unique advantages which include availability, simplicity of operation, low cost, speed, precision and accuracy; hence making them a powerful tool in chemical analysis.

Contents

* Corresponding author. Tel.: +98 511 8797022; fax: +98 511 8795457.
E-mail address: ashraf-n@um.ac.ir (N. Ashraf).

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1. Introduction

Spectrophotometric methods have been in general use for about 40 years and over this period are the most commonly used techniques and continue to enjoy wide popularity [1]. In many applications, other techniques could be employed but none rival UV–Vis spectrophotometry for its availability, simplicity, versatility, speed, accuracy, precision, and cost-effectiveness. This technique is routinely used in analytical chemistry for quantitative determination of different analytes such as transition metal ions, highly conjugated organic compounds, and biological macromolecules.

UV–Vis spectrophotometry has become the most important analytical technique in modern day laboratories. With recent advances in sensitive array detectors, fiber optic wave guides, high speed electronics and powerful software, many new generations of spectrometers have been developed. A quick glance at today's instrumentation market indicates the popularity of the charged coupled devices (CCDs) and photodiode arrays as a replacement to photomultipliers and avalanche photodiodes used in conventional spectrometers. Because of the unique combination of sensitivity, high speed, low noise, compactness, instantaneous capture of full spectra, low cost and robustness, these detectors have revolutionized the spectroscopic detections. The overwhelming benefits of array detectors are simultaneous and multi wavelength data acquisition [2–5]. Also, the use of fiber optics as light guidance allows a great modularity and flexibility in setting up an optical measurement system. In addition, optical fibers have high light focalization which makes them suitable for spectroscopic applications [6].

The low concentrations of many analytes in the complex real samples make it difficult to directly measure by spectrophotometry, even by these new instruments. Moreover, the wide bandwidth in the UV–Vis spectrum of the species makes the technique unselective. Therefore, a sample preparation step is necessary before spectroscopic measurements to improve the selectivity and sensitivity [7].

The sample preparation is a critical step in the overall scheme of analysis which has a direct impact on accuracy, precision and quantization limits and is often the rate determining step of the analytical process, especially for trace determinations [8].

Liquid–liquid extraction (LLE) based on the transfer of analytes from an aqueous sample to a water-immiscible solvent is a versatile classical sample preparation technique which is widely employed. However, conventional liquid–liquid extraction uses large amounts of potentially toxic organic solvents which are often hazardous and expensive. To reduce these disadvantages, liquid phase microextraction (LPME) techniques have been developed. LPME is often rapid, inexpensive and uses minimal volumes of solvent with negligible exposure to toxic organic solvents. LPME is normally performed between a small volume of water-immiscible solvent (in the μL or sub-μL range) and an aqueous phase containing the analytes of interest and allows high enrichment factors. Since, the publication of the first paper on LPME in 1996 [9], different approaches to LPME have been developed [10].

There are different operating modes in LPME such as single drop microextraction (SDME), dispersive liquid–liquid microextraction (DLLME), cold induced aggregation microextraction (CIAME), in situ solvent formation microextraction (ISSFME), ultrasound assisted emulsification microextraction (USAEME), solidified floating organic drop microextraction (SFODME), and hollow fiber based liquid phase microextraction (HF-LPME) which have been used in combination with UV–Vis spectrophotometry for determination of various species in different matrices. Of course, these combinations require the replacement of microvolume cells with conventional spectrophotometric cells or the use of commercially nanodrop® instruments which was firstly introduced for bioanalytical purposes [11].

Although LPME has been long and widely used in combination with various measurement techniques such as gas chromatography (GC) and high performance liquid chromatography (HPLC) [12], electrophoresis [13], atomic absorption spectrometry [14], etc.; however, only recently its application with spectrophotometers is growing. In 2007, Shokoufi et al. [1], reported the first application of LPME (i.e., DLLME) in combination with UV–Vis spectrophotometry. Since then, several efforts have been directed toward the application of various LPME techniques in combination with UV–Vis spectrophotometry for determination of many organic and inorganic species. Although, very recently a review has been published [15] that dealt with the recent advances in coupling single-drop and dispersive liquid–liquid microextraction techniques with UV–Vis spectrophotometry and the related detection techniques; however, this review is not comprehensive and does not include all the microextraction techniques utilized in combination with UV–Vis spectrophotometric detection. Therefore, the aim of this review is to discuss extensively the different applications of microextraction techniques for the extraction of different analytes and their determinations by UV–Vis spectrophotometer. So, we devote this review to discuss these combinations and their performances and to inspect the advantages and drawbacks.

2. Microextraction techniques combined with UV–Vis spectrophotometry

2.1. Single drop microextraction (SDME)

SDME has been gained importance since Jeannot and Cantwell [16] introduced this technique. SDME is based on the principle of distribution of the analytes between a microdrop of extracting solvent at the tip of a microsyringe, or a small PTFE rod and an aqueous phase. Since the extraction medium is in the form of a single drop, this type of microextraction is called SDME [17].

In SDME, commercial materials and equipments are used, and a separate droplet is used for each extraction to avoid across contamination.

In practice, two main approaches can be used to perform SDME [10]:

1) Direct immersion DI-SDME
2) Headspace HS-SDME.

Among the different modes of SDME, headspace sampling (HS-SDME) techniques, introduced in 2001 [18,19] has become a powerful alternative pre-treatment technique for extraction and preconcentration of volatile and semivolatile analytes as well as volatiles after derivatization owing to the high enrichment factors typically obtained, the high degree of clean-up achieved and the possibility of using green extractant phases such as ionic liquids or aqueous drops [20,21].

The combination of SDME with conventional UV–Vis spectrophotometry is difficult to accomplish because of the high volumes needed (~1 mL) in comparison with microdrop volumes (typically 1–3 μL) used in SDME. Several attempts to decrease the volume for performing a spectrophotometric measurement can be found in the literature. The simplest approach is the use of a microvolume cell (commonly in the range of 50–500 μL) and diluting the drop prior to UV–Vis spectrophotometric measurements. However, cuvetteless micro-spectrophotometers, in which a 1–2 μL drop is held during measurement between a pair of sample pedestals, made of stainless steel and quartz fiber by

surface tension only, provides a more elegant solution. This sample-retention technology is employed in microvolume UV–Vis spectrometers marketed by Thermo Fisher Scientific (Nanodrop®) [22]. In addition, microvolume systems, such as liquid droplets [23–28], liquid films/droplets [29] and falling drop [30] system have been developed in the past years [31]. Advances in microvolume UV–Vis spectrophotometry mainly derive from efforts to miniaturize the sample compartment. In this sense, different UV–Vis spectrometric systems and accessories have been developed in recent years, and some of them can currently be found in the market, including confined drop-based systems, liquid-core waveguides (LCWs), microcells, UV-transmissive pipette tips and variable path-length systems [11].

The relevant applications of the single drop microextraction techniques combined with spectrophotometry (Table 1) are divided into headspace and direct immersion modes as described below.

2.1.1. Headspace single drop microextraction

In 2009, Pena-Pereira et al. [31] used a microdrop of *N,N′* Dimethylformamide (DMF) as an extractant phase for separation and preconcentration of the iodine generated in situ by HS-SDME (Fig. 1). The procedure consisted of exposing the droplet to the headspace of an acidic aqueous solution containing Na_2SO_4. Addition of H_2O_2 for in situ iodine generation was performed. This procedure has been applied for determination of iodine in water, pharmaceutical and food samples. HS-SDME provides efficient matrix separation and large enrichment factors (623) in only 7 min of microextracion.

At the same time, Sharma et al. [32] presented another application of the HS-SDME combined with a Nanodrop® UV–Vis spectrophotometer to detect trace amounts of free chlorine, chlorine dioxide and total chlorine in water. Determination of chlorine/chlorine dioxide has been performed by headspace in-drop reaction with alternative reagents, viz., mixed phenylhydrazine-4-sulphonic acid and *N*-(1-naphthyl)ethylenediamine dihydrochloride, *o*-dianisidine, *o*-tolidine, and *N,N*-diethyl-*p*-phenylenediamine. Comparison of features of merit of analytical methods suggests that the proposed miniaturized method is better than conventional spectrophotometry and is less sensitive to interferences.

Chloride has also been determined in water samples, inorganic compounds and cement by Pillai and co-workers [33] using HS-SDME in combination with a NanoDrop® spectrophotometer. The method involves the oxidation of chloride with permanganate in sulfuric acid medium, and reaction of the generated chlorine with a 2 μL drop of starch-iodide reagent suspended at the tip of a microsyringe needle in the headspace of the reaction mixture. The method was highly selective and a number of ions which severely interfered in other methods did not affect the results.

Another strategy used by Pena-Pereira et al. [21] for the determination of iodate on the basis of the iodometric reaction:

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

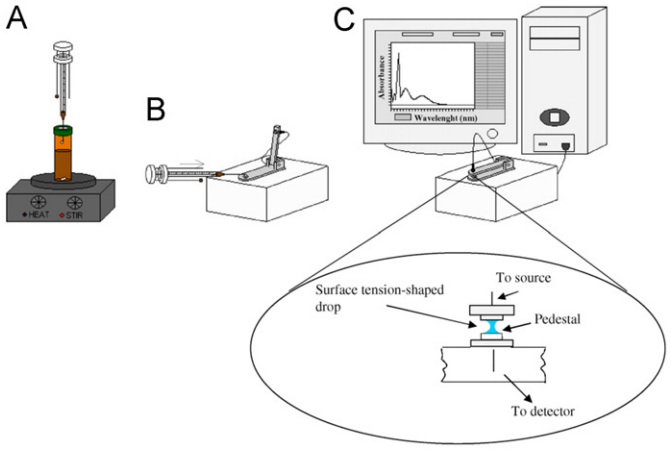

Fig. 1. Schematic representation of the different steps for the determination of iodine by HS-SDME combined with a Nanodrop® spectrophotometer: (A) Headspace single-drop microextraction of iodine generated in situ. (B) Deposition of the microdrop on the lower pedestal of the Nanodrop® spectrophotometer and (C) absorption spectra acquisition [31].

Table 1
Application of SDME modes in conjunction with UV–Vis spectrophotometry.

Extraction technique	Extractant phase	Analyte	Sample matrix	λ	LOD	%RSD	Linear range	Ref.
HS-SDME	Dimethylformamide	Iodide/Iodine	Water; Food; Pharmaceuticals	295	0.69 μg L^{-1}	4.7	5–200 μg L^{-1}	31
HS-SDME	Phenylhydrazine-4-sulphonic acid + *N*-(1-naphthyl)ethylenediamine dihydrochloride	Chlorine/Chlorine dioxide	Water	517	13 μg L^{-1}	3.4	0.07–7.5 μg L^{-1}	32
HS-SDME	*O*-dianisidine in sulphuric acid	Chlorine/Chlorine dioxide	Water	449	0.6 μg L^{-1}	1.1	0.007–1.8 μg L^{-1}	32
HS-SDME	*O*-tolidine in sulphuric acid	Chlorine/Chlorine dioxide	Water	440	5 μg L^{-1}	2.4	0.05–3.5 μg L^{-1}	32
HS-SDME	*N,N*-diethyl-*p*-phenylenediamine in sulphuric acid	Chlorine/Chlorine dioxide	Water	547	9 μg L^{-1}	4.6	0.03–3.5 μg L^{-1}	32
HS-SDME	Starch + Iodide	Chloride	Inorganic compounds; Cemenet	553	2.8 μg L^{-1}	3.9	0.025–4 mg L^{-1}	33
HS-SDME	Dimethylformamide	Iodate	Water	295	1.1 μg L^{-1}	4.2	7.5–175 μg L^{-1}	21
HS-SDME	Xylene + Picric acid	Trimethylamine - nitrogen	Fish	410	6×10^{-4} mg/100 g	5	5×10^{-5}–3×10^{-4} mg/100 g	34
HS-SDME	Aqueous drop containing sulphanilic acid + α − naphtylamine	Nitrite	Water	540	1.5 μg L^{-1}	3.5	10–100 μg L^{-1}	20
DI-SDME	Tetraoctylammonium bromide + Toluene	Thiols	Pharmaceuticals	470	–	–	–	32
DI-SDME	Dithizone + Carbon tetrachloride	Cd(II)	Rice; Water	610	0.5 ng l^{-1}	3.2	Up to 50 ng L^{-1}	36
DS-SDME	1-Octanaol	Nitrobenzene	Water	258	–	3.82	0.08–1.2 mg L^{-1}	39
DS-SDME	Malachite green (ion pairing agent) + Methyl isobutyl keton	Phosphate	Water	627	6.1 nM	2.7	0.05–1.5 μM	37
In-situ SDME	Dithizone + Carbon tetrachloride	Hg(II)	Water	475	0.2 μg L^{-1}	4.7	2-50 μg $L-^{1}$	40
Triple phase SDME	KI + Starch + Water (Third phase)	Iodide/Iodine	Table salt; Seawater; Pharmaceuticals	553	10 μg L^{-1}	2.9–5.7	25–750 μgL^{-1}	32

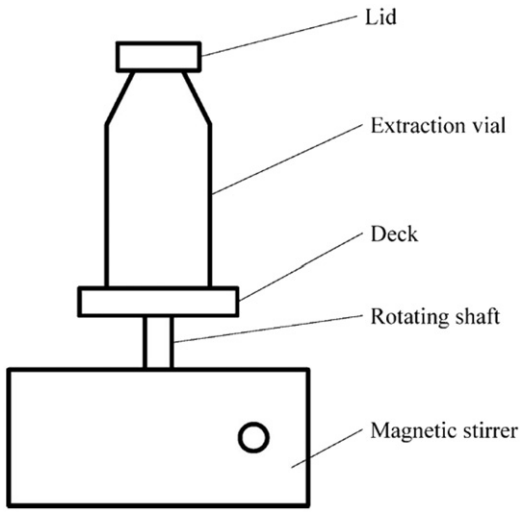

Fig. 2. The experimental setup of the novel DS-SDME microextraction method [39].

Vapor iodine which is generated in situ was extracted and preconcentrated onto a headspace DMF droplet. With only 7 min of extraction time, the relative recovery ranges from 94–104%. The proposed method has been employed for the analysis of different natural water samples.

The same authors [34] also employed HS-SDME for trimethylamine-nitrogen (TMA-N) determination in fish samples. A picric acid-containing xylene microdrop exposed to the headspace of a closed vial was employed as extractant phase of TMA-N which is a miniaturization of the AOAC official method and gives rise to a considerable improvement of sensitivity and rapidity. The AOAC official method 971.14 for determination of TMA-N in fish samples [35], encompasses a liquid–liquid extraction of TMA-N with toluene and its subsequent reaction with picric acid reagent to form a yellow complex. The low limit of detection of the proposed method, together with a high freedom from interferences, allows the determination of TMA-N within a short time.

Another strategy has been described by Senra-Ferreiro et al. [20] by the use of SDME-spectrophotometry for a sensitive determination of nitrite in water samples. The miniaturized Griess assay would allow the determination of nitrite in a variety of samples at low concentrations with minimal sample handling. The enrichment factor of 193 was achieved for water samples.

2.1.2. Direct immersion single drop microextraction

In DI-SDME, a drop of a water-immiscible solvent is suspended directly from the tip of a microsyringe needle immersed in the aqueous sample. In 2009, Sharma et al. [32] introduced a DI-SDME-spectrophotometry technique for determination of thiols involving their reaction with the Ellman reagent. The thiolate ion formed was then extracted into the organic phase as an ion pair.

At the same time, these authors [32] were the first to employ the triple phase SDME in conjunction with a spectrophotometer for determination of iodide/total iodine. In this procedure, the iodide is oxidized using 2-iodosobenzoate into iodine, then extracted into an organic solvent, and finally back-extracted into an aqueous starch-iodide reagent drop held in the organic phase.

In recent years, Wen et al. [36] have developed a SDME technique using carbon tetrachloride (CCl_4) as extraction solvent for spectrophotometric determination of cadmium in rice and water samples. To overcome the negative effects of subsequent dilution, four parallel samples were simultaneously operated in the process.

A modification to the conventional SDME was performed by Pena-Pereira and his co-workers [37] in which a directly suspended droplet microextraction (DS-SDME) was combined with spectrophotometry. This technique which does not require the use of a microsyringe, involves adding 5–100 μL portion of a water immiscible organic solvent directly in the vortex of a stirred aqueous sample. Stirring at a constant speed (typically 1000 rpm) produces a velocity gradient vertically in solution, being higher near the stirring peddle, and draws the extraction solvent into the aqueous solution [38]. This miniaturized methodology was applied for determination of phosphate in water samples. The method is based on the extraction of the ion pair formed between 12-molybdophosphate and malachite green onto a microdrop of methyl isobutyl ketone (MIBK) and subsequent spectrophotometric determination with no dilution. An enrichment factor of 325 was obtained after 7.5 min of microextraction.

In 2009, Mingyuan and co-workers [39] introduced a novel DS-SDME in which a rotating vial was served to provide a very stable flow field and solvent spreading along the parabolic surface of the aqueous phase and hence reduced the mass transfer resistance (Fig. 2). Potential emulsification was avoided using the centrifugation effect of the rotating vial. During sampling, the shape of the 1-octanol organic solvent droplet changed upon insertion of a needle, causing the droplet height to increase approximately 3–4 folds. This increase in droplet height made the solvent sampling much more convenient and allowed the use of smaller 1-octanol volumes, which enhanced the mass transfer process and enrichment factor.

Yang et al. [40] introduced a novel setup for microextraction and detection by spectrophotometry, namely, in situ SDME. This sensitive method was developed for mercury determination in water samples using a droplet of dithizone-CCl_4 as extraction phase which was hanged on a rolled PTFE tube. LED light was adjusted carefully to pass through the centre of the droplet and the entrance slit of the CCD detector. The radiation intensities before and after the SDME were recorded for quantification. Besides a high enrichment factor, the merits of this method include low cost, low organic reagent consumption and easy operation. This miniaturized system opened a promising avenue for sensitive field analysis.

2.1.3. Features of SDME in combination with UV–Vis spectrophotometry

At present, there are three different modes of SDME which have been applied in conjunction with UV–Vis spectrophotometry. All of the SDME modes involve non-equilibrium processes which are far away from equilibrium. These modes can be classified as: headspace, direct immersion, and directly suspended droplet microextraction techniques; which demonstrate the versatility of the method.

Selection of a suitable microextraction technique requires the careful considering of several parameters, mainly, the characteristics of the analytes, the sample matrix, and the type of organic solvent (as extractant phase).

HS-SDME is applicable only for extraction of volatile and semivolatile analytes as well as analytes which forms volatile species after a derivatization process. On the other hand, DI-SDME and DS-SDME modes are not usually suitable for dirty samples, since suspended particles may disturb the drop or even make it very unstable.

Considering the extractant phase, There are a good number of organic solvents, e.g., hexane, cyclohexane, toluene, xylene, isooctane, anisole, chloroform, 1-octanol, etc., that can be used in the modes in which the solvent drop directly come in contact with aqueous sample (i.e., DI-SDME and DS-SDME). Thus, water

immiscibility of solvent is a critical factor. In the case of DI-SDME, adequate viscosity to adhere to the tip of the syringe needle must be also considered. On the other hand, in DS-SDME, only solvents with densities lower than that of water can be used, e.g., 1-octanol, toluene, etc. There is much freedom in choosing solvent in HS-SDME mode. Essentially, non-volatility of solvent is the main criterion. Thus, butanol, octanol, benzyl alcohol, ethylene glycol, toluene, dodecane and water have been used [38].

As a choice for sample preparation, SDME method is characterized by its simplicity in operation, low instrumental costs, speed, low cost, and freedom from analyte carryover.

In general, SDME can provide very high enrichment factors due to the high ratio of sample volume to organic phase volume which increases the sensitivity [20]. Also, the negligible consumption of extractant phase and, therefore, the reduced waste makes this method environmentally friendly.

On the contrary, SDME shows some disadvantages especially at high temperatures, long extraction periods and high stirring rates which cause drop volume variation during the process of extraction and thus affects the drop stability and as a result, analytical precision [9]. Formation of a slightly bigger drop for extraction than the volume withdrawn into syringe after extraction helps to avoid problems due to drop size variation, or accidental withdrawal of some of aqueous sample [38]. On the other hand, because the droplet is placed on the tip of a microsyringe needle, it is easily dislodged during stirring. Thus, large droplets and any factors leading to flow field disturbances must be avoided. Also, SDME is also not suitable for samples containing particles [39] and implementation of SDME is currently limited by the unavailability of commercial equipments.

On the other hand, high stirring speed and larger organic drops, in the situation of DS-SDME, are responsible for reduction of extraction time, and high enrichment factor [38]. However, clean-up of extract would be needed after initial extraction whilst dealing with samples of complex matrices.

HS-SDME provides many more advantages including the elimination of interference of dirty or complex matrix and particulate matter, freedom from restrictions on sample stirring rate, and on organic solvent. Also, high clean-up is possible by HS-SDME of volatile substances or those which are rendered so after derivatization [38].

2.2. Dispersive liquid–liquid microextraction (DLLME)

A novel high performance and powerful microextraction technique termed dispersive liquid–liquid microextraction (DLLME) was demonstrated by Rezaee and co-workers in 2006 for the first time [41]. In this extraction method, any component in the solution, directly or indirectly after derivatization, is extracted and concentrated into a small volume of the remained phase. In this procedure, an appropriate mixture of the extraction and disperser solvents is injected into the aqueous sample by a syringe which forms a cloudy solution. As a result, fine droplets of the extraction solvent is formed and dispersed in the sample solution. The cloudy solution would then be centrifuged and the fine droplets are sedimented at the bottom of the conical test tube. Determination of analytes in the remaining phase can be performed by instrumental techniques. Hyphenation of such a procedure with cylindrical micro-cell, optical fibers and CCD-linear array detector (Table 2) allows the multi wavelength scan of the low volume of the remained phase after DLLME [1].

The first conjunction between DLLME and UV–Vis spectrophotometry was proposed by Shokoufi et al. [1] for determination of palladium and cobalt in water samples. In this procedure, an appropriate mixture of ethanol (the disperser solvent) and 1,2-dichlorobenzene (the extraction solvent) was injected rapidly into the water sample containing palladium and cobalt after complex formation using 1-(2-pyridylazo)-2-naphthol (PAN) reagent. After phase separation, the sedimented phase containing the enriched analytes was determined by a fiber optic linear array detector (FO-LADS).

The same procedure has been also applied for preconcentration of cobalt from real water samples by Gharehbaghi and co-workers [42]. In this method, chloroform was dissolved in pure ethanol, and injected into the water sample containing Co-PAN complex. The enrichment factor of 125 shows an efficient extraction and preconcentration procedure.

They also focused on the use of ionic liquids as extracting media for coupling DLLME to UV–Vis spectrophotometry [43] in which a hydrophobic ionic liquid, namely, 1-hexyl-3-methylimmidazolium bis(trifluormethylsulfonyl)imid ([HMIM][Tf_2N]), was used as an extracting solvent, which had been dissolved in aceton. The binary solution was injected into the water sample containing mercury cations and complexed by 4,4′-bis(dimethylamino)thiobenzophenone (TMK) in the presence of sodium dodecyl sulphate as the anti-sticking agent to prevent the sticking of ionic liquid to the test tube wall.

In recent years, Ding and Liu [44] have developed the application of DLLME-Spectrophotometry for determination of trace vanadium. Vanadium was extracted from acetate buffer solution using PAN, chloroform and ethanol. The enrichment factor of 50 was achieved at the optimal conditions.

Another DLLME has been developed by Bavili Tabrizi [45] for determination and speciation of Fe ions. The procedure is based on the complexation of Fe(II) with *O*-phenanthroline (*O*-Phen), followed by subsequent ion-association formation with picrate anion, and then extraction of the complex using chloroform and methanol as the extractant system. Study of the interference of several cations and anions showed that the method is nearly free from interferences.

Biparva and co-workers [46] used a mode of DLLME technique coupled with spectrophotometric detection for determination of rhodamine 6G. A mixture of acetone (disperser solvent) and chloroform (extractant solvent) was used for the microextraction procedure. After centrifugation, the sedimented phase was evaporated and dissolved in small amounts of methanol and measured by UV–Vis spectrophotometry.

Bidari et al. [47] proposed the same strategy for determination of total anionic surfactantss. Indeed, the official reference methods (ASTM D2330-02, ISO 7875-1), which require tedious procedures, were replaced with a modified method. The SDS-MB ion-pairs is extracted into chloroform.

The mentioned procedure has also been used by Ezodin et al. [48] for preconcentration and determination of Cu(II) as its complex with 4-benzylpiperidineditiocarbamate (BPDC) in urine and water samples. FO-LADS has been applied for detection using a cylindrical microcell. The enrichment factor was 160.

Recently, DLLME procedure using tetrachloromethane (CCl_4) as extraction solvent was proposed by Wen et al. [49] for spectrophotometric determination of cadmium and copper by dithizone and diethyldithiocarbamate as complexing agents, respectively.

A method which involves ionic liquid-based dispersive liquid–liquid microextraction method was proposed by gharehbaghi and shemirani [50] for preconcentration of molybdenum in water and plant leaves samples as a prior step to its enhanced spectrophotometric determination by FO-LADS. Pyrogallol red was employed as complexing agent and *N*-cetyl-*N*-*N*-*N*-trimethyl ammonium chloride (CTAC) as the sensitizing agent to assess the extraction procedure.

In 2011, Bidari et al. [51] developed a new surfactant enhanced DLLME procedure for the assay of trace amounts of MG in aquatic environment of Trout fish.

Table 2
Application of DLLME in combination with UV–Vis spectrophotometry.

Extraction technique	Complexing agent	Extractant solvent	Disperser solvent	Analyte	Sample matrix	λ	LOD	%RSD	Linear range	Ref.
DLLME	1-(2-pyridylazo)-2-naphtol	1,2-dichlorobenzene	Ethanol	Pd(II)	Water	680	0.25 μg L^{-1}	< 4	2–100 μg L^{-1}	1
DLLME	1-(2-pyridylazo)-2-naphtol	1,2-dichlorobenzene	Ethanol	Co(II)	Water	640	0.2 μg L^{-1}	< 4	1–70 μg L^{-1}	1
DLLME	1-(2-pyridylazo)-2-naphtol	Chloroform	Ethanol	Co(II)	Water	577	0.5 μg L^{-1}	2.5	2-50 μg L^{-1}	42
DLLME	4,4′-bis(dimethylamino) thiobenzophenon	[HMIM][Tf_2N]	Aceton	Hg(II)	Water; mineral serum	575	3.9 μg L^{-1}	1.7	12–140 μg L^{-1}	43
DLLME	1-(2-pyridylazo)-2-naphtol	Chloroform	Ethanol	*V*	Ore; water	–	0.79 μg L^{-1}	–	8–180 μg L^{-1}	44
DLLME	*O*-phenanthroline	Chloroform	Methanol	Fe(II), Fe(III)	Water	510	7.5 μg L^{-1}	1.2	0.025–1 μg mL^{-1}	45
DLLME	–	Chloroform	Aceton	Rhodamine 6G	Waste water	530	2.39 ng mL^{-1}	2.88	5–900 ng ml^{-1}	46
DLLME	Methylene Blue (ion pairing agent)	Chloroform	Aceton	Anionic surfactant	Water	650	2 μg L^{-1}	4.5	6–80 μg L^{-1}	47
DLLME	4-benzylpiperidine dithiocarbamat	Chloroform	Ethanol	Cu(II)	Urine; Water	436	0.34 μg L^{-1}	1.39	2–70 μg L^{-1}	48
DLLME	CN^-(complexing) and Astra Phloxine (ion pairing agnet)	Carbon Tetrachloride+Toluene	Methanol	Au(I)	Water	556	–	3.7	0.39–4.7 mg L^{-1}	57
DLLME	Dithizone	Carbon Tetrachloride	Methanol	Cd(II)	Water; Tea; Milk powder	615	0.01 ng L^{-1}	2.6	Up to 2.5 μg L^{-1}	49
DLLME	Diethyldithiocarbamate	Carbon Tetrachloride	Methanol	Cu(II)	Water; Tea; Milk powder	437	0.5 ng L^{-1}	1.9	Up to 200 μg L^{-1}	49
DLLME	Pyrogallol red	[HMIM][Tf_2N]	Acetone	Mo (VI)	Water; Plants leaves	612	1.43 μg L^{-1}	2.8	15–100 ng mL^{-1}	50
DLLME	SDS (ion pairing agent)	Chloroform	Ethanol	Malachite green	Trout fish	620	10^{-8} mol L^{-1}	4.5	Up to 5×10^{-7}	51
DLLME	*p*-dimethylaminobezaldehyde	Chloroform	Methanol	Barbituric acid	Pharmaceuticals; biological samples	468	2 ng mL^{-1}	1.64	5–200 ng mL^{-1}	52
DLLME	Dimethylindoaninearocy	Amyl acetate+ tetrachlorommethane	Acetonitrile	Thiocyanate	Saliva	555	0.11 mg L^{-1}	–	3.13–28.2 mg L^{-1}	60
DLLME	1,2-naphthoquione-4-sulphonic acid	Chloroform	Methanol	Azidirine	Food simulant	430	1.0 ng mL^{-1}	2.5	2.0–350 ng mL^{-1}	53
DLLME	*o*-phthaldialdehyde	Chloroform	Ethanol	Sulfite	Water; Food samples	542	0.2 μg L^{-1}	2.8	2–100 μg L^{-1}	54
DLLME	–	[HMIM][PF_6]	Ethanol	Rhodamine B	Tap Water; Liquid soap; Match tip; Pencil; Textile dye	556	1.05 μg L^{-1}	1.3	5–100 μg L^{-1}	55
DLLME	–	[HMIM][PF_6]	Ethanol	Formal-ehyde	Water; Cosmetics	375	0.02 ng mL^{-1}	2.5	0.1–20 ng mL^{-1}	56
SI-DLLME	Dimethylindoaninearocy	Amyl acetate+t etrachloromwthane	Acetonitrile	Thiocyanate	Saliva	555	0.017 mg L^{-1}	6.5	0.29–5.81 mg L^{-1}	60

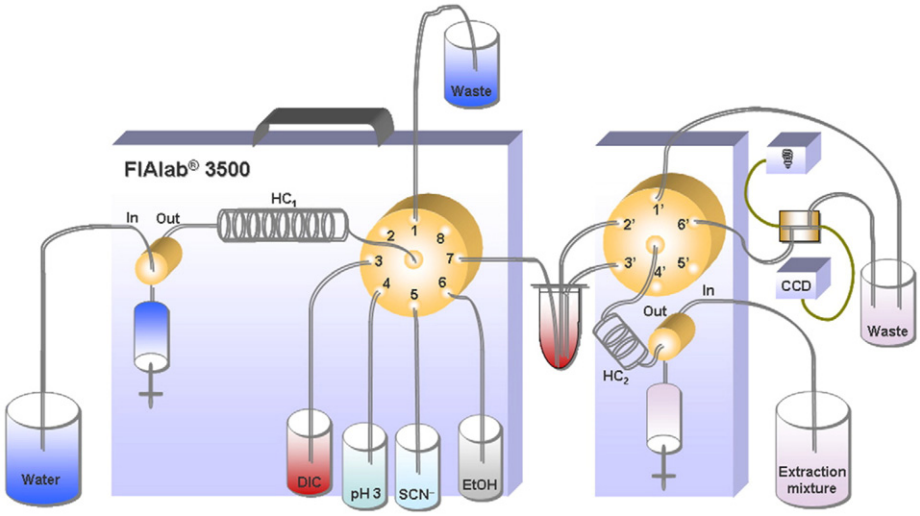

Fig. 3. Automated on-line sequential injection dispersive liquid–liquid microextraction (SI-DLLME) manifold [60].

Zarei and gholamian [52] reported a DLLME procedure for determination of barbituric acid in pharmaceutical formulation and biological samples. The procedure is based on color reaction of barbituric acid with *p*-dimethylaminobenzaldehyde and extraction of the color product using the DLLME technique.

Zarei and his co-workers [53] also applied DLLME for preconcentration of azidirine in food simulants. Their method is based on derivatization of aziridine with Folin's reagent (1,2-naphthoquione-4-sulphonic acid) and extraction of color product.

Filik and Çetintaş [54] reported the preconcentration of sulfite ions from aqueous samples as a prior step to its determination by fiber optic-linear array detection spectrophotometry. The procedure is based on the color reaction of sulfite with *o*-phthaldialdehyde (OPA) in the presence of ammonia to form isoindole and extraction of the formed isoindole derivative using the DLLME technique.

Ionic liquid-based dispersive liquid–liquid microextraction (IL-based DLLME) method has been utilized by Taziki et al. [55] for sensitive determination of trace amounts of rhodamine B in aqueous samples containing very high salt concentrations by fiber optic-linear array detection spectrophotometry (FO-LADS). The method is based on the DLLME of rhodamine B from aqueous solution using ionic liquid. The robustness of microextraction system against high salt concentration (up to 40%, w/v) is increased by introducing a common ion of the ionic liquid into the sample solution.

Spectrophotometry in combination with ionic liquid-based DLLME has been applied by Arvand et al. [56] for determination of formaldehyde in real samples. The method is based on the reaction of formaldehyde with methyl acetoacetate in the presence of ammonia.

It is impossible to use an extractant solvent which has a density lower than that of water in DLLME like toluene, xylene, etc. In order to overcome this shortcoming, a novel approach based on the use of an auxiliary solvent for the adjustment of density presented by Kocurova et al. [57]. The procedure utilizes a solvent system consisting of disperser, extractant, and auxiliary solvents. The suggested approach could be an alternative to procedures which have been devoted for solving the same problem [58,59]. The efficiency of the method is demonstrated through the determination of gold based on the formation of the ion pair $[Au(CN)_2]^-$ anion with Astra Phloxine (*R*) reagent and its extraction using the DLLME procedure with subsequent UV–Vis spectrophotometric and graphite furnace atomic absorption spectrometric detection. A triple solution containing methanol as disperser solvent, toluene as extraction solvent, and CCl_4 as auxiliary solvent was used throughout the experiment.

An interesting approach for sequential injection-DLLME (Fig. 3) has been suggested by Andruch et al. [60]. The method is based on the aspiration and mixing of a sample and all required aqueous reagents in the holding coil, delivering it into a conical tube and adding in a mixture of extraction solvent, auxiliary solvent and disperser solvent, resulting in the formation of a cloudy state and the extraction of an analyte.

2.2.1. *Features of DLLME in combination with UV–Vis spectrophotometry*

Nowadays, the use of DLLME technique and its modified modes in combination with UV–Vis spectrophotometer has became very popular because of its usefulness, high EFs, speed, simplicity, low cost and environmental friendliness. This technique which is available to virtually all analytical laboratories, presents some major benefits such as: the negligible volumes of extraction solvents used; the very large surface area between the fine droplets of the extraction solvent and the aqueous sample; and the accordingly fast extraction kinetics that result in the rapid achieving of a state of equilibrium [61], and the high enrichment factor usually obtained [62]. DLLME can easily be modified for a particular purpose and connected to other sample-preparation techniques [63].

Several shortcomings have been emerged with DLLME. First, there are some limitations related to the choice of extraction and disperser solvents. The extraction solvent has to be denser than water. Since the number of organic solvents meeting this requirement is relatively small, usually hazardous solvents such as halogenated hydrocarbons are used. In some cases, ionic liquids have been applied as green solvents. However, they are too expensive. On the other hand, a suitable disperser solvent has to be miscible with both aqueous and organic phases in order to ensure the formation of the cloudy state that enhances the contact between two phases, thus facilitating extraction. However, at the same time, the disperser solvent can complicate the process of phase separation [62]. Also, one main drawback of DLLME is the consumption of higher volumes (i.e., mL) of disperser solvent. Therefore, the number of extraction solvents and disperser available for use with the method is limited, and the choice of the extraction solvent thus becomes the method's primary drawback.

In additions, centrifugation which is considered to be the method's most time-consuming step needs to be applied in the majority of conventional DLLME procedures. Moreover, centrifugation of larger volumes is simply too difficult to carry out [64]. Another great disadvantage is that the procedure is entirely manual and not yet suitable as a routine applicable on-line preconcentration procedure.

Also, the fundamental theory of DLLME needs further improvement. There is no equation in DLLME for calculating the volume of sedimented phase without further experimental test. Development of equations that show the relationship between the four important factors in DLLME (types and volumes of the extracting and disperser solvents) needs some progress. The performance of DLLME in aqueous samples is excellent; however, it is not yet suitable in complex matrixes such as biological samples. Therefore, it needs further improvement [65].

To overcome these various drawbacks, researchers have offered some useful approaches. For example, solvents with a density lower than that of water can be used. However, instead of collecting of the extraction solvent in the bottom of a conical centrifuge tube, a special narrowed neck tube is used and the extraction phase is collected on the top of solution.

Also, to make the procedure automated, on-line sequential injection dispersive liquid–liquid microextraction (SI-DLLME) has been suggested which offers several important advantages: faster operation in micro-scale analysis, extremely low analysis time, low cost, low consumption of organic solvent, simple manifold (no need of separation unit), high recovery and high enhancement factor [65]. Also, in comparison with conventional DLLME, it offers two important benefits: it is not necessary that the extraction solvent have a density higher than that of water, since the extraction takes place in a moving stream, and the separation of the organic phase is not based on centrifugation, but on retention, and most importantly, the process is fully automated. Although some progress has been made to automate DLLME, but further research is still needed to complete the experiences in this area.

Comparison of DLLME and SDME shows that DLLME is a very simple and rapid method (extraction time is less than 3 min) and has higher preconcentration factor and extraction recoveries [65].

2.3. Cold induced aggregation microextraction (CIAME)

A new mode of homogeneous liquid liquid microextraction technique based on ionic liquids termed cold induced aggregation microextraction (CIAME) was developed by Baghdadi and Shemirani [66]. In this technique (Fig. 4), there is no interface between the water and the extractant phase. After the formation of the extractant phase, a cloudy solution is formed by controlling the temperature. The hydrophobic species are collected by the extractant phase, and the extraction process is complete after the centrifuging of the solution. As a result, mass transfer from aqueous phase into the separated phase has no significant effect on the extraction step. Table 3 gives a list of papers utilizing this technique in combination with UV–Vis spectrophotometry.

They applied this new technique for determination of mercury(II) in real water samples; in which a very small amounts of 1-hexyl-3-methylimidazolium hexafluorophosphate [HMIM][PF_6] and 1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide [HMIM][Tf_2N] (as extractant solvents) were dissolved in a sample solution containing Michler thioketone (TMK, as complexing agent) and triton X-114 (as an anti-sticking agent). Then, the solution was cooled in the ice bath and a cloudy solution was formed. After centrifuging, the fine droplets of extractant phase were settled to the bottom of the conical-bottom glass centrifuge tube. Also, Gharehbaghi and co-workers [67] applied the same method for extraction of cobalt as its complex with PAN from water samples.

2.3.1. Features of CIAME in combination with UV–Vis spectrophotometry

This method is simple, rapid, safe and robust against high content of salt and water-miscible organic solvent. CIAME provides high recovery and has low toxicity since only very small amount of an IL as a "green extraction solvent" is used. In addition, the method offers good sensitivity in comparison to the other combination methods which were used with UV–Vis spectrophotometer as the detection technique [67]. The disadvantages associated with CIAME include the high extraction time, high viscosity of ILs which obligates further dilution (before detection), and high expenses of preparing ionic liquid.

2.4. In situ solvent formation microextraction (ISSFME)

Another mode of homogeneous liquid–liquid microextraction (HLLME) based on ionic liquids termed in situ solvent formation microextraction (ISSFME) was also introduced by Baghdadi and Shemirani [68]. First, a hydrophilic ionic liquid is added to the sample

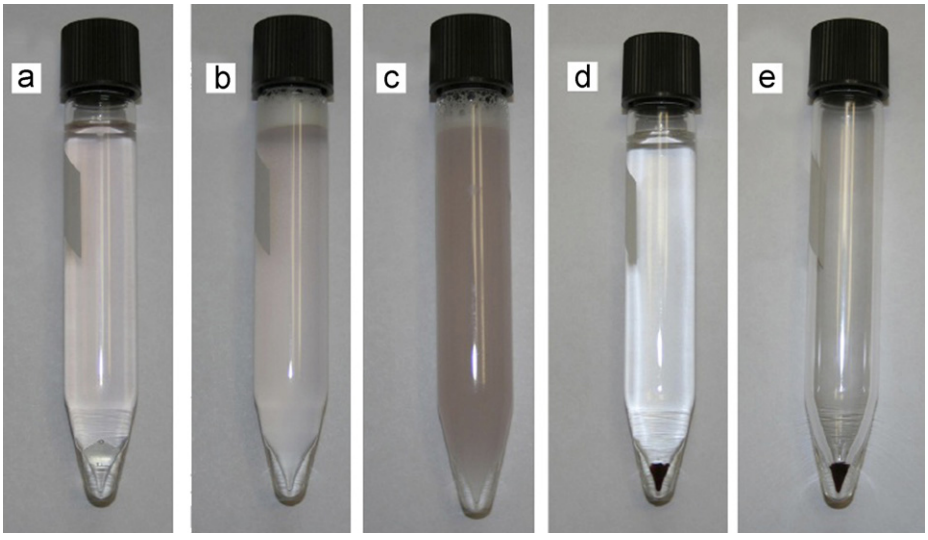

Fig. 4. Photography of different steps in CIAME: (a) after adding ionic liquid in the sample solution, (b) after shaking and dissolving the ionic liquid, (c) after cooling and phase separation, (d) after centrifuging and (e) after removing the bulk aqueous phase [66].

Table 3
Applications of cold induced aggregation microextraction **(CIAME),** in situ solvent formation microextraction **(ISSFME),** modified cold induced aggregation microextraction **(M-CIAME)** and solidified floating organic drop microextraction **(SFODME)** in combination with UV–Vis spectrophotometry.

Extraction technique	Complexing agent	Extractant solvent	Analyte	Sample matrix	λ	LOD	%RSD	Linear range	Ref.
CIAME	4,4′-Bis(dimethylamino) thiobenzophenon	[HMIM][PF_6]+ [HMIM][TF_2N]	Hg(II)	Water	570	0.3 ng mL^{-1}	1.32	Up to 150 ng mL^{-1}	66
CIAME	1-(2-pyridylazo)-2-naphtol	[HMIM][PF_6]+ [HMIM][TF_2N]	Co(II)	Water	570	0.14 ng mL^{-1}	2.32	1.5–65 ng mL^{-1}	67
ISSFME	4,4′-Bis(dimethylamino) thiobenzophenon	[HMIM][BF_4]+ $NaPF_6$	Hg(II)	Water	570	0.7 ng mL^{-1}	1.94	Up to 150 ng mL^{-1}	68
M-CIAME	4,4′-Bis(dimethylamino) thiobenzophenon	[HMIM][BF_4]+ $NaPF_6$	Au(III)	Water	545	0.7 ng mL^{-1}	1.65	1.8–160 μg L^{-1}	69
M-CIAME	4,4′-Bis(dimethylamino) thiobenzophenon	[HMIM][BF_4]+ $NaPF_6$	Pd(II)	Blood; Tea; Water;	530	0.2 ng mL^{-1}	1.7	0.6–10 ng mL^{-1}	70
M-CIAME	1-(2-pyridylazo)-2-naphtol	[HMIM][BF_4]+ $NaPF_6$	Pd(II)	Geological SRM; Seawater;	665	0.4 ng mL^{-1}	2.23	5–100 ng mL^{-1}	71
M-CIAME	4,4′-Bis(dimethylamino) thiobenzophenone	[HMIM][BF4]+ $NaPF_6$	Ag	Photographic waste; Water	530	0.4 ng mL^{-1}	1.8	1–12 ng mL^{-1}	72
USAEME	–	Dichloromethane	Formaldehyde	Cosmetics	410	0.02 μg g^{-1}	5.9	–	77
USAEME	–	[C_6MIM][PF_6]+SDS	Triclosan	Cosmetics	372	0.018 μg g^{-1}	2.6	0.5–200 μg g^{-1}	78
USAEME	–	[C_6MIM][PF_6]+SDS	Triclosan	Wastewater	372	0.005 μg mL^{-1}	1.7	0.02–0.18 μg L^{-1}	78
SFODME	8-Hydroxyquinoline	1-Undecanol	V(V)	Water samples	383	0.97 μg L^{-1}	3.9	3–100 μg L^{-1}	83
DLLME-SFO	2-Thenoyltrifluoroacetone	1-Undecanol+ Ethanol (disperser)	Fe(II), Fe(III)	Power plant; Drum water	–	Fe(II): 25 μg L^{-1} Fe(III): 8 μg L^{-1}	Fe(II):4.2 Fe(III):3.9	Fe(II): 95–1070 μg L^{-1} Fe(III): 31–380 μg L^{-1}	84

solution. Then, a sparingly soluble ionic liquid (extractant phase) is formed in situ by addition of a suitable salt as an ion-pairing agent. The extraction process is completed after the formation and centrifugation of fine droplets of the extractant phase. Indeed, in this case as the previous one, mass transfer from aqueous phase into separated phase has no significant effect on the extraction step. In this section, the applications of ISSFME with UV–Vis spectrophotometry are reviewed (Table 3). This method was applied for determination of mercury(II) in water samples. Sodium hexafluorophosphate ($NaPF_6$, as an ion-pairing agent) was added to the sample solution containing 1-hexyl-3-methylimidazolium tetrafluoroborate ([HMIM][BF_4], as hydrophilic ionic liquid). A cloudy solution was formed as a result of formation of fine droplets of [HMIM][PF_6] and mercury is extracted as Hg-TMK. After centrifuging, the fine droplets of the extractant phase was settled at the bottom of a conical-bottom glass centrifuge tube [68].

In 2010, Mahpishanian and Shemirani [69] proposed an alternative extraction method based on the combinations of ISSFME and CIAME, namely, modified cold-induced aggregation microextraction (M-CIAME); in which, excess sodium hexafluorophosphate ($NaPF_6$) was used in order to decrease the solubility of IL-phase in saline solutions. The method was applied for determination of gold in saline solutions in which $NaPF_6$ was added to the sample solution containing Au-TMK complex and 1-hexyl-3-methylimidazolium tetrafluoroborate [HMIM][BF_4].

At the same time, this technique was used by Vaezzadeh and co-workers [70] for determination of palladium in high salts content solutions. In this research, palladium species is extracted into ionic liquid as its Michler thioketone (TMK) complex.

Also, Zarei and Shemirani used this technique for determination of palladium in saline solution. 1-(2-pyridylazo)-2-naphtol (PAN) was chosen as the complexing agent [71].

The extraction of silver was preformed by Vaezzadeh et al. [72] in the presence of 4,4'-bis(dimethylamino)thiobenzophenone (TMK) as the complexing agent.

2.4.1. Features of ISSFME in combination with UV-Vis spectrophotometry

The merits of this method include low organic reagent consumption and easy operation. In comparison with DLLME, no pure disperser solvent is used which can reduce the extraction recovery. Furthermore, in order to have a cloudy system; no syringe is required. In comparison with CIAME, ISSFME is faster and simpler and is applicable for solutions containing higher concentrations of salt. In the presence of high contents of salts, the solubility of ionic liquids increases and phase separation cannot occur. However, according to the common ion effect, the solubility of ionic liquids decreases in the presence of excess $NaPF_6$. Consequently, the volume of the extractant phase does not alter. This is one of the interesting properties of ionic liquids. Because of the high density of ionic liquids, even in saturated solutions (40%, w/v) the fine droplets of extractant phase can settle.

2.5. Ultrasound-assisted emulsification microextraction (USAEME)

Combination of microextraction systems and ultrasound (US) radiation provides an efficient preconcentration technique such as ultrasound-assisted emulsification microextraction (USAEME) for determination of analytes at trace levels. This technique was first developed by Regueiro et al. [73]. The US radiation is an efficient tool to facilitate the emulsification phenomenon and accelerates the mass-transfer process between two immiscible phases, leading to an increment in the extraction efficiency of the technique in a minimum amount of time [74,75]. In addition, the use of ultrasound energy eliminates the need for a disperser solvent, commonly used in DLLME [76].

Utilization of USAEME in combination with spectrophotometric detection (Table 3) was proposed by Lavilla et al. [77] in 2010, who applied the in situ derivatization for determination of formaldehyde in very complex matrices such as cosmetics. The use of a powerful ultrasound source promotes the mass transfer between the involved phases as well as the Hantzsch reaction which is employed for analyte derivatization. The proposed methodology involves an important miniaturization of the European official method of analysis of formaldehyde in cosmetic products as well as an important improvement in sample throughput. Taking into account the tedious sample treatments usually involved, a simplified sample treatment is reached. Also, high sensitivity is obtained as a result of the 34-fold enrichment factor (Table 4).

Table 4
Application of hollow fiber liquid liquid microextraction **(HFLLME)** in conjuction with UV–Vis spectrophotometer.

Extraction technique	Organic phase	Acceptor phase	Analyte	Sample matrix	λ	LOD	%RSD	Linear range	Ref.
HFLLME	Dibutylbutylphosphat + tributyl phosphate	Alkaline water	As(V)	Water	840	27 μg mL^{-1}	< 3.0	200–2000 μ g L^{-1}	88
HFLLME	Dodecanol	Alkaline water	Carbamate pesticide	Vegetable	245	1 ng mL^{-1}	2.7	0.0033–1 μ g mL^{-1}	89

Another report on USAEME procedure in conjuction with microvolume UV–Vis spectrophotometry has been accomplished by Cabaleiro et al. [78] for triclosan determination in cosmetic and wastewater samples. A diazotation reaction was simultaneously developed in order to quantify the yellow azo-derivative formed. The enrichment factor of 180 was achieved for wastewater using a 7 mL sample.

2.5.1. Features of USAEME in combination with UV-Vis spectrophotometry

The method is easy, simple, and an equilibrium liquid-phase microextraction. No disperser solvent is used in this method, and the amount of organic solvent is minimized, both of which contribute to the low level of pollution [79]. Sonication provokes the dispersion of organic extractants into the aqueous phase as fine droplets that accelerate the the mass transfer (of analyte) between the involved phases [77]. In comparison with conventional DLLME, higher extraction times and more expensive equipments are needed.

2.6. Solidified floating organic drop microextraction (SFODME)

In 2007, Khalili Zanjani and co-workers [80] introduced Solidified floating organic drop microextraction (SFODME) as a new microextraction method. In this method, a droplet of an immiscible organic solvent (extractant solvent) is floated on the surface of an agitated aqueous sample. The organic solvent must have a melting point in the range of 10–30 °C. The vial is then transferred into an ice bath and after a short period of time, the extractant solvent is solidified and transferred into a small conical vial using a small spatula [80–82].

Combination of this microextraction technique with UV–Vis spectrophotometry has been proposed by Dadfarnia et al. [83] for determination of vanadium in water samples. 8-Hydroxyquinoline (oxine) was used as the chelating agent and 1-undecanol applied as extracting solvent.

Rohani Moghadam et al. [84] proposed a new technique on the basis of SFOME and DLLME for speciation of iron in water samples. In this method, an appropriate mixture of ethanol (as the disperser solvent) and 1-undecanol (as the extracting solvent) containing appropriate amount of 2-thenoyltrifluoroacetone (TTA, as complexing agent) was injected rapidly into the water sample containing iron(II) and iron(III) species. At this stage, a cloudy solution containing many dispersed fine droplets of TTA in 1-undecanol was formed which was then centrifuged. The extracting solvent droplets floated on the surface of the aqueous solution due to their low density. The vial was transferred into an ice bath and the organic solvent was solidified.

2.6.1. Features of SFODME in combination with UV–Vis spectrophotometry

In SFODME the solvent needs to melt near the room temperature (e.g., 1-undecanol and 1-dodecanol) [38] which limits the choice of extraction solvent. In comparison with single drop microextraction, higher stirring rates are possible in SFODME, since no holder is required for the organic microdrop [81].

Combination of SFO with DLLME solves some of problems. In comparison with DLLME, DLLME-SFO uses lower toxicity solvents and has higher extraction recovery. Further, it is cheap and has higher preconcentration factor [65]. In addition, higher extraction time is needed in comparison with DLLME.

2.7. Hollow fiber based liquid phase microextraction (HF-LPME)

To avoid the drop instability in SDME, HF-LPME was introduced in 1999 by the hand of Pedersen-Bjergaard and Rasmussen [85] as a LPME technique in which analytes are firstly extracted into a supported liquid membrane (SLM) sustained in the pores of a hydrophobic porous HF, and later into an acceptor solution placed inside the lumen of the fiber. HF-LPME modes can be classified according to the number of phases involved in the system into two-phase or three-phase HF-LPME [86].

Membrane extraction has been evolved to be a viable alternative to conventional sample preparation. It facilitates extraction without the mixing of two phases, thus eliminating emulsion formation and the need for high solvent usage. An important advantage of a membrane process is that a sample and an extractant can be in contact continuously, thus providing the basis for a continuous, real-time process leading to automation and on-line connection to instruments. Conventional membrane extraction modules can be fabricated using hollow fibers or flat sheets, the former having a tubular geometry. Each shape has its intrinsic advantages, and the module designs are based on the membrane geometry. Typical hollow fiber modules are fabricated in a shell and tube design with multiple parallel fibers to provide high packing density [87]. These modules offer the advantage of providing higher surface area per unit of volume compared to their flat counterparts.

A micro-fluidic membrane extraction using a conventional hollow fiber membrane was used for continuous, on-line extraction of arsenic by Hylton and Mitra [88]. In this procedure, a polypropylene hollow fiber was soaked in dibutylphosphonate (DBBP)/tributyl phosphate (TBP) (90:10, v/v) mixture and then placed in the channel of the microfluidic extractor, and the ends were attached to the respective inlets and outlets. A syringe filled with acceptor solution (NaCl) was attached to the inlet of the fiber lumen which was flushed to remove excess of the organic extractant. The donor was pumped through the microfluidic channel around the hollow fiber and the acceptor was pumped through the fiber lumen which was finally collected. Arsenic detection was carried out using a spectrophotometric method employing the colorimetric reagent molybdenum blue.

There is also the procedure of Fu and co-workers [89] who proposed a simple, convenient, sensitive, and environmentally friendly analysis method for carbamate pesticide residues in vegetable samples by using electrokinetic flow analysis (EFA) with on-line hollow fiber liquid–liquid–liquid microextraction (LLLME) and ultraviolet spectrophotometry (UV). Carbamate pesticides in a sample solution were extracted into the dodecanol phase immobilized on the hollow fiber and back-extracted into the alkaline solution inside the hollow fiber. The high enrichment

factor of 300 was obtained by introducing 5 mL of sample solution within 22 min.

2.7.1. Features of HF-LPME in combination with UV–Vis spectrophotometry

The major advantage of this technique is that the sample may be stirred or vibrated vigorously without any loss of the extracting liquid because it is mechanically protected [90]. Moreover, there is a remarkable clean-up efficiency because high molecular mass compounds cannot pass through the membrane barrier. Also, it is suitable for inorganic and organic analytes over a wide range of polarity [91–94].

Compared with DLLME, when dealing with more complicated matrices such as soil and beverage samples, HF-LPME proves to be more useful than DLLME. Also, the repeatability of HF-LPME is better than that of DLLME [65]. The advantages of DLLME over HF-LPME include short extraction time and suitability for simultaneous treatment of batches of samples. In addition, a higher extraction recovery is obtained by DLLME in comparison with HF-LPME.

3. Prospects and trends

Microextraction methods have been used in combination with various analytical instruments. Although, the preferred analytical technique is gas chromatography, they have been also combined with high performance liquid chromatography, inductively coupled plasma, mass spectrometry, graphite furnace atomic absorption spectrometry, flame atomic absorption spectrometry, capillary electrophoresis and very recently, with different molecular spectroscopic techniques, namely, UV–Vis spectrophotometry, fluorospectrometry, and infrared spectroscopy. UV–Vis spectrometry has become a widespread analytical technique due to its inherent features (e.g., availability, simplicity, ease of operation, convenience, economy, precision and accuracy). Combinations of UV–Vis spectrophotometric detection system with microextraction techniques whose main advantages are their speed and negligible solvent volume use has been overviewed in this work. Integration of these unique advantages with the advantages of UV–Vis spectrophotometry provides a powerful tool in chemical analysis. Single drop microextraction (SDME), dispersive liquid–liquid microextraction (DLLME), cold induced aggregation microextraction (CIAME), in situ solvent formation microextraction (ISSFME), ultrasound assisted emulsification microextraction (USAEME), solidified floating organic drop microextraction (SFODME), and hollow fiber based liquid phase microextraction (HF-LPME) are the microextraction techniques which have been used in conjunction with UV–Vis spectrophotometry to date for determination of various organic and inorganic species in different matrices. DLLME and SDME are the approaches which have been widely used. Due to its better compatibility with UV–Vis spectrophotometry, LPME has gain more attention in comparison with solid phase microextraction (SPME) and it is expected to be an important future sample preparation technique.

Miniaturization of detection systems is a challenge that has been met with different degrees of success in analytical chemistry. Work in this area is in progress, and the near future should produce some commercial equipment for LPME. This equipment should be fully automated and compatible with common laboratory robotics and auto-samplers [90]. More developments are expected to be evolved in the near future which might be as follows: (a) introduction of new microextraction techniques which would not require centrifugation as a necessary step to reduce the cost and time of analysis; (b) application of microextraction system as online with the detection system; (c) miniaturization of detection systems to prevent from additional dilution in order to increase the method sensitivity; (d) the application of chemometrics approaches to decrease the effects of interferences and thus to increase the selectivity. Therefore, the research in this field and quest for combination of new microextraction techniques is still being continued.

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