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Latest trends, green aspects, and innovations in liquid-phase–based microextraction techniques: a review

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Abstract: Liquid-phase microextraction (LPME) methods including single-drop microextraction (SDME), hollow-fiber LPME (HF-LPME), and dispersive liquid-liquid microextraction (DLLME) have in the very short time since their invention grabbed the attention of scientists. Up to now, LPME methods have shown important innovations for the extraction and preconcentration of both inorganic and organic trace analytes from different matrices. These LPME methods offer unique advantages such as high preconcentration factor for target analytes in a single step, low cost, simplicity, excellent preconcentration capability, sample cleanup and integration of steps, and combined use with almost every analytical measurement technique. We describe the milestones and the combined use of different types of LPME methods as well as the green aspects and advantages and shortcomings of known LPME protocols. In addition, we discuss the main results and innovations of different types of LPME published in the period 2010–2016 and we compare the performance of these techniques to that of other recent techniques.

Key words: Separation, preconcentration, liquid-phase microextraction, solvent microextraction, sample preparation, green chemistry, green solvent

1. Introduction

The sample pretreatment process has a special role in chemical analysis, especially for the separation, preconcentration, and determination of analytes from complex matrices.[1–3] Despite important developments in analytical measurement systems and applications in recent years, sample pretreatment is frequently required prior to instrumental detection of analytes, especially for trace analytes in complex matrices, which show potential interference effects in the determination of trace analytes.[4–6]

A number of sample preparation methods have been used for the separation and preconcentration of trace analytes, such as liquid–liquid extraction (LLE), solid phase extraction (SPE), co-precipitation, and cloud point extraction (CPE).[4–8] However, these methods have the following important disadvantages: (1) the need for volumes of potentially toxic solvents that are often toxic because of their high vapor pressure, (2) their producing secondary wastes during the process, (3) the need for large and complex equipment, (4) their requiring time consuming, tedious, and multistage operations, (5) their having insufficient sensitivity for trace analysis, and (6) their using large amounts of real samples.[9–11]

In order to overcome the disadvantages mentioned above, many green methods based on principles of green analytical chemistry have been developed in recent years, and scientific journals have published

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guidelines or recommendations regarding green analytical chemistry practice in research and applied laboratory applications.[12,13] Considering the twelve principles of green analytical chemistry, in recent years, current trends in sample pretreatment have led to the introduction of new types of liquid-phase microextraction (LPME) methods such as single-drop microextraction (SDME), hollow-fiber LPME (HF-LPME), and dispersive liquid-liquid microextraction (DLLME).[14–17] These techniques are cheap and quick and useful when selecting suitable solvents and apparatus for the effective extraction of different analytes. Since microliter solvent is used, interaction with the toxic solvent is limited.[14] Moreover, they combine separation, preconcentration, and sample introduction in one step.[15] The most significant advantage of these methods is that almost all of the microliter volumes of the organic extraction phase can be introduced into the detection systems while only limited volume of the concentrated solvent is introduced in conventional preconcentration and extraction methods. LPME methods are not detailed, and only a small part of the analytes is extracted/preconcentrated for measurements.[14–17] Efforts to find innovative and simpler applications in LPME are continuing and an average of over a hundred papers each year are published.

During the last decade or so (2002–2016), there has been a dramatic increase in the number of scientific articles on LPME methods. Among them, there are approximately 1200 papers on LPME methods for the determination of organic and inorganic analytes (Figure 1a). Almost 61% of them were published in the last five years. Furthermore, more than 70% of these articles have suggested techniques for the determination of organic compounds and metabolites, whereas only 25% have proposed techniques for inorganic analytes. In these procedures, different detection systems have been used. The % proportional distribution of the measurement systems including LC, GC, HPLC, AAS, ICP-MS, ICP-OES, CE, UV-VIS, MALDI-MS, and LIBS are 29%, 25%, 19%, 10%, 6%, 5%, 4% 2%, 0.5%, and 0.4%, respectively (Figure 1b).

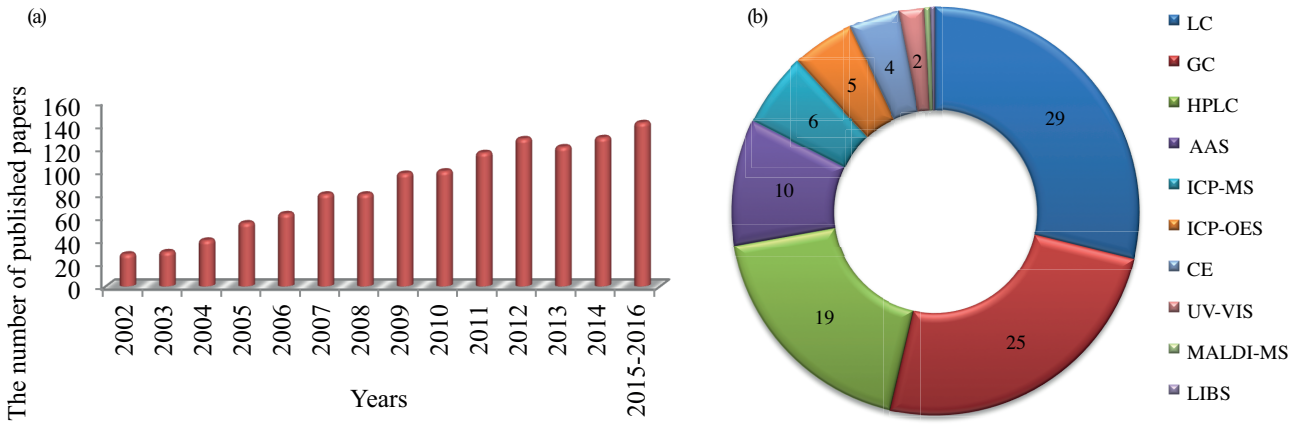

Figure 1. (a) Evaluation of number of publications concerning the combination of LPME methodologies (Source: Web of Science; Keywords: Liquid phase microextraction, liquid-phase microextraction, liquid-liquid microextraction, liquid liquid microextraction, liquid phase based microextraction, liquid phase based solvent microextration, LLME, LPME, LL-ME, LP-ME, Single-drop microextraction, Single drop microextraction, Hollow fiber based LPME, Hollow fiber based Liquid phase microextraction, hollow fiber Liquid phase microextraction, Dispersive liquid–liquid microextraction, Dispersive liquid liquid microextraction). (b) The % proportional distribution of the measurement systems used with different types of LPME.

This review is focused on the recent developments, variations, and innovations in LPME coupled with different detections systems over the five-year period 2010 to 2016 for the preconcentration and sequential determination of analytes in different samples. During this period, more than 700 papers based on LPME have been published. At the same time, we compared the performance of these techniques to that of other recent techniques.

1.1. Classification of LPME

1.2. Single-drop microextraction (SDME)

Single-drop microextraction (SDME) is one of the most commonly used and simplest types of LPME methods.[18] This technique is applied for the extraction of analytes from an aqueous solution by forming an acceptor single liquid drop, replacing the coated fiber. After extraction, the drop is withdrawn and analyzed by suitable spectroscopic and chromatographic techniques (AAS, ICP-MS, AES, AFS, GC, LC, HPLC, LC-MS, GC-MS, CE, etc.). This is shown in Figure 2.

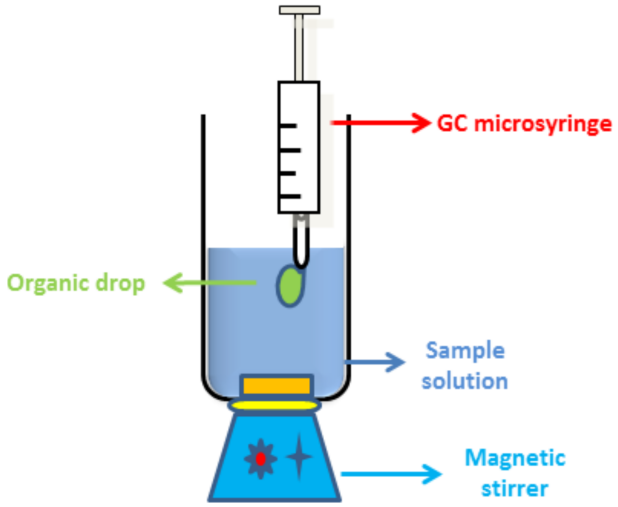

Figure 2. Direct immersion single-drop microextraction.

The method is based on the distribution ratio of the target analyte between a microvolume single drop of extraction solvent on the tip of either a Teflon rod or the needle tip of a microsyringe and a sample solution. Hence, this mode of liquid-phase microextraction is named SDME.[19,20]

The application of a single drop as an acceptor phase for analytes can be traced to the study by Dasgupta in the mid-1990s. In that study, a liquid was used to extract sodium dodecyl sulfate from the aqueous sample solution.[21]

The first SDME technique directly combined with chromatographic determination was developed by Cantwell's research group. They used a Teflon rod with a spherical recess to hold an 8-μL single drop of octane immersed in a stirred sample solution and this method was termed solvent microextraction (SME).[22] After extraction, the rod was removed, and a GC syringe was used for the sampling and injection of the single drop solvent into a GC.

In their other paper,[22] for the first time, they used a GC syringe needle to keep the extraction phase on the surface of the sample solution and inject the extraction phase ion into the GC. SDME provides wonderful

advantages such as high extraction capability, short extraction time, low cost, simple operation, and no need for special apparatus.

One of the developments introduced to SDME is the use of ionic liquids (ILs) as extraction solvents, which let the use of stable large drop, thus increasing extraction efficiency.[23] ILs show some good and significant physicochemical properties, like good extraction capacity for inorganic and organic analytes, non-flammability and negligible vapor pressure, analytes.

Liu et al. reported the first study regarding the use of ILs in SDME. In this report, IL based SDME coupled with HPLC was applied for the preconcentration and analysis of polycyclic aromatic hydrocarbons.[24] Because of the unique features of ILs, the use of IL has increased rapidly with each passing day as a green alternative to organic solvents in LPME methods.[24,25] The modes of SDME can be broadly classified as direct immersion SDME (DI-SDME), head space SDME (HS-SDME), and continuous flow microextraction (CFME).

1.2.1. DI-SDME

In DI-SDME, a drop (0.3–3.0 μL) of a water-immiscible extraction solvent phase is suspended directly from the tip of a microsyringe needle immersed in the aqueous sample. The equipment used in DI-SDME is as follows: an extraction vial with a septum cap, a small volume of extracting solvent, a stir bar, a magnetic stirrer, and a microsyringe.[26] A simple DI-SDME apparatus is illustrated in Figure 2. The important advantages of DI-SDME are the simplicity of the apparatus used, low cost, low volume of extraction solvent, and low amount of sample needed for analysis.[27,28] An important feature of this method is that it is also easily and completely automated with spectroscopic (AAS, ICP-MS, ICP-OES, HPLC-ICP-MS, etc.) and chromatographic (GC, LC, LC-MS, HPLC, etc.) determination techniques with software.[29] Automation has also been achieved with sequential injection manifold systems.[29]

DI-SDME can be used in two different modes (static and dynamic modes) for the extraction and determination of different types of hydrocarbons. The advantages mentioned above make it a very green analytical procedure. The unstableness of the droplet at high stirring speeds and in complicated matrix samples is the most important disadvantage of DI-SDME.[30] Hence, careful and elaborate manual operations are required. Typical stirring rates for this method are lower than 1000 rpm. This problem can be solved by making some alterations such as modification of the needle tip and use of a 1-μL microsyringe in place of a 10-μL one. However, the organic drop is still not resistant for a stirring speed of more than 1700 rpm.[31] This negative situation causes the slowing of analyte transfer from the aqueous phase to the extraction phase because of the low diffusion coefficients in liquids. This leads to a lengthening of the extraction time in DI-SDME compared to other SDME methods.[30,31]

1.2.2. Headspace SDME (HS-SDME)

In 2001, Theis et al. reported a single-drop microextraction procedure termed headspace solvent microextraction (HSME) or more usually headspace single-drop microextraction (HS-SDME).[32] The working principle of HS-SDME is similar to that of DI-SDME but the extractor drop is held above the aqueous sample solution (Figure 3). The HS-SDME method is preferred to DI-SDME and is applied for the extraction of volatile and nonvolatile analytes from different matrices.[33,34]

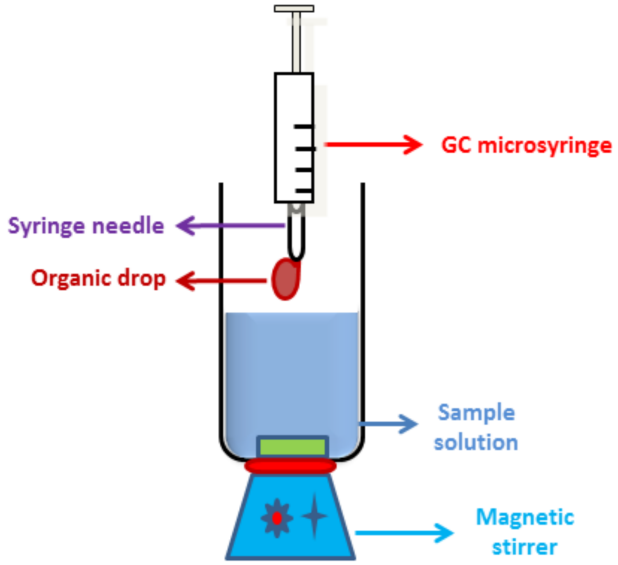

Figure 3. Headspace single–drop microextraction.

In HS-SDME, a drop of extractor is formed and the aqueous sample solution is stirred (∼1000 rpm). The extraction of target analytes is performed by suspending a microliter drop of an extractor from the tip of a microsyringe situated in the headspace of a sample. The extraction system is heated at a suitable temperature for a certain time. The drop, which stands at the tip of the microsyringe along the extraction period, interacts with the analytes in the sample solution.[35,36] Then the drop is drawn off into the syringe after extraction and the derived analytes in the extraction phase are analyzed with an instrumental technique.

In the HS-SDME procedure, the analytes are distributed among three phases: the headspace, water sample, and organic drop.[35,36] The rate determining step is the analyte mass transfer, which means that a high stirring speed of the sample solution usually has a positive influence on the extraction performance.[35–37]

HS-SDME provides many unique features such as removal of interference of a dirty or complex matrix and particulate matter, and being independent from the limitations on sample stirring rate and on extractor phase. Nevertheless, the solvent should not be very volatile as evaporation is a faster procedure in the headspace than in the immersed position of the drop. HS-SDME is also affected by some of the same limitations as DI-SDME as follows: drop dislodgement, limited extractor volume, volatility of extraction solvent, and low preconcentration factors for semivolatile analytes.[37–39]

1.2.3. Continuous-flow microextraction (CFME)

In 2000, Liu and Lee reported a new dynamic SDME procedure called continuous-flow microextraction (CFME). In this procedure, a microdrop extraction solvent is put into a glass chamber by using a conventional microsyringe and kept at the outlet tip of a PTFE connecting tube.[40] An aqueous sample solution flows continuously at 0.05 mL/min or above flow rate by using an HPLC solvent delivery system.

The extraction drop is then moved to the outlet of the PEEK tubing (within the chamber), where it remains. The sample solution is continually flowed "around" the extraction drop for the extraction of analytes from the aqueous sample to the extraction drop phase. After extraction, in order to collect the extraction drop, a microsyringe needle is introduced into the chamber.[40,41]

1.3. Hollow fiber-based LPME (HF-LPME)

To solve the drop instability problem in SDME, in 1999, Pedersen-Bjergaard and Rasmussen reported a different LPME notion called hollow fiber-based liquid phase microextraction (HF-LPME).[42] For the first time, the authors utilized the basic basis of the supported liquid membrane (SLM) in simple, cheap, disposable extraction units utilizing commercial polypropylene HFs as the membrane. In this procedure, the microvolume of the extractor solvent is contained within the lumen of a porous hollow fiber. Therefore, the extraction solvent is not in direct contact with the sample solution. In the first step, the HF is sucked in the hydrophobic extraction liquid, which results in the formation of a thin layer within the wall of the HF.[42,43] The HF is then put into a sample vial including sample solution. The sample solution can be vibrated vigorously or stirred without any loss of the extraction solvent due to the mechanical protection of extraction solvent in the lumen and the sample and extraction solutions can be in contact continuously. Analytes are firstly extracted into a supported liquid membrane (SLM) sustained in the pores of a hydrophobic porous HF, and later into an extraction solvent fitted inside the lumen of the fiber.

The introduction and collection of the extraction solvent placed inside the lumen of a porous HF are carried out by two needles (Figure 4).[44] The procedure provides major advances like high extraction yield, effective mass transfer, and applicability for a constant, real-time process leading to on-line connection and automation with the detection systems.

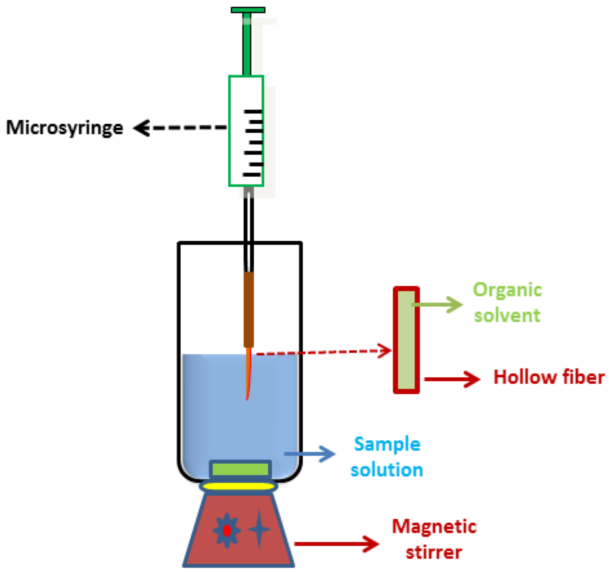

Figure 4. Hollow fiber-based LPME.

HF-LPME can be applied in two-phase and three-phase mode. In two-phase mode, the acceptor phase is the same extraction phase and the analytes are extracted in an extraction phase that is coupled with a GC. However, in three-phase mode, the acceptor solvent is another aqueous solvent, and the target analytes are extracted from an aqueous sample through the thin film of the extraction solvent into an aqueous acceptor solvent. Hence, this method is combined with different instrumental techniques.[44,45]

1.4. Dispersive liquid–liquid microextraction (DLLME)

In 2006, Rezaee and co-workers developed a novel, rapid, economical, environmental, and powerful microextraction method called dispersive liquid–liquid microextraction (DLLME) for the first time.[46] This method has attracted considerable attention from scientists because of the wide range of applications for organic and inorganic analytes in different samples.[47,48] The basis of the method is the use of a ternary solvent component system consisting of an aqueous phase, an apolar extraction solvent, and a polar water miscible solvent named a dispersive solvent.

This method involves a ternary solvent system in which a small volume of extraction solvent and dispersive solvent is rapidly added to the aqueous analyte solution.[49–51] After shaking the mixture by different techniques such as manual, vortex, magnetic stirring, up-and-down-shaker, and air-assisted, a cloudy solution consisting of fine droplets of extraction solvent fully dispersed in the aqueous phase is created.[51–54] The schematic illustration is shown in Figure 5.

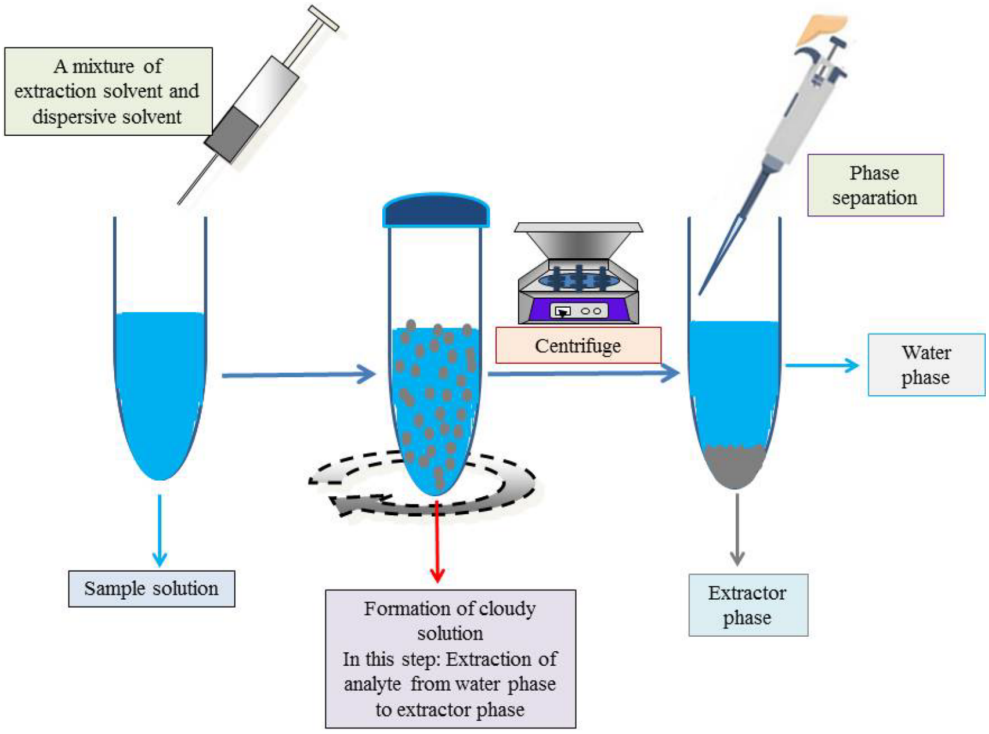

Figure 5. Schematic illustration of DLLME.

The surface area between the aqueous phase and the extraction phase becomes extremely large, and hence rapid, efficient mass extraction occurs. The dispersion is removed by centrifugation and the extraction phase containing analytes is collected with a micropipette or microsyringe and analyzed.[47–56]

The most important parameters are the selection of extraction and dispersive solvents for the extraction of analytes. A suitable dispersive solvent has to be miscible with both extraction and aqueous phases for the generation of the cloudy solution that increases the interaction between the two phases and the interactions cause high extraction efficiency.

Ethanol, methanol, acetone, and acetonitrile are generally used as dispersing solvents. The extraction solvent has to be insoluble in the aqueous phase while it has to be soluble in dispersive solvent. After extraction,

in order to achieve phase separation, the density of the extraction solvent has to differ greatly from the density of the aqueous phase.[47–56]

Different types of extraction solvents such as CCl_4, $CHCl_3$, and CS_2, which are denser than water, are most usually used because phase separation is simple by sample centrifugation. However, the number of them is limited and the requirement to eliminate toxic solvents, like chlorinated hydrocarbons, has led to the search for new types of solvents to be used in DLLME.

Many developments have been introduced to the normal DLLME to increase extraction efficiency, make the method completely free from toxic organic solvents, make it suitable for combined use with a wide range of measurement techniques, and eliminate the matrix effect of co-existing ions in the sample solution. The innovations are shown in Figure 6. In the next parts of this section, we will describe briefly the improvements made in DLLME.

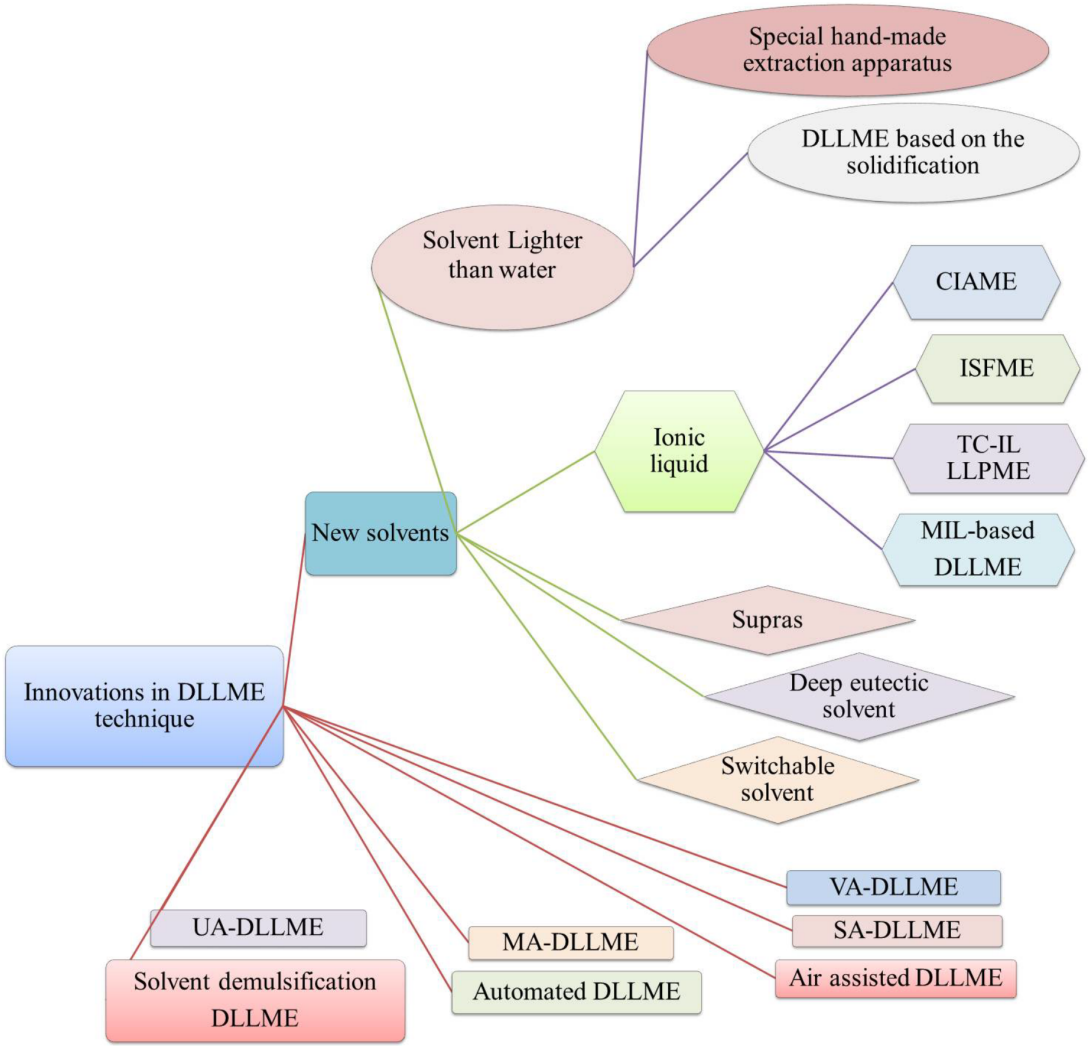

Figure 6. Novel solvents and innovative methodologies in the field of DLLME.

As an alternative, the new type extraction solvents such as organic solvents lighter than water,[57] ionic liquids (IL),[54] supramolecular solvents (SUPRAs),[58] deep eutectic solvents (DESs),[59] and switchable solvents

(Ss)[60] have led to the development of the new liquid phase microextraction techniques discussed below. One possible route of enabling the utilization of such solvents in DLLME is the use of assisting extraction steps such as shaking, stirring, temperature, vortex, and ultrasound radiation.[51−54,61] These special steps are used to obtain a fine cloudy solution and the acceleration of the emulsification of microliter volumes of extraction solvents in aqueous solutions, and they speed the analyte transfer between the sample and extraction phases and reduce the extraction time. Hence, the resulting innovative designs and methodological approaches were developed in DLLME (Figure 6), e.g., ionic-liquid–based dispersive liquid–liquid microextraction (IL-DLLME),[62] solidified floating organic drop dispersive liquid–liquid microextraction (SFO-DLLME),[63] supramolecular solvent-based dispersive liquid–liquid microextraction (SUPRAs-DLLME),[58] deep eutectic solvent-based dispersive liquid–liquid microextraction (DES-DLLME),[59] and switchable solvent-based dispersive liquid–liquid microextraction (Ss-DLLME).[60] In these DLLME methods, various dispersion methods have been used for mixing the extraction solvent and sample solution (Figure 6), e.g., ultrasound-assisted dispersive liquid–liquid microextraction (USA-DLLME),[64] vortex-assisted dispersive liquid–liquid microextraction (VA-DLLME),[65] air-assisted dispersive liquid–liquid microextraction (AA-DLLME),[66] magnetic stirring-assisted dispersive liquid–liquid microextraction (MSA-DLLME),[67] and microwave-assisted dispersive liquid–liquid microextraction (MWA-DLLME).[68] One of the improvements in DLLME is the use of organic solvents (e.g., 1-dodecanol, 1-undecanol, and hexadecanol) that are lighter than water as extraction solvents.[57]

In 2007, Khalili Zanjani et al. suggested solidified floating organic drop microextraction (SFODME) as a novel DLLME procedure that uses less dense extraction solvents (e.g., 1-dodecanol, 1-undecanol, and hexadecanol) than water.[67] In this procedure, a mixture of extractant solvent (a melting point near room temperature) and dispersive solvent is injected into the aqueous phase. The mixture is then centrifuged.[67−69] A droplet of extractor phase floats on the surface of the aqueous sample because of its low density. The sample is then put in an ice bath to make the SFO easy due to its lower melting point. Then the solidified droplet is transferred to a conical vial by a small spatula, rapidly melted, and introduced into the analytical instrument for analyte determination.[68,69]

In 2009, Farajzadeh and coworkers reported a new DLLME procedure for the preconcentration of organophosphorus pesticides by using extraction solvent that is lighter than water.[57] In this procedure, the extraction is performed in special extraction devices. A mixture of cyclohexane as extractor and acetone as dispersive solvent was injected into the sample solution and this led to the formation of the cloudy state. Then the extraction phase was collected at the top of the water phase by centrifugation, elevated to the narrow side of the extraction vessel, collected by a microsyringe, and analyzed with GC-FID.[57]

One of the developments introduced to DLLME is the utilization of ionic liquids as extraction solvents. The utilization of ILs in DLLME was first reported by Zhou et al.[70] and Baghdadi and Shemirani.[71] However, the first description of the conventional IL-DLLME was reported by Liu et al.[72] for the preconcentration and separation of heterocyclic insecticides in water prior to HPLC-DAD determination. IL ($C_6MIm\text{-}PF_6$) was used as the extractor and methanol as the dispersive solvent.

The use of ultrasonic radiation in ultrasound-assisted liquid-liquid methods (USA-LLE) was reported by Luque de Castro and Priego-Capote for the first time for extraction of some polar and nonpolar compounds in solid plant samples.[73] Regueiro and coworkers used a miniaturized technique in USA-LLE for the microextraction of emergent contaminants and pesticides in environmental waters by using a microvolume of extraction solvent to supply the benefits of both DLLME and USA-LLE.[74] The method was termed ultrasound-assisted

emulsification–liquid–liquid microextraction (USAE-LLME) and used as a simple and effective separation and preconcentration method for organic analytes in sample solutions.[74] Another DLLME method is vortex-assisted emulsification liquid–liquid microextraction (VA-ELLME).[75] In this approach, the emulsification is formed by physical mixing agitation. Vortex agitation is cheaper than ultrasonic radiation and the phase separation is easier.

Elimination of a dispersive solvent and simple phase separation after centrifugation are important advantages of the ultrasound and vortex-assisted emulsification–liquid–liquid microextraction procedures. Furthermore, a very small amount of extraction solvent provides importantly high interface area between the two immiscible phases and increases the mass transfer of analytes from the water phase to the extraction phase.

Saleh et al. developed a hand-made centrifuge glass vial for ultrasound-assisted emulsification microextraction (USA-EME) based on using low density organic solvents prior to GC determination of polycyclic aromatic hydrocarbons in water samples.[76] In this method, 14 μL of toluene as extractor was injected into the sample solution and the mixture was placed in an ultrasonic water bath for emulsification.[76]

DLLME with ILs was also used without dispersive solvent. Liang et al. reported a new approach called ionic liquid-based ultrasound-assisted emulsification microextraction (IL-USA-EME).[77] In this method, ILs were used as extraction phase instead of organic solvent in the USA-EME technique for the extraction of different type fungicides in water samples prior to HPLC determination.[77]

Zhou and coworkers reported an alternative IL-based microextraction method called temperature-controlled ionic liquid dispersive liquid-phase microextraction to determine organophosphorus pesticides in environmental samples.[61] In this method, the sample solution including IL is heated until a homogeneous liquid is formed. The solution is cooled down and a cloudy mixture is obtained. Then the ionic liquid phase containing analytes is separated by centrifugation and analyzed with an analytical measurement technique using a suitable analytical instrument.[61]

Anderson et al. reported an in situ metathesis IL-DLLME procedure. In this method, a hydrophilic IL as extractant solvent is fully dissolved in the aqueous sample solution. Then an ion-exchange reagent is added to promote a metathesis reaction. A cloudy solution with fine IL microdroplets is obtained, and the hydrophilic IL phase is transformed into a hydrophobic IL phase. In this step, the analyte is to be extracted into the IL phase. The IL phase is separated and analyzed with an analytical measurement technique.[78,79]

Moreover, scientists have consequently attempted to find green dispersive solvents in place of harmful toxic solvents and as a result one of the developments introduced to DLLME was the utilization of surfactants as dispersive solvents. Three new methods were introduced: surfactant-assisted dispersive liquid–liquid microextraction (SA-DLLME), ion pair-based surfactant assisted microextraction (IP-SA-ME), and surfactant-enhanced emulsification microextraction (SE-ME).[80−83] These methods were combined with ultrasonic radiation, vortex agitation, and solidification improvements.[80−83]

The work by scientists to develop green solvents for different chemical purposes resulted in three new solvent types: supramolecular solvent (SUPRAs), deep eutectic solvent (DES), and switchable solvent (Ss).

Another kind of DLLME, called supramolecular based dispersive liquid–liquid microextraction (SUPRAs-DLLME), was developed by Gòmez and coworkers as a quick, simple, and efficient sample treatment procedure.[84] Supramolecular solvents (SUPRASs) are water-immiscible solvents made up of supramolecular assemblies dispersed in a continuous phase. SUPRAS are nanostructured solvents obtained from amphiphiles through a self-assembly global process occurring on two scales, nano and molecular.[58,85] The external effects such as pH, electrolyte concentration, and temperature of the sample and the type and amount of solvent are important in

the self-assembly global process. In these methods, coacervates consisting of the reverse micelles (size 3–500 nm) of long chain alcohols or carboxylated acids dispersed in an aqueous solution of tetrahydrofuran are injected into the aqueous sample solution. At the end of the extraction, the hydrophobic phase is separated from the sample by centrifugation. The supramolecular solvents have different kinds of interactions (e.g., hydrogen bonding and hydrophobic) with the analytes in aqueous sample phase for effective mass extraction.[85,86]

In 2012, Farajzadeh and Mogaddam provided a new application of the DLLME method called air-assisted liquid–liquid microextraction (AA-LLME). In this method, a lower amount of extraction solvent is used, and there is no need to use a dispersive solvent.[87] The effective extraction of analyte from the sample solution phase to the extraction solvent phase is conducted by sucking and injecting the mixture of sample solution and extraction solvent with a syringe many times in a centrifuge tube. Then the extraction phase is separated from the aqueous phase by centrifugation. After extraction, the analyte concentration in the enriched phase is determined by an analytical measurement technique.[88]

Karimi et al. introduced a new procedure called deep eutectic solvent based liquid phase microextraction (DES-LPME).[59] This was the first report on the utilization of DES as an extraction solvent for LPME. Deep eutectic solvents (DESs) show physical properties similar to ILs such as tunable miscibility, low volatility, high conductivity, and good thermal stability. However, DESs were introduced by Abbot et al. (2003) to eliminate the disadvantages of ILs such as dangers to health and the environment and high price.[89] Some DESs are drinkable and are prepared by simply mixing two safe components together; they are easily accessible, cheap, biodegradable, renewable, nonflammable, and nonvolatile.[89,90] The preparation facility of hydrophobic or hydrophilic DESs is the most important property of DESs in extraction studies and provides a suitable extraction medium for different polarity analytes.[59,89–91]

Lasarte-Aragonés et al. introduced for the first time a novel homogeneous liquid–liquid microextraction approach, based on the utilization of switchable hydrophilicity solvents (SHs) as extraction solvent for the extraction of polycyclic aromatic hydrocarbons.[92] Jessop et al. firstly examined the behavior of switchable hydrophilicity solvents for industrial purposes.[93] A switchable polarity solvent (SPs) is a solvent that creates water-miscible hydrophilic form in the presence of an atmosphere of CO_2 at 1 bar, but separates from water and creates hydrophobic form when CO_2 is removed with a phase transition trigger such as bubbling air, argon, nitrogen, or another inert gas under heating and addition of acids and bases.[93–97]

In Ss-LPME, a hydrophilic form of Ss as extractant solvent is completely dissolved in the aqueous sample solution. Then a phase transition trigger is introduced to create the hydrophobic form of Ss. At this stage, a cloudy solution with fine Ss microdroplets is formed and analyte is extracted into the hydrophobic form of Ss. Then the analyte concentration in the extraction phase is analyzed with an analytical measurement technique.[60,92]

2. Innovative applications of LPME from 2010 to 2016

In this section, the latest applications of SDME, HF-LPME, and DLLME for the separation and preconcentration of trace inorganic, organic, and biological analytes in environmental and biological samples is discussed.

2.1. Single-drop microextraction (SDME)

From the first discovery of the SDME method up to the present, innovative and effective applications of different types of SDME to environmental and biological samples have been reported.[98–123] These innovations from 2010

up to this time are illustrated in Table 1. As shown in Table 1, most procedures have been applied for water and food samples. In addition, a small number of papers have focused on biological samples.

Xu and coworkers[98] developed a simpler and more environmentally friendly UA-HS-SDME procedure for the preconcentration of hexanal and heptanal in human blood prior to HPLC determination. Methyl cyanide was used as extraction solvent. Guo et al.[118] reported an ionic liquid-based SDME method coupled with HPLC for the preconcentration and determination of sulfonamides in environmental water samples. This method is based on the exposure of the needle of a microsyringe including 10 μL of IL to the sample solution. Next, a magnetic stirrer was turned on to start the extraction of the sulfonamides from a 15-mL aqueous sample solution to the IL phase at the tip of the needle. At the end of the extraction, the extraction phase was retracted into the microsyringe and injected for HPLC analysis.

Martinis and Wuilloud[119] proposed an alternative extraction method called cold vapor ionic liquid-assisted headspace single-drop microextraction (CV-ILAHS-SDME) for the determination of Hg species in different types of samples. In this method, the authors' aim was the separation, preconcentration, and determination of inorganic (InHg) and organomercury (OrgHg) species by in situ cold vapor (CV) generation followed by headspace extraction with a suspended microdrop of a low cost IL and direct injection in ETAAS.

Carrillo-Carrion and coworkers[120] developed a new type of SDME procedure called ionic liquid-based head-space single-drop microextraction (IL-HS-SDME) and QD-based fluorimetric detection of trimethylamine in fish samples. They used a combination of ionic liquids and quantum dots as the extraction phase. After in situ generation of volatile trimethylamine (TMA) from fish samples, for the extraction of trimethylamine (TMA), a 20-μL microdrop of (QD) IL was subjected for 2 min to the headspace of a 5-mL sample solution located in a 10-mL vial with stirring and thermostated at 50–60 °C. For the measurement, the fluorescence signal of analyte (λ_{em} = 570 nm, λ_{exc} = 400 nm) was measured.

Almeida et al.[121] introduced a UA-SDME method combined with high-resolution continuum source electrothermal atomic absorption spectrometry (HR-CS-ET-AAS). They used a two-level full-factorial design program for optimization of analytical parameters. The microextraction procedure was conducted in an ultrasonic water bath at 46 °C. A 5-μL drop of 0.1 mol L^{-1} HNO_3 in a syringe was utilized as extractor. The needle of the syringe was immersed into the vegetable oil sample and sonication was applied to the system. After extraction, the extraction drop was transported by the autosampler to the HR-CS-ET-AAS for the determination of cadmium.

Amde et al.[122] used the advantages of nanoparticles and ionic liquids in SDME for the simultaneous preconcentration of three types of fungicides in water samples prior to their analysis by HPLC-VWD. They prepared a nanofluid by dispersing ZnO nanoparticles (ZnO NPs) in 1-hexyl-3-methylimidazolium hexafluorophosphate and used the extraction phase.

George et al.[123] extracted some growth hormones in bovine urine by using the mixed-solvent bubble-in-drop single drop microextraction method (BID–SDME) coupled with GC-MS. In this method, 1 μL of chloroform as extracting solvent was drawn into the syringe, followed by 0.5 mL of air. These contents were brought into contact with the sample solution by gentle depression of the plunger, causing the air to form a bubble contained within the microdroplet. Following a period of extraction under static conditions, the extraction solvent phase was carefully taken into the syringe, and analyzed with GC–MS.

Table 1. Different applications of SDME for organic and inorganic analytes.

Type of SDME	Analyte	Sample	Measurement technique	Extraction solvent	LOD μg L^{-1}	EF	RSD %	Ref.
UA-HS-SDME	Hexanal and heptanal	Human blood	HPLC	Methyl cyanide	0.79, 0.80 nmol L^{-1}	-	9.8	98
IL-SDME	UV filters	Water	LC-UV	IL	0.06–3.0	100	2.8–8.8	99
IL-SDME	Lead	Water	ETAAS	IL	0.0032	32	4.9	100
In situ-SDME	Mercury	Water	CCD detector	IL	0.2	69	4.9	101
IL-HS-SDME	Musk fragrances	Water	GC–IT-MS/MS	IL	0.010–0.030	-	3–11	102
Carrier-mediated-SDME	Amino acid	Human urine	CE		70–500 nM	120	2–3.7	103
IL-SDME	2,4,6-tricholoroanisole	Water and wine	IMS	IL	0.0001	-	<3	104
UNE-HGFT-HS-SDME	Essential oil	*Zanthoxylum bungeanum* Maxim	GC-MS		-	-	1.5–6.7	105
IL-SDME	Copper	Water and food	UV-VIS	IL	0.15	33	3.4	106
SDME	Organic pollutants	Water and grape juice	GC–FID	n-Hexanol	2–112	141–214	2.9–4.5	107
SDME	Cadmium	Water and rice	UV-VIS	CCl_4	0.0005	128	3.2	108
DI-SDME	Alkaloids	Human urine	CE	1-Octanol	8.1–14.1	231–524	4.8–8.1	109
E-SDME	Ethanol	Cosmetic	Fluoro spectrometry	Aqueous drop	9×10^{-5} mM	-	5.3	110
IL-SDME	Cadmium	Water and rice	W-coil ET-AAS	IL	0.015	42	5.2	111
SDME	Arsenic	Water	CE	1-Octanol	–	390–1300	1–15	112
UA-HS-SDME	Organophosphorus pesticides	Soil	GC	Ethanol	0.1–2.0 ng g^{-1}	1.4-12.7	2.1–6.9	113
Automated-HS-SDME	Ethanol	Wine	Fiber-optic spectrophotometer	-	–	-	<5	114
HS-SDME	Short-chain fatty acids	RuO_4 oxidation products of asphaltenes	GC-FID	1-Butanol	20–300	-	3.7–5.0	115
DI-SDME	Heterocyclic amine	Fried food	CE	IL modified nanomaterial	290	-	2.52	116
HS-SDME	Ammonia	Concrete walls	CE	Phosphoric acid	30 μg kg^{-1}	-	3–5	117
IL-SDME	Sulfonamides	Water	HPLC	IL	1–1500	5–55	2.8–9.9	118
CV-ILAHS-SDME	Mercury	Sea water, fish tissues, hair, and wine	ETAAS	IL	0.010	75	4.6	119
HS-SDME	Trimethylamine	Fish	FL	**(CdSe/ZnS QDs)-ionic liquid**	14	-	3.5	120
UA-SDME	Cadmium	Vegetable oils	HR-CS-ETAAS	HNO_3	–	-	3	121
SDME	Fungicides	Water	HPLC	Nanosized ZnO-IL	0.13–0.19		<4.82 <7.04	122
BID–SDME	Hormones	Bovine urine	GC-MS	$CHCl_3$	0.01–0.03	-	<10	123

2.2. Hollow fiber-based LPME (HF-LPME)

The innovative developments of HF-LPME published in the literature are shown in Table 2.[124−147] As seen, organic compounds are mostly extracted and determined by using HF-LPME.

Yang et al.[124] proposed HF-LPME coupled with HPLC for the preconcentration and determination of three types of *Aconitum* alkaloids in urine samples. Analytes in urine sample were extracted into the 1-octanol membrane phase impregnated in the pores of the HF wall, and then extracted back into an acidified aqueous solution in the lumen of the HF. At the end of the extraction, the concentration of analytes in the acceptor phase was measured directly by HPLC.

In the same year, Emidio et al.[126] used HF-LPME for the separation of cannabinoids prior to GC–MS/MS analysis. They used a fractional factorial design and a central composite design to optimize important analytical factors. A butyl acetate impregnated accurel Q3/2 polypropylene HF membrane was used for extraction of analytes contained in the hair digestion solution. A 50-μL syringe was utilized to introduce the acceptor phase, and another was used for its removal. After extraction, 1-μL portions of the last phase were introduced into the GC–MS/MS for the measurement of the concentrations of analytes. In 2010, a different HF-LPME method was suggested by Luciano et al. for extraction and preconcentration of cadmium.[128] They investigated the applicability of polypropylene porous membrane for the hollow fiber renewal liquid membrane (HFRLM) method in a U-shape configuration for extraction and preconcentration of Cd(II) prior to FAAS determination. Cd(II) ions in the aqueous phase were complexed with ammonium O,O-diethyl dithiophosphate and this neutral hydrophobic complex was extracted to the organic solvent phase immobilized inside the polypropylene porous membrane by using stirring for a predetermined time. The extraction phase was collected and directly analyzed by FAAS.

Ghambarian et al.[132] suggested a new type of the three-phase HF-LPME procedure based on two immiscible organic solvents for the extraction of tramadol in urine and plasma samples prior to GC-MS determination. In this method, the three phases included are a donor aqueous solution, a very small volume of organic solvent (n-dodecane) immobilized in the pores of the HF, and a small volume of another organic solvent (acetonitrile or methanol) inside the lumen of the HF. The chemometric approach was applied for the optimization of the procedure. In this procedure, a new hollow fiber was immersed for 5 s into the n-dodecane for impregnation. After impregnation, organic acceptor solvent (acetonitrile) was added to the HF with a microsyringe, and afterwards the fiber was brought into contact with the sample solution by magnetic stirring. After extraction, the acceptor phase was injected into the GC–MS for measurements. In the same year, Zeng et al.[137] used ionic liquids in HF-LPME for the speciation of Cr(VI) and Cr(III) species. The method is based on the extraction of Cr(VI) into the lumen of hollow fiber as Cr(VI)-diethyldithiocarbamate (DDTC) complex, whereas Cr(III) remained in aqueous solutions. The extraction organic phase was introduced into FAAS for the analysis of Cr(VI). The concentration of total Cr was analyzed after oxidizing Cr(III) to Cr(VI) and using the suggested HF-LPME method.

In 2011, Shrivas and Patel[140] used ultrasound irradiation in HF-LPME to facilitate the extraction of selenium from the aqueous phase into 3.5 μL of N-octyl acetamide phase placed inside the hollow fiber. The extraction of selenium was conducted in the pH range of 0.8–3.0. They used this UA-HF-LPME method coupled to GF-AAS for the determination of selenium from different types of vegetable and fruit samples. In 2012, Liu et al.[138] used water-miscible ionic liquid (IL) for the first time as a new multifunctional acceptor phase in the three-phase HF-LPME method. This method was applied for the isolation and preconcentration of polycyclic

Table 2. Different applications of HF-LPME for organic and inorganic analytes.

Type of HF-LPME	Analyte	Sample	Measurement technique	Extraction solvent	LOD, μg L^{-1}	EF, %	RSD, %	Ref.
HF-LPME	Aconitine, hypaconitine, and mesaconitine	Urine	HPLC	1-Octanol	0.7–1.5	98–288	0.99–7.22	124
HF-LLLME	Desipramine	Plasma and urine	VD	Propyl benzoate	-	234–301	6.2	125
HF-LPME	Cannabinoids	Human hair	GC–MSMS	Butyl acetate	-		3.3–8.9	126
HF-LPME	Amphetamine, caffeine and ketamine	Drug abuser urine samples	GC-FID	o-Xylene	8, 82	5–227	6.9–14.1	127
HFRLM	Cadmium	Environment	FAAS	Toluene	1.5	107	4.0	128
HF-LPME	Ochratoxin A and T-2 toxin	Alcoholic beverages	UHPLC–MS/MS	1-Octanol	-	-	<12	129
HF-LPME	Rosiglitazone	Biological fluids	CE and HPLC	Dihexyl ether	0.18, 2.83 and 0.56, 5.00		10.9, 13.2	130
HF-LPME	Tellurium and selenium	Water and soil	ETAAS	Toluene	0.004 and 0.005	520 and 480	3.5 and 3.1	131
Three -phase HF-LPME	Tramadol	Urine and plasma	GC-MS	n-Dodecane	0.08	546	6.4	132
HF-LPME	Pesticide	Cucumber	UHPLC–MS/MS	chloroform	-	100–147	<20	133
HF-LPME	Mercury	Water	ETAAS	Toluene	0.06	270	3.2	134
PT-HF-LPME	Co, Pd, Cd, Bi	Water and urine	ETV-ICP-MS	Toluene	0.0037–0.0083	110–393	6.2–12.9	135
HF-LPME	Sulfonamides and metabolites of sulfonamides	Water	HPLC	1-Octanol	0.0003–0.00033	175–1000	0.8–1.2	136
HF-LPME	Cr(III) and Cr(VI)	Water	FAAS	1-Octanol	0.0007	175	4.9	137
IL-three phase HF-LPME	Polycyclic aromatic hydrocarbons	Water	HPLC	IL	0.00025	45–54	4.93–5.54	138
HF-LPME	Sulfonamide compounds	Water	CE	1-Octanol	0.000033–0.00044	121–996	0.7–1.2	139
UA-HF-LPME	Selenium	Vegetable and fruit	GF-AAS	N-octyl acetamide	0.08	35	2.5–4.4	140
IL-HF-LPME	Ultraviolet filters	Water	HPLC	IL	0.3–0.5	25–221	1.1–8.2	141
TP-HF-LPME	Echinacoside	Parkinson's disease rat plasma	HPLC	n-Octanol	2.0	337	5.43	142
UPP-HF-LLLME	Phthalate esters	Plastic-bottled beverages	HPLC	1-Octanol	0.01–0.02	182–218	3.0–5.8	143
IL-HF-LPME	Kanamycin sulfate	Water and milk	ECL	IL	0.67	-	-	144
IL-HF-LPME	Neutral red dye	Three soft drink samples	UV-VIS or ECL	IL	0.36	-	2.90–8.64	145
IL-HF-LPME	Ag, Al, As, Mn, and Ti	Diesel and gasoline	ICP-OES	IL	0.04–0.09	112–405	<5	146
Automatic HF-LPME	Organophosphate esters	Water	GC–MS	Toluene	0.0026–0.120	–	2.1–10.4	147

aromatic hydrocarbons (PAHs) in river water. The determination of PAHs in the last volume was conducted by LC.

In 2013, Chao et al.[143] combined ultrasound-assisted push/pull perfusion and hollow-fiber liquid–liquid–liquid microextraction for online extraction of phthalate esters in liquid samples and called ultrasound-assisted push/pull perfusion UPP-HF-LLLME. They used ultrasonic irradiation to speed up the analyte transfer and a push/pull syringe pump as the driving source to spray the acceptor phase and reduce the perfusion pressure, permitting on-line coupling of HF-LLLME to HPLC. The pores of the HF membrane were filled with 1-octanol and MeCN was used as acceptor solvent.

In 2014, Wang et al.[144] suggested a three-phase HF-LPME method for the extraction of kanamycin sulfate combined with electrochemiluminescence detection. In this procedure, 1-octyl-methylmidazolium hexafluorophosphate ([OMIM]PF_6) as extraction solvent and a hollow fiber supported liquid membrane between the sample solution containing analyte and aqueous solution (pH 10) as acceptor phase were used. In 2014, a HF-LPME method for the simultaneous extraction and preconcentration of Ag, Al, As, Mn, and Ti as ammonium pyrrolidine dithiocarbamate (APDC) complexes in [C_6MIM][PF_6] ionic liquid was proposed by Nomngongo et al.[146] They used multivariate techniques for the optimization of analytical parameters. The gasoline samples were digested by using a microwave assisted digestion system prior to applying the HF-LPME. IL as the extraction solvent phase was impregnated into hollow fiber membrane pores of the hollow fiber wall. The target analytes extracted in the IL phase were then transferred to an aqueous phase by adding different concentrations of nitric acid. They sonicated the mixture for 10 min. After centrifugation, the upper nitric acid phase was collected for the determination of the analyte concentrations with the ICP-OES.

2.3. Dispersive liquid–liquid microextraction (DLLME)

The resulting new applications and methodological approaches in DLLME are shown in Table 3.[148–173] As shown, the DLLME method has been successfully used for the extraction and determination of a wide variety of organic and inorganic analytes from a variety samples such as environmental, food, and biological samples.

Yamini et al.[148] used a mode of the DLLME-SFO method combined with ICP-OES for the analysis of heavy metals in water samples. In this method, 1-(2-thenoyl)-3,3,3-trifluoraceton (TTA) as complexing agent was added to the sample solution to obtain a hydrophobic metal complex. Then a suitable mixture of extraction solvent (140 μL of 1-undecanol) and dispersive solvent (2.0 mL of acetone) were added to the aqueous samples including metal ion complex and this resulted in a cloudy solution. After centrifugation, the fine droplets of the extraction solvent were gathered at the top of the centrifuge tube. The sample solution was cooled with ice pieces for solidification of the extraction solvent phase. The extraction phase was melted in a different vial and dissolved in 1-propanol. The metal concentrations were measured by a flow injection system connected with ICP-OES.

In 2010, Mahpishanian and Shemirani[149] reported a preconcentration procedure called ionic liquid-based modified cold-induced aggregation microextraction (IL-M-CIAME) for the extraction of gold in saline solutions. In this procedure, sodium hexafluorophosphate ($NaPF_6$) was injected into the sample solution containing Au-TMK complex and 50 μL of 1-hexyl-3-methylimidazolium tetrafluoroborate [Hmim][BF_4]. Subsequently, the solution was left in an ice bath and a cloudy solution formed. After phase separation, the volume of the IL phase was completed to 350 μL with ethanol and analyzed with a UV-VIS spectrophotometer at 545 nm. In the same year, Yan et al.[150] reported a simple ultrasound-assisted dispersive liquid–liquid microextraction method (UA-

Table 3. Different applications of DLLME for organic and inorganic analytes.

Type of DLLME	Analyte	Sample	Meas. tech.	Extraction solvent	LOD, μg L^{-1}	EF	RSD, %	Ref.
DLLME–SFO	Mn, Cr, Co, Cu	Water	ICP-OES	1-Undecanol	0.1–0.3	57–96		148
M-CIAME	Au	Water	UV-VIS	IL	0.7	28	1.65	149
UA-DLLME	Pyrethroids	Water	HPLC	Tetrachloromethane	0.11–0.30	767–1033	<8.7	150
VALLME	Octylphenol, nonylphenol and bisphenol-A	Water	HPLC	Octanol	0.01–0.07	150–690	2.1–8.0	151
SA-DLLME	Chlorophenols	Water	HPLC	1-Octanol	0.1	187–353	4.7–6.9%	152
TC-IL-LLPME	Pb	Water	FAAS	IL	9.5	–	4.4	153
ISFME	Cd	Water and salt	FAAS	IL	0.07	78	2.42	154
UASEME	Carbamate pesticides	Water	HPLC	Chlorobenzene and chloroform	0.1–0.3	170, 246	3.2–4.8	155
MSA-DLLME	UV filters	Water	HPLC	1-Octanol	0.2–0.8	59–107	1.4– 4.8.	156
LDS-SD-DLLME	Polycyclic aromatic Hydrocarbons	Water	GC–MS	n-Hexane	0.003.7–0.0391	-	<11	157
IL-based MA-DLLME	Sulfonamides	Water, honey, milk, and animal plasma	HPLC	IL	0.0005	97.8–106	1.5–7.3	158
DLLME	Cu	Water	UV–VIS	Amyl acetate	5	-	1.3–5.4	159
SALLME	Iodine	Table salts	HPLC–UV	Ethanol	3.7	280	7.9	160
DLLME	Volatile nitrosamines	Meat products	GC–MS	Carbon tetrachloride	0.003–0.014	220–342	2.1–10	161
DUSA-DLLME	Nitroaromatic explosives	Water	GC–MS	Chlorobenzene	0.03–0.91	-	6	162
IL-UA-DLLME	Rh	Water and leaves	FAAS	IL	0.37	29.3	1.63	163
Online-IL-DLLME	Se	Water and garlic	ETAAS	IL	0.015	20	5.1	164
IL-CIA-DLLME	Phthalate esters	Water	HPLC	IL	0.68–1.36	174–212	2.2– 3.7	165
DLLME	Phosphatidylethanol	Blood	LC-MS	Dichloromethane	0.01	-	<15	166
DLLME	Synthetic food colorants	Food	HPLC	IL	0.015–0.32	–	–	167
UESA–DLLME	Pathogenic bacteria	Blood and serum	MALDI–MS	Chlorobenzene	–	–	–	168
MIL-based DLLME	Triazine herbicides	Vegetable oils	LC	IL	1.31–1.49	–	<7.7	169
MWA–DLLME	Organophosphorus pesticide residues	Water and fruit juice	GC–FID	1,2–DBE	0.65–1.3	1340–1900	2–7	170
LDS–DLLME	Polycyclic aromatic hydrocarbons	Water	GC–MS	1–Octanol	0.023–0.058	–	4.8–7.3	171
GA–DLPME	Cu	Water	UV–VIS	IL	0.07	122	3.9	172
dual–UADLLME	20(S)–protopanaxadiol and 20(S)–protopanaxatriol	Rat plasma	UHPLC–MS/MS	Bromocyclohexane	0.010–0.085	164–182	–	173
Ss–LLME	Cu	Food and water	FAAS	Supras	0.52	60	<3	58
DESs–LPME	Cd, Pb	Edible oils	ETAAS	DES	–	195–198	2.0–8.3	59
SS–LPME	Cu	Water, food, and hair	FAAS	Switchable solvent	1.80	25	3.8	60

DLLME) coupled to HPLC for the extraction and determination of six pyrethroids in actual water samples. The effective extraction was conducted with ultrasonic treatment. The ultrasonic treatment caused the formation of fine droplets and could extract target analytes towards equilibrium faster due to a larger specific surface area and shorter diffusion distance. In this study, 20 μL of tetrachloromethane (extraction solvent) and 1.0 mL of acetone (dispersive solvent) were used.

Yiantzi et al.[151] used a vortex mixer for the dispersion of microvolumes of a low density extractant organic solvent into the aqueous sample and increased mass transfer tool for the first time. The method was called vortex-assisted liquid–liquid microextraction (VA-LLME) and was applied for the trace determinations of octylphenol, nonylphenol, and bisphenol-A in water samples. In this procedure, 50 μL of octanol as extraction solvent was added to a 20-mL aqueous sample solution including all target analytes. The mixture was then strongly shaken by a vortex mixer and fine droplets were formed. After centrifugation, the floating octanol phase was collected with a microsyringe and used for HPLC analysis.

Moradi et al.[152] used a method called surfactant-assisted dispersive liquid–liquid microextraction (SA-DLLME) for the sample preparation of chlorophenols in water samples. In this method, a cationic surfactant (cethyltrimethyl ammonium bromide (CTAB)) was selected as a dispersive solvent, while 1-octanol was utilized as an extraction solvent. After extraction, the analyte concentration was measured with HPLC.

Bai et al.[153] developed a procedure called temperature-controlled ionic liquid–liquid-phase microextraction (TC-IL-LLPME) for lead quantification. In this application, lead was extracted into the infinite IL drops as dithizone complex at 80 °C. In this step, the IL was dissolved completely and mixed entirely with the sample solution to transfer the chelate transfer to the IL phase after cooling with an ice-water bath and was then centrifuged. The lead concentration in the extraction phase was measured by FAAS.

The development of new devices has provided important advantages for different applications of DLLME. In 2011, Zhang et al.[156] used a new DLLME including the use of a new device of UV filters in environmental water samples. In this study, they used a specially designed flask with two narrow open necks, one of which has a capillary tip, to simplify the DLLME procedure. By using such an apparatus, the extraction and subsequent phase separation were properly realized. 1-Octanol was used as low density extraction solvent and a disperser solvent was not used. The mass transfer was facilitated by magnetic stirring of the two phases. No centrifugation step used in classical DLLME was necessary. After extraction, phase separation was easily achieved by leaving the extraction system static for a while. The extraction phase, floating above the sample solution, was elevated and concentrated into the narrow open tip of the flask by adding pure water into it via the other port, which was withdrawn with a microsyringe for the subsequent HPLC determinations.

In 2011, Guo and Lee[157] used low density solvents for demulsification DLLME of polycyclic aromatic hydrocarbons in water samples prior to GC–MS analysis. In the LDS-SD-DLLME method, the authors used a flexible and disposable polyethylene pipette as the extraction device. A mixture of n-hexane (extraction solvent) and acetone (dispersive solvent) was added to the sample solution to obtain an emulsion. A second 500-μL aliquot of acetone was then added to the aqueous sample solution for demulsification, which formed clear and was separated into two phases. The novel application expands the use of DLLME to a wider range of solvents. Additionally, the method eliminates some of the extra experiment steps usually used in conventional DLLME such as ultrasonication or agitation, centrifugation, and refrigeration of the extraction system.

Xu and coworkers[158] developed a new preconcentration procedure named ionic liquid-based microwave-assisted dispersive liquid–liquid microextraction (IL-based MA-DLLME) and used this method for the determination of sulfonamides in river water, honey, milk, and animal plasma. In this preconcentration method, 100

μL of IL as an extraction solvent, 0.75 mL of methanol as a dispersive solvent, and 200 μL of fluorescamine solution as a derivatization reagent were added rapidly to the sample solution. A cloudy solution was obtained and then the mixture in a centrifuge tube was subjected to microwave irradiation at a microwave power of 240 W for 90 s. At this step, the analytes were extracted to the IL phase. The mixture was centrifuged and the IL phase was collected for HPLC analysis. In 2011, Gupta et al.[160] reported a procedure for the determination of iodine in table salt by HPLC. This method was called salt-assisted liquid–liquid microextraction (SA-LLME). In this system, ethanol was utilized as extraction solvent and the phase separation occurred with the addition of a salt such as ammonium sulfate. In 2011, a quantification method for Se species determination in water and garlic samples based on the use of an on-line IL-dispersive microextraction system combined with ETAAS was reported by Martinis et al.[164] The method is based on the highly selective extraction of Se(IV). Se(VI) was reduced and then indirectly analyzed. In this method, the Se(IV) species was selectively extracted as Se–ammonium pyrrolidine dithiocarbamate (Se–APDC) complex from the aqueous sample phase to the IL phase. After the DLLME step, the IL phase was adsorbed on a microcolumn for retention and separation. Then the IL phase was eluted with 200 μL of methanol acidified to 10% (v/v) HNO_3 by using the on-line system and the enriched phase was determined by ETAAS.

Wu et al.[167] reported a new application of DLLME for the simultaneous extraction of different food colorants in soft drinks and sugar- and gelatin-based confectionery by HPLC. The method is based on manual shaking for the easier dispersion of IL and extraction of analytes into the IL phase. In this DLLME method, ultrasonication, heat, a dispersive solvent, or additional chemical reagents are not necessary.

Nowadays, the combined use of magnetic nanoparticles and ILs has become a novel area and a hot topic of research in LPME methods.[25–28] A novel type of magnetic ionic liquids (MILs) with a single component has been developed. MILs provide an excellent response to an external magnetic field[28] and have attracted interest as effective extraction solvents to take the place of routine nonmagnetic extraction solvents in DLLME. In 2014, Wang et al.[169] used MILs in DLLME for the preconcentration and determination of triazine herbicides in vegetable oils by LC. In this method, 1-hexyl-3-methylimidazolium tetrachloroferrate ($[C_6mim]$ $[FeCl_4]$) was used as the extractor phase. The authors reported that the phase separation was shortened in this method by using magnetic separation.

From 2014 up to the present, a revolution in the use of green solvents for LPME has occurred and analytical chemists have focused on these solvents to develop green preconcentration methods. LPME methods have taken on a new perspective with the use of supramolecular solvents (SUPRAs), deep eutectic solvents (DESs), and switchable solvents (Ss).

In 2014, Yilmaz and Soylak[58] used supramolecular solvents (SUPRAs) made up of reverse micelles of 1-decanol in tetrahydrofuran (THF):water as a green and new solvent system in LPME for the extraction of copper in environmental samples. In this system, the extraction solution consists of 1-decanol and THF was added to the sample solution including Cu(II)-dimethyl dithiocarbamate complex and the mixture was incubated in an ultrasonic bath for formation of the nano-sized and micro-sized supramolecular solvent system. At this stage, the analyte was extracted to SUPRAs phase. After centrifugation, the extraction solvent phase was collected and the copper concentration in the last volume was measured by FAAS using a microsampling system. In 2015, Karimi et al. used deep eutectic solvent (DES) in LPME for the first time. They applied this method to the ligandless extraction of lead and cadmium in edible oils. In this method, a deep eutectic solvent consisting of choline chloride (ChCl) and urea and 200 μL of 2% nitric acid was added to an oil sample. The mixture was vortexed and incubated in a water bath at 50 °C and stirred for 5 min. After the extraction was completed, the phases

were separated by centrifugation, and the concentrations of analytes in the DES phase were measured by ETAAS. In the same year Yilmaz and Soylak[60] developed a switchable solvent-based liquid phase microextraction (Ss-LPME) method for the quantification of copper in an aqueous sample solution prior to microsampling FAAS determination. In this method, triethylamine (TEA) and protonated triethylamine carbonate (P-TEA-C) as green and cheap switchable solvents were used. They synthesized the P-TEA-C, which is a polar form extraction solvent, from TEA, which is an apolar form of extraction solvent. The synthesis of P-TEA-C is based on the reaction of CO_2 with TEA in water. First 1.0 mL of P-TEA-C was added to the aqueous sample solution including the Cu(II)-1-(2-pyridylazo)-2 naphthol (PAN) complex. Then 2.0 mL of 10 M NaOH solution was injected into the centrifuge tube and a cloudy solution appeared. At this stage, P-TEA-C was turned into TEA and the Cu(II)-PAN complex was transferred into fine droplets of the TEA phase. The TEA phase was collected on the surface of the aqueous phase by centrifugation at 4000 rpm for 10 min. Finally, the copper concentration in the TEA phase was measured with FAAS.

Guo et al.[171] reported an automated determination method combining low density solvent-based solvent demulsification DLLME with GC-MS for polycyclic aromatic hydrocarbons (PAHs) in environmental water samples. A Gerstel Maestro software program was used to control the automated DLLME method. They added a mixture of 1-octanol (extraction solvent) and acetonitrile (dispersive solvent) to aqueous samples for the demulsification. In the same year, Akhond et al.[172] used ILs and an Ar gas system as extraction solvent and as disperser in IL-DLPME. They combined this method with UV-Visible spectrophotometer for the speciation and determination of both Cu(I) and Cu(II) species in water samples.

In future new generation green solvents including new ferrofluids, deep eutectic solvents, and magnetic ionic liquids may be preferred and used in liquid-phase microextraction studies. Moreover, studies will be focused on the automation of liquid-phase microextraction of analytes.

Abbreviations

SPE	Solid phase extraction
CPE	Cloud point extraction
LLE	Liquid–liquid extraction
UA-HS-SDME	Ultrasound-assisted headspace liquid-phase microextraction
LC-UV	Liquid chromatography-ultraviolet spectrophotometry detection
IL-SDME	Ionic liquid-based single-drop microextraction
In situ-SDME	In situ single-drop microextraction
MHS-SDME	Multiple headspace single-drop microextraction
IL-HS-SDME	Ionic liquid-based headspace single drop microextraction
GC–IT-MS/MS	Gas chromatography and ion trap tandem mass spectrometry
CE	Capillary electrophoresis
IMS	Ion mobility spectrometry
UNE-HGFT-HS-SDME	Ultrasonic nebulization extraction-heating gas flow transfer combined with head space single drop microextraction
GC–FID	Gas chromatography–flame ionization detection
E-SDME	Enzymatic single drop microextraction
W-coil ET-AAS	Tungsten coil electrothermal atomic absorption spectrometry
DI-SDME	Direct immersion single drop microextraction
CV-ILAHS-SDME	Cold vapor ionic liquid-assisted head space single drop microextraction
FL	Fluorimeter
HR-CS-ETAAS	High resolution continuum source electrothermal atomic absorption spectrometer
BID–SDME	Bubble-in-drop single drop microextraction

M-CIAME	Modified-cold-induced aggregation microextraction
UA-DLLME	Ultrasound-assisted dispersive liquid–liquid microextraction
VALLME	Vortex-assisted liquid–liquid microextraction
SA-DLLME	Surfactant assisted dispersive liquid–liquid microextraction
TC-IL-LLPME	Temperature-controlled ionic liquid–liquid-phase microextraction
FAAS	Flame atomic absorption spectrometry
ISFME	In situ solvent formation microextraction
UASEME	Ultrasound-assisted surfactant-enhanced emulsification microextraction
MSA-DLLME	Magnetic stirring-assisted dispersive liquid–liquid microextraction
LDS-SD-DLLME	Low-density solvent-based solvent demulsification dispersive liquid–liquid microextraction
IL-based MA-DLLME	Ionic liquid-based microwave-assisted dispersive liquid–liquid microextraction
SALLME	Salt-assisted liquid–liquid microextraction
DUSA-DLLME	Direct ultrasound-assisted dispersive liquid–liquid microextraction
IL-UA-DLLME	Ionic liquid ultrasound assisted dispersive liquid–liquid microextraction
Online-IL-DLLME	On-line ionic liquid dispersive microextraction
IL-CIA-DLLME	Ionic liquid cold-induced aggregation dispersive liquid–liquid microextraction
UESA-DLLME	Ultrasound enhanced surfactant-assisted dispersive liquid–liquid microextraction
MALDI-MS	Matrix assisted laser desorption/ionization mass spectrometry
MIL-based DLLME	Magnetic ionic liquid-based dispersive liquid–liquid microextraction
MWA–DLLME	Microwave-accelerated dispersive liquid–liquid microextraction
GA-DLPME	Gas-assisted dispersive liquid-phase microextraction
dual-UADLLME	Dual ultrasonic-assisted dispersive liquid–liquid microextraction
UHPLC–MS/MS	Ultra high performance liquid chromatography tandem mass spectrometry
SS-LPME	Switchable solvent-based liquid phase microextraction
HF-LLLME	Hollow fiber-based liquid–liquid–liquid microextraction
VD	Voltammetric determination
GC–MS/MS	Gas chromatography–tandem mass spectrometry
HFRLM	Hollow fiber renewal liquid membrane
UHPLC–MS/MS	Ultra high pressure liquid chromatography coupled to tandem mass spectrometry
PT-HF-LPME	Phase transfer hollow fiber liquid phase microextraction.
ETV-ICP-MS	Electrothermal vaporization inductively coupled plasma mass spectrometry
UA-HFLPME	Ultrasound assisted-hollow fiber-liquid microextraction
UPP-HF-LLLME	Ultrasound-assisted push/pull perfusion hollow-fiber liquid–liquid–liquid microextraction
ECL	Electrochemiluminescence detection
HPLC	High performance liquid chromatography
ICP-OES	Inductively coupled plasma-optical emission spectrometry
ETAAS	Electrothermal-atomic absorption spectrometry
MALDI-MS	Matrix-assisted laser desorption/ionization mass spectrometry
LIBS	Laser-induced breakdown spectrometry

References

1. Wu, M.; Chen, W.; Wang, G.; He, P.; Wang, Q. *Food Chem.* **2016**, *209*, 154-161.
2. Feist, B. V. *Food Chem.* **2016**, *209*, 37-42.
3. Asfaram, A.; Ghaedi, M.; Goudarzi, A. *Ultrason. Sonochem.* 2016, *32*, 407-417.
4. Tiwari, S.; Sharma, N.; Saxena, R. *New J. Chem.* **2016**, *40*, 1412-1419.
5. Gholami, A.; Masoum, S.; Mohsenikia, A.; Abbasi, S. *Spectrochim. Acta A* **2016**, *153*, 108-117.
6. Yilmaz, E.; Ocsoy, I.; Ozdemir, N.; Soylak, M. *Anal. Chim. Acta* **2016**, *906*, 110-117.

7. Gürkan, R.; Korkmaz, S.; Altunay, N. *Talanta*, **2016**, *155*, 38-46.
8. Shamsipur, M.; Yazdanfar, N.; Ghambarian, M. *Food Chem.* **2016**, *204*, 289-297.
9. Tong, S.; Jia, Q.; Song, N.; Zhou, W.; Duan, T.; Bao, C. *Microchim. Acta* **2011**, *172*, 95-102.
10. Jalbani, N.; Yilmaz, E.; Alosmanov, R. M.; Soylak, M. *Des. Water Treat.* **2016**, *57*, 2834-2842.
11. Unsal, Y. E.; Tuzen, M.; Soylak, M. *Turk. J. Chem.* **2014**, *38*, 173-181.
12. Dadfarnia, S.; Haji Shabani, A. M.; Amirkavei, M. *Turk. J. Chem.* **2013**, *37*, 746-755.
13. Dadfarnia, S.; Mirzaei, M.; Shabani, A. M. H.; Ramazanzadeh, B. *Turk. J. Chem.* **2012**, *36*, 614-623.
14. Eskandari, H. *Turk. J. Chem.* **2012**, *36*, 631-643.
15. Dadfarnia, S.; Shabani, A. M. H.; Mirshamsi, A. *Turk. J. Chem.* **2011**, *35*, 625-636.
16. Yazdi, A. S.; Yazdinezhad, S. R.; Heidari, T. *Journal of Advanced Research* **2015**, *6*, 957-966.
17. Kazemi, M. S. J. *Anal. Chem+* **2015**, *70*, 1330-1335.
18. Alothman, Z. A.; Dawod, M.; Kim, J.; Chung, D. S. *Anal. Chim. Acta* **2012**, *739*, 14-24.
19. Mirmoghaddam, M.; Kaykhaii, M.; Hashemi, M. *Anal. Methods* **2016**, *8*, 2456-2462.
20. Piryaei, M.; Nazemiyeh, H. *Nat. Prod. Res.* 2016, *30*, 991-994.
21. Liu, S.; Dasgupta, P. K. *Anal. Chem.* **1995**, *67*, 2042-2049.
22. Jeannot, M. A.; Cantwell, F. F. *Anal. Chem.* **1996**, *68*, 2236-2240.
23. Herrador, E. A.; Lucena, R.; Cárdenas, S.; Valcárcel, M. *J. Chromatogr. A* **2009**, *1216*, 5580-5587.
24. Liu, J.; Jiang, G.; Chi, Y.; Cai, Y.; Zhou, Q.; Hu, J. T. *Anal. Chem.* **2003**, *75*, 5870-5876.
25. Qin, W.; Li, S. F. Y. *Electrophoresis* **2002**, *23*, 4110-4116.
26. Liu, W.; Lee, H. K. *Anal. Chem.* **2000**, *72*, 4462-4467.
27. Przyjazny, A.; Kokosa, J. M. *J. Chromatogr. A* **2002**, *977*, 143-153.
28. Jeannot, M. A.; Przyjazny, A.; Kokosa, J. M. *J. Chromatogr. A* **2010**, *1217*, 2326-2336.
29. Ahmadi, F.; Assadi, Y.; Milani Hosseini, S. M. R.; Rezaee, M. *J. Chromatogr. A* **2006**, *1101*, 307-312.
30. Xu, L.; Basheer, C.; Lee, H. K. *J. Chromatogr. A* **2007**, *1152*, 184-192.
31. Theis, A. L.; Waldack, A. J.; Hansen, S. M.; Jeannot, M. A. *Anal. Chem.* **2001**, *73*, 5651-5654.
32. Deng, C.; Yao, N.; Wang, A.; Zhang, X. *Anal. Chim. Acta* **2005**, *536*, 237-244.
33. Chamsaz, M.; Arbad-Zavar, M. H.; Nazari, S. *J. Anal. Atom. Spectrom.* **2003**, *18*, 1279-1282.
34. Shariati-Feizabadi, S.; Yamini, Y.; Bahramifar, N. *Anal. Chim. Acta* **2003**, *489*, 21-31.
35. Zhao, F.; Lu, S.; Du, W.; Zeng, B. *Microchim. Acta* **2009**, *165*, 29-33.
36. Fiamegos, Y. C.; Stalikas, C. D. *Anal. Chim. Acta* **2007**, *599*, 76-83.
37. Khajeh, M.; Yamini, Y.; Hassan, J. *Talanta* **2006**, *69*, 1088-1094.
38. Piryaei, M.; Nazemiyeh, H.; *Nat. Prod. Res.* **2016**, *30*, 991-994.
39. Kokosa, J. M. *TrAC -Trend. Anal. Chem.* **2015**, *71*, 194-204.
40. Liu, W.; Lee, H. K. *Anal. Chem.* **2000**, *72*, 4462-4467.
41. Li, Y.; Zhang, T.; Liang, P. *Anal. Chim. Acta* **2005**, *536*, 245-249.
42. Pedersen-Bjergaard, S.; Rasmussen, K. E. *Anal. Chem.* **1999**, *71*, 2650-2656.
43. Kim, H. Y.; Yoon, S. H.; Jeong, T. Y.; Yu, S.; Kim, S. D. *Des. Water Treat.* **2016**, *57*, 16024-16033.
44. Basheer, C.; Suresh, V.; Renu, R.; Lee, H. K. *J. Chromatogr. A* **2004**, *1033*, 213-220.
45. Pedersen-Bjergaard, S.; Rasmussen, K. E.; Halvorsen, T. G. *J. Chromatogr. A* **2000**, *902*, 91-105.

46. Rezaee, M.; Assadi, Y.; Hosseini, M. R. M.; Aghaee, E.; Ahmadi, F.; Berijani, S. *J. Chromatogr. A* **2006**, *1116*, 1-9.
47. Šandrejová, J.; Campillo, N.; Viñas, P.; Andruch, V. *Microchem. J.* **2016**, *127*, 184-186.
48. Herrera-Herrera, A.; Asensio-Ramos, M.; Hernández-Borges, J.; Rodríguez Delgado, M. A. *TrAC-Trend Anal. Chem.* **2010**, *29*, 728-751.
49. Farahani, H.; Norouzi, P.; Dinarvand, R.; Ganjali M. R. *J. Chromatogr. A* **2007**, *1172*, 105-112.
50. Shamsipur, M.; Yazdanfar, N.; Ghambarian, M. *Food Chem.* **2016**, *204*, 289-297.
51. Bashiry, M.; Mohammadi, A.; Hosseini, H.; Kamankesh, M.; Aeenehvand, S.; Mohammadi, Z. *Food Chem.* **2016**, *190*, 1168-1173.
52. Rocha, B. A.; Da Costa, B. R. B.; De Albuquerque, N. C. P.; De Oliveira, A. R. M.; Souza, J. M. O.; Al-Tameemi, M.; Campiglia, A. D.; Barbosa, F. *Talanta* **2016**, *154*, 511-519.
53. Pouyan, M.; Bagherian, G.; Goudarzi, N. *Microchem J.* **2016**, *127*, 46-51.
54. Wang, H.; Gao, J.; Yu, N.; Qu, J.; Fang, F.; Wang, H.; Wang, M.; Wang, X. *Talanta* **2016**, *154*, 381-391.
55. Sobhanzadeh, E.; Bakar, N. K. A.; Abas, M. R. B.; Nemati, K. *J. Hazard. Mater.* **2011**, *186*, 1308-1313.
56. Zhang, J.; Gao, H.; Peng, B.; Li, S.; Zhou, Z. *J. Chromatogr. A* **2011**, *1218*, 6621-6629.
57. Farajzadeh, M. A.; Seyedi, S. E.; Shalamzari, M. S.; Bamorowat, M. *J. Sep. Sci.* **2009**, *32*, 3191-3200.
58. Yilmaz, E.; Soylak, M. *Talanta* **2014**, *126*, 191-195.
59. Karimi, M.; Dadfarnian, S.; Shabani, A. M. H.; Tamaddon, F.; Azadi, D. *Talanta* **2015**, *144*, 648-654.
60. Yilmaz, E.; Soylak, M. *J. Anal. At. Spectrom.* **2015**, *30*, 1629-1635.
61. Zhou, Q.; Bai, H.; Xie, G.; Xiao, J. *J. Chromatogr. A* **2008**, *1177*, 43-49.
62. Shirkhanloo, H.; Ghazaghi, M.; Mousavi, H. Z. *J. Mol. Liq.* **2016**, *218*, 478-483.
63. Barfi, B.; Asghari, A.; Rajabi, M.; Mirkhani, N. *RSC Adv.* 2015, *5*, 106574-106588.
64. Zhou, Q.; Zhang, X.; Xiao J. *J. Chromatogr. A* **2009**, *1216*, 4361-4365.
65. Jia, C.; Zhu, X.; Wang, J.; Zhao, E.; Chen, M. H. L.; Yu, P. *J. Chromatogr. A* **2010**, *1217*, 5868-5871.
66. Farajzadeh, M. A.; Mogaddam, M. R. A. *Anal. Chim. Acta* **2012**, *728*, 31-38.
67. Mohammadzadeh, A.; Ramezani, M.; Niazi, A. *Des. Water Treat.* **2016**, *57*, 9745-9755.
68. Ganjali, M. R.; Sobhi, H. R.; Farahani, H.; Norouzi, P.; Dinarvand, R.; Kashtiaray, A. *J. Chromatogr. A* **2010**, *1217*, 2337-2341.
69. Dadfarnia, S.; Shabani, A. M. H.; Kamranzadeh, E. *Talanta* **2009**, *79*, 1061-1065.
70. Zhou, Q.; Bai, H.; Xie, G.; Xiao, J. *J. Chromatogr. A* **2008**, *1188*, 148-153.
71. Baghdadi, M.; Shemirani, F. *Anal. Chim. Acta* **2008**, *613*, 56-63.
72. Liu, Y.; Zhao, E.; Zhu, W.; Gao, H.; Zhou, Z. *J. Chromatogr. A* **2009**, *1216*, 885-891.
73. Pérez-Serradilla, J. A.; Priego-Capote, F.; Luque de Castro, M. D. *Anal. Chem.* **2007**, *79*, 6767-6774.
74. Regueiro, J.; Llompart, M.; Garcia-Jares, C.; Garcia-Monteagudo, J. C.; Cela, R. *J. Chromatogr. A* **2008**, *1190*, 27-38.
75. Moreno-González, D.; Huertas-Pérez, J. F.; García-Campaña, A. M.; Gámiz-Gracia, L. *Talanta*, **2015**, *139*, 174-180.
76. Saleh, A.; Yamini, Y.; Faraji, M.; Rezaee, M.; Ghambarian, M. *J. Chromatogr. A* **2009**, *1216*, 6673-6679.
77. Liang, P.; Wang, F.; Wan, Q. *Talanta* **2013**, *105*, 57-62.
78. Yao, C.; Jared, L. *Anal. Bioanal. Chem.* **2009**, *395*, 1491-1502.
79. Baghadi, M.; Shemirani, F. *Anal. Chim. Acta* **2009**, *634*, 186-191.

80. Vichapong, J.; Srijaranai, S.; Santaladchaiyakit, Y.; Kanchanamayoon, W.; Burakham, R. *Food Anal. Method.* **2016**, *9*, 1120-1127.
81. Molaei, K.; Asgharinezhad, A. A.; Ebrahimzadeh, H.; Shekari, N.; Jalilian, N.; Dehghani, Z. *J. Sep. Sci.* **2015**, *38*, 3905-3913.
82. Rajabi, M.; Ghanbari, H.; Barfi, B.; Asghari, A.; Haji-Esfandiari, S. *Food Res. Int.* **2014**, *62*, 761-770.
83. Yousefi, S. M.; Shemirani, F. *J. Hazard. Mater.* **2013**, *254*, 134-140.
84. Ballesteros-Gomez, A.; Rubio, S.; Perez-Bendito, D. *J. Chromatogr. A* **2009**, *1216*, 530-539.
85. Aydin, F.; Yilmaz, E.; Soylak, M. *RSC Adv.* **2015**, *5*, 94879-94886.
86. Yilmaz, E.; Soylak, M. *RSC Adv.* **2014**, *4*, 47396-47401.
87. Farajzadeh, M. A.; Mogaddam, M. R. A. *Anal. Chim. Acta* **2012**, *728*, 31-38.
88. You, X.; Xing, Z.; Liu, F.; Jiang, N. *J. Chromatogr. A* **2013**, *1311*, 41-47.
89. Abbott, A. P.; Capper, G.; Davies, D. L.; Raymond K. Chem. Commun. **2003**, 70-71.
90. Habibia, E.; Ghanemi, K.; Fallah-Mehrjardi, M.; Dadolahi-Sohra, A. *Anal. Chim. Acta* **2013**, *762*, 61-67.
91. Bi, W.; Tian, M.; Row, K. H. *J. Chromatogr.* A **2013**, *1285*, 22-30.
92. Lasarte-Aragonés, G.; Lucena, R.; Cárdenas, S.; Valcárcel, M. *Talanta* **2015**, *131*, 645-649.
93. Khan, M.; Soylak, M. *RSC Adv.* **2016**, *6*, 24968-24975.
94. Phan, L.; Brown, H.; White, J.; Hodgson, A.; Jessop P. G. *Green Chem.* **2009**, *11*, 53-59.
95. Boyd, A. R.; Champagne, P.; McGinn, P. J.; MacDougal, K. M.; Melanson, J. E.; Jessop, P. G. *Bioresource Technol.* **2012**, *118*, 628-632.
96. Hardy, S.; Wispelaere, I. M.; Leitnera, W.; Liauw, M. A. *Analyst* **2013**, *138*, 819-824.
97. Du, Y.; Schuur B.; Samorì, C.; Tagliavini, E.; Brilman, D. W. F. *Bioresource Technol.* **2013**, *149*, 253-260.
98. Xu, H.; Lv, L.; Hu, S.; Song, D. *J. Chromatogr. A* **2010**, *1217*, 2371-2375.
99. Vidal, L.; Chisvert, A.; Canals, A. *Talanta* **2010**, *81*, 549-555.
100. Martinis, E. M.; Bertón, P.; Altamirano, J. C.; Hakala, U.; Wuilloud, R. G. Talanta **2010**, 80, 2034-2040.
101. Yang, F.; Liu, R.; Tan, Z.; Wen, X.; Zheng, C.; Lv, Y. J. Hazard. Mater. **2010**, 183, 549-553.
102. Vallecillos, L.; Pocurull, E.; Borrull, F. Talanta **2012**, 99, 824-832.
103. Choi, J.; Choi, K.; Kima, J.; Yacin, A.; Ahmed, B. H.; Al-Othman, Z. A.; Chunga, D. S. *J. Chromatogr. A* **2011**, *1218*, 7227-7233.
104. Márquez-Sillero, I.; Aguilera-Herrador, E.; Cárdenas, S.; Valcárcel, M. Anal. Chim. Acta 2011, 702, 199-204.
105. Wang, Z.; Ding, L.; Li, T.; Zhou, X.; Wang, L.; Zhang H.; Liu, L.; Li, Y.; Liu, Z.; Wang, H.; et al. J. Chromatogr. A **2006**, 1102, 11-17.
106. Wen, X.; Deng, Q.; Guo, J. Biomolecular Spectroscopy **2011**, 79, 1941-1945.
107. Farajzadeh, M. A.; Djozan, D.; Khorram, P. Talanta **2011**, 85, 1135-1142.
108. Wen, X.; Deng, Q.; Guo, J.; Yang, S. Spectrochim. Acta Part A 2011, *79*, 508-512.
109. Gao, W. H.; Chen, G. P.; Chen, T. F.; Zhang, X. S.; Chen, Y. W.; Hu, Z. D. *Talanta* **2011**, *83*, 1673-1679.
110. Cabaleiro, N.; Calle, I.; Bendicho, C.; Lavilla, I. Anal. Chim. Acta **2012**, 733, 28-33.
111. Wen, X.; Deng, Q.; Wang, J.; Yang, S.; Zhao, X. *Spectrochim. Acta A* **2013**, *105*, 320-325.
112. Cheng, K.; Choi, K.; Kim, J.; Sung, I. H.; Chung, D. S. *Microchem. J.* **2013**, *106*, 220-225.
113. Salemi, A.; Rasoolzadeh, R.; Nejad, M. M.; Vosough, M. Anal. Chim. Acta **2013**, 769, 121-126.
114. Šrámková, I.; Horstkotte, B.; Solich, P.; Sklenárová, H. *Anal. Chim. Acta* **2014**, *828*, 53-60
115. Li, Y.; Xiong Y.; Liang, Q.; Fang, C.; Wang, C. J. Chromatogr. A **2010**, 1217, 3561-3566.

116. Laura Soriano, C. R. P. M.; Valcárcel, M. *Talanta* **2014**, *125*, 72-77.
117. Timofeeva, I.; Khubaibullin, I.; Kamencev, M.; Moskvin, A.; Bulatov, A. *Talanta* **2015**, *133*, 34-37.
118. Guo, X.; Yin, D.; Peng, J.; Hu, X. *J. Sep. Sci.* **2012**, *35*, 452-458.
119. Martinis, E. M.; Wuilloud, R. G. *J. Anal. At. Spectrom.* **2010**, *25*, 1432-1439.
120. Carrillo-Carrion, C.; Simonet, B. M.; Valcarcel, M. *Analyst* **2012**, *137*, 1152-1159.
121. Almeida, J. S.; Anunciação, T. A.; Brandão, G. C.; Dantas, A. F.; Lemos, V. A.; Leonardo S. G. *Spectrochim. Acta B* **2015**, *107*, 159-163.
122. Amde, M.; Tan, Z. Q.; Liu, R.; Liu, J. F. *J. Chromatogr. A* **2015**, *1395*, 7-15.
123. George, M. J.; Marjanovic, L.; Bradley, D.; Williams, G. *Talanta* **2015**, *144*, 445-450.
124. Yang, Y.; Chen, J.; Shi, Y. P. *J. Chromatogr. B* **2010**, *878*, 2811-2816.
125. Saraji, M.; Farajmand, B.; Ensafi, A. A.; Allafchian, A. R.; Zare, Z. M. *Talanta* **2010**, *82*, 1588-1593.
126. Emídioa, E. S.; Prata, V. M.; Santana, F. J. M.; Dórea, H. S. *J. Chromatogr. B* **2010**, *878*, 2175-2183.
127. Xionga, J.; Chenb, J.; Hea, M.; Hua, B. *Talanta* **2010**, *82*, 969-975.
128. Luciano, R. M.; Bedendo, G. C.; Carletto, J. S.; Carasek, E. *J. Hazard. Mater.* **2010**, *177*, 567-572.
129. Romero-González, R.; Frenich, A. G.; Vidal, J. L. M.; Aguilera-Luiz, M. M. *Talanta* **2010**, *82*, 171-176.
130. Azzama, K. M. A.; Makahleaha, A.; Saada, B.; Mansor, S. M. *J. Chromatogr. A* **2010**, *1217*, 3654-3659.
131. Ghasemi, E.; Najafia, N. M.; Raofie, F.; Ghassempour, A. *J. Hazard. Mater.* **2010**, *181*, 491-496.
132. Ghambarian, M.; Yamini, Y.; Esrafili, A. *J. Pharmaceut. Biomed.* **2011**, *56*, 1041-1045.
133. Wang, J.; Du, Z.; Yu, W.; Qu, S. *J. Chromatogr. A* **2012**, *1247*, 10-17.
134. López-García, I.; Rivas, R. E.; Hernández-Córdoba, M. *Anal. Chim. Acta* **2012**, *743*, 69-74.
135. Guo, X.; He, M.; Chen, B.; Hu, B. *Talanta* **2012**, *101*, 516-523.
136. Payán, M. R.; López, M. Á. B.; Fernández-Torres, R.; Navarro, M. V.; Mochón, M. C. *J. Chromatogr. B* **2011**, *879*, 197-204.
137. Zeng, C.; Lin, Y.; Zhou, N.; Zheng, J.; Zhang, W. *J. Hazard. Mater.* **2012**, *237*, 365-370.
138. Liu, W.; Wei, Z.; Zhang, Q.; Wu, F.; Lin, Z.; Lu, Q.; Lin, F.; Chen, G.; Zhang, L. *Talanta* **2012**, *88*, 43-49.
139. Tong, F.; Zhang, Y.; Chen, F.; Li, Y.; Ma, G.; Chen, Y.; Liu, K.; Dong, J.; Ye, J.; Chu, Q. *J. Chromatogr. B* **2013**, *942*, 134-140.
140. Shrivas, K.; Patel, D. K. *Food Chem.* **2011**, *124*, 1673-1677.
141. Ge, D.; Lee, H. K. *J. Chromatogr. A* **2012**, *1229*, 1-5.
142. Zhou, J.; Zeng, P.; Sun, J. B.; Wang, F. Q.; Zhang, Q. *J. Pharm. Biomed. Anal.* **2013**, *81-82*, 27-33.
143. Chao, Y. Y.; Jian, Z. Z.; Tu, Y. M.; Huang, Y. L. *Microchem. J.* **2013**, *110*, 386-394.
144. Wang, H.; Wu, W. W.; Wei, D. Y.; Guo, Z. Y.; Wang, S. *J. Electroanal. Chem.* **2014**, *735*, 136-141.
145. Wang, S. R.; Wang, S. *J. Food Drug. Anal.* **2014**, *22*, 418-424.
146. Nomngongo, P. N.; Ngila, J. C.; Msagati, T. A. M.; Moodley, B.; *Microchem. J.* **2014**, *114*, 141-147.
147. Wang, X.; He, Y.; Lin, L.; Zeng, F. *Sci. Total Environ.* **2014**, *470-471*, 263-269.
148. Yamini, Y.; Rezaee, M.; Khanchi, A.; Faraji, M.; Saleh, A. *J. Chromatogr. A* **2010**, *1217*, 2358-2364.
149. Mahpishanian, S.; Shemirani, F. *Miner. Eng.* **2010**, *23*, 823-825.
150. Yan, H.; Liu, B.; Du, J.; Yang, G.; Row, K. H. *J. Chromatogr. A* **2010**, *1217*, 5152-5157.
151. Yiantzi, E.; Psillakis E.; Tyrovola, K.; Kalogerakis, N. *Talanta* **2010**, *80*, 2057-2062.
152. Moradi, M.; Yamini, Y.; Esrafili, A.; Seidi, S. *Talanta* **2010**, *82*, 1864-1869.

153. Bai, H.; Zhou, Q.; Xie, G.; Xiao, J. *Talanta* **2010**, *80*, 1638-1642.

154. Mahpishanian, S.; Shemirani, F. *Talanta* **2010**, *82*, 471-476.

155. Wu, Q.; Chang, Q.; Wu, C.; Rao, H.; Zeng, X.; Wang, C.; Wang, Z. *J. Chromatogr. A* **2010**, *1217*, 1773-1778.

156. Zhang, P. P.; Shi, Z. G.; Yu, Q. W.; Feng, Y. Q. *Talanta* **2011**, *83*, 1711-1715.

157. Guo, L.; Lee, H. K. *J. Chromatogr. A* **2011**, *1218*, 5040-5046.

158. Xu, X.; Su, R.; Zhao, X.; Liu, Z.; Zhang, Y.; Li, D.; Li, X.; Zhang, H.; Wang, Z. *Anal. Chim. Acta* **2011**, *707*, 92-99.

159. Škrlíková, J.; Andruch, V.; Balogh, I. S.; Kocúrová, L.; Nagy, L.; Bazel, Y. *Microchem. J.* **2011**, *99*, 40-45.

160. Gupta, M.; Pillai, A. K. K. V.; Singh, A.; Jain, A.; Verma, K. K. *Food Chem.* **2011**, *124*, 1741-1746.

161. Campillo, N.; Viñas, P.; Martínez-Castillo, N.; Hernández-Córdoba, M. *J. Chromatogr. A* **2011**, *1218*, 1815-1821.

162. Cortada, C.; Vidal, L.; Canals, A. *Talanta* **2011**, *85*, 2546-2552.

163. Molaakbari, E.; Mostafavi, A.; Afzali, D. *J. Hazard. Mater.* **2011**, *185*, 647-652.

164. Martinisa, E. M.; Escuderoa, L. B.; Bertona, P.; Monasterio, R. P.; Filippini, M. F.; Wuilloud, R. G. *Talanta* **2011**, *85*, 2182-2188.

165. Zhang, H.; Chen, X.; Jiang, X. *Anal. Chim. Acta* **2011**, *689*, 137-142.

166. Cabarcos, P.; Cocho, J. Á.; Moreda, A.; Míguez, M.; Tabernero, M. J.; Fernández, P.; Bermejo, A. M. *Talanta* **2013**, *111*, 189-195.

167. Wu, H.; Guo, J.; Du, L.; Tian, H.; Hao, C.; Wang, Z.; Wang, J. *Food Chem.* **2013**, *141*, 182-186.

168. Abdelhamid, H. N.; Bhaisare, M. L.; Wu, H. F. *Talanta* **2014**, *120*, 208-217.

169. Wang, Y.; Sun, Y.; Xu, B.; Li, X.; Jin, R.; Zhang, H.; Song, D. *J. Chromatogr. A* **2014**, *1373*, 9-16.

170. Farajzadeh, M. A.; Asghari, A.; Feriduni, B. *J. Food Compos. Anal.* **2016**, *48*, 73-80.

171. Guo, L.; Tan, S.; Li, X.; Lee, H. K. *J. Chromatogr. A* **2016**, *1438*, 1-9.

172. Akhond, M.; Absalan, G.; Pourshamsi, T.; Ramezani, A. M. *Talanta* **2016**, *154*, 461-466.

173. Zhao, X. E., Lv, T.; Zhu, S.; Qu, F.; Chen, G.; He, Y.; Wei, N.; Li, G.; Xia, L.; Sun, Z.; et al. *J. Chromatogr. A* **2016**, *1437*, 49-57.