Journal of Chromatography A, 1217 (2010) 2337–2341

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Review

Solid drop based liquid-phase microextraction

Mohammad Reza Ganjali [a,d,*], Hamid Reza Sobhi [b], Hadi Farahani [c], Parviz Norouzi [a,d], Rassoul Dinarvand [e], Amir Kashtiaray [b]

[a] *Center of Excellence in Electrochemistry, University of Tehran, Tehran, Iran*
[b] *Department of Chemistry, Tehran Payamenoor University, Tehran, Iran*
[c] *Industrial and Environmental Protection Division, Research Institute of Petroleum Industry (RIPI), Tehran, Iran*
[d] *Endocrinology & Metabolism Research Center, Tehran University of Medical Sciences, Tehran, Iran*
[e] *Medical Nanotechnology Research Center, Tehran University of Medical Sciences, Tehran, Iran*

ARTICLE INFO

Article history:
Available online 13 November 2009

Keywords:
Solid drop liquid-phase microextraction
Sample preparation
Review

ABSTRACT

Solid drop based liquid-phase microextraction (SDLPME) is a novel sample preparation technique possessing obvious advantages of simple operation with a high pre-concentration factor, low cost and low consumption of organic solvent. SDLPME coupled with gas chromatography (GC), high-performance liquid chromatography (HPLC), and atomic absorption spectrometry (AAS) has been widely applied to the analyses of a different variety of samples. The basic principles, parameters affecting the extraction efficiency, and the latest applications of SDLPME are reviewed in this article.

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1. Introduction

Sample preparation is a tedious and yet unavoidable procedure in analytical chemistry [1]. The objective of this challenging and critical step is to transfer the analyte into a form that is pre-purified, concentrated and compatible with the analytical system [2,3]. The extracted and enriched analytes of interest from the sample matrix are often accomplished by procedures such as liquid-liquid-extraction (LLE) [4,5] and solid phase extraction (SPE) [6,7]. The invention of solid phase microextraction (SPME) by Arthur and Pawliszyn [8] basically initiated the interest for microextraction techniques in analytical chemistry. SPME satisfies most of the requirements of a good sample preparation technique including: simplicity of use, automation, and low consumption of materials [9]. Thus, it has been applied to determine a broad range of organic compounds in numerous types of samples [10].

* Corresponding author at: Center of Excellence in Electrochemistry, University of Tehran, Tehran, Iran. Tel.: +98 21 61112788; fax: +98 21 66405141.
E-mail address: ganjali@khayam.ut.ac.ir (M.R. Ganjali).

0021-9673/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2009.11.026

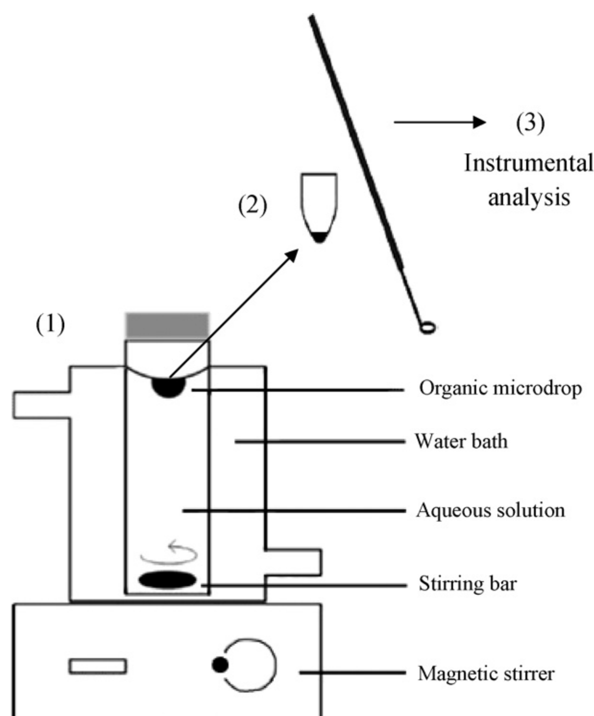

Fig. 1. Solid drop based liquid-phase microextraction procedure.

An alternative solvent-minimized sample preparation approach to complement SPME appeared in the middle-to-late 1990s [11–13]; liquid-phase microextraction (LPME) utilizes only a small amount of solvent (low microliter range) for concentrating analytes from aqueous samples. It is simply a miniaturized format of LLE and overcomes many of its disadvantages as well as some of those of SPME (e.g. non-dependence on a commercial supplier and sample carryover). LPME is simple to implement and use, generally fast, and is also characterized by its affordability and reliance on widely available apparatus or materials [14]. The applications of LPME in environmental and biological analysis have been described in several papers [15–17].

LPME can be classified as two- [13,18,19] and three-phase [20–22] categories. Two-phase microextraction is usually performed by suspending a drop (a few microliters) of organic solvent on the tip of either a Teflon rod or the needle tip of a microsyringe immersed in the stirred aqueous sample solution. Analytes are extracted into the organic solvent and then directly injected into a gas chromatograph (GC) for analysis. Hollow fiber protected two-phase microextraction has also been developed to enhance the extraction efficiency and to stabilize the extracted solvent microdrop [23]. In three-phase microextraction, the ionizable analytes in the aqueous sample are extracted through a thin phase of organic solvent inside the pores of a polypropylene hollow fiber or an organic solvent layer held within a Teflon ring and then back-extracted into another aqueous acceptor solution. Following this procedure the acceptor solution could be analyzed by capillary electrophoresis (CE) or high-performance liquid chromatography (HPLC) without further treatment.

In 2007, Yamini and co-workers [24] developed a novel two-phase LPME method based on a solid drop in which the acceptor to donor phase ratio is greatly reduced compared with other methods. In solid drop liquid-phase microextraction (SDLPME, Fig. 1), an appropriate volume of suitable organic solvent (less than 20 μL) is delivered to the surface of the aqueous solution located in a glass vial. The organic solvent must have a melting point near room temperature (in the range of 10–30 °C). The aqueous phase is stirred for a desired time and then the sample vial is transferred into an ice bath. After a short period of time (about 5 min) the organic solvent is solidified and transferred into a small conical vial using a miniature spatula. The solid organic solvent known as the 'solid drop' melts quickly at room temperature. Finally, it is retracted by a microsyringe and injected into an analytical instrument for final analysis. Due to excellent accuracy and precision this quantitative technique seems to be an efficient and satisfactory analytical procedure.

The present review builds on the principles, effective factors and also previous reports regarding the application of SDLPME.

2. The principle of SDLPME

Equations describing effects of several parameters of the efficiency of SDLPME method are similar to those of LLE. The related equations are as follows:

$$C_{o,f} = KC_{aq,f} = \frac{KC_{aq,i}}{1 + KV_o/V_{aq}} \quad (1)$$

$$\frac{dC_o}{dt} = \frac{A_i\beta}{V_o(KC_{aq} - C_o)} \quad (2)$$

where $C_{o,f}$ is the final concentration of the analyte in the organic phase; $C_{aq,f}$ and $C_{aq,i}$ are the final and initial analyte concentrations in the aqueous phase, respectively; V_o and V_{aq} are the organic and aqueous phase volumes, respectively; K is the distribution coefficient; C_o and C_{aq} are the analyte concentrations in the organic and aqueous phases at the time t, respectively; A_i is the interfacial area and β is the overall mass transfer coefficient with respect to the organic phase [13,25].

The pre-concentration factor (PF) can be calculated based on the following equation:

$$\mathrm{PF} = \frac{C_{o,f}}{C_{aq,i}} \quad (3)$$

$C_{o,f}$ was calculated from a suitable calibration curve obtained from the direct injection of the standards into an analytical instrument.

3. Parameters affecting the extraction efficiency of SDLPME

The extraction efficiency for the target analytes in SDLPME is influenced by many factors such as the: kind of extracting solvent and its volume, sample solution temperature, salt addition, stirring rate, sample pH and extraction time.

3.1. Selection of extracting solvent

The selection of an appropriate extracting solvent is of great importance for the optimization of the LPME process [26]. To choose a suitable organic extracting solvent the following criteria should be considered. Firstly, the selected solvent should be immiscible with water and exhibit a high boiling point with low vapor pressure in order to reduce the evaporation risk during the extraction time [27]. Secondly, it should exhibit a good chromatographic behavior and thirdly, improve appropriate extraction efficiency to yield high PFs [28]. Finally, it must demonstrate a melting point near room temperature (in the range of 10–30 °C) [24]. Accordingly, several extracting solvents, including 1-undecanol, 1-dodecanol, 2-dodecanol, 1-bromohexadecane, 1-hexadecane, 1,10-dichlorodecane and 1-chlorooctadecane meet the above criteria (Table 1). But amongst those, 1-undecanol and 1-dodecanol have been commonly used.

Table 1
Usable organic extracting solvents and their corresponding melting points.

Extracting solvent	Melting point (°C)
1-Undecanol	13–15
2-Dodecanol	17–18
1-Dodecanol	22–24
1-Bromohexadecane	17–18
n-Hexadecane	18
1,10-Dichlorodecane	14–16
1-Chlorooctadecane	20–23

3.2. Sample solution temperature

Raising the temperature of the sample solution can influence the mass transfer rate and the partition coefficient of the analyte. Therefore, it affects the extraction kinetics and consequently, the time required to reach equilibrium diminishes [29,30]. The effect of sample solution temperature on the extraction efficiency is commonly studied in the range of 20–70 °C by floating the extracting solvent microdrop during the extraction time. It is clear that by increasing the temperature, the extraction efficiency of the analyte increases. However, at higher temperatures (>60 °C) the over-pressurization of the sample vial makes the extraction system unstable. Thus, in this method the sample solution temperature should not exceed 60 °C.

3.3. Salt addition

The salting-out effect has been widely applied to LLE and SPME [31,32]. However in SDLPME and LPME in general, some contradictory results have been reported [33,34]. One of them is an observed decrease in extraction efficiency at higher salt concentrations. This can be explained by the fact that the addition of salt can restrict the transport of the analyte to the extracting solvent drop due to an increase of sample viscosity. By increasing the salt concentration, diffusion of analytes towards the organic solvent becomes more and more difficult [35]. On the other hand, in some reports the addition of salt promotes the transfer of the analyte into the extracting solvent. It can be explained by the fact that water molecules form hydration spheres around the salt ions. These hydration spheres reduce the concentration of water available to dissolve analyte molecules; thus it was expected that this would drive additional analytes into the extracting solvent [36].

3.4. Volume of extracting solvent

Based on Eq. (2), the rate of analyte transfer into the microdrop is directly related to the interfacial area between the two liquid-phases and inversely related to the organic-phase volume. Thus by increasing the drop volume, the effect of the interfacial area predominates and the analytical signal increases [37–39]. By further increase of the microdrop volume, the effect of the solvent volume dominates and the analytical signal decreases [40,41]. Moreover, since in most cases a fixed amount of the drop is injected for final analysis (not the whole); once the volume of extracting phase is increased there is always a competition between the rise in extraction efficiency on the one hand and dilution effect on the other hand. Due to the dual mentioned effect the selected volume varies in the range of 7.0–10.0 μL.

3.5. Stirring rate

Magnetic stirring enhances extraction and reduces the time required to reach thermodynamic equilibrium. It also facilitates the mass transfer process and thus improves the extraction efficiency [42–44]. In SDLPME, since a specific holder is not required for supporting the organic microdrop, stirring of the sample solution at high speeds is feasible. The stirring rate however should not exceed too far at the cost of instability of the organic drop. Moreover, by using a multi-stirrer parallel extraction of many samples is possible.

3.6. Extraction time

The amount of analyte extracted at a given time depends upon the mass transfer of analyte from the aqueous phase to the organic phase [45,46]. To increase repeatability of extraction it is necessary to choose an extraction time during which equilibrium between the aqueous and organic phase is reached. However, it is not practical to wait for equilibrium to occur; the extraction time should be just long enough for the extraction rate to slow down for an improved precision. Usually the extraction time for the method varies from 20 to 35 min. Therefore, the method is not exhaustive.

3.7. Sample pH

Acidic and basic compounds in water samples can be neutral or ionized depending on the choice of sample pH. The pH must be adjusted so that analytes are neutralized, i.e. carrying no charge otherwise the analytes cannot diffuse and dissolve into the organic phase [47]. This shows the extraction of ionizable targets including polar drugs, metal ions etc is significantly under control of the sample pH.

4. Applications of SDLPME

As a novel sample preparation method SDLPME can be coupled with GC, HPLC, and AAS (atomic absorption spectrometry) for application. It has been widely applied to the analyses of organic pollutants, some metal ions, and so on. The typical applications are discussed in detail in the following sections and also shown in Table 2.

Table 2
Applications of solid drop based liquid-phase microextraction.

Analyte	Matrix	Analytical method	Extracting solvent	PF	LOD (μg L^{-1})	Reference
PAHs	Water	GC-FID	1-Undecanol	594–1940	0.07–1.67	[24]
2-Pyrazoline derivatives	Biological samples	GC-FID	1-Undecanol	183–538	5.0–10.0	[48]
Aliphatic alcohols	Water	GC-FID	1-Undecanol	13–358	3.0–56.0	[49]
Phthalate esters	Water	GC–MS	1-Dodecanol	307–412	0.02–0.05	[50]
Organochlorine pesticides	Water	GC-ECD	1-Dodecanol	708–1337	0.007–0.019	[51]
Trihalomethanes	Water	GC–MS	1-Undecanol	366–482	0.03–0.08	[52]
Fat-soluble vitamins	Water	HPLC-UV	1-Undecanol	30–35	1.0–3.5	[53]
Pb (II)	Water	GF-AAS	1-Undecanol	500	0.0009	[54]
Co (II), Ni (II)	Water	GF-AAS	1-Undecanol	497, 502	0.0003, 0.0004	[55]
Cd (II)	Water	FI-FAAS	1-Undecanol	640	0.008	[56]

4.1. GC

Since the used extracting solvents in SDLPME can be directly injected into GC without additional pre-treatment, the method is very compatible with GC in most cases. Therefore, SDLPME-GC technique has achieved relatively rapid development in a short time. Monitoring pollutants in water is one of the most important environmental analyses. SDLPME-GC is easy to operate and applicable for different verity of samples. In 2007, Yamini and co-workers [24] developed the coupled technique mentioned above as a novel method for the determination of some polycyclic aromatic hydrocarbons (PAHs) in complex water matrices (sea and well waters). In their study 8 μL of 1-undecanol was first delivered to the surface of the solution (20 mL) containing the analytes. Secondly, the temperature of the solution was set at 60 °C using a water bath. The solution was then stirred for 30 min and once the extraction time was over, the sample vial was cooled – by inserting it into an ice bath for 5 min. The produced solid drop was transferred into another suitable conical vial, where it melted immediately; then, 2 μL of it was injected into the GC for final analysis. High PFs in the range of 594–1940 were achieved for different PAHs. The calibration curves were linear in the concentration ranges of 0.2–400 $\mu g L^{-1}$, with correlation coefficients (r^2) in the range of 0.9943–0.9999 for different PAHs. The limits of detection (LODs) at a signal-to-noise ratio of 3 (S/N = 3) were in the range of 0.07–1.67 $\mu g L^{-1}$. The recovery of the PAHs from sea-water at a spiked level of 8.0 $\mu g L^{-1}$ varied from 84 up to 104%. Further development shows that Sobhi et al. [48] developed the extraction and determination of 2-pyrazoline derivative compounds in biological samples, (including urine) with high recovery and precision. Also, this group successfully managed to extract and analyze trace amounts of some low-molecular weight aliphatic alcohols in a different variety of aqueous samples including waste-water [49]. Later on, Farahani et al. [50] developed the combination of SDLPME with gas chromatography–mass spectrometry (GC–MS) for the extraction and determination of very low amounts of phthalate esters in water samples. The LODs were in the range of 0.02–0.05 $\mu g L^{-1}$, while a broad linear range (0.05–100 $\mu g L^{-1}$) was obtained. They also developed the method in conjunction with (GC-ECD) for screening eleven organochlorine pesticides in water samples [51]. Furthermore, the applicability of SDLPME method was successfully tested for the extraction and determination of trihalomethanes pollutants in drinking water with GC–MS [52].

4.2. HPLC

Orthogonal array experimental design (OAD) based on Taguchi's method was employed to screen the SDLPME conditions for the extraction determination of vitamins A, D_2 and D_3 in different aqueous samples [53]. According to the report the most important factors contributing to the extraction efficiency were stirring rate (59%) followed by extraction time (25%). In the method, the whole solid drop (about 15 μL) was injected into the HPLC for quantification. The mobile phase was pure methanol with a flow-rate of 1.0 mL min^{-1}. Ultraviolet (UV) detection was carried out simultaneously at two different wavelengths of 264 and 325 nm for the Vitamins D (D_2 and D_3) and A, respectively.

4.3. AAS

SDLPME combined with graphite furnace atomic absorption spectrometry (GF-AAS) was initially proposed by Dadfarnia and co-workers [54] for simultaneous separation/enrichment and determination of trace amounts of lead (II) ions. 1-Undecanol containing dithizone as the chelating agent was transferred to the water samples containing lead ions. Under the optimized conditions, a good relative standard deviation (RSD) of ±5.4% at 10 ng L^{-1} and LOD of 0.9 ng L^{-1} were obtained. The procedure was successfully applied to the analysis of lead ions in tap, well, river and sea-water. In a further development, the above mentioned research group proposed the prior method for simultaneous separation/enrichment and determination of trace amounts of nickel (II) and cobalt (II) in surface and sea-water [55]. In this work, 1-(2-pyridylazo)-2-naphthol (PAN) was used as the chelating agent. Later on they also combined DSLPME with flow injection flame atomic absorption spectrometry (FI-FAAS) as a simple and selective method for the separation and pre-concentration of cadmium (II) in water samples [56]. Under the optimized conditions, a pre-concentration factor of 640, detection limit of 0.0079 $\mu g L^{-1}$ and good RSD of ±5.4% at 5.0 $\mu g L^{-1}$ were obtained. The procedure was applied for the analysis of cadmium in tap, well, and sea-water samples.

5. Conclusions

SDLPME is a relatively new sample pre-treatment method combining sampling, extraction, and pre-concentration all together. Compared with traditional extraction methods it has the advantages of simplicity of operation, rapidity, low cost, high recovery and high pre-concentration factor. However, the main drawback of the proposed method is the limitation of selecting an extracting solvent, because just a few organic solvents are close to the melting point of room temperature, as well as overlapping of the solvent peaks with those of the analytes. Since a fresh portion of organic solvent is used for each extraction, there is no memory effect and since the volume of the organic phase is only at few microliter levels, large pre-concentration factors are achievable. It is likely that SDLPME will be developed further in the following aspects: (1) more applications in the analysis of samples with complex matrices – since most of the target compounds analyzed by SDLPME till now are relatively simple matrices, it is important to make this method more applicable to the samples with complex matrices including biological ones; (2) to investigate as to whether SDLPME is capable of being coupled to other analytical instruments.

Acknowledgment

The authors would honor the memory of M.R. Khalili-Zanjani who first came up with the idea of SDLPME.

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