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Determination of organic compounds in water using dispersive liquid–liquid microextraction

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Abstract

A new microextraction technique termed dispersive liquid–liquid microextraction (DLLME) was developed. DLLME is a very simple and rapid method for extraction and preconcentration of organic compounds from water samples. In this method, the appropriate mixture of extraction solvent (8.0 μL C_2Cl_4) and disperser solvent (1.00 mL acetone) are injected into the aqueous sample (5.00 mL) by syringe, rapidly. Therefore, cloudy solution is formed. In fact, it is consisted of fine particles of extraction solvent which is dispersed entirely into aqueous phase. After centrifuging, the fine particles of extraction solvent are sedimented in the bottom of the conical test tube (5.0 ± 0.2 μL). The performance of DLLME is illustrated with the determination of polycyclic aromatic hydrocarbons (PAHs) in water samples by using gas chromatography-flame ionization detection (GC-FID). Some important parameters, such as kind of extraction and disperser solvent and volume of them, and extraction time were investigated. Under the optimum conditions the enrichment factor ranged from 603 to 1113 and the recovery ranged from 60.3 to 111.3%. The linear range was 0.02–200 μg/L (four orders of magnitude) and limit of detection was 0.007–0.030 μg/L for most of analytes. The relative standard deviations (RSDs) for 2 μg/L of PAHs in water by using internal standard were in the range 1.4–10.2% ($n = 5$). The recoveries of PAHs from surface water at spiking level of 5.0 μg/L were 82.0–111.0%. The ability of DLLME technique in the extraction of other organic compounds such as organochlorine pesticides, organophosphorus pesticides and substituted benzene compounds (benzene, toluene, ethyl benzene, and xylenes) from water samples were studied. The advantages of DLLME method are simplicity of operation, rapidity, low cost, high recovery, and enrichment factor.

Keywords: Dispersive liquid–liquid microextraction (DLLME); Sample preparation; Water analysis; Gas chromatography (GC); Polycyclic aromatic hydrocarbons (PAHs)

1. Introduction

The sample preparation step in an analytical process typically consists of an extraction procedure that results in the isolation and enrichment of components of interest from a sample matrix. Extraction can vary in degree of selectivity, speed and convenience and depends not only on the approach and conditions used but also on the geometric configurations of the extraction phase [1]. Liquid–liquid extraction (LLE) is among the oldest of the preconcentration and matrix isolation techniques in analytical chemistry [2]. However, LLE is time-consuming and requires large amounts of organic solvent. Solid-phase extraction (SPE) uses much less solvent than LLE, but can be relatively expensive. Supercritical fluid extraction (SFE) can also be relatively expensive [3].

Recent research activities are oriented towards the development of efficient, economical, and miniaturized sample preparation methods. As a result, solid-phase microextraction (SPME) [4–6] and solvent microextraction (SME) [7,8] have been developed, among the others. Compared with LLE, SPME is a solvent-free process developed by Arthur and Pawliszyn [9] that includes simultaneous extraction and preconcentration of analytes from aqueous samples or the headspace of the samples. However, SPME is also expensive, its fiber is fragile and has limited lifetime and sample carry-over can be a problem [10]. Jeannot and Cantwell developed a liquid–liquid microextraction (LLME) system by which extraction was achieved into a single drop [11]. He and Lee reported liquid-phase microextraction (LPME) in

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1997 [12,13]. Single drop microextraction (SDME) was developed as a solvent-minimized sample pretreatment procedure which is inexpensive, and since very little solvent is used, there is minimal exposure to toxic organic solvents [14,15]. However, the disadvantages of these methods are as follows: fast stirring would tend to break up the organic drop; air bubble formation [3]; extraction is time-consuming and equilibrium could not be attained after a long time in most cases [15]. Furthermore, as a result of the demand for ultra-trace analysis, the need for powerful methods has increased in particular for environmental analysis. Therefore, simple, rapid, clean and efficient techniques that can be performed easily are required.

Cloud-point extraction (CPE) uses surfactants for extraction of materials. Surfactants for extraction have been known to human beings for long for their capability to enhance the solubility of hydrophobic material [16,17]. The advantage of CPE is the preferable use of water as the solvent in the micellar solution, which is benign to the environment, as compared with the organic solvents still used in other preconcentration procedures. Despite many benefits of using cloud-point extraction, the choices of the surfactants often bring the nuisance to the analysis of analytes using some instruments analyses such as GC and HPLC [18,19]. In addition, the use of anionic surfactants as effective extractant in the cloud-point extraction separation often requires of salts and adjustments of pH [20,21]. Pressure and temperature effect in CPE. Hence, it is very important to optimize them in order to obtain the good recovery [22].

Homogeneous liquid–liquid extraction (HLLE) utilizes the phase separation phenomenon from a homogeneous solution, and the target solutes are extracted into a separated phase. In homogeneous liquid–liquid extraction, the initial condition (before phase separation) is homogeneous solution; namely, there is no interface between the water phase and the water-miscible organic solvent phase. In other words, the surface area of the interface is infinitely large initially. Accordingly, no vigorous mechanical shaking is necessary. The procedure is simple and requires only the addition of a reagent. The ternary component solvent system and the perfluorinated surfactant system are the two usual modes of homogeneous liquid–liquid extraction [23–26].

However, HLLE has some problem; for instance, sometimes it is not compatible with some instrumental analysis and also it requires the addition of reagent such as acid, base, salt, etc. As a result of that, probably some interested compounds are destroyed; moreover, the addition of reagent causes to release of heat during extraction.

The authors demonstrated a novel microextraction technique as a high performance and powerful preconcentration method which is dispersive liquid–liquid microextraction (DLLME). It is based on ternary component solvent system such as HLLE and CPE. In this method, the appropriate mixture of extraction solvent and disperser solvent is injected into aqueous sample by syringe, rapidly. Thereby, cloudy solution is formed. The advantages of DLLME method are simplicity of operation, rapidity, low cost, high recovery, and enrichment factor. The performance of DLLME is illustrated with the determination of polycyclic aromatic hydrocarbons (PAHs) in water samples by using gas chromatography-flame ionization detection (GC-FID). The effects of various experimental parameters on the extraction of PAHs from water samples were investigated. Also, the ability of DLLME technique in the extraction of other organic compounds such as organochlorine pesticides (OCPs), organophosphorus pesticides (OPPs) and benzene, toluene, ethyl benzene and xylenes (BTEX) from water samples was studied.

2. Experimental

2.1. Reagents and standards

All PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, flouranthene, pyrene, benzofluorene, benzo[a]anthracene, chrysene, benzo[e]acephenanthylene, benzo[e]pyrene, benzo[a]pyrene, perylene, and benzo[ghi]perylene) used were purchased from Aldrich (USA). Tetrachloroethylene (for spectroscopy), carbon tetrachloride (GR), and carbon disulfide (GR) were obtained from Merck (Germany). These solvents were distillated at least four times and were used as extraction solvents. Acetone, acetonitrile, and methanol as disperser solvent (suprasolv for gas chromatography) were obtained from Merck, along with dichloromethane and biphenyl (as internal standard). Bidistilled water was used for preparation of aqueous solution.

0.00100 g of each PAHs was dissolved in 20 mL mixture of acetonitrile and dichloromethane (1:1) to obtain a standard stock solution with a concentration of 50 mg/L. A fresh 2 mg/L standard solution containing the 16 PAHs was prepared in acetonitrile every week and stored at 4 °C.

Surface, well and river water samples, used for evaluation of the method were collected in glass bottle from Tehran (Iran), and stored at 4 °C. Water samples were filtrated through a 0.45 μm PTFE syringe filter (Osmonics).

2.2. Instrumentation

A gas chromatograph (Shimadzu GC 2010) with a split/splitless injector system, and a flame ionization detector was used for separation and determination of PAHs. Ultra pure helium (99.9999%, Air products, UK) was made to pass through a molecular sieve trap and oxygen trap (Crs, USA) was used as the carrier gas at constant linear velocity of 35 cm/s. The injection port was held at 340 °C and used in the splitless mode with splitless time 1 min. Separation was carried out on a BP-5, 30 m × 0.22 mm capillary column with a 0.25 μm stationary film thickness, 95% methyl–5% phenyl copolymer column (SGE). The oven temperature was programmed as follows: initial 90 °C, from 90 °C (held 5 min) to 290 °C at the rate of 10 °C/min, and held at 290 °C for 10 min. The total time for one GC run was 35 min. The FID temperature was maintained at 330 °C, hydrogen gas was generated with hydrogen generator (OPGU–2200s, Shimadzu) for FID at a flow of 40 mL/min. The flow of zero air (99.999, Air Products) for FID was 400 mL/min. The Centurion Scientific Ltd. (model 2010D, UK) was used for centrifuging.

2.3. Dispersive liquid–liquid microextraction procedure

A 5.00 mL of bidistilled water was placed in a 10 mL screw cap glass test tube with conic bottom and spiked at the level of 2 μg/L of PAHs and biphenyl (as internal standard). 1.00 mL of acetone (as disperser solvent) containing 8.0 μL C_2Cl_4 (as extraction solvent) was injected into a sample solution by using 1.00 mL syringe, rapidly and then the mixture was gently shaken. A cloudy solution (water, acetone, and tetrachloroethylene) was formed in a test tube (the cloudy state was stable for a long time). Then the mixture was centrifuged for 1.5 min at 6000 rpm. Accordingly, the dispersed fine particles of extraction phase were sedimented in the bottom of conical test tube. The 2.00 μL of sedimented phase was removed using a 2.00 μL microsyringe (zero dead volume, Hamilton) and injected into GC. The volume of the sedimented phase was determined using a 10 μL microsyringe which was about 5.0 μL. The extraction steps are illustrated in Fig. 1.

2.4. Calculation of enrichment factor, extraction recovery and relative recovery

The enrichment factor (EF) was defined as the ratio between the analyte concentration in the sedimented phase (C_{sed}) and the initial concentration of analyte (C_0) within the sample:

$$\mathrm{EF} = \frac{C_{sed}}{C_0} \tag{1}$$

The C_{sed} was obtained from calibration graph of direct injection of PAHs standard solution in the C_2Cl_4 at the range of 0.5–2.5 mg/L.

The extraction recovery (ER) was defined as the percentage of the total analyte amount (n_0) which was extracted to the sedimented phase (n_{sed}).

$$\mathrm{ER} = \frac{n_{sed}}{n_0} \times 100 = \frac{C_{sed} \times V_{sed}}{C_0 \times V_{aq}} \times 100 \tag{2}$$

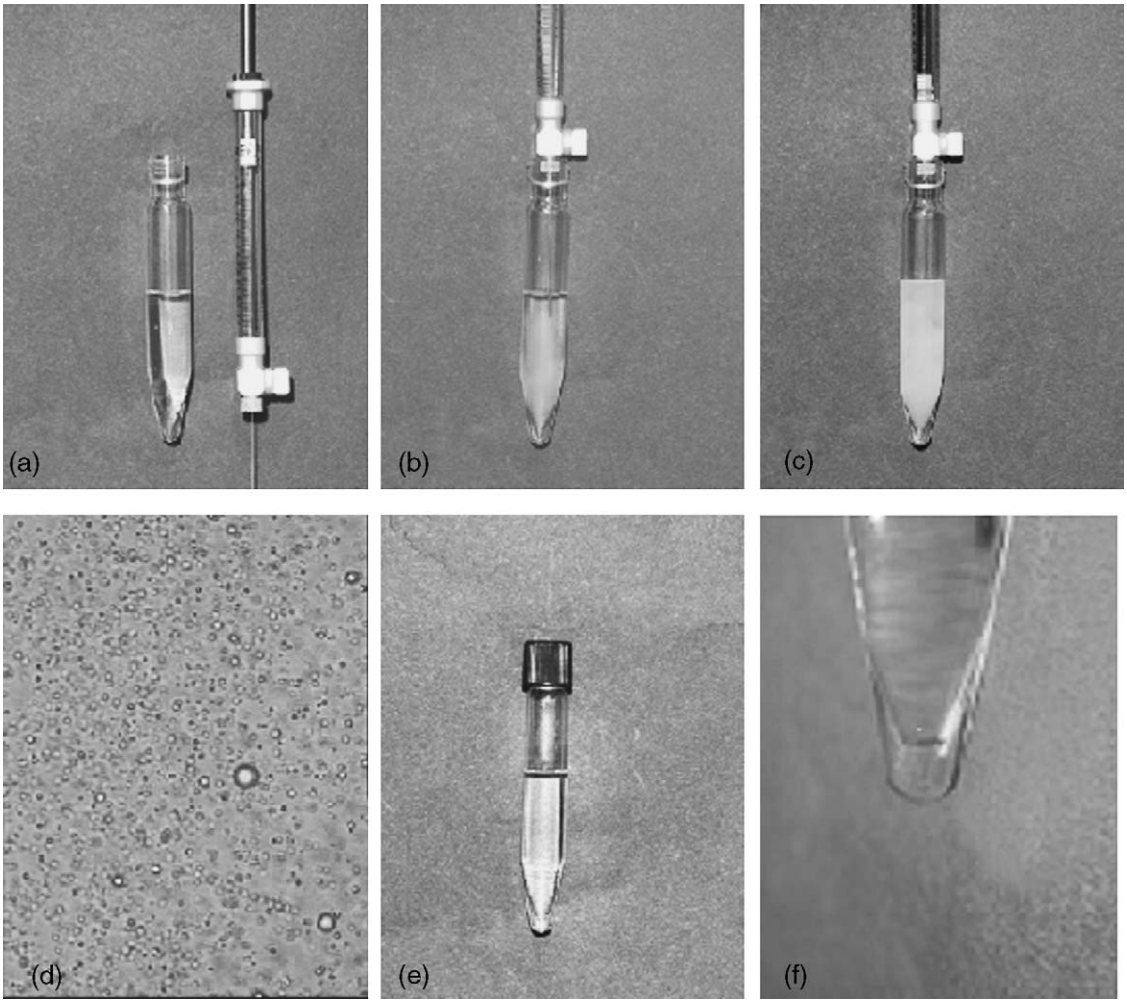

Fig. 1. Photography of different steps in DLLME: (a) before injection of mixture of disperser solvent (acetone) and extraction solvent (C_2Cl_4) into sample solution, (b) starting of injection, (c) end of injection, (d) optical microscopic photography, magnitude 1000 (that shows fine particles of C_2Cl_4 in cloudy state), (e) after centrifuging and (f) enlarged view of sedimented phase (5.0 ± 0.2 μL).

$$\mathrm{ER} = \left(\frac{V_{\mathrm{sed}}}{V_{\mathrm{aq}}}\right) EF \times 100 \quad (3)$$

where V_{sed} and V_{aq} are the volumes of sedimented phase and sample solution, respectively.

The relative recovery (RR) was obtained as the following equation:

$$\mathrm{RR} = \frac{C_{\mathrm{founded}} - C_{\mathrm{real}}}{C_{\mathrm{added}}} \times 100 \quad (4)$$

where C_{founded}, C_{real}, and C_{added} are the concentrations of analyte after addition of known amount of standard in the real sample, the concentration of analyte in real sample and the concentration of known amount of standard which was spiked to the real sample, respectively.

3. Result and discussion

There are different factors that affect the extraction process. Some of them are selection of suitable extraction solvent, selection of suitable disperser solvent, volume of extraction solvent, volume of disperser solvent, and extraction time. It is very important to optimize them in order to obtain the good recovery strategy forms. We selected eight compounds as representative of the PAHs, and showed their behavior under these extraction conditions.

3.1. Selection of extraction solvent

Organic solvents are selected on the basis of higher density rather than water, extraction capability of interested compounds, and good gas chromatography behavior. The selection of an appropriate solvent is more important for the DLLME process. Carbon disulfide, carbon tetrachloride, and tetrachloroethylene were compared in the extraction of PAHs. The density values of the selected organic solvents are 1.26 (CS_2), 1.59 (CCl_4) and 1.62 g/mL (C_2Cl_4). A series of sample solution was studied by using 1.00 mL of acetone contains different volumes of extraction solvent to achieve 5.0 μL volume of sedimented phase, thereby, 8.0, 13.0, and 25.0 μL volumes of C_2Cl_4, CCl_4, and CS_2 are selected, respectively. The results revealed that C_2Cl_4 has the highest extraction efficiency (60.3–111.3%) in comparison with the CS_2 (16.7–48.5%) and CCl_4 (24.6–74.8%). Thereby, C_2Cl_4 was selected as the extraction solvent. The average recovery (triplicate) and standard deviation (SD) were shown in Table 1 for different extraction solvents.

3.2. Selection of disperser solvent

Miscibility of disperser solvent in organic phase (extraction solvent) and aqueous phase is the main point for selection of disperser solvent. Thereby, acetone, acetonitrile, and methanol are selected for this purpose. A series of sample solution was studied by using 1.00 mL of each disperser solvent containing 8.0 μL C_2Cl_4 (as extraction solvent). The results were illustrated in Table 2. The recoveries by using acetone, acetonitrile, and methanol (as disperser solvents) were ranged 60.3–111.3%, 58.5–102.6%, and 66.3–105.3%, respectively. According to these results, variations of recoveries using different disperser solvent are not remarkable, thus, acetone is selected, because of less toxicity and low cost.

3.3. Effect of extraction solvent volume

To examine the effect of extraction solvent volume, solutions containing different volumes of C_2Cl_4 were subjected to the same DLLME procedures. The experimental conditions were fixed and included the use of 1.00 mL acetone containing different volumes of C_2Cl_4 (8.0, 13.0, 18.0 and 23.0 μL). Figs. 2–4 show the curves of volume of sedimented phase, recovery and enrichment factor versus volume of extraction solvent (C_2Cl_4),

Table 1
Efficiency of different extraction solvent evaluated for extraction of PAHs by DLLME[a]

Compounds	Recovery (%)		
	Tetrachloroethylene, mean ± SD (n = 3)	Carbon tetrachloride, mean ± SD (n = 3)	Carbon disulfide, mean ± SD (n = 3)
Naphthalene	60.3 ± 1.3	24.6 ± 2.4	16.7 ± 3.0
Acenaphthylene	71.5 ± 1.4	38.4 ± 2.5	31.1 ± 1.3
Acenaphthene	111.3 ± 7.0	41.5 ± 6.8	34.2 ± 1.6
Fluorene	90.2 ± 1.8	49.8 ± 3.8	35.5 ± 1.0
Phenanthrene	94.1 ± 2.1	57.5 ± 4.6	41.2 ± 2.9
Anthracene	95.4 ± 2.3	53.1 ± 4.2	40.2 ± 2.5
Fluoranthene	101.6 ± 4.3	72.5 ± 4.4	47.7 ± 2.2
Pyrene	104.6 ± 5.0	73.1 ± 5.7	48.2 ± 2.4
Benzofluorene	106.0 ± 5.2	74.8 ± 5.6	48.4 ± 3.0
Benzo[a]anthracene	104.7 ± 6.8	70.2 ± 4.7	48.5 ± 2.9
Chrysene	102.9 ± 6.6	71.1 ± 4.1	47.9 ± 2.5
Benzo[e]acephenanthylene	96.6 ± 5.8	69.8 ± 4.2	48.0 ± 3.4
Benzo[e]pyrene	96.8 ± 4.3	68.8 ± 4.8	47.8 ± 2.9
Benzo[a]pyrene	97.1 ± 7.3	57.4 ± 6.5	44.3 ± 2.2
Perylene	90.5 ± 4.9	47.3 ± 5.1	41.3 ± 2.3
Benzo[ghi]perylene	92.4 ± 3.5	64.5 ± 6.3	30.0 ± 4.5

[a] Extraction conditions: water sample volume, 5.00 mL; disperser solvent (acetone) volume, 1.00 mL; extraction solvent volumes, 8.0 μL C_2Cl_4, 13.0 μL CCl_4 and 25 μL CS_2; sedimented phase volume, 5.0 ± 0.2 μL; room temperature; concentration of each PAHs, 2.0 μg/L.

Table 2
Efficiency of different disperser solvent evaluated for extraction of PAHs by DLLME[a]

Compounds	Recovery (%)		
	Acetone, mean ± SD ($n = 3$)	Acetonitrile, mean ± SD ($n = 3$)	Methanol, mean ± SD ($n = 3$)
Naphthalene	60.3 ± 1.3	58.5 ± 4.7	66.3 ± 4.8
Acenaphthylene	71.5 ± 1.4	68.8 ± 5.5	74.3 ± 4.9
Acenaphthene	111.3 ± 7.0	99.5 ± 13.4	105.3 ± 9.6
Fluorene	90.2 ± 1.8	84.1 ± 7.1	84.9 ± 6.3
Phenanthrene	94.1 ± 2.1	88.3 ± 7.5	87.6 ± 6.7
Anthracene	95.4 ± 2.3	87.2 ± 7.4	87.9 ± 4.7
Fluoranthene	101.6 ± 4.3	95.2 ± 8.9	90.4 ± 8.4
Pyrene	104.6 ± 5.0	102.6 ± 13.4	95.4 ± 1.9
Benzofluorene	106.0 ± 5.2	100.1 ± 11.0	91.1 ± 9.2
Benzo[a]anthracene	104.7 ± 6.8	95.8 ± 11.1	86.6 ± 9.1
Chrysene	102.9 ± 6.6	94.8 ± 10.5	84.5 ± 8.3
Benzo[e]acephenanthylene	96.6 ± 5.8	95.7 ± 9.7	81.7 ± 7.5
Benzo[e]pyrene	96.8 ± 4.3	90.3 ± 9.1	79.5 ± 6.1
Benzo[a]pyrene	97.1 ± 7.3	87.2 ± 8.6	75.5 ± 4.9
Perylene	90.5 ± 4.9	83.3 ± 7.9	72.5 ± 4.2
Benzo[ghi]perylene	92.4 ± 3.5	89.1 ± 8.6	75.3 ± 3.3

[a] Extraction conditions: water sample volume, 5.00 mL; disperser solvent (acetone, acetonitrile and methanol) volume, 1.00 mL; extraction solvent (C_2Cl_4) volume, 8.0 μL; sedimented phase volume, 5.0 ± 0.2 μL; room temperature; concentration of each PAHs, 2.0 μg/L.

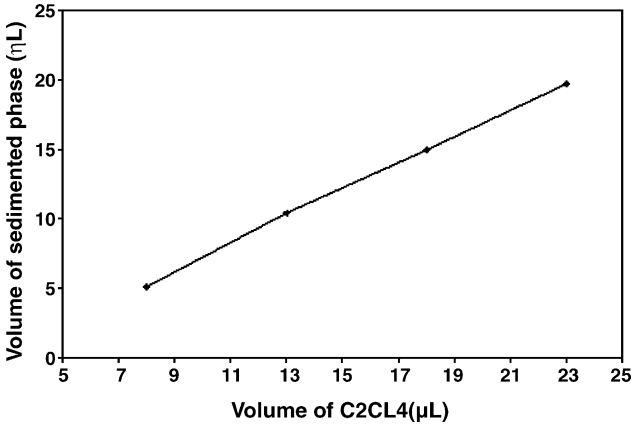

Fig. 2. Effect of the volume of C_2Cl_4 on the volume of sedimented phase in DLLME. Extraction conditions: water sample volume, 5.00 mL; disperser solvent (acetone) volume, 1.00 mL; room temperature.

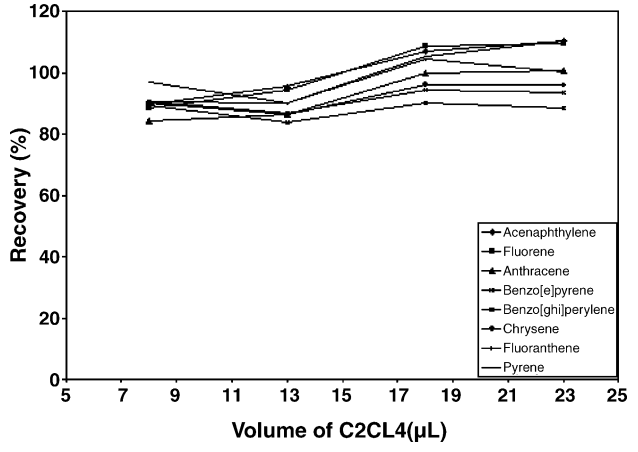

Fig. 3. Effect of the volume of C_2Cl_4 on the recovery of PAHs obtained from DLLME. Extraction conditions, as with Fig. 2; concentration of each PAHs, 2.0 μg/L.

respectively. According to Fig. 2, it is clear that by increasing the volume of C_2Cl_4 from 8.0 to 23.0 μL, the volume of the sedimented phase increases from 5.0 to 20.0. Regarding Fig. 3, by increasing the volume of C_2Cl_4, extraction recovery for the most of analytes is slightly constant, which indicates the quantitative extraction and high distribution coefficients of PAHs in this condition (even at the low volume of C_2Cl_4). However, as the volume of the sedimented phase increases, enrichment factor decreases with increasing the volume of C_2Cl_4 as shown in Fig. 4. Subsequently, at low volume of extraction solvent, high enrichment factor and good recovery are obtained. Thereby, the gain in sensitivity was achieved by using 8.0 μL volume of C_2Cl_4.

3.4. Effect of disperser solvent volume

Variation of the volume of acetone (as disperser solvent) causes change in the volume of sedimented phase; hence, it is

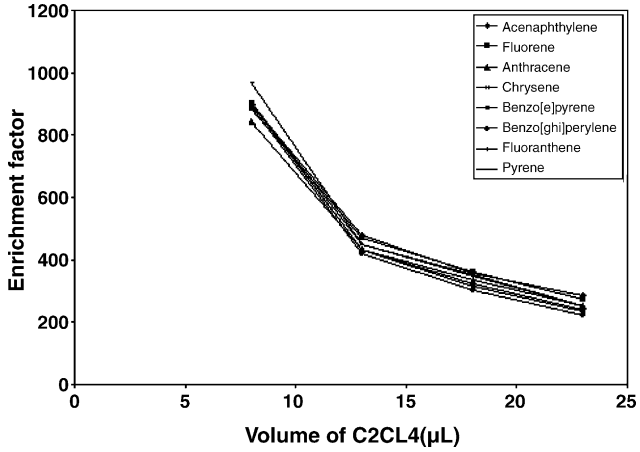

Fig. 4. Effect of the volume of C_2Cl_4 on the enrichment factor of PAHs obtained from DLLME. Extraction conditions, as with Fig. 2; concentration of each PAHs, 2.0 μg/L.

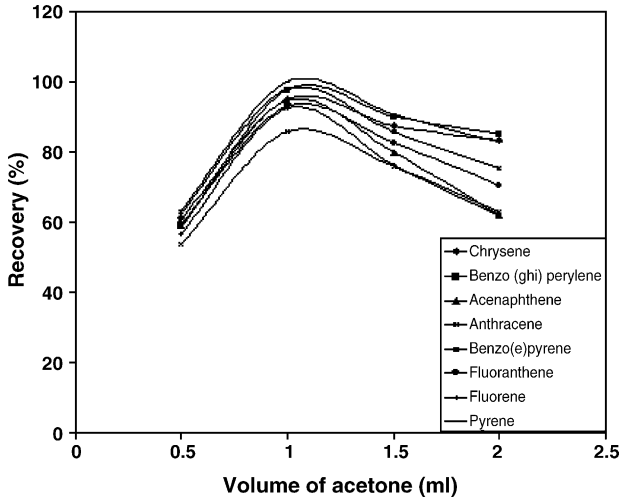

Fig. 5. Effect of the volume of acetone on the recovery of PAHs obtained from DLLME. Extraction conditions: water sample volume, 5.00 mL; sedimented phase volume, 5.0 ± 0.2 μL; room temperature; concentration of each PAHs, 2.0 μg/L.

impossible to consider the influence of the volume of acetone on the extraction efficiency. To avoid this matter and in order to achieve a constant volume of sedimented phase, the volume of acetone and C_2Cl_4 were changed spontaneously. The experimental conditions were fixed and included the use of different volumes of acetone 0.50, 1.00, 1.50, and 2.00 mL containing 7.3, 8.0, 10.3, and 12.4 μL of C_2Cl_4, respectively. Under these conditions, the volume of the sedimented phase was constant (5.0 ± 0.2 μL). The results are shown in Fig. 5. According to the curve, at first the extraction efficiency increases and then decreases by increasing the volume of acetone. It seems, at a low volume of acetone, cloudy state is not formed well, thereby, the extraction recovery decreases. At the high volume of acetone, the solubility of PAHs in water increases, therefore, the extraction efficiency decreases. A 1.00 mL of acetone was chosen as optimum volume.

3.5. Effect of extraction time

Extraction time is one of the most important factors in most of the extraction procedures, especially in microextraction methods such as SPME and LPME. In DLLME extraction, time is defined as an interval time between injection of mixture of disperser solvent (acetone) and extraction solvent (C_2Cl_4), and before starting to centrifuge. The effect of time was examined in the range of 0–60 min with constant experimental conditions. Fig. 6 shows the extraction recovery of PAHs versus extraction time. According to the curve, time has no influence on extraction efficiency. It is revealed that the surface area between extraction solvent and aqueous phase (sample) is infinitely large (it is confirmed by optical microscopic photography as shown in Fig. 1d). Thereby, transfer of analytes from aqueous phase (sample) to extraction phase is fast. Subsequently, equilibrium state is achieved quickly; as a result of that the extraction time is very short. This is the most important advantage of DLLME technique. Table 3 compares the extraction time of PAHs from

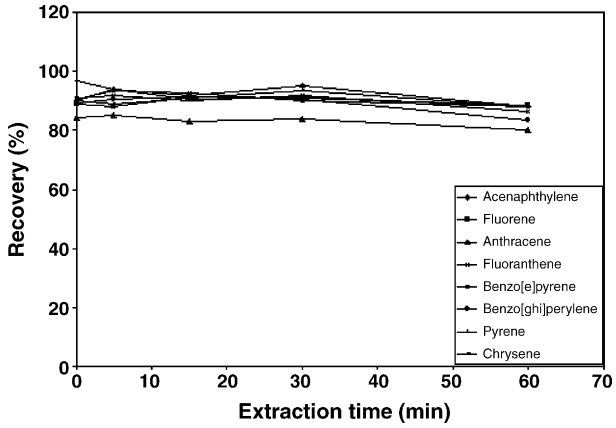

Fig. 6. Effect of extraction time on the recovery of PAHs obtained from DLLME. Extraction conditions, as with Fig. 2; concentration of each PAHs, 2.0 μg/L.

water samples by using DLLME, LPME, and SPME. The comparison of this method in the term of extraction time with other methods indicates that this novel method needs very short extraction time as shown in Table 3. Since SPME is equilibrium extraction method, the time to reach absorption equilibrium determines the maximum amount of analyte that can be extracted by the fiber and, therefore, controls the sensitivity of the method, but equilibrium time for SPME is large. Also, LPME is non-equilibrium extraction method in the most cases [15,27]. However, DLLME reaches equilibrium state, immediately (a few seconds). In this method, time-consuming step is centrifuging of sample solution in extraction procedure, which is about 2 min.

3.6. Quantitative analysis

The characteristic of calibration curves shown in Table 4 was obtained under optimized conditions. Linearity of calibration curve was observed at the range of 0.02–200 μg/L (four order magnitude) for most of the analytes. Coefficient of correlation (r^2) ranged from 0.9992 to 0.9999 with internal standard and from 0.9990 to 0.9999 without internal standard. The enrichment factors of PAHs were high and from 603 to 1113. The reproducibility in peak responses was investigated on five replicate experiments under the optimized conditions. The relative standard deviations (RSDs %) of PAHs were from 1.4 to 10.2% with internal standard and 2.1 to 10.6% without internal standard. The limit of detections (LODs), based on signal-to-noise ratio (S/N) of 3 ranged from 0.007 to 0.030 μg/L, which is very low by using FID.

Table 3
Comparison of extraction time of PAHs from aqueous sample by using DLLME, SPME and LPME

Extraction methods	Extraction time	Reference
DLLME	A few seconds	Proposed method
SPME	60 min	[28]
LPME	20 min	[29]

Table 4
Quantitative result of DLLME and GC-FID of PAHs from water sample[a]

PAHs	RSD %[b], $n=5$	RSD %[c], $n=5$	EF[d]	LR[e] (μg/L)	r^{2}[f]	r^{2}[g]	LOD[h] (μg/L)
Naphthalene	1.4	2.5	603	0.02–200	0.9993	0.9998	0.010
Acenaphthylene	1.6	1.7	715	0.02–200	0.9997	0.9999	0.010
Acenaphthene	10.2	10.6	1113	0.02–200	0.9995	0.9990	0.007
Fluorene	1.5	2.1	902	0.02–200	0.9996	0.9998	0.008
Phenanthrene	3.7	2.8	941	0.02–200	0.9995	0.9995	0.009
Anthracene	8.4	7.0	954	0.02–100	0.9992	0.9995	0.009
Fluoranthene	7.7	6.9	1016	0.02–200	0.9996	0.9994	0.010
Pyrene	5.6	5.3	1046	0.02–200	0.9997	0.9994	0.010
Benzofluorene	9.3	8.6	1060	0.02–20	0.9996	0.9995	0.010
Benzo[a]anthracene	9.8	9.3	1047	0.02–20	0.9996	0.9995	0.010
Chrysene	9.0	8.3	1029	0.02–20	0.9996	0.9995	0.010
Benzo[e]acephenanthylene	4.3	4.6	966	0.05–20	0.9999	0.9996	0.015
Benzo[e]pyrene	4.2	4.5	968	0.05–20	0.9999	0.9996	0.015
Benzo[a]pyrene	7.6	7.7	971	0.05–20	0.9999	0.9996	0.020
Perylene	8.8	7.9	905	0.05–20	0.9993	0.9996	0.020
Benzo[ghi]perylene	3.3	4.3	924	0.05–20	0.9993	0.9995	0.030

[a] Extraction conditions: water sample volume, 5.00 mL; disperser solvent (acetone) volume, 1.00 mL; extraction solvent (C_2Cl_4) volume, 8.0 μL; sedimented phase volume, 5.0 ± 0.2 μL; room temperature; concentration of internal standard (biphenyl), 2.0 μg/L.
[b] RSD % by using internal standard at a concentration of 2 μg/L of each PAHs.
[c] RSD % without using internal standard at a concentration of 2 μg/L of each PAHs.
[d] EF, enrichment factor.
[e] LR, linear range.
[f] r^{2} by using internal standard.
[g] r^{2} without using internal standard.
[h] LOD, limit of detection for a S/N = 3.

3.7. Real water analysis

River, well, and surface water were collected from Tehran (Iran), and were extracted using the DLLME method and the extracts analyzed by GC-FID. The results for well, river, and surface waters showed that they were free of PAHs contamination. River, well, and surface waters were spiked with PAHs standards at the concentration of 5.0 μg/L to assess matrix effects. Fig. 7 shows the chromatogram obtained for surface water by spiking PAHs. Results of relative recovery of surface water are shown in Table 5. The data show that for all PAHs the relative recoveries were between 82.0 and 111%. Same results were obtained for river and well water. These results demonstrate that the surface, river and well waters matrices, in our present context, had little effect on DLLME.

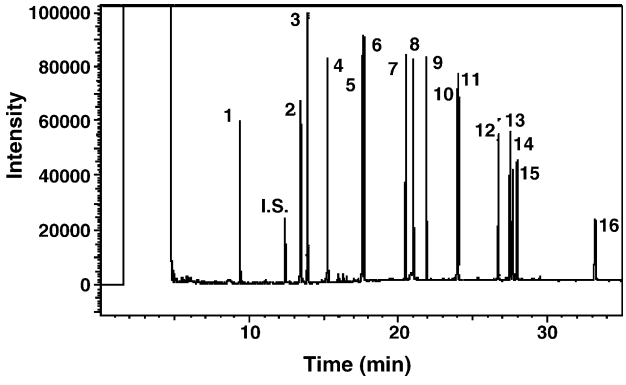

Fig. 7. Chromatogram of surface water spiked at concentration level of 5.0 μg/L of PAHs obtained by using DLLME combined GC-FID. Peak identification: (1) naphthalene, (2) acenaphthylene, (3) acenaphthene, (4) fluorene, (5) phenanthrene, (6) anthracene, (7) fluoranthene, (8) pyrene, (9) benzofluorene, (10) benzo[a]anthracene, (11) chrysene, (12) benzo[e]acephenanthylene, (13) benzo[e]pyrene, (14) benzo[a]pyrene, (15) perylene and(16) benzo[ghi]perylene, (I.S.) biphenyl.

3.8. Application range

DLLME is a simple and rapid extraction procedure and can be used for a wide range of organic compounds. To make clear the application range of the proposed method, the capability of DLLME was also investigated for the extraction of some organic compounds from water sample. Figs. 8–10 illustrate typical chromatograms of BTEX, OCPs, and OPPs in water sample

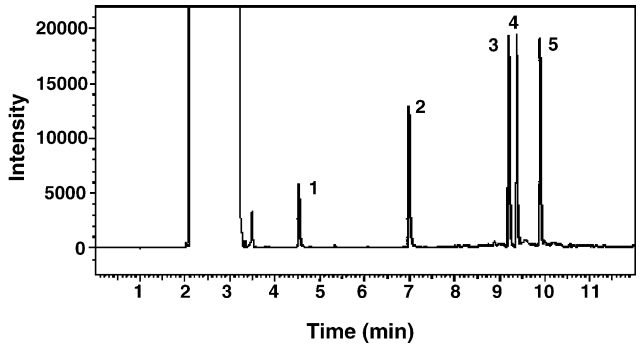

Fig. 8. DLLME–GC-FID analysis of BTEX in water sample. Extraction conditions: water sample volume, 5.00 mL; disperser solvent (acetonitrile) volume, 1.00 mL; extraction solvent (CS_2) volume, 30 μL; sedimented phase volume, 10.0 ± 0.5 μL; room temperature; concentration of each BTEX, 10 μg/L. Peak identification: (1) benzene, (2) toluene, (3) ethyl benzene, (4) *m*- or *p*-xylene and (5) *o*-xylene.

Table 5
Relative recoveries and standard deviation of PAHs from spiked surface water[a]

PAHs	Surface water sample concentration (μg/L)	Added concentration (μg/L)	Founded concentration (SD, $n=3$)[b] (μg/L)	Relative recovery (%)
Naphthalene	nd[c]	5.00	4.93 (0.17)	98.6
Acenaphthylene	nd	5.00	4.86 (0.69)	97.2
Acenaphthene	nd	5.00	4.10 (0.23)	82.0
Fluorene	nd	5.00	4.59 (0.27)	91.8
Phenanthrene	nd	5.00	4.94 (0.40)	98.8
Anthracene	nd	5.00	4.76 (0.45)	95.2
Fluoranthene	nd	5.00	4.53 (0.46)	90.6
Pyrene	nd	5.00	5.55 (0.45)	111.0
Benzofluorene	nd	5.00	5.06 (0.28)	101.2
Benzo[a]anthracene	nd	5.00	5.13 (0.51)	102.6
Chrysene	nd	5.00	4.69 (0.49)	93.8
Benzo[e]acephenanthylene	nd	5.00	4.42 (0.10)	88.4
Benzo[e]pyrene	nd	5.00	5.10 (0.91)	102.0
Benzo[a]pyrene	nd	5.00	5.08 (0.13)	101.6
Perylene	nd	5.00	4.81 (0.10)	96.2
Benzo[ghi]perylene	nd	5.00	5.04 (0.13)	100.8

[a] Extraction conditions: water sample volume, 5.00 mL; disperser solvent (acetone) volume, 1.00 mL; extraction solvent (C_2Cl_4) volume, 8.0 μL; sedimented phase volume, 5.0 ± 0.2 μL; room temperature; concentration of internal standard (biphenyl), 2.0 μg/L.
[b] SD, standard deviation.
[c] nd, not detected.

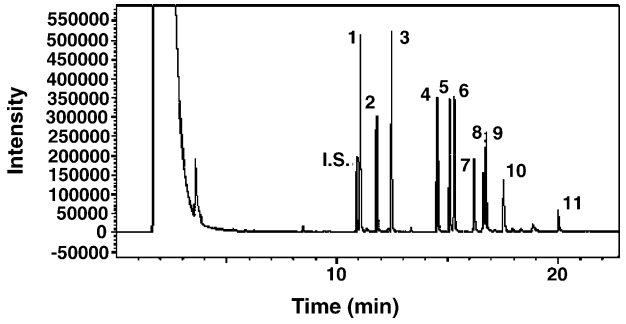

Fig. 9. DLLME–GC-ECD analysis of OCPs in water sample. Extraction conditions: water sample volume, 5.00 mL; disperser solvent (acetone) volume, 1.00 mL; extraction solvent (CS_2) volume, 25 μL; sedimented phase volume, 5.0 ± 0.3 μL; room temperature; concentration of each OCPs, 0.50 μg/L. Peak identification: (1) lindane, (2) heptachlor, (3) aldrin, (4) α-endosulfan, (5) *p,p*-DDE, (6) dieldrin, (7) endrin, (8) β-endosulfan, (9) DDD, (10) *p*-DDT and (11) methoxychlor, (I.S.) pentachloronitrobenzene.

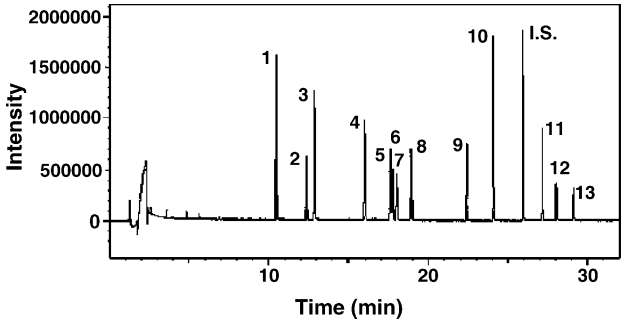

Fig. 10. DLLME–GC-FPD analysis of OPPs in water sample. Extraction conditions: water sample volume, 5.00 mL; disperser solvent (acetone) volume, 1.00 mL; extraction solvent (chlorobenzene) volume, 12 μL; sedimented phase volume, 5.0 ± 0.2 μL; room temperature; concentration of each OPPs, 0.50 μg/L. Peak identification: (1) phorate, (2) diazinon, (3) disolfotan, (4) methy parathion, (5) sumithion, (6) chloropyrifos, (7) malathion, (8) fenthion, (9) profenphose, (10) ethion, (11) phosalone, (12) azinphose-methyl and (13) co-ral, (I.S.) triphenyl phosphate.

by using DLLME (extraction conditions are shown in figures). The results show the ability of DLLME technique for the extraction of wide range of organic compounds from water sample.

4. Conclusion

In the present study, a new mode of microextraction technique was described as a dispersive liquid–liquid microextraction (DLLME) which has been developed. DLLME provides high recovery and enrichment factor within a very short time (a few seconds). PAHs were employed as model compounds to assess the extraction procedure and were determined by GC-FID. The performance of this procedure in the extraction of PAHs from surface, river, and well waters was excellent. Also, the ability of DLLME technique in the extraction of other organic compounds such as OCPs, OPPs, and BTEX from water samples shows satisfactory results. The comparison of the new method with other methods such as LPME and SPME demonstrated that DLLME is fast, simple, and inexpensive.

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