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Low-density solvent-based solvent demulsification dispersive liquid–liquid microextraction for the fast determination of trace levels of sixteen priority polycyclic aromatic hydrocarbons in environmental water samples

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ABSTRACT

For the first time, the low-density solvent-based solvent demulsification dispersive liquid–liquid microextraction was developed for the fast, simple, and efficient determination of 16 priority polycyclic aromatic hydrocarbons (PAHs) in environmental samples followed by gas chromatography–mass spectrometric (GC–MS) analysis. In the extraction procedure, a mixture of extraction solvent (*n*-hexane) and dispersive solvent (acetone) was injected into the aqueous sample solution to form an emulsion. A demulsification solvent was then injected into the aqueous solution to break up the emulsion, which turned clear and was separated into two layers. The upper layer (*n*-hexane) was collected and analyzed by GC–MS. No centrifugation was required in this procedure. Significantly, the extraction needed only 2–3 min, faster than conventional DLLME or similar techniques. Another feature of the procedure was the use of a flexible and disposable polyethylene pipette as the extraction device, which permitted a solvent with a density lighter than water to be used as extraction solvent. This novel method expands the applicability of DLLME to a wider range of solvents. Furthermore, the method was simple and easy to use, and some additional steps usually required in conventional DLLME or similar techniques, such as the aforementioned centrifugation, ultrasonication or agitation of the sample solution, or refrigeration of the extraction solvent were not necessary. Important parameters affecting the extraction efficiency were investigated in detail. Under the optimized conditions, the proposed method provided a good linearity in the range of 0.05–50 μg/L, low limits of detection (3.7–39.1 ng/L), and good repeatability of the extractions (RSDs below 11%, $n = 5$). The proposed method was successfully applied to the extraction of PAHs in rainwater samples, and was demonstrated to be fast, efficient, and convenient.

1. Introduction

Sample extraction plays a key role in modern analytical methodology, which affects the accuracy and precision of the final results. However, traditional sample extraction procedures, based on conventional liquid–liquid extraction (LLE) are often considered to be time-consuming, labor-intensive, and environmentally unfriendly due to usage of significant amount of potentially toxic organic solvents. In the past few years, many research efforts have been oriented towards the development of efficient, miniaturized and environmentally benign sample extraction methods, such as solid-phase microextraction (SPME) [1–6] and liquid-phase microextraction (LPME) [7–11].

SPME, which combines extraction and pre-concentration in a single step, is an efficient and solvent-free technique. It has some drawbacks, however. SPME fibers are generally fragile, expensive, have a limited lifetime, and can also suffer from analyte carryover. LPME approaches are much more cost-effective, and can be used in many different modes, such as single drop microextraction [12], dynamic LPME [13,14], hollow fiber protected LPME [15–17], solvent bar microextraction [18], headspace LPME [19], and continuous flow LPME [20], among others. They are solvent-minimized, effective, and economical sample extraction procedures. However, to conduct these extractions to completion (equilibrium or non-equilibrium states), a considerable extraction time is required.

In 2006, a rapid LPME method, dispersive liquid–liquid microextraction (DLLME), was introduced [21]. In this procedure, a mixture of high density organic solvent (serving as extraction solvent) and water miscible polar dispersive solvent (dispersive solvent) is rapidly injected into an aqueous sample to form an emulsion consisting of fine droplets of the extraction solvent, dispersive solvent, and water. Due to the extraction solvent being highly dispersed in the aqueous phase, the surface area between extraction solvent and sample solution is infinitely large, thus speeding up the extraction.

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After extraction, the extract can be sedimented at the bottom of the extraction vial (usually a conical tube) by centrifugation. DLLME features rapid analysis, simple operation, and high enrichment and recovery [22,23], and has been reported for the extraction of a wide variety of organic compounds, i.e., phenols [24], herbicides [25], pesticides [26–30], polychlorinated biphenyls [31,32], carbendazim and thiabendazole [33], auxin [34], heavy metals [35,36].

The main disadvantage of DLLME is that the extraction solvent is generally limited to solvents with higher density than water in order to be sedimented by centrifugation, typically chlorinated solvents such as chlorobenzene, chloroform, and tetrachloromethane, all of them are potentially toxic to humans and the environment. In addition, the use of high density solvents as extractants limits a wider applicability of DLLME due to more limited choices since there are more low-density than high-density solvents. In recent years, this limitation has been recognized and there have been several reports of the application of low density solvents in DLLME [37–40].

Typically, most DLLME methods have a centrifugation step, which is the extra time-consuming step in the extraction. Very recently, solvent-terminated DLLME was developed by Li and co-workers [41] as an alternative approach, which avoided centrifugation, thereby simplifying the operation and speeding up the extraction procedure. This method was also applied to the determination of organochlorine pesticides in water samples [42].

In the present study, the low-density solvent-based solvent demulsification dispersive liquid–liquid microextraction (LDS-SD-DLLME) was for the first time applied for the fast determination of trace levels of sixteen polycyclic aromatic hydrocarbons (PAHs) listed as priority pollutants by the US Environmental Protection Agency (EPA) in rainwater samples followed by analysis with gas chromatography–mass spectrometry (GC–MS). In the proposed procedure, a solvent of lower density than water, *n*-hexane, was employed as extraction solvent and injected into the aqueous samples with acetone (as dispersive solvent). After a 2 min extraction, a second aliquot of acetone (as demulsifier) was injected into the solution to break the emulsion [42]. This step made centrifugation unnecessary. The emulsion rapidly turned clear and separated into two phases, and the upper layer (organic extract) was collected and analyzed. In order to evaluate the proposed method, traditional DLLME and low density solvent based DLLME were carried out for comparison with the performance of LDS-SD-DLLME. Under the optimized microextraction conditions, the developed method was applied to analyze genuine rainwater samples.

2. Experimental

2.1. Chemicals and materials

The PAH standards (acenaphthene (Ace), acenaphthylene (Acp), anthracene (Ant), benz[*a*]anthracene (BaA), benzo[*a*]pyrene (BaP), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), chrysene (Cry), dibenz[*a*,*h*]anthracene (DBA), indeno[1,2,3-*cd*]pyrene (InP), fluoranthene (Flt), benzo[*g*,*h*,*i*]perylene (BghiP), fluorene (Flu), naphthalene (Nap), phenanthrene (Phe), and pyrene (Pyr)) were bought from Supelco (Bellefonte, PA, USA) as a kit (PAH Kit 610-N). All these 16 PAHs are listed as priority pollutants by the USEPA.

HPLC-grade methanol, acetone, acetonitrile, chloroform, and *n*-hexane were purchased from Tedia Company (Fairfield, OH, USA). 1-Octanol was bought from Merck (Darmstadt, Germany) while toluene and cyclohexane were from Fisher (Loughborough, UK). The *o*-xylene was obtained from Sigma–Aldrich (St. Louis, MO, USA). Ultrapure water was produced on a Nanopure water purification system (Barnstead, Dubuque, IA, USA)

The soft polyethylene Pasteur pipette (5-mL capacity, ~216 mm length) is manufactured by Continental Lab Products (San Diego, CA, USA) and was purchased from Practical Mediscience Pte., Ltd. (Singapore). A 1.0 mL syringe used for injection of extraction solvent and a 50 μL blunt tip microsyringe used for collection of the organic extract were purchased from Hamilton Bonaduz AG (Bonaduz, Switzerland). A 10 μL microsyringe used for GC injection was form SGE (Sydney, Australia). The 5-mL syringe was bought from HSW (Tuttlingen, Germany).

2.2. GC–MS analysis

Sample analyses were carried out on a Shimadzu (Kyoto, Japan) QP2010 GC–MS system equipped with a Shimadzu AOC-20i auto sampler and a DB-5 MS (J&W Scientific, Folsom, CA, USA) fused silica capillary column (30 m × 0.25 mm internal diameter (i.d.), 0.25 μm film thickness). Helium (purity 99.9999%) was employed as the carrier gas at a flow rate of 1.7 mL/min. samples (1 μL) were injected in splitless mode. The injector temperature was set at 280 °C and the interface temperature maintained at 300 °C. The GC oven was initially held at 70 °C for 2 min and then programmed to 190 at 15 °C/min. After being kept at 190 °C for 1 min, the oven was programmed to 260 at 10 °C/min. Finally, it was programmed to 285 at 5 °C/min and held for 5 min. The solvent cut time was 6 min. The masses monitored by the detector were set as follows: 6–8 min, *m*/*z* 128, 129, 127, 102; 8–9.5 min, *m*/*z* 152, 153, 151, 154; 9.5–10.8 min, *m*/*z* 166, 165, 167, 139; 10.8–13 min, *m*/*z* 178, 176, 179, 152; 13–16 min, *m*/*z* 202, 203, 200, 101; 16–20 min, *m*/*z* 228, 226, 229, 227, 252; 20–23 min, *m*/*z* 253, 252, 250, 126; 23–28 min, *m*/*z* 276, 278, 277, 138. PAH standards and samples were analyzed in selective ion monitoring (SIM) mode for quantitative determination of the analytes: Nap, *m*/*z* 128, 129, 127, 102; Acp, *m*/*z* 152, 153, 151; Ace, 153, 154, 152; Flu, *m*/*z* 166, 165, 167; Phe, *m*/*z* 178, 176, 179; Ant, *m*/*z* 178, 179, 176; Flt, *m*/*z* 202, 203, 200, 101; Pyr, *m*/*z* 202, 200, 203, 101; Cry, *m*/*z* 228, 226, 229; BaA, *m*/*z* 228, 226, 227, 229, 252; BbF, *m*/*z* 252, 253, 250; BkF, *m*/*z* 252, 250, 126; BaP, *m*/*z* 252, 253, 250, 126; InP, *m*/*z*, 276, 277, 138; DBA, *m*/*z* 278, 276; BghiP, *m*/*z* 276, 277, 138.

2.3. Sample preparation

A stock solution containing 10 mg/L of each analyte was prepared by dissolving them in methanol. This was stored in the refrigerator at 4 °C until use. Water samples were prepared by spiking ultrapure water with analytes at known concentrations (25 μg/L) to study extraction performance and optimize the extraction conditions as indicated in the individual experiments. Quantification of the analytes was done by external calibration, for which a series of standard solution was prepared by diluting the stock solution and analyzing with GC–MS to obtain linear calibration plots for each analyte based on the chromatographic peak areas.

Genuine rainwater samples were collected from three locations in the campus of the National University of Singapore using precleaned glass bottles. The bottles were covered with aluminum foil to prevent exposure to light. All collected rainwater samples were transported to the laboratory immediately, and stored in the refrigerator at 4 °C. The rainwater samples were extracted and analyzed without any prior treatment or filtration to avoid loss of PAHs.

2.4. LDS-SD-DLLME

Fig. 1 shows the LDS-SD-DLLME procedure. Briefly [41], an aliquot of 5 mL of sample solution was placed in a 5-mL soft polyethylene Pasteur pipette using a 5-mL syringe. A mixture of 50 μL of *n*-hexane (serving as extraction solvent) and 500 μL ace-

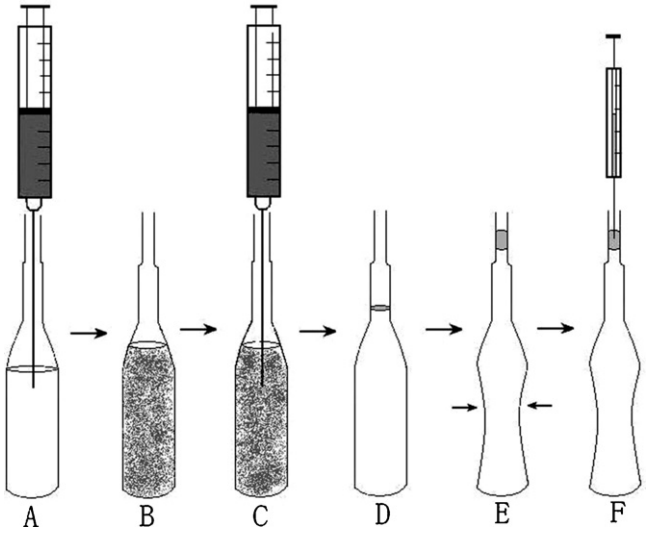

Fig. 1. The LDS-SD-DLLME procedure.

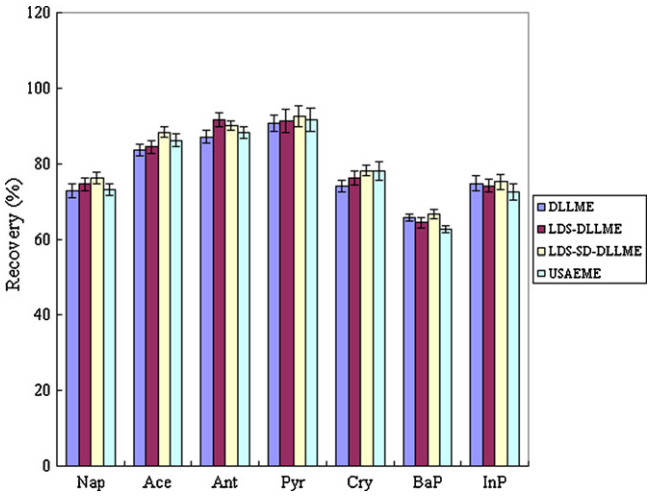

Fig. 2. Comparison of DLLME, USAEME, LDS-DLLME, and LDS-SD-DLLME.

tone (dispersive solvent) was injected rapidly into the sample solution through a 1.0 mL syringe. An emulsion of the extraction solvent, dispersive solvent, and aqueous sample was formed in the pipette. In this step, analytes were extracted into multiple *n*-hexane droplets in a few seconds. After 2 min extraction, a second 500 μL aliquot of acetone (serving as demulsification solvent) was injected into the solution to break down the emulsion. The mixture cleared and separated into two phases. The pipette bulb was then squeezed slightly. The upper layer comprising the organic extract (~35 μL) moved into the narrow stem of the pipette, facilitating its retrieval using a 50 μL microsyringe. One microlitre of the extract was immediately injected into the GC–MS for analysis.

3. Results and discussion

3.1. Comparative studies

The performance of LDS-SD-DLLM was compared with conventional DLLME, low density solvent-based DLLME (LDS-DLLME), and ultrasound-assisted emulsification liquid–liquid microextraction (USAEME). Spiked ultrapure water samples (5 μg/L for each PAH) were used for the comparative extractions.

3.1.1. Conventional DLLME

For DLLME, a 5 mL water sample was placed in a 10 mL conical centrifuge tube. A mixture of 500 μL acetone (dispersive solvent) and 50 μL chloroform (extraction solvent) was rapidly injected into the aqueous solution. Immediately, an emulsion was formed. After centrifugation at 4000 rpm for 4 min, the organic extract (~42 μL) was sedimented at the bottom of the conical centrifuge tube and was collected using a 50 μL microsyringe. One microliter of extract was injected into the GC–MS system for analysis. The conditions used here were most favorable for extraction.

3.1.2. LDS-DLLME

To proceed with the extraction, a 5-mL aqueous sample was placed in a 5-mL soft polyethylene pipette. A mixture of 50 μL of *n*-hexane (extraction solvent) and 500 μL acetone (dispersive solvent) was injected rapidly into the sample solution through a 1.0 mL syringe. An emulsion formed in the pipette. The emulsion was centrifuged at 4000 rpm for 4 min to separate the mixture into two phases. The upper layer comprising the organic extract (~37 μL) was removed using a 50 μL microsyringe. One microliter of the extract was analyzed by GC–MS.

3.1.3. USAEME

A 5-mL soft polyethylene Pasteur pipette was filled with a 5-mL of aqueous sample. The pipette was immersed in an ultrasonic water bath, and a 50 μL volume of extraction solvent (*n*-hexane) was injected into the sample solution. The extraction was performed at 35 Hz of ultrasound frequency, and was maintained at 25 °C. An emulsion formed in the pipette. After 2 min of extraction, the emulsion was separated into two phases by centrifugation at 4000 rpm for 4 min. The upper layer (organic extract, ~40 μL) was collected and 1 μL of the extract was analyzed by GC–MS.

It can be clearly seen from Fig. 2 for the 7 representative PAHs that all four procedures gave comparatively acceptable extraction recoveries (data for all 16 PAHs are shown in the supplementary materials section (Figure 1)). However, the *n*-hexane, used as extraction solvent in the proposed method, is much less toxic in comparison with the chlorinated solvents widely used as extraction solvents in conventional DLLME. Furthermore, the proposed method uses a low density solvent as extractant, overcoming the limited variety of high density extraction solvents necessitated by the centrifugation-based collection of the extractant. Most importantly, the proposed technique was faster than conventional DLLME, LDS-DLLME, and USAEME because centrifugation is unnecessary, which, although it is only for 4 min, is the most time-consuming step in the other three methods compared. In addition, there was no extra equipment or apparatus required for the proposed method including a centrifuge or an ultrasonicator, which are both widely used in normal DLLME approaches. Needing only a plastic pipette, without the necessity of a centrifuge and an ultrasonicator, the present approach provides the potential of performing DLLME in the field.

3.2. Optimization

In order to determine the most favorable conditions of the LDS-SD-DLLME procedure, the effect of different extraction parameters including the type and volume of extraction solvent, the type and volume of dispersive solvent and demulsification solvent, and extraction time, were studied in terms of the extraction recovery of analytes. All optimization experiments were performed in triplicate.

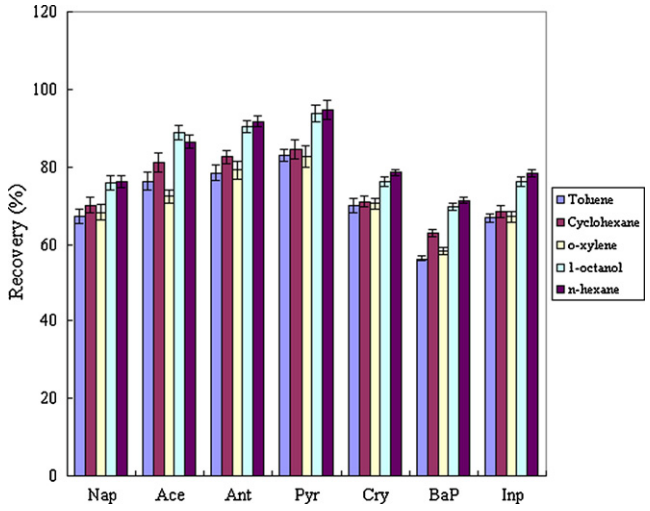

Fig. 3. Effect of type of extraction solvent on extraction efficiency.

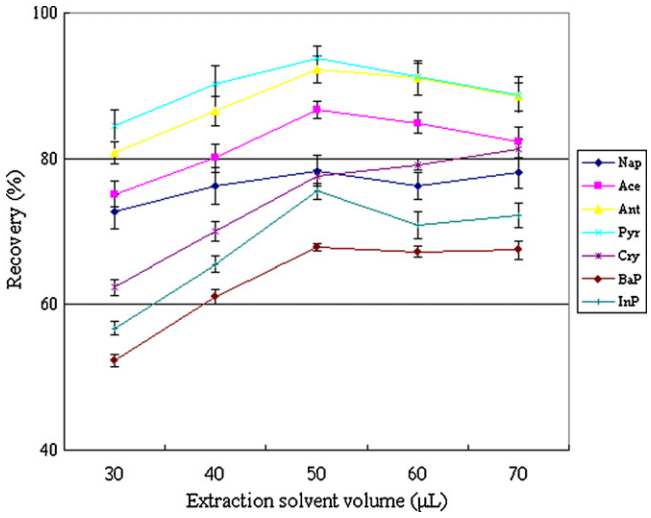

Fig. 4. Effect of extraction solvent volume on extraction efficiency.

The extraction recovery, R, was calculated using the following equation:

$$R = \frac{C_O V_O}{C_0 V_{aq}} \times 100$$

where C_O, C_0, V_O, and V_{aq} are the concentration of analytes in the upper layer, the spiked concentration of analytes in aqueous solution, the volume of upper layer (organic extract), and the volume of aqueous solution, respectively.

3.2.1. The selection of extraction solvent

An appropriate extraction solvent is a crucial factor in an extraction. It should meet the following requirements: (1) high extraction affinity to the analytes; (2) low solubility in the aqueous solution; (3) lower density than water (for our purpose); (4) good gas chromatographic performance. Five low density organic solvents were evaluated as extraction solvent including 1-octanol (density, $d = 0.827\,g\,mL^{-1}$), n-hexane ($d = 0.659\,g\,mL^{-1}$), toluene ($d = 0.865\,g\,mL^{-1}$), cyclohexane ($d = 0.779\,g\,mL^{-1}$), and o-xylene ($d = 0.88\,g\,mL^{-1}$). A series of experiments were performed using 500-μL acetone as dispersive solvent and another 500-μL acetone as demulsification solvent. In order to achieve an equal recovery volume in the upper layer for different extraction solvents after extraction, different initial volumes of extraction solvents were used, based on their solubility in aqueous solution. Recoveries of different extraction solvents were compared and the results for the 7 representative PAHs are shown in Fig. 3 (data for all 16 PAHs are shown in the supplementary materials section (Figure 2)). The figure shows that n-hexane and 1-octanol have comparable extraction recoveries which were higher than those obtained by other solvents for most analytes. Considering its good GC–MS performance (better peak shapes), n-hexane was chosen as the extraction solvent. We believe, however, that, 1-octanol could be used as well as an alternative if n-hexane was unavailable.

3.2.2. The volume of the extraction solvent

In DLLME, the volume of extraction solvent is a very important parameter, as it impacts on the enrichment factor. The effect of extraction solvent volume was studied with 500 μL acetone and different volumes of n-hexane (30, 40, 50, 60, and 70 μL). As can be seen from Fig. 4 for the 7 representative PAHs, the extraction recoveries for most PAHs increased with the increase of extraction solvent volume from 30 to 50 μL; beyond 50 μL, there was either a flattening out of the profile, or slight decrease, depending on the analytes (data for all 16 PAHs are shown in the supplementary materials section (Figure 3)). This observation has been reported previously [37,41]. In the proposed method, the initial volume of extraction solvent of less than 30 μL resulted in difficulty in collecting the upper layer. On the other hand, a much higher volume led to a lower precision due to the evaporation of the upper layer [37], and was also disadvantageous in terms of the enrichment factor. Thus, 50 μL was adopted for subsequent experiments as extraction solvent volume; not only for the above reasons, but also that maximum extraction was achieved.

3.2.3. Selection of dispersive solvent and demulsification solvent

In DLLME, the extraction solvent is dispersed into the aqueous phase to form micro droplets, which enhance the contact between both entities, achieving rapid extraction. Therefore, the effective emulsion depends greatly on the dispersive solvent. The most important consideration for the selection of a suitable dispersive solvent is its miscibility with the extraction solvent and the aqueous sample solution. Three commonly used dispersive solvents, acetone, acetonitrile, and methanol, were evaluated in this work. A series of sample solutions were extracted with a mixture of 500 μL of each dispersive solvent and 50 μL of n-hexane. To simplify the selection process, another 500 μL of the same solvent was used as demulsifier. From Fig. 5 (data for 7 PAHs are shown here; results for all 16 PAHs are shown in the supplementary materials section (Figure 4)), it is clear that the highest extraction recovery was obtained when acetone was used as dispersive and demulsification solvent, followed by acetonitrile and methanol.

3.2.4. Volume of the dispersive solvent and demulsification solvent

Furthermore, the effect of the volume of dispersive solvent and demulsification solvent on the extraction efficiency was investigated. A series of volumes of acetone (600, 800, 1000, 1500, and 2000 μL) were divided into two equal aliquots. An aliquot was injected into sample solution with 50 μL extraction solvent, serving as dispersive solvent. After a certain extraction time, the other aliquot was injected into the aqueous sample to break the emulsion. The results are shown in Fig. 6 (results for all 16 PAHs are shown in the supplementary materials section (Figure 5)). It may be observed that higher extraction efficiency was obtained using 1000 μL (500 + 500) of acetone.

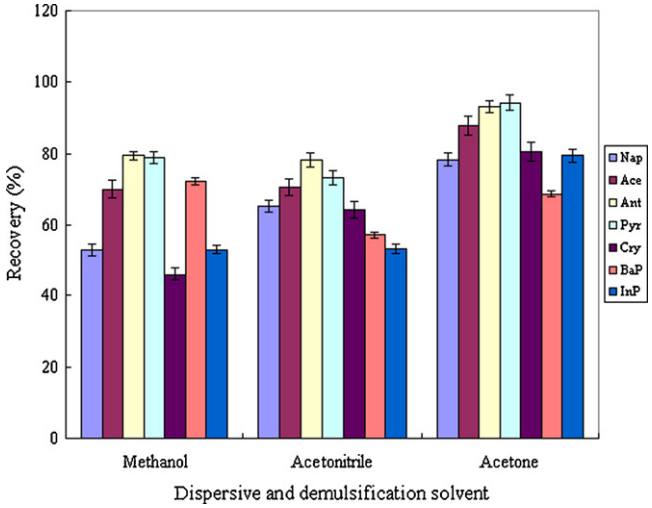

Fig. 5. Effect of type of dispersive solvent and demulsification solvent on extraction efficiency.

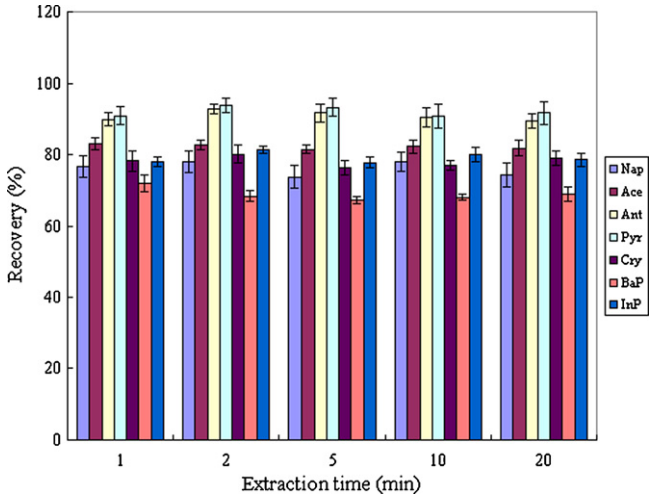

Fig. 7. Extraction time profiles of LDS-SD-DLLME.

3.2.5. Extraction time profiles

In LDS-SD-DLLME, the extraction time is defined as the time between the injection of the mixture of extraction solvent and dispersive solvent, and that at which the demulsification solvent was injected [41]. In order to evaluate the effect of extraction time, extraction was carried out for 1, 2, 5, 10, and 20 min, respectively. Fig. 7 shows the extraction time profiles (results for all 16 PAHs are shown in the supplementary materials section (Figure 6)). The extraction time has no significant effect on the extraction efficiencies for all PAHs. Extraction time also has no influence on extraction efficiencies in conventional DLLME [3,5]. One min of extraction time was enough to achieve high extraction recovery, and prolonged extraction time did not contribute significantly to an increase in extraction recovery.

In the emulsion phase of the DLLME procedure, the extraction solvent was in the form of fine droplets that were highly dispersed in the aqueous phase. The contact area between the extraction solvent and the aqueous phase was extremely large, hence facilitating the migration of analytes from the aqueous phase to the extraction solvent droplets. The mass transfer equilibrium between extraction solvent and aqueous phase could be reached quickly; subsequently the extraction could be completed very rapidly. The extraction time was set at 2 min, rather than at, for example, 1 min to ensure complete extraction.

On the basis of the above discussion, the most suitable extraction conditions for LDS-SD-DLLME were as follows: 50 μL *n*-hexane as extraction solvent with 500 μL acetone as dispersive solvent; extraction for 2 min; and demulsification with 500 μL acetone. All the following experiments were carried out under these conditions. Fig. 8 shows a chromatogram of spiked ultrapure water sample (25 μg/L of each analyte) after extraction by the developed method under these described conditions.

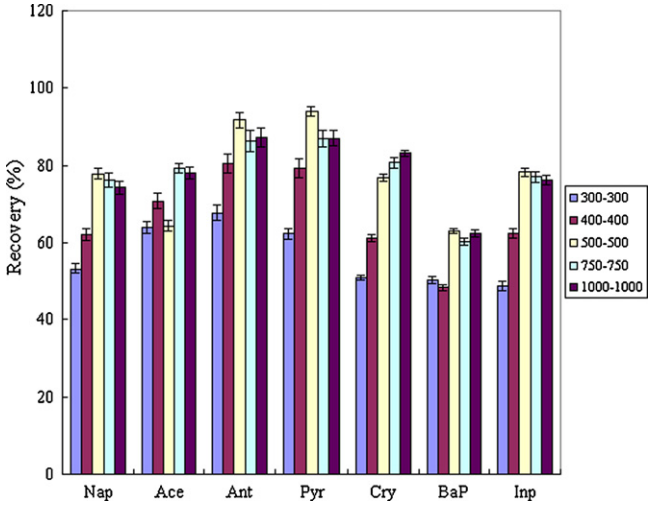

Fig. 6. Effect of volume of dispersive solvent and demulsification solvent on extraction efficiency.

3.3. Method validation

In order to investigate the practicality of the developed method, validation parameters including the linear range, repeatability, limits of detection (LODs), limits of quantification (LOQs), and recoveries were studied under the described extraction conditions using spiked ultrapure water samples. The data obtained are summarized in Table 1.

The linearity of the method was studied with a series of concentrations, and the calibration curves were obtained by plotting the mean peak area against the sample concentration. Depending on the compounds, calibration curves gave satisfactory linearity in the range of 0.05–50 μg/L, 0.1–50 μg/L, and 0.2–50 μg/L, with correlation coefficients ranging between 0.9803 and 0.9965 for all the analytes, indicating the method could be used for the determination of PAHs at trace level concentrations. The repeatability was studied for five replicate analyses of the spiked samples (at concentrations close to the LOQs) under the same operational parameters. The relative standard deviations (RSDs) were satisfactory, ranging from 3.5% to 11% for all the PAHs, showing the good repeatability of the method.

The LODs (calculated at a signal-to-noise ratio of 3 based on peak-to-peak noise) ranged between 3.7 and 39.1 ng/L. The LOQs (calculated as a signal-to-noise ratio of 10 based on peak-to-peak noise) were from 0.01 to 0.15 μg/L. These results were comparable with those obtained by DLLME-GC-flame ionization detection [21], low toxic DLLME-GC–MS [43], DLLME-solidification of floating organic droplet coupled to HPLC-variable wavelength detector [44], USAEME coupled to GC–MS [38,45], solid-phase extraction (SPE)-GC–MS [46,47], SPE-HPLC-ultraviolet detection [48] with mutiwalled carbon nanotubes sorbent, SPE-HPLC-diode array detection-fluorescence detection [49], SPME-GC–MS [4,50],

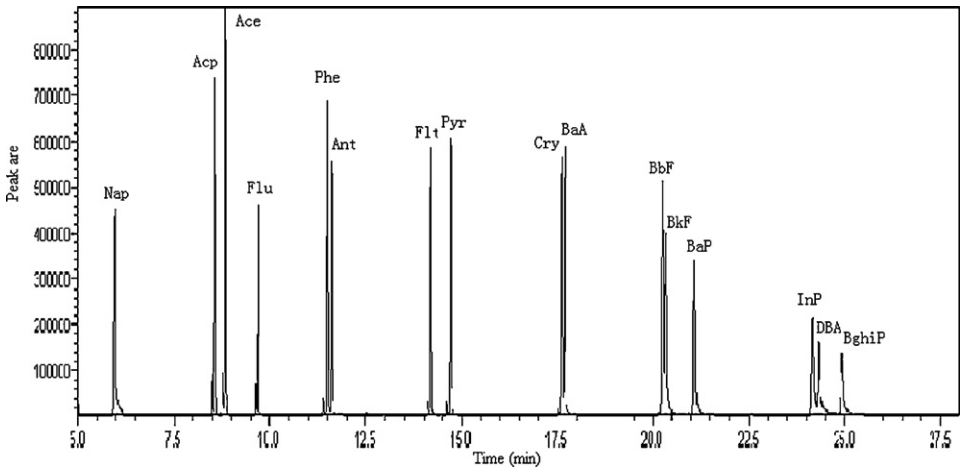

Fig. 8. Chromatogram of spiked ultrapure water sample extract under the most favorable extraction conditions as described in the text.

Table 1
Linear range, limits of detection, limits of quantification, recovery, and precision of PAHs of LDS-SD-DLLME method.

Analyte	Linear range (μg/L)	Correlation coefficient (*r*)	LOD (ng/L)	LOQ (μg/L)	Recovery (%)	RSD (%, *n* = 5)
Nap	0.1–50	0.9876	32.8	0.11	78.9	6.2
Acp	0.1–50	0.9902	21.3	0.09	82.3	9.4
Ace	0.05–50	0.9891	19.5	0.07	88.7	6.6
Flu	0.05–50	0.9943	15.6	0.06	90.1	5.1
Phe	0.05–50	0.9910	3.7	0.01	85.2	5.6
Ant	0.05–50	0.9907	10.9	0.04	89.5	3.5
Flt	0.05–50	0.9853	4.8	0.02	91.4	4.1
Pyr	0.05–50	0.9965	6.7	0.03	94.6	4.3
Cry	0.1–50	0.9928	16.6	0.06	75.2	7.5
BaA	0.1–50	0.9922	29.2	0.15	78.3	8.3
BbF	0.1–50	0.9879	28.4	0.12	81.9	6.9
BkF	0.1–50	0.9936	21.2	0.08	74.8	9.3
BaP	0.2–50	0.9869	39.1	0.14	68.3	9.9
InP	0.2–50	0.9914	28.6	0.11	77.1	8.6
DBA	0.2–50	0.9803	33.0	0.11	67.5	10.2
BghiP	0.2–50	0.9881	27.3	0.13	81.7	8.7

3.4. Genuine water sample analysis

The developed approach was applied to determine PAHs in genuine rainwater samples. Each rainwater sample was divided into three parts and analyzed in parallel. The results are summarized in Table 2. PAHs were found in all analyzed samples. Concentrations ranging from non-detected to 0.61 μg/L, dominated by low molecular weight PAHs, Nap, Acp, Ace, and Phe, due to their relatively higher water solubility, were measured. Especially, the predominant concentration of Nap would conceivably be a result of its lower vapor pressure and higher water solubility in comparison with other PAHs. In addition, Nap is easily trapped by rain droplets in the atmosphere [4,51,52]. Similar concentration levels of PAHs were reported in previous studies [4,5,53,54]. The results indicated

Table 2
PAHs in genuine rainwater samples determined by LDS-SD-DLLME.

	Sampling site 1		Sampling site 2		Sampling site 3	
	Concentration (μg/L)	RSD (%, *n* = 3)	Concentration (μg/L)	RSD (%, *n* = 3)	Concentration (μg/L)	RSD (%, *n* = 3)
Nap	0.53	8.2	0.61	10.7	0.44	6.3
Acp	0.24	6.8	0.15	7.6	0.22	8.9
Ace	0.13	8.1	0.16	9.4	0.16	7.7
Flu	nd		nd		nd	
Phe	0.12	11.3	0.12	6.2	0.11	10.6
Ant	nd		nd		nd	
Flt	nd		nd		nd	
Pyr	nd		nd		nd	
Cry	0.03	9.5	0.01	7.4	0.01	8.2
BaA	nd		nd		nd	
BbF	nd		nd		nd	
BkF	0.05	11.2	0.02	9.9	0.02	8.5
BaP	0.08	7.2	0.11	9.1	0.08	10.3
InP	nd		nd		nd	
DBA	0.13	10.5	0.12	7.9	0.12	11.8
BghiP	nd		nd		nd	

nd: non-detected or below the limits of detection.

that the present method was suitable for the determination of PAHs in environmental water samples.

4. Conclusion

In the present study, low-density solvent-based solvent demulsification dispersive liquid–liquid microextraction (LDS-SD-DLLME) was developed and for the first time applied for determining PAHs in rainwater samples. A low density solvent, *n*-hexane, which is less toxic than chlorinated solvents widely used in conventional DLLME, was successfully used in conjunction with a soft polyethylene pipette that allowed convenient operation of the procedure. The use of low density solvents expands the applicability of DLLME. As is well known, speed of extraction is the most significant feature of DLLME. This present technique was demonstrated to have this characteristic, as well as high extraction efficiency. The extraction could be achieved in 2 min and no other steps were required. Coupled with GC–MS analysis, the proposed method exhibited good linearity and acceptable repeatability, and particularly good LODs in the sub-parts-per-billion range (ng/L). There are several disadvantages of LDS-SD-DLLME in comparison with ultrasound-assisted liquid–liquid microextraction (USAEME). One could argue that more dispersive solvent is needed, this may result in greater solubility of the analytes in the aqueous sample in certain cases [42], possibly leading to reduced extraction efficiency. Also, slightly more extraction solvent is required in LDS-SD-DLLME than in USAEME. On the other hand, LDS-SD-DLLME, does not need electricity-driver equipment (ultrasonicator and centrifuge), and thus has the potential to be performed in the field. Overall, LDS-SD-DLLME has been shown to be a fast, simple, effective, and cost-effective method for the determination of PAHs in environmental water samples.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2011.05.069.

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