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# Development of a dispersive liquid–liquid microextraction method for the determination of polychlorinated biphenyls in water

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**Abstract**

A very simple and powerful microextraction procedure, the dispersive liquid–liquid microextraction (DLLME), was used for the determination of the content of 10 polychlorinated biphenyls (PCBs) in water samples, using gas chromatography coupled with electron-capture detection (GC–ECD). The appropriate amount of acetone (disperser solvent) and chlorobenzene (extraction solvent) at the microlevel volume was used for this procedure. The conditions for the microextraction performance were investigated and optimized. The optimized method exhibited a good linearity ($R^2 > 0.996$) over the studied range (0.005–2 $\mu g\,L^{-1}$), illustrating a satisfactory precision level with R.S.D. values between 4.1% and 11.0%. The values of the detection limit (S/N = 3) were found to be lower than 0.002 $\mu g\,L^{-1}$. Furthermore, a large enrichment factor for the analytes (up to a 540-fold) was achieved in a very short time for only a 5.00-mL water sample. The effectiveness of the method towards real samples was tested by analyzing well, river and seawater samples. The relative recoveries of the well, river and seawater samples, which had been spiked with different levels of PCBs were equal to 92.0–114.0%, 97.0–102.0% and 96.0–103.0%, respectively. The attained results demonstrated that DLLME combined with GC–ECD was a fast and inexpensive technique for the PCBs determination in water samples.


*Keywords:* Dispersive liquid–liquid microextraction; Sample preparation; Polychlorinated biphenyls; Water analysis; Gas chromatography–electron-capture detection

## 1. Introduction

Polychlorinated biphenyls (PCBs) constitute a class of ubiquitous persistent environmental pollutants of great concern, because of their potential risks for the human health and the ecosystems. Although they have been banned in the industrialized countries for years and in some instances for decades, PCBs are still routinely found throughout the world and continue to cause many ecotoxicological problems [1–4]. Owing to their very poor aqueous solubility, PCBs concentration levels in water are typically very low. In order to determine the PCBs trace levels in water samples, an extraction and a preconcentration step is often required prior to their analysis by gas chromatography (GC) [1] or high-performance liquid chromatography (HPLC) [5]. Extraction and preconcentration techniques, such as liquid–liquid extraction (LLE) [6], solid-phase extraction (SPE) [7] and solid-phase microextraction (SPME) [1], are widely applied to determine PCBs in water samples.

New sample preparation methods, especially in the microextraction category, are always of great interest. The reason is to diminish complicated, labor intensive and time-consuming sample preparation procedures uses large amounts of sample and toxic organic solvents cause environmental pollution, health hazards to laboratory personnel and extra operational costs for waste treatment. Therefore, new sample-preparation techniques which are fast, easy to use, inexpensive, environmental friendly and compatible with a range of analytical instruments would be outspreaded. More recently, efforts have been placed on the miniaturization of the LLE extraction procedure by greatly reducing the solvent to aqueous phase ratio, leading to the development of the liquid-phase microextraction (LPME) methodology. LPME provides the advantage of the analyte extraction in only a few microliters of the organic solvents. Up to now, several different LPME modes have been developed, such

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as single drop microextraction (SDME) [8], hollow fiber LPME [9], headspace LPME [10] and dynamic LPME [11].

The recently innovating LPME mode is the dispersive liquid–liquid microextraction [12–23]. DLLME possesses very simple principles and it is based on a ternary component solvent system. The dispersion of the extraction solvent (assisted by the disperser solvent) within the aqueous solution leads to the generation of a significantly large contact area between the extraction solvent and the aqueous phase. Apart from the characteristics of simplicity and rapidity, the consumption of the extraction solvent at the microlevel volume and the compatibility with analytical instruments [13,18,20,21] are some other features of DLLME, illustrating its importance as a sample pretreatment method. At present it is competing with other techniques like SPE, SPME and SDME for the extraction of analytes from various aqueous samples.

In this paper, the efficiency of the DLLME method was thoroughly investigated for the PCBs analysis in water samples. The analytes were firstly microextracted from the water samples and, then, detected using a gas chromatography–electron-capture detection (GC–ECD) system.

## 2. Experimental

### 2.1. Reagents and standards

Ten PCBs were selected to be monitored in this study, based on their reported abundance and toxicity. These compounds were obtained from Dr. Ehrenstorfer (Augsburg, Germany) and were the following: 2,4,4′-trichlorobiphenyl (PCB NO. 28), 2,2′,5,5′-tetrachlorobiphenyl (PCB NO. 52), 2,2′,4,5,5′-pentachlorobiphenyl (PCB NO. 101), 2,3,3′,4,4′-pantachlorobiphenyl (PCB NO. 105), 2,3′,4,4′,5-pantachlorobiphenyl (PCB NO. 118), 3,3′,4,4′,5-pantachlorobiphenyl (PCB NO. 126), 2,2′,3,4,4′,5′-hexachlorobiphenyl (PCB NO. 138), 2,2′,4,4′,5,5′-hexachlorobiphenyl (PCB NO. 153), 2,2′,3,3′,4,4′,5-heptachlorobiphenyl (PCB NO. 170) and 2,2′,3,4,4′,5,5′-heptachlorobiphenyl (PCB NO. 180). The PCBs stock solution (100 mg $L^{-1}$) was prepared in acetone. Acetone (suprasolv for gas chromatography), acetonitrile (hyper grade for liquid chromatography), methanol (suprasolv for gas chromatography), carbon disulfide (for spectroscopy), sodium chloride (analytical grade) and chlorobenzene were obtained from Merck (Darmstadt, Germany). For further purification, chlorobenzene was distillated four times before use.

The well, river and seawater samples, used for the design of the method, were collected from Northern Iran in glass bottles, stored in the dark at 4 °C and analyzed within 48 h of collection without any previous treatment or filtration. Ultra pure water (Ghazi Co., Tabriz, Iran) was used throughout the experiments for the dilutions and the standard preparations.

### 2.2. Instrumentation

The PCBs determinations were performed with the use of a gas chromatographic system, equipped with an ECD detection. The GC–ECD system was a Shimadzu GC-2010 gas chromatograph (Kyoto, Japan) with a $^{63}Ni$ electron capture detector and a split/splitless injection port. The separations were carried out with a BPX-5 capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness, 95% methyl, 5% phenyl), purchased from SGE (Victoria, Australia).

Ultra pure helium (99.9999%, Air Products, West Sussex, UK), passing through a molecular sieve trap and an oxygen trap (Chromatography Research Supplies, Louisville, USA), was employed as the carrier gas at the constant linear velocity of 30 cm $s^{-1}$. Ultra pure nitrogen (99.9999%, Air Products) was employed as the makeup gas for ECD, passing through a molecular sieve trap and an oxygen trap (Chromatography Research Supplies) at the flow of 30 mL $min^{-1}$. The injection port was held at 300 °C and used in the splitless mode at the splitless time of 0.50 min and at the split ratio of 1:50.

PCBs were separated after setting the following oven temperature program: 3 min at 100 °C, first ramp at 25 °C $min^{-1}$ to 200 °C, second ramp at 5 °C $min^{-1}$ to 290 °C (held for 2 min). Concerning the carbon disulfide usage as extraction solvent, the column temperature was initially adjusted to 35 °C. The ECD temperature was maintained at 300 °C. Additionally, a Centurion Scientific (Arundel, UK) model 1020D centrifuge was used.

### 2.3. Labware cleaning

To remove any organic contamination and to well sediment the fine droplets of the extraction solvent (chlorobenzene) in the centrifugation step, all of the 10-mL screw cap conical bottomed glass test tubes (extraction vessels) were heated at 500 °C for 30 min in a furnace (Carbolite, model CWF 1200, Hope Valley, UK).

### 2.4. Microextraction procedure

The microextraction of 10 PCBs spiked water samples (at the spiking level of 0.100 μg $L^{-1}$) was conducted under the optimized conditions, requiring 5.00 mL from the spiked water samples in a screw cap conical bottom test tube. DLLME was performed by a rapid injection of 500 μL acetone (disperser solvent, miscible in water sample), containing 10.0 μL of chlorobenzene (extraction solvent, immiscible in water sample), to the spiked water sample by a 500-μL syringe (Gastight, Hamilton, Reno, NV, USA). This injection led to a cloudy water solution, caused by the fine droplets dispersion of the immiscible extraction solvent (chlorobenzene) in the aqueous sample. The result of this phenomenon was the generation of a high contact area between the aqueous phase and the extraction solvent.

The final step of the microextraction procedure was centrifugation (2 min at 5 000 rpm) to collect the dispersed tinny chlorobenzene droplets in the bottom of the conical test tube. The volume of the sedimented phase, which was about 5.0 ± 0.2 μL was determined with a 10.0-μL microsyringe. For the detection of the enriched analytes (PCBs), 0.50 μL of the sedimented phase were removed with the aid of a 1.00-μL microsyringe (zero dead volume, cone tip needle, SGE) and injected into GC.

Table 1
Enrichment factor of different extraction solvents evaluated for extraction of PCBs by DLLME[a]

| Compounds | Enrichment factor | |
|---|---|---|
| | Chlorobenzene, mean (S.D.[b], $n=3$) | Carbon disulfide, mean (S.D.[b], $n=3$) |
| PCB 28 | 540 (32) | 213 (37) |
| PCB 52 | 529 (33) | 216 (42) |
| PCB 101 | 468 (28) | 157 (49) |
| PCB 105 | 490 (35) | 134 (36) |
| PCB 118 | 439 (33) | 144 (39) |
| PCB 126 | 492 (40) | 161 (39) |
| PCB 138 | 464 (40) | 149 (46) |
| PCB 153 | 443 (50) | 81 (18) |
| PCB 170 | 378 (28) | 120 (45) |
| PCB 180 | 383 (30) | 112 (45) |

[a] Extraction conditions: water sample volume, 5.00 mL; disperser solvent (acetone) volume, 500 μL; extraction solvent volumes, 10.0 μL chlorobenzene and 19.5 μL carbon disulfide; sedimented phase volume, 5.0 ± 0.2 μL; room temperature; concentration of each PCBs 0.100 μg $L^{-1}$.
[b] Standard deviation.

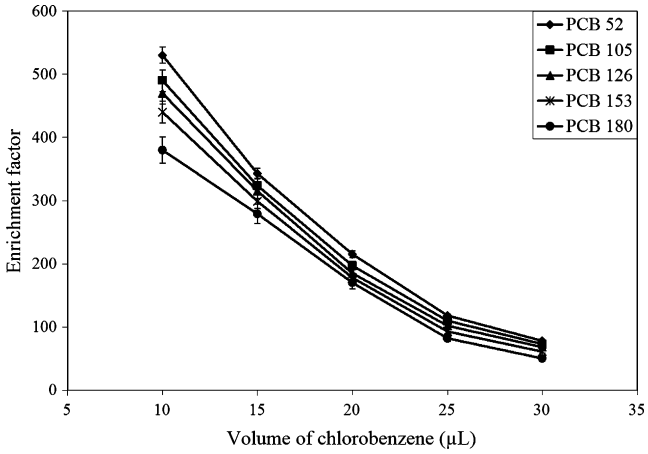


Fig. 1. The effect of the volume of extraction solvent (chlorobenzene) on the enrichment factor of some PCBs obtained from DLLME. Extraction conditions: water sample volume, 5.00 mL; disperser solvent (acetone) volume, 500 μL; sedimented phase volume, 5.0 ± 0.2 μL; room temperature; no salt addition; concentration of each PCBs, 0.100 μg $L^{-1}$. The results for the other PCBs are very similar.

## 3. Results and discussion

The parameters, affecting the DLLME procedure, such as the type of the extraction and the disperser solvents as well as their volume, the salt addition and the extraction time were optimized. For this purpose, the one-variable-at-a-time optimization was used. It should be noted that the optimization procedure was conducted using spiked samples.

The enrichment factor (EF) was defined as the ratio of the analyte concentration in the sedimented phase to the analyte concentration in the aqueous sample. The analyte concentration in the sedimented phase was calculated from the direct calibration graph (10–50 μg $L^{-1}$ PCBs in chlorobenzene).

### 3.1. Effect of the extraction solvent type and the volume

According to the DLLME principles [12], the extraction solvent should demonstrate special characteristics: low solubility in water, extraction capability of the target compounds, good chromatographic behavior and higher than water density. The densest solvents are the halogenated ones and the halogenated compounds present a strong response with a severe tailing in ECD. Therefore, there are some limitations on the selection of the extraction solvent, especially in the GC–ECD analysis system.

Carbon disulfide (density: 1.2 g $mL^{-1}$; boiling point: 46 °C; solubility in water at 20 °C: 2.1 g $L^{-1}$) and chlorobenzene (density: 1.1 g $mL^{-1}$; boiling point: 131.6 °C; solubility in water at 20 °C: 0.4 g $L^{-1}$), with a much lower response factor than that of the analytes in ECD, were selected as extraction solvents and tested for their performance. In detail, a series of sample solutions were microextracted using 500 μL acetone contain 10.0 μL chlorobenzene or 19.5 μL carbon disulfide. The volume of the sedimented phase for both extraction solvents was approximately 5.0 μL. According to the results (Table 1), chlorobenzene displayed higher extraction efficiency and a lower relative standard deviation than those of carbon disulfide. Consequently, chlorobenzene was selected as the optimum extraction solvent.

To examine the effect of the extraction solvent volume, 500 μL acetone solutions with different chlorobenzene volumes were subjected to the same DLLME procedure. With the increase of the chlorobenzene volume from 10.0 to 30.0 μL, the volume of the sedimented phase increased from 5.0 to 25.4 μL. Fig. 1 depicts the variation of the enrichment factor versus the volume of the extraction solvent. In line with this figure, enrichment factors decrease with the increase of the chlorobenzene volume, owing to the sedimented phase volume increase. Thereby, the best sensitivity was achieved with the employment of 10.0 μL chlorobenzene. This volume could not be set lower than 10.0 μL, on the grounds that the sedimented phase volume would become less than 5.0 μL, causing difficulties in its removal with a microsyringe and encountering systematic errors.

### 3.2. Influence of the disperser solvent type and volume

As explained before [12], the disperser solvent should be miscible in water and dissolve the extraction solvent. The polar solvents, like acetone, acetonitrile and methanol, exhibit these properties and were used to investigate the influence of these solvents on the DLLME performance. Several sample solutions were analyzed using 500 μL of each disperser solvent containing 10.0 μL chlorobenzene (extraction solvent). The results (Table 2) show that the enrichment factor values are almost equal for acetone (378–540), acetonitrile (385–522) and methanol (372–534). Subsequently, acetone was chosen among these solvents, due to its lower toxicity and cost.

The influence of the disperser solvent amount on the extraction efficiency was tested over the range of 250–1500 μL, but the variation of the acetone volume (disperser solvent) caused changes in the sedimented phase volume. Hence, it

Table 2
Enrichment factor of different disperser solvents evaluated for extraction of PCBs by DLLME[a]

| Compounds | Enrichment factor | | |
|---|---|---|---|
| | Acetone, mean (S.D.[b], $n=3$) | Acetonitrile, mean (S.D.[b], $n=3$) | Methanol, mean (S.D.[b], $n=3$) |
| PCB 28 | 540 (32) | 522 (37) | 534 (26) |
| PCB 52 | 529 (33) | 514 (27) | 523 (35) |
| PCB 101 | 468 (28) | 479 (34) | 452 (33) |
| PCB 105 | 490 (35) | 476 (25) | 488 (36) |
| PCB 118 | 439 (33) | 453 (42) | 426 (48) |
| PCB 126 | 492 (40) | 501 (45) | 477 (28) |
| PCB 138 | 464 (40) | 446 (32) | 419 (33) |
| PCB 153 | 443 (50) | 439 (43) | 454 (41) |
| PCB 170 | 378 (28) | 385 (31) | 372 (34) |
| PCB 180 | 383 (30) | 390 (35) | 394 (37) |

[a] Extraction conditions: water sample volume, 5.00 mL; disperser solvent (acetone, acetonitrile or methanol) volumes, 500 μL; extraction solvent (chlorobenzene) volume, 10.0 μL; sedimented phase volume, 5.0 ± 0.2 μL; room temperature; concentration of each PCBs 0.100 μg $L^{-1}$.
[b] Standard deviation.

was impossible to consider independently the influence of the acetone volume on the extraction efficiency in DLLME. To avoid this problem and in order to attain a constant volume of the sedimented phase, the acetone and chlorobenzene volumes were changed simultaneously. The experimental conditions were fixed and included the use of different acetone volumes: 250, 500, 750, 1000, 1250 and 1500 μL, containing 9.5, 10.0, 11.3, 13.0, 14.5 and 16.5 μL of chlorobenzene, respectively. Under these conditions, the sedimented phase volume remained constant (5.0 ± 0.2 μL). In agreement with the respective results (Fig. 2), the extraction efficiency initially increases, while, afterwards, it reduces as the acetone volume increases. This observation could be attributed to the fact that at lower acetone volumes, the cloudy suspension of the chlorobenzene droplets was not formed well, resulting in a decrease in the extraction recovery. At higher acetone volumes, the PCBs solubility in water increased and the extraction efficiency reduced. Therefore, the acetone volume of 500 μL was selected as the optimum volume for the disperser solvent.

### 3.3. Salt influence

Salt addition is frequently used to adjust the ionic strength, improve the extraction efficiency and reduce the detection limit. The effect of the ionic strength on the PCBs extraction efficiency by DLLME was examined across the concentration range of 0–5% (w/v) NaCl. The data from these experiments presented that the salt addition did not influence the enrichment factor significantly for any of the analytes. As a consequence, all the extraction experiments were carried out without salt addition. The practicability of the method was also confirmed in saline samples up to 5% (w/v) NaCl. Concentration values higher than 5% (w/v) NaCl were abandoned, due to the higher density than the water solution gained, preventing the chlorobenzene sedimentation.

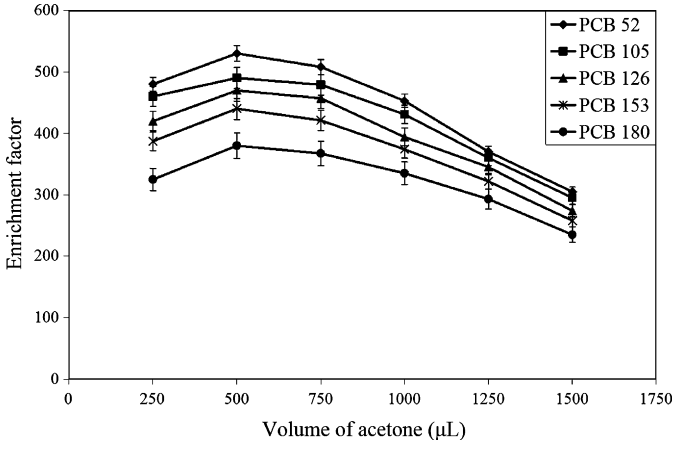


Fig. 2. The effect of the volume of acetone (disperser solvent) on the enrichment factor of some PCBs obtained from DLLME. Extraction conditions: as in Fig. 1; extraction solvent (chlorobenzene) volume, 10.0 μL. The results for the other PCBs are very similar.

Table 3
Quantitative results of DLLME and GC–ECD of PCBs from water sample[a]

| Compounds | R.S.D.%[b] ($n=8$) | EF[c] | LR[d] (μg $L^{-1}$) | $R^2$[e] | LOD[f] (μg $L^{-1}$) |
|---|---|---|---|---|---|
| PCB 28 | 4.1 | 540 | 0.005–2 | 0.9961 | 0.0010 |
| PCB 52 | 4.8 | 529 | 0.005–2 | 0.9984 | 0.0020 |
| PCB 101 | 6.3 | 468 | 0.005–2 | 0.9986 | 0.0015 |
| PCB 105 | 6.9 | 490 | 0.005–2 | 0.9991 | 0.0015 |
| PCB 118 | 7.5 | 439 | 0.005–2 | 0.9991 | 0.0015 |
| PCB 126 | 7.4 | 492 | 0.005–2 | 0.9992 | 0.0010 |
| PCB 138 | 7.8 | 464 | 0.005–2 | 0.9994 | 0.0010 |
| PCB 153 | 7.8 | 443 | 0.005–2 | 0.9995 | 0.0020 |
| PCB 170 | 10.2 | 378 | 0.005–2 | 0.9996 | 0.0015 |
| PCB 180 | 11.0 | 383 | 0.005–2 | 0.9996 | 0.0010 |

[a] Extraction conditions: water sample volume, 5.00 mL; disperser solvent (acetone) volume, 500 μL; extraction solvent (chlorobenzene) volume, 10.0 μL; sedimented phase volume, 5.0 ± 0.2 μL; room temperature.
[b] At concentration of 0.100 μg $L^{-1}$ for each PCBs.
[c] Enrichment factor.
[d] Linear range.
[e] Correlation coefficient.
[f] Limit of detection for S/N = 3.

Table 4
Relative recoveries and standard deviations of PCBs from spiked well, river and seawater samples[a]

| Compounds | Well water | | | River water | | | Seawater | | |
|---|---|---|---|---|---|---|---|---|---|
| | Added ($\mu g\,L^{-1}$) | Found (S.D. $n=3$) ($\mu g\,L^{-1}$) | Relative recovery (%) | Added ($\mu g\,L^{-1}$) | Found (S.D.[b], $n=3$) ($\mu g\,L^{-1}$) | Relative recovery (%) | Added ($\mu g\,L^{-1}$) | Found (S.D.[b], $n=3$) ($\mu g\,L^{-1}$) | Relative recovery (%) |
| PCB 28 | 0.0200 | 0.0184 (0.0017) | 92.0 | 0.200 | 0.195 (0.018) | 97.5 | 2.00 | 2.06 (0.08) | 103.0 |
| PCB 52 | 0.0200 | 0.0228 (0.0028) | 114.0 | 0.200 | 0.201 (0.016) | 100.5 | 2.00 | 2.05 (0.08) | 102.5 |
| PCB 101 | 0.0200 | 0.0210 (0.0026) | 105.0 | 0.200 | 0.196 (0.013) | 98.0 | 2.00 | 2.03 (0.10) | 101.5 |
| PCB 105 | 0.0200 | 0.0206 (0.0021) | 103.0 | 0.200 | 0.194 (0.014) | 97.0 | 2.00 | 2.05 (0.10) | 102.5 |
| PCB 118 | 0.0200 | 0.0197 (0.0022) | 98.5 | 0.200 | 0.194 (0.019) | 97.0 | 2.00 | 1.99 (0.07) | 99.5 |
| PCB 126 | 0.0200 | 0.0211 (0.0021) | 105.5 | 0.200 | 0.196 (0.016) | 98.0 | 2.00 | 2.00 (0.09) | 100.0 |
| PCB 138 | 0.0200 | 0.0195 (0.0024) | 97.5 | 0.200 | 0.198 (0.015) | 99.0 | 2.00 | 1.99 (0.09) | 99.5 |
| PCB 153 | 0.0200 | 0.0203 (0.0020) | 101.5 | 0.200 | 0.195 (0.011) | 97.5 | 2.00 | 2.00 (0.07) | 100.0 |
| PCB 170 | 0.0200 | 0.0188 (0.0020) | 94.0 | 0.200 | 0.202 (0.014) | 101.0 | 2.00 | 1.92 (0.08) | 96.0 |
| PCB 180 | 0.0200 | 0.0184 (0.0021) | 92.5 | 0.200 | 0.204 (0.012) | 102.0 | 2.00 | 1.95 (0.06) | 97.5 |

[a] Extraction conditions: water sample volume, 5.00 mL; disperser solvent (acetone) volume, 500 μL; extraction solvent (chlorobenzene) volume, 10.0 μL; sedimented phase volume, $5.0 \pm 0.2$ μL; room temperature.
[b] Standard deviation.

Table 5
Comparison of DLLME–GC–ECD with other extraction methods for determination of PCBs in water

| Method | Sample consumption (mL) | R.S.D.[a] (%) | LOD[b] ($ng\,L^{-1}$) | Volume of the extraction or elution solvent (mL) | Estimated sample preparation time[c] (min) | Reference |
|---|---|---|---|---|---|---|
| LLE–GC–ECD | 500 | 1.1–9.8 | <200 | 100 | >90 | [6] |
| LLE–GC–MS | 500 | 0.61–6.32 | <200 | 100 | >90 | [6] |
| LLME–GC–ECD | 500 | 1.7–26.9 | 40 | 2 | >30 | [24] |
| SPE(disk)–GC–ECD | 1000 | 1–8 | 0.25–1 | 30 | >30 | [7] |
| SBSE[d]–GC–MS | 8 | 3.3–29.7 | 0.05–0.15 | Thermodesorption | >120 | [25] |
| HS-SPME[e]–GC–MS | 100 | 5 | 0.3 | Thermodesorption | 30 | [26] |
| SPME–GC–MS | 30 | 8–14 | 30–110 | Thermodesorption | 50 | [27] |
| OMMLLE[f]–GC–ECD | 1 | 2–5 | 2–3 | 0.007 | >10 | [28] |
| EPA[g] method 608 | 1000 | 20–48.8 | 65 | 120 | >40 | [29] |
| HFMM[h]–GC–MS | 10 | 1–9 | 0.04–0.21 | 0.100 | >40 | [30] |
| DLLME–GC–ECD | 5 | 4.1–11.0 | 1–2 | 0.010 | <3 | (Represented method) |

[a] Relative standard deviation.
[b] Limit of detection.
[c] The time needed for conditioning of sorbent, analyte desorption, solvent evaporation and sample cleanup is not considered.
[d] Stir bar sorptive extraction.
[e] Headspace solid-phase microextraction.
[f] On-line microporous membrane liquid–liquid extraction–gas chromatography.
[g] Environmental Protection Agency.
[h] Hollow fiber membrane microextraction.

### 3.4. The extraction time effect

Mass-transfer is a time-dependent process. For this reason, it is important to establish the extraction-time profiles of the target analytes so as to configure the optimized time. In DLLME, extraction time is defined as the time between the injection of the disperser solvent, containing the extraction solvent, and the centrifugation initiation. Extractions were performed in a period of 0, 5, 10 and 15 min, respectively. The resulting data, displaying that the extraction time has no significant effect on the extraction efficiency for all the target compounds. It was revealed that after the formation of the cloudy solution, the contact area between the extraction solvent and the aqueous phase was considerably large, delineating why the extraction equilibrium could be established very fast. The most time-consuming procedure was the centrifugation of the sample solution in the extraction procedure, which was about 2 min. Unlike SDME and SPME, the establishment of the equilibrium in DLLME was not a time-consuming step. On the other hand, there is a possibility for the SDME and SPME techniques not to reach equilibrium. Extraction time is one of the distinct primacies of the DLLME method in comparison with SDME and SPME.

### 3.5. Quantitative aspects

The optimized DLLME–GC–ECD procedure was validated with respect to precision, enrichment factor, correlation coefficient, linear dynamic range and detection limit (Table 3). The precision of the method was evaluated by carrying out eight independent microextraction measurements of the studied compounds at 0.100 $\mu g\,L^{-1}$. The obtained results showed that the relative standard deviations (R.S.D.s) values could be considered as acceptable, between 4.1% and 11.0%. The calibration data could fit a linear model for all the 10 PCBs with a typical correlation coefficient ($R^2$), exceeding 0.996. The detection limit values (LODs) of the 10 PCBs (listed in Table 3), based on a signal-to-noise ratio of 3 (S/N = 3) for the extraction of a 5.00-mL water sample, were found to be lower than 0.002 $\mu g\,L^{-1}$. Finally, the high enrichment factors (378–540) were obtained for PCBs only for small volume of water samples (5.00 mL).

### 3.6. Real water analysis

To demonstrate the applicability and reliability of the proposed trace enrichment method for environmental purposes, the procedure was applied to the PCBs determination in natural water samples (well, river and seawater). The investigation revealed that none of the 10 target PCBs were found in these real water samples. Fig. 3 presents the chromatograms for (a) the river water samples and (b) the spiked river water samples at the spiking level of 0.200 $\mu g\,L^{-1}$. The spike recovery of the target PCBs in the real water samples at different concentration levels are summarized in Table 4 (the recoveries obtained in different samples were compared to those obtained from distilled water having the same concentrations relative to analytes). The data indicated that the recommended method could be used in the analysis of the environmental water samples (no matrix effect was observed).

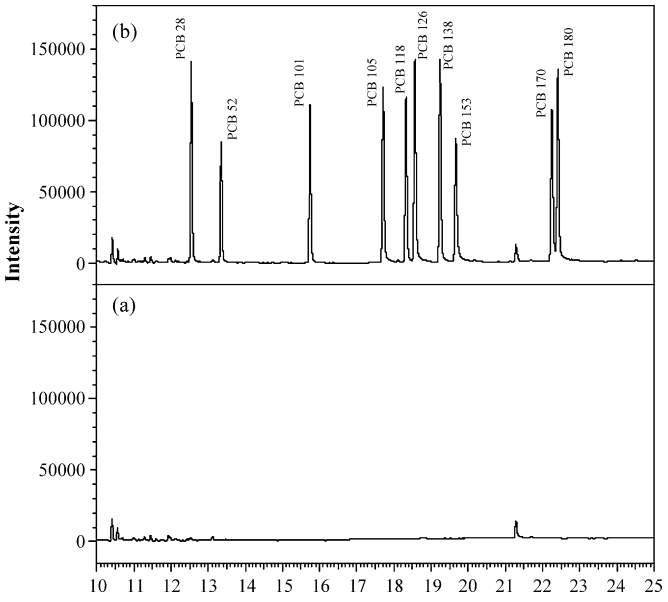


Fig. 3. The chromatograms of the river water (a) and the spiked river water at the concentration level of 0.200 $\mu g\,L^{-1}$ for each PCBs (b) obtained by using DLLME combined with GC–ECD. Extraction conditions: water sample volume, 5.00 mL; extraction solvent (chlorobenzene) volume, 10.0 μL; disperser solvent (acetone) volume, 500 μL; sedimented phase volume, 5.0 ± 0.2 μL; room temperature.

### 3.7. Comparison of DLLME with other methods

The performance of the proposed method in the PCBs microextraction and determination from water samples were compared with the corresponding performance of other methods with reference to sample volume, R.S.D.s, LODs and estimated sample preparation time (Table 5). As it can be seen, the obtained R.S.D.s are comparable with other methods in relation to the fact that sample volume consumption and significantly sample preparation time is much reduced. LODs are lower than many of the mentioned techniques, considering very low sample consumption volume, except stir bar sorptive extraction (SBSE) and hollow fiber membrane microextraction (HFMM) employing mass detector [25,30]. We must take into account that many analytical laboratories cannot support such equipment because of their high price and expensive maintenance. Besides, stir bar sorptive extraction requires a special device for thermal desorption therefore, expenses increase. DLLME employs simple equipment and is applicable for most of the analytical laboratories. Moreover, the extraction equilibrium establishes within a few seconds. All these results disclosed that DLLME was a sensitive, rapid and reproducible technique. In addition to the mentioned benefits, DLLME did not involve any labor intensive and time-consuming steps.

## 4. Conclusion

This study illustrated that DLLME–GC–ECD is an accurate and reliable method for the PCBs determination in environmental water samples. It appears to be a time-saving technique, mainly for laboratories performing analysis of a large number of samples with a rapid reporting time. Since the method demonstrated a sufficient reliability, accuracy and repeatability, it was applied to real water samples.

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