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Dispersive liquid–liquid microextraction combined with gas chromatography–electron capture detection for the determination of polychlorinated biphenyls in soils

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ABSTRACT

In this article, dispersive liquid–liquid microextraction (DLLME) and gas chromatography–electron capture detection (GC–ECD) were presented for the extraction and determination of five polychlorinated biphenyls (PCBs) in soil samples. Acetone was used as extraction solvent for the extraction of PCBs from soil samples. In DLLME, the target analytes in the extraction solvent were rapidly transferred from the acetone extract to chlorobenzene when the extraction process began. The main advantages of this method are quick speed, high enrichment factor, high recovery and good repeatability. Under the optimum conditions, the method yields a linear calibration curve in the concentration range from 2 to 2000 $\mu g\,kg^{-1}$ for PCB 52, and 0.4 to 400 $\mu g\,kg^{-1}$ for other target analytes. Coefficients of correlation (r^2) ranged from 0.9993 to 0.9999. The repeatability was tested by spiking soil samples at a concentration level of 10 $\mu g\,kg^{-1}$ for PCBs. The relative standard deviations (RSDs, $n = 11$) varied between 2.2% and 6.4%. The limits of detection (LODs), based on signal-to-noise (S/N) of 3, were between 0.20 and 0.50 $\mu g\,kg^{-1}$. The relative recoveries of the five PCBs from soil S1, S2 and S3 at spiking levels of 10, 20 and 50 $\mu g\,kg^{-1}$ were in the range of 88.70–103.8%, 82.50–106.3% and 82.30–113.6%, respectively. Therefore, DLLME combined with GC–ECD can be successfully applied for the determination of trace PCB residues in real soil samples.

1. Introduction

Polychlorinated biphenyls (PCBs) are one kind of the most widespread and persistent environmental pollutants since the middle of the last century [1], and they are mainly used in transformers, capacitors and paper and paint industry. Migration of chemicals from soil to water and vice versa may cause an accumulation of multiple residues in water and agricultural products designed for animal or human consumption [2]. Due to their low water solubility, hydrophobic character and resistance to metabolic degradation, PCBs can represent a risk to environmental and human health. In recent years, the production of PCBs has been phased out. However, these chemicals have already occurred in the environment and in food chains, it is very important to investigate the concentration levels of PCBs in environmental samples. The European Environmental Agency (Directive 76/464/EEC and its daughter Directives) has drawn up a list of pollutants including PCBs for priority monitoring, which need to be analyzed with sensitive instrumental methods [3].

PCB residues are often at trace level in the environment, so it is necessary to use a preconcentration step before their analysis. Many reliable analytical techniques to improve this extraction step and reduce the use of organic solvents have been reported [4–10]. Although the Soxhlet extraction method, developed in 1879 [4], is still used in many laboratories, several novel extraction methods, such as liquid–liquid extraction (LLE) [5], solid-phase extraction (SPE) [6], solid-phase microextraction (SPME) [7], and liquid-phase microextraction (LPME) [8] have been carried out to determine PCBs in environmental samples. The most frequently used sample pretreatment methods for PCBs determination are LLE and SPE [9,10]. LLE and SPE need either large amounts of sample and organic solvents, or are time-consuming and the materials used are not reusable, and expensive [11]. SPME is a practical solvent-free alternative for the extraction of organic compounds. It is easily automated, involves fewer extraction steps and consumes less time. However, SPME is expensive, the fiber used is fragile and has a limited lifetime, and sample carryover can be a problem [12]. LPME provides the advantage of the analyte extraction in only a few

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microliters of organic solvent. Nevertheless, LPME suffers from some disadvantages as follows: fast stirring often tend to form air bubble [13], the extraction process is time-consuming and equilibrium cannot be achieved after a long time in most cases [14].

Dispersive liquid–liquid microextraction (DLLME) developed by Assadi and co-workers [15], which is based on a ternary component solvent system like homogeneous liquid–liquid extraction (HLLE) [16] and cloud point extraction (CPE) [17]. It is a miniaturized, simple, rapid, sensitive preconcentration and microextraction technique. At present it is competing with other methods like SPE, SPME and LPME for the extraction of analytes from different samples. It has been successfully used for the extraction and preconcentration of many trace substances from water samples [18–27]. The performance of DLLME was also illustrated with the determination of organophosphorus pesticides (OPPs) in vegetable samples [28].

As far as our information goes, only one paper reported the application of DLLME technique for the determination of PCBs in water samples [29]. However, no data are available on the determination of PCBs in soil samples by DLLME. In the present work, DLLME combined with gas chromatography–electron capture detection (GC–ECD) was investigated for the determination of PCBs in soil samples. The influence of various experimental parameters on the extraction of PCBs in S1, S2 and S3 soil samples was studied in detail. The results show that DLLME is a simple, rapid and sensitive method that can be used in detecting trace PCB residues in soil samples.

2. Experimental

2.1. Materials

2,2′,5,5′-tetrachlorobiphenyl (PCB 52), 2,2′,4,5,5′-pentachlorobiphenyl (PCB 101), 2,2′,3,4,4′,5′-hexachlorobiphenyl (PCB 138), 2,2′,4,4′,5,5′-hexachlorobiphenyl (PCB 153), and 2,2′,3,4,4′,5,5′-heptachlorobiphenyl (PCB 180) were selected as representative congeners of PCBs. Polychlorinated biphenyls (PCB 52, PCB 101, PCB 138, PCB 153, PCB 180) were obtained from AccuStandard, USA. The individual stock standard solution were prepared in acetone at a concentration of 100 μg mL^{-1} and stored at −20 °C at the refrigerator. The standard working solutions were daily obtained by appropriate dilution of the stock standard solution. Acetonitrile, methanol, acetone and *n*-hexane were purchased from Merck (Darmstadt, Germany). All of the reagents used as extraction solvent in this experiment (chlorobenzene, carbon tetrachloride and tetrachloroethane) were purchased from Sinopharm Chemical Reagent (Shanghai, China) and were of analytical grade. They were redistilled at least three times before use. Sodium chloride was of the highest purity available from the Merck (Darmstadt, Germany). Deionized water was produced by a Milli-Q water purification system (Millipore, Bedford, MA, USA).

Soil samples S1, S2 and S3 were collected at upper, middle and lower reaches of the Ao River, Wenzhou, China, respectively. Soil samples were air-dried, pulverized and sieved to a grain size of 2 mm. The spiking levels of PCBs in soil samples were 10, 20 and 50 μg kg^{-1}, respectively. Then, the soil sample was homogenized by mixing and shaking for 30 min on a mechanical shaker at 250 rpm, remained at room temperature for 90 min in order to attain the equilibrium state of adsorption–desorption.

2.2. Apparatus

Separation and determination of PCBs were performed on an Agilent 6890 series gas chromatography equipped with ECD. One microliter of sample was injected in the splitless mode, with splitless time of 0.75 min. The injection port temperature was 300 °C. The detector temperature was 300 °C with N_2 as make-up gas. N_2 was used as the carrier gas at a flow rate of 1.6 mL min^{-1}. Chromatographic separation was accomplished on a HP-5 (5% phenyl, 95% methylpolysiloxane), 30 m × 320 μm i.d. × 0.25 μm capillary column. The oven program was started at 140 °C held for 5 min, programmed at 20 °C min^{-1} to 200 °C held for 5 min, then programmed at 3 °C min^{-1} to 240 °C held for 5 min.

An 80-2 model centrifuge (Changzhou Guohua Electrical Appliance Co. Ltd., China) was used for centrifuging. 10-mL glass test tube with conical bottom as extraction vessel was heated at 250 °C in a furnace (Carbolite, UK; model CWF 1200) to remove organic compounds.

2.3. Extraction procedures

The procedures for the extraction of PCBs from soil samples were as follows: aliquots (1.0 g) of soil samples were loaded into a 50 mL conical flask. Samples were extracted with 10 mL acetone for 30 min at 250 rpm on a mechanical shaker. The upper solution was transferred into a 10 mL glass test tube.

For DLLME operations, 5.0 mL ultra pure water was placed in a 10 mL screw cap glass test tube with conical bottom. 30.0 μL chlorobenzene was added to 1.0 mL acetone extract used as the extraction solvent. Then, 1 mL of acetone solution was rapidly added into the aqueous solution by using a 1.0 mL syringe (Shanghai, China). Then the mixture was gently shaken several seconds by hand. A cloudy solution (water, acetone and chlorobenzene) was formed in the glass test tube. In this step, PCBs were extracted into the fine droplets of chlorobenzene. The mixture was then centrifuged for 3 min at 3000 rpm, the chlorobenzene phase was sedimented at the bottom of the centrifuge tube. The sedimented phase (20.0 ± 1.0 μL) was completely transferred to another test tube with conical bottom by using a 25 μL micro-syringe. After evaporation of the extract solvent by a gentle nitrogen flow, the residue was dissolved in 20.0 μL *n*-hexane. Aliquots (1.00 μL) of the *n*-hexane phase was removed by a 5.00 μL micro-syringe and injected into GC for analysis.

3. Results and discussion

The possibility of combination of DLLME with GC–ECD was investigated to preconcentrate and determine PCBs in soil samples. There are several parameters that affect DLLME performance, including type of extraction solvent used for soil sample, type of extraction and disperser solvent and their volume in DLLME procedure, salt addition and extraction time. We selected five compounds as PCB representative congeners and studied their extraction efficiency under various conditions.

3.1. Selection of organic solvent for the extraction of PCBs from soils

The extraction solvent for soil samples must play two kinds of role in this investigation, one is that it can efficiently extract analytes of interest from soil samples and the other is that it can act as a phase, for example dispersive solvent, in DLLME procedures. The selection of dispersive solvents in DLLME is based on its miscibility with both organic (extraction solvent in DLLME) and aqueous (sample solution) phases. In view of the above considerations, acetone, acetonitrile and methanol were evaluated for this purpose. Since different dispersive solvent often lead to the different volume of the sedimented phase with constant volume of extraction solvent, in order to avoid this case and achieve a constant volume of sedimented phase (20.0 ± 1.0 μL), the kind of dispersive solvent and the volume of chlorobenzene were changed simultaneously. Several water solutions (5 mL) were performed using 1.0 mL of acetone, acetonitrile and methanol solution containing 30.0, 32.0, and 36.0 μL of C_6H_5Cl, respectively. The effect of various dispersive sol-

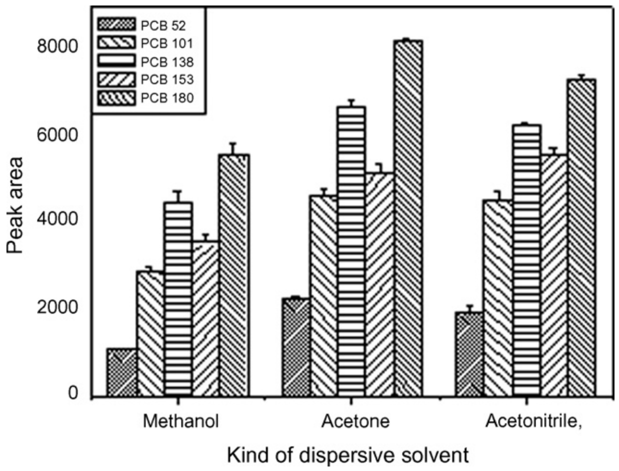

Fig. 1. Effect of different dispersive solvents on extraction efficiencies of PCBs by DLLME. Extraction conditions: sample volume, 5.0 mL; disperser solvent (methanol, acetone, acetonitrile) volume, 1.0 mL; extraction solvent (chlorobenzene) volumes, 36.0, 30.0, 32.0 μL, respectively; room temperature and without salt addition; sedimented phase volume, 20.0 ± 1.0 μL; concentration of each PCBs, 1.0 μg L^{-1}.

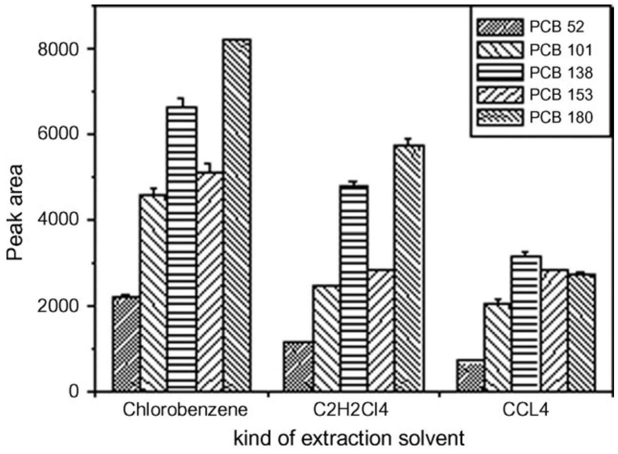

Fig. 2. Effect of different extraction solvents on extraction efficiencies of PCBs by DLLME. Extraction conditions: sample volume, 5.0 mL; disperser solvent (acetone) volume, 1.0 mL; extraction solvent volumes, 30.0 μL chlorobenzene, 26.0 μL tetrachloroethane and 42.0 μL carbon tetrachloride; room temperature and without salt addition; sedimented phase volume, 20.0 ± 1.0 μL; concentration of each PCBs, 1.0 μg L^{-1}.

vents on the extraction of PCBs with chlorobenzene as extraction solvent is shown in Fig. 1. As compared with other disperser solvents, acetone gave better extraction efficiency for the target PCBs. Therefore, acetone was chosen as extraction solvent for soil samples and as dispersive solvent in DLLME procedures in the subsequent experiments.

3.2. Selection of the extraction solvent for DLLME

In general, extraction solvent used in DLLME procedures must possess the following properties: (1) higher density than water; (2) good chromatographic behavior; (3) high extraction capability of interested compounds; (4) low solubility in water and (5) forming a cloudy solution (very fine droplets) in the presence of a dispersive solvent when injected to an aqueous solution [22]. Most of the solvents with all of the above properties are halogenated compounds. Considering the strong response with a high tailing peak of the halogenated solvents in ECD, we evaporated the extraction solvent after DLLME process in water bath by nitrogen, and the residue was dissolved in 20.0 μL *n*-hexane.

We examined three chlorinated solvents, carbon tetrachloride, tetrachloroethane and chlorobenzene, in order to find the most suitable solvent for DLLME. The densities of the selected organic solvents are 1.59 g mL^{-1} (CCl_4), 1.60 g mL^{-1} ($C_2H_2Cl_4$) and 1.10 g mL^{-1} (C_6H_5Cl), respectively. A series of sample solutions was tested using 1.0 mL of acetone (disperser solvent), which contained different volumes of the extraction solvents to achieve a volume of 20.0 μL of the sedimented phase. Accordingly, 42.0, 26.0 and 30.0 μL of CCl_4, $C_2H_2Cl_4$ and C_6H_5Cl were employed, respectively. As can be seen from Fig. 2, chlorobenzene showed the highest extraction efficiencies in comparison with the other tested solvents. Consequently, chlorobenzene was selected as the optimum extraction solvent.

3.3. Effect of volume of extraction solvent

The volume of extraction solvent was another important factor that could affect the extraction efficiency. To examine the influence of extraction solvent volume, 1.00 mL acetone containing different volumes of chlorobenzene (30.0, 40.0, 50.0, 60.0 and 70.0 μL) was subjected to the same preconcentration procedure. By increasing the volume of chlorobenzene from 30.0 to 70.0 μL, the volume of the sedimented phase increases from 20.0 to 69.0 μL. Figs. 3 and 4 present the variation of the sedimented phase

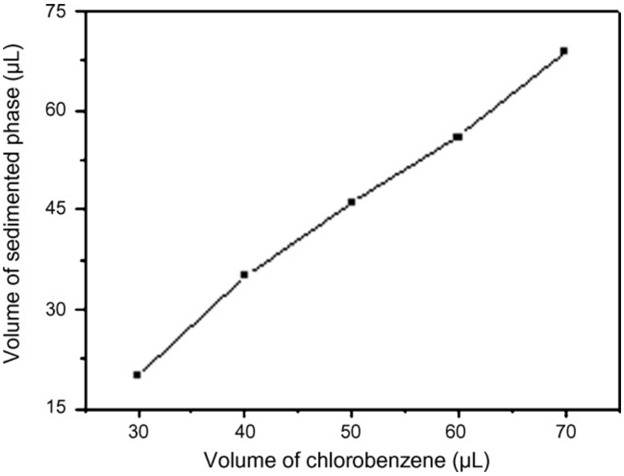

Fig. 3. Effect of the volume of chlorobenzene on the volume of sedimented phase by DLLME. Extraction conditions: sample volume, 5.0 mL; disperser solvent (acetone) volume, 1.0 mL; room temperature and without salt addition; concentration of each PCBs, 1.0 μg L^{-1}.

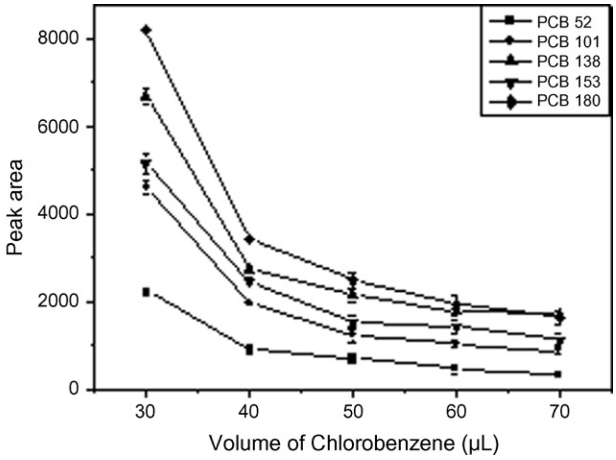

Fig. 4. Effect of extraction solvent (chlorobenzene) volumes on extraction efficiencies of PCBs by DLLME. Extraction conditions: as in Fig. 3.

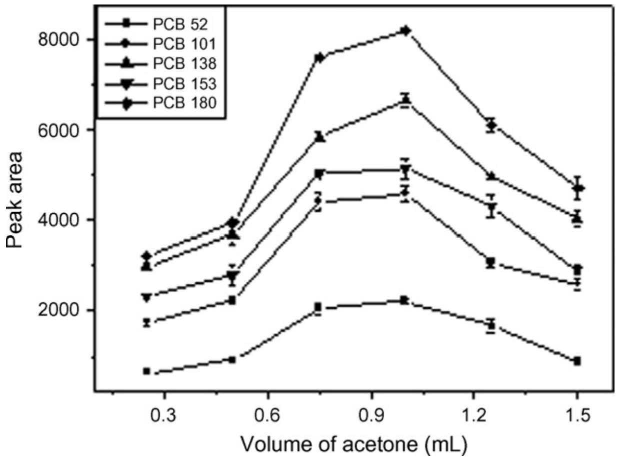

Fig. 5. Effect of dispersive solvent (acetone) volumes on extraction efficiencies of PCBs by DLLME. Extraction conditions: sample volume, 5.0 mL; extraction solvent (chlorobenzene) volumes, 30.0 μL; room temperature and without salt addition; sedimented phase volume, 20.0 ± 1.0 μL; concentration of each PCBs, 1.0 μg L^{-1}.

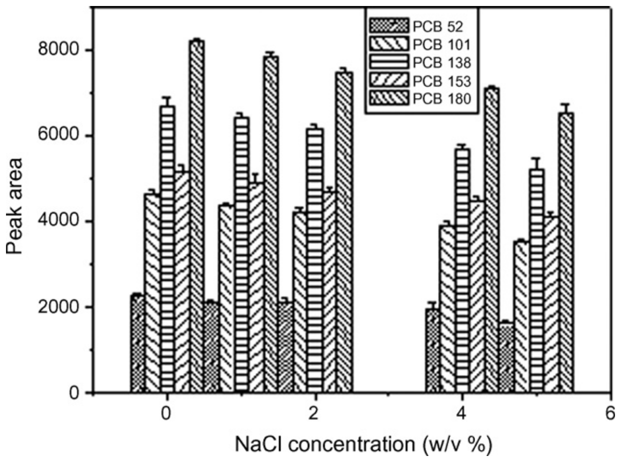

Fig. 6. Effect of the concentration of NaCl on extraction efficiencies of PCBs by DLLME. Extraction conditions: sample volume, 5.0 mL; disperser solvent (acetone) volume, 1.0 mL; extraction solvent (chlorobenzene) volumes, 30.0 μL; room temperature; concentration of each PCBs, 1.0 μg L^{-1}.

volume and peak area of the PCBs versus the volume of the extraction solvent. It was obvious that the peak areas of analytes were decreased with the increase of the chlorobenzene volume because the sedimented phase volume increased. As a consequence, 30.0 μL of chlorobenzene was selected in order to obtain low detection limit.

3.4. Effect of volume of disperser solvent

After selecting acetone as the disperser solvent, its volume should be optimized. At low volume, acetone cannot disperse extraction solvent properly and cloudy solution is not formed completely. However, at high volume, the solubility of PCBs in water increases, which will result in the decrease of the extraction efficiency. To obtain optimized volume of acetone, various experiments were performed by using different volumes of acetone (0.25, 0.5, 0.75, 1.0, 1.25 and 1.50 mL) containing the corresponding volume chlorobenzene (28.0, 28.2, 28.6, 30.0, 30.6 and 31.0 μL) were studied to attain the constant volume of the settled phase (20.0 ± 1.0 μL). Fig. 5 shows that the effect of disperser solvent (acetone) volume on the extraction efficiency of five target PCBs. As could be seen, extraction efficiency increased with the increase of the volume of acetone when it less than 1.0 mL. Reduction in extraction efficiency was observed after the volume of acetone exceeded 1.0 mL. According to the results, 1.0 mL was chosen as the optimum volume of the disperser solvent.

3.5. Effect of extraction time

Mass transfer is a time-dependent process, and thus it is important to set up the extraction time profile of the target analytes so as to optimize the time parameter. In DLLME, extraction time is defined as an interval between the injection of the mixture of disperser solvent (acetone) and extraction solvent (chlorobenzene) and starting to centrifuge. The extraction time was studied in the range of 0–60 min under constant other experimental conditions. It is obvious from the data that the extraction time has no significant effect on the extraction efficiency for PCBs. After formation of cloudy solution, the surface area between the extraction solvent and the aqueous phase is infinitely large, explaining why the extraction equilibrium could be established very fast. As a result, the extraction time has no significant effect on extraction efficiency, which is also a remarkable advantage of DLLME technique. In DLLME procedures, the most time-consuming step is the centrifuging of sample solution in the extraction process, which is about 3 min.

3.6. Effect of the ionic strength

The salt addition to the sample solution may have several influences on the extraction efficiency. Generally speaking, salt addition decreases the solubility of target compounds in water sample and enhances their partitioning into the adsorbent (for SPME) or organic phase (for LLE). In DLLME, various experiments were performed to investigate the effect of the ionic strength by adding different NaCl amounts (0–5%, w/v), while other experimental conditions were kept constant. The effects of NaCl concentration on extraction efficiency of five PCBs are shown in Fig. 6. It was obvious that the peak area decreased with the increase of NaCl concentration (0–5%, w/v). The increase of ionic strength led to decrease of chlorobenzene solubility in aqueous phase, which further increased the volume of sedimented phase (from 20.0 to 24.0 μL) and decreased enrichment factors. Thus, no salt was added in all the extraction experiments.

In general, the optimum DLLME conditions were as follows: 5.0 mL water sample; 30.0 μL chlorobenzene as extraction solvent; 1.0 mL acetone solution as disperser solvent; no addition of salt and 3.0 min centrifugation at 3000 rpm at room temperature.

3.7. Quantitative analysis

Under the above optimum conditions, the proposed method was applied to a series of standard solutions containing different concentrations of PCBs in order to obtain the respective calibration curves. The characteristics of calibration curves are summarized in Table 1. Linearity was observed in the concentration range from 2 to 2000 μg kg^{-1} for PCB 52, and 0.4 to 400 μg kg $^{-1}$ for other target analytes. Correlation coefficients (r^2) ranged from 0.9993 to 0.9999. The repeatability was studied by extracting the spiked soil samples at a concentration level of 10 μg kg^{-1} for five PCB congeners. The relative recoveries were high and ranged from 81.00% to 106.5%. The relative standard deviations (RSDs, $n = 11$) were calculated in the range of 2.2–6.4%. The limits of detection (LODs), based on signal-to-noise ratio of three (S/N = 3), ranged from 0.20 to 0.50 μg kg^{-1}.

3.8. Real soil sample analysis

In order to investigate performance of the proposed method, soil samples, collected from upper, middle and down reaches of

Table 1
Quantitative results of PCBs by DLLME–GC–ECD from soil samples[a].

Compounds	RSD (%)[b] $n = 11$	LR[c] ($\mu g\,kg^{-1}$)	[d] r^2	LOD[e] ($\mu g\,kg^{-1}$)
PCB 52	2.2	2–2000	0.9993	0.50
PCB 101	6.4	0.4- 400	0.9995	0.21
PCB 138	2.5	0.4- 400	0.9999	0.29
PCB 153	5.3	0.4- 400	0.9998	0.20
PCB 180	3.1	0.4- 400	0.9997	0.25

[a] Extraction conditions: water sample volume, 5.00 mL; disperser solvent (acetone) volume, 1.00 mL; and; extraction solvent (chlorobenzene) volume, 30.0 μL; room temperature and without salt addition; sedimented phase volume, 20.0 ± 1.0 μL.

[b] RSD without using internal standard at concentration of each PCBs 1.0 $\mu g\,L^{-1}$.

[c] LR, linear range.

[d] r^2, coefficients of correlation.

[e] LOD, limit of detection for S/N = 3.

Ao River, Wenzhou, China, were first extracted using acetone, then concentrated by DLLME technique and finally analyzed by GC–ECD. The results showed that all the analyzed soil samples contained detectable levels of the target analytes, ranged from 1.92 to 6.60 $\mu g\,kg^{-1}$. Fig. 7 shows the chromatograms of PCBs in real soil S3 (a) and spiked soil sample (b) at the spiking level of 50 $\mu g\,kg^{-1}$. The five kinds of certified PCBs congeners were first spiked to soil S1, S2 and S3 to obtain a series of

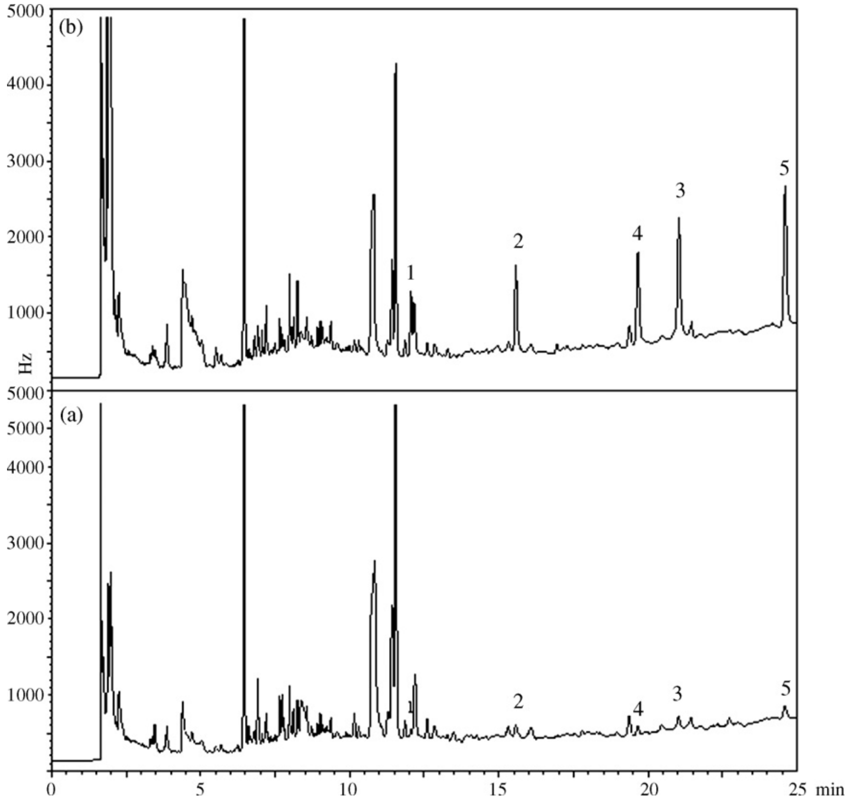

Fig. 7. Chromatogram of soil S3 (a) and spiked soil S3 (b) at the concentration level of 50.0 $\mu g\,L^{-1}$ for each PCBs obtained by using DLLME combined with GC–ECD. Extraction conditions: sample volume, 5.0 mL; disperser solvent (acetone) volume, 1.0 mL; extraction solvent (chlorobenzene) volumes, 30.0 μL; room temperature and without salt addition; sedimented phase volume, 20.0 ± 1.0 μL. Peak identification: (1) PCB 52, (2) PCB 101, (3) PCB 138, (4) PCB 153, (5) PCB 180.

Table 2
Relative recoveries and standard deviations of PCBs from spiked soil S1, S2, S3 samples.

Analytes	Soil samples[a]											
	S1				S2				S3			
	Real ($ng\,g^{-1}$)	Added ($ng\,g^{-1}$)	RSD (%) ($n = 11$)	RR (%)	Real ($ng\,g^{-1}$)	Added ($ng\,g^{-1}$)	RSD (%) ($n = 11$)	RR (%)	Real ($ng\,g^{-1}$)	Added ($ng\,g^{-1}$)	RSD (%) ($n = 11$)	RR (%)
PCB 52	5.60	10.0	6.5	90.4	5.61	20.0	5.2	82.5	4.59	50.0	3.1	82.3
PCB 101	1.92	10.0	5.4	98.0	4.85	20.0	3.3	90.5	6.60	50.0	1.8	105.5
PCB 138	1.97	10.0	3.9	96. 2	4.70	20.0	2.5	85.4	5.46	50.0	4.3	107.2
PCB 153	3.15	10.0	2.7	103.8	8.57	20.0	4.6	106.3	4.32	50.0	2.9	113.6
PCB 180	2.98	10.0	2.9	88.7	6.53	20.0	3.4	104.5	5.25	50.0	2.4	99.5

[a] Soil sample quality: 1.0000 g, Extraction conditions: water sample volume, 5.00 mL; disperser solvent (acetone) volume, 1.00 mL, enriched each PCB; extraction solvent (chlorobenzene) volume, 30.0 μL; room temperature and without salt addition; sedimented phase volume, 20.0 ± 1.0 μL.

Table 3
Comparison of DLLME–GC–ECD with other extraction methods for the determination of PCBs in soil samples.

Methods	LOD (μg kg^{-1})	Volume of organic solvent required (mL)	References
LLE–GC–MS	0.20	>200	[30]
MUSE –GC–MS	0.003–0.006	>100	[31]
DLLME–GC–ECD	0.20–0.50	10	Represented method

standard concentrations (10, 20 and 50 μg kg^{-1}), and then studied the recovery in soil by the proposed method. The results of relative recovery of soil samples are listed in Table 2. The recoveries of PCBs from Soil S1, S2 and S3 were in the range of 88.70–103.8%, 82.50–106.3% and 82.30–113.6%, respectively, indicating that no significant matrix effect was observed. The preceding results demonstrate that the recommended method can be applied for the trace analysis of PCBs in environmental soil samples.

3.9. *Comparison of DLLME with other published methods*

Table 3 summarizes the limit of detection (LOD) and the volume of organic solvent required in the liquid–liquid extraction (LLE) [30], miniaturized ultrasonic solvent extraction (MUSE) [31], and DLLME (represented method) for the extraction and determination of PCBs in soil samples. It was obvious that DLLME possesses the comparable LOD with those of LLE and MUSE methods. Besides, DLLME technique has the advantage of lower consumption of organic solvent (about 10 mL) than other kinds of methods. All these results indicate that DLLME is a fast, simple, inexpensive and benign to environment technique that can be used for trace residue analysis of PCBs from soil samples.

4. Conclusion

This paper describes a DLLME–GC–ECD method for the analysis of five representative PCBs congeners in soil samples. The developed procedure is a good alternative to conventional pretreatment techniques, such as Soxhlet extraction and SPE, since it reduces largely organic solvents consumption. The proposed method gives comparable detection limit (0.20 to 0.50 μg kg^{-1}**)** with the previous studies, but provides good repeatability and good extraction efficiency within a short time. Especially, this method can be used for the extraction of PCBs in solid matrices. As far as our information goes, this is the first report on the application of DLLME for the determination of PCBs in solid matrices. In conclusion, DLLME–GC–ECD method is a simple, rapid, sensitive method for trace analysis of PCBs in soil samples.

Acknowledgements

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