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Article

Determination of Organophosphorus Pesticides in Soil by Dispersive Liquid–Liquid Microextraction and Gas Chromatography

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In this article, a rapid and sensitive sample pretreatment technique for the determination of organophosphorus pesticides (OPPs) in soil samples is developed by using dispersive liquid–liquid microextraction (DLLME) combined with gas chromatography–flame photometric detection. Experimental conditions, including the kind of extraction and disperser solvent and their volumes, the extraction time, and the salt addition, are investigated, and the following experiment factors are used: 20 μL chlorobenzene as the extraction solvent; 1.0 mL acetonitrile as the disperser solvent; no addition of salt; and an extraction time of 1 min. Under the optimum conditions, the linearities for the three target OPPs (ethoprophos, chlorpyriphos, and profenofos) are obtained by five points in the concentration range of 2.5–1500 μg/kg, and three replicates are used for each point. Correlation coefficients vary from 0.9987 to 0.9997. The repeatability is tested by spiking soil samples at a concentration level of 5.0 μg/kg. The relative standard deviation ($n = 3$) varied between 2.0% and 6.6%. The limits of detection, based on a signal-to-noise ratio (S/N) of 3, range from 200 to 500 pg/g. This method is applied to the analysis of the spiked samples S1, S2, and S3, which are collected from the China Agriculture University's orchard, lawn, and garden, respectively. The recoveries for each target analyte are in the range between 87.9% and 108.0%, 87.4% and 108.0%, and 86.7% and 107.2%, respectively.

Introduction

Organic agrochemicals are widely used in China for agricultural activities due to their highly effective ability to control pests. However, the widespread application of organic agrochemicals results in their occurrence in adjacent environmental systems such as soil. Soil is an important component of the ecosystem, and closely related to human survival. As part of the human environment, contaminated soil may cause a serious risk to human health. Organophosphorus pesticides (OPPs) enter the soil ecosystem because of direct spraying on the soil surface during pesticide application in agriculture; the drop from the foliage and stems by the washing of rain and the rotting of plant bodies containing OPPs residues in the soil. The majority of OPPs demonstrate high acute toxicity (1, 2). Therefore, the analysis of OPPs residue in the soil plays an important role in environmental protection and human health.

Sample pretreatment is one of the most important and crucial procedures in the field of pesticide residue analysis. Traditionally, the determination of trace levels of pesticide residues relies on the use of liquid–liquid extraction (LLE) and solid-phase extraction (SPE) (3). However, the main drawbacks of LLE include its high expense, prolonged run time, and the large volumes of toxic organic solvents it requires. SPE typically is less time-consuming than LLE, but it requires column conditioning and elution with organic solvents. In the latest decade, more environmental friendly techniques, such as supercritical fluid extraction, microwave-assisted extraction, and accelerated solvent extraction (4–6) have been developed to determine pesticides in soil samples. All of these techniques have the advantages of a short extraction time and the require less organic solvents (7), but the instruments required are expensive. Hence, there is an increasing demand to develope a rapid, easy, and sensitive sample pretreatment method for the determination of such OPPs in soil.

Recently, miniaturized sample preparation techniques, such as solid-phase microextraction (SPME) and liquid-phase microextraction (LPME) (8), have been developed as alternatives to conventional sample preparation procedures. SPME, a more recent procedure that is a simple and organic solvent-free technique (9), has been used for the determination of pesticides in soil (10–13). However, SPME fibers are expensive, fragile, have a limited lifespan; in addition, sample carry-over is also a problem (14). LPME is a fairly new method of sample preparation. LPME has been used for the pre-concentration of compounds from aqueous samples (15–18). LPME has been previously applied to the pre-concentration of compounds from soil samples (19–21).

Very recently, a novel microextraction technique termed as dispersive liquid–liquid microextraction (DLLME) has been developed by Rezaee (22). Since its introduction, this technique has been used for the determination of trace organic pollutants in liquid samples (23) and solid samples (24, 25). However, only a few papers reported the application of a DLLME technique for the determination of pesticides in soil (25–27), and none of the literature reported that acetonitrile was used as an extraction solvent for the extraction of OPPs from soil samples, nor as a dispersive solvent in the DLLME procedure.

In this work, DLLME combined with gas chromatography–flame photometric detection (GC–FPD) was investigated for the determination of OPPs in soil samples. The influence of various experimental parameters, such as the extraction time, the salt concentration, and the kind and volume of the extraction solvent and disperser solvent has been discussed. The developed method has been applied for the analysis of real soil samples.

Experimental

Reagents and materials

The individual stock standard solutions of 2000 μg/mL for each pesticide (ethoprophos, chlorpyrifos, and profenofos)

prepared in acetonitrile were obtained from the Agricultural Environmental Protection Institution in Tianjin, China. The standard working solutions were obtained daily by the appropriate dilution of the stock standard with deionized water. The stock and working standard solutions were stored in the dark at 4°C until use. Carbon tetrachloride (CCl_4), chlorobenzene (C_6H_5Cl), and 1,2-dichlorobenzene ($C_6H_4Cl_2$) were purchased from the Beijing Chemical Reagents Company (Beijing, China). The acetone and acetonitrile (MeCN) were from the Sinopharm Chemical Reagent Co., Ltd. (Tianjin, China). All the reagents were HPLC-grade unless otherwise stated. Deionized water was purified with a Milli-Q purification system (Millipore, Bedford, MA), which was used throughout this work.

Sample preparation

Soil samples S1, S2, and S3 were collected from the China Agriculture University's orchard, lawn, and garden, respectively. All the soil samples were air-dried at room temperature, pulverized, and passed through 250 μm sieves. The extraction procedures were as follows: 1.0 g of the soil sample was accurately weighed and loaded into a 50-mL flask centrifuge tube, and then the soil was extracted with 5.0 mL acetonitrile for 30 min at 250 rpm on a mechanical shaker, followed by centrifuging at 3500 rpm for 5 min. The upper solution (acetonitrile extract) was filtered through a 0.45-μm membrane filter to obtain a clear solution, and then an aliquot of 1.0 mL of acetonitrile extract was subjected to the DLLME procedure.

Instrumentation

The chromatographic analysis was performed on an Agilent 6890 series GC equipped with a FPD system (Agilent Technologies, Palo Alto, CA). The chromatographic separation was accomplished on a HP-5 (5% phenyl, 95% methylpolysiloxane, 30 m × 0.32 mm i.d. × 0.25 μm) capillary column, purchased from J&W Scientific (Folsom, CA). The injection port was made in the splitless mode at 230°C with a splitless time of 0.5 min. The detector temperature was 250°C, and it was fed with 75 mL/min of hydrogen (>99.999%), 100 mL/min of purified compressed air, and 60 mL/min of nitrogen (>99.999%) as the auxiliary gas. Nitrogen was used as the carrier gas at a flow rate of 1.0 mL/min. The oven program was started at 150°C, then programmed at 5°C/min ramp to 220°C, followed by a 20°C/min ramp to 260°C, and held for 2 min. The total analytical time was 18 min. The identification of the analytes was confirmed based on the retention time.

DLLME procedure

For the DLLME, a 5.00-mL aliquot of deionized water was placed into a 10-mL screw-cap glass centrifuge tube with a conic bottom. The target analytes were extracted from the soil with acetonitrile (see the Sample preparation section), and 20 μL chlorobenzene (as an extraction solvent in the DLLME procedure) was then added into 1.0 mL of the described acetonitrile extract (as a dispersive solvent in the DLLME procedure) to form a mixture. After that, the mixture was rapidly added into the 10 mL screw-cap glass centrifuge tube by using a 5.0 mL syringe (Hamilton, Shanghai, China). The sample was then gently shaken for 1 min by hand. A cloudy solution (water, acetonitrile, and chlorobenzene) was formed in the glass centrifuge tube. During this step, the OPPs were extracted into the fine droplets of chlorobenzene. In order to separate the organic phase from the aqueous phase, the mixture was then centrifuged for 3.0 min at 3500 rpm, causing the chlorobenzene phase to be sedimented at the bottom of the conical test tube. The volume of the sedimented phase was determined by a 50.0 μL micro syringe, and was completely transferred to another test tube with a conical bottom. Afterwards, 1.0 μL of the sedimented phase was withdraw by a 10.0 μL micro syringe and injected into the GC for further instrument analysis.

Results and Discussion

Selection of the extraction solvent for DLLME

The selection of an appropriate extraction solvent for the DLLME process is very critical. Generally, the extraction solvent used in DLLME procedures must fulfill the following requirements: it should have a higher density than water, a low solubility in water, a high extraction capability of the target analytes, and have good chromatographic behaviors during the course of chromatographic separation. Based on these facts, three extraction solvents, CCl_4, C_6H_5Cl, and $C_6H_4Cl_2$, were examined for the extraction of the target analytes. A series of samples were studied using 1.0 mL of MeCN (the disperser solvent), containing different volumes of the extraction solvents in order to achieve a volume of 13.0 μL of the settled phase. As shown in Figure 1, chlorobenzene showed the best extraction efficiencies in comparison with the other two solvents. Therefore, chlorobenzene was selected as the extraction solvent for further experiments.

Effect of extraction solvent volume

In order to study the influence of the extraction solvent volume, different volumes of chlorobenzene (20.0, 25.0, 30.0, and 35.0 μL) and a constant volume of the disperser solvent, MeCN (1.0 mL), were examined. An extraction solvent volume

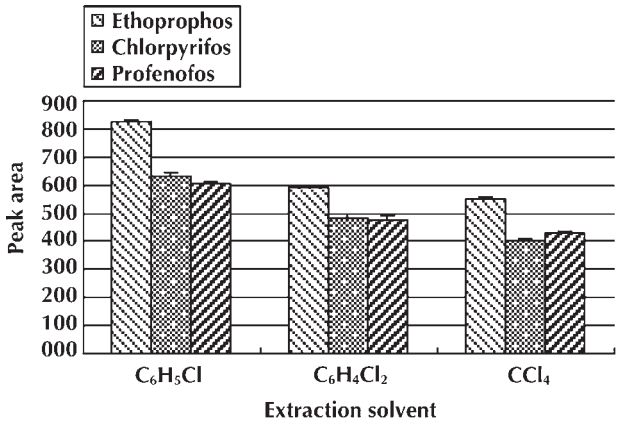

Figure 1. The effect of extraction solvent on DLLME. Extraction conditions: water sample volume, 5.0 mL; disperser solvent (acetonitrile) volume, 1.0 mL; extraction time, 1 min; and without salt addition. The concentration of each OPP was 5 ng/mL.

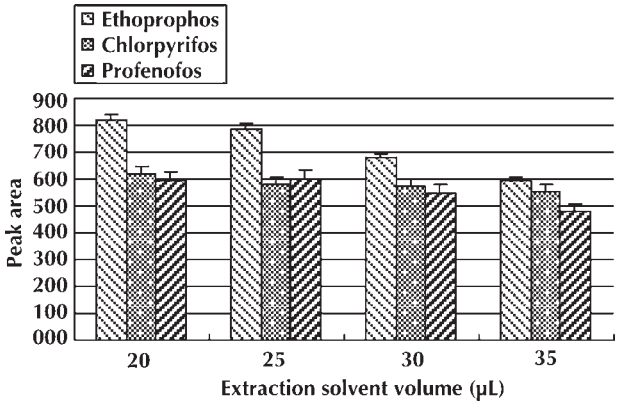

Figure 2. The effect of extraction solvent volume on DLLME. Extraction conditions: water sample volume, 5.0 mL; disperser solvent (acetonitrile) volume, 1.0 mL; extraction time, 1 min; and without salt addition. The concentration of each OPP was 5 ng/mL.

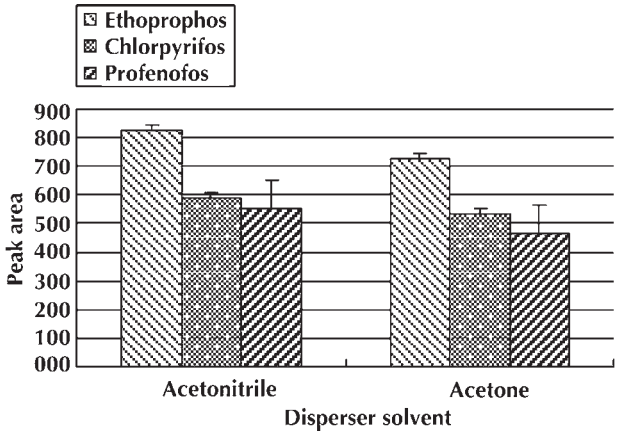

Figure 3. The effect of disperser solvent on DLLME. Extraction conditions: water sample volume, 5.0 mL; extraction solvent (chlorobenzene) volume, 20.0 μL; extraction time, 1 min; and without salt addition. The concentration of each OPP was 5 ng/mL.

less than 20 μL was avoided, as it would be hard to be collected in the final sedimented phase. By increasing the volume of chlorobenzene from 20.0 to 35.0 μL, the volume of the sedimented phase increased from 13.0 to 28.0 μL. Figure 2 shows the variation of the peak areas of the OPPs versus the extraction solvent volume. It was obvious that the peak areas of the OPPs decreased with the increase of the chlorobenzene volume. Consequently, 20 μL of chlorobenzene was selected for further study.

Selection of disperser solvent

For a DLLME method, the disperser solvent must play two roles. Firstly, it must efficiently extract analytes from soil samples. Secondly, it must be used as a disperser solvent in the DLLME step. The selection of the disperser solvent is based on its miscibility with both the organic and the aqueous phase. MeCN and acetone were the most used solvents for the extraction of OPPs from the samples; all of them have demonstrated acceptable recoveries (28). In view of these considerations, MeCN and acetone were evaluated for this study. A series of sample solutions were investigated by using 1.0 mL each of the disperser solvents containing 20.0 μL chlorobenzene. As shown in Figure 3, the best extraction efficiencies were obtained when MeCN was used as a disperser solvent. Hence, MeCN was selected.

Effect of disperser solvent volume

The effect of the disperser solvent volume was investigated by using different volumes of HPLC-grade acetonitrile (0.50, 1.0, and 1.5 mL) containing 20 μL chlorobenzene. The results shown in Figure 4 demonstrate that the extraction efficiencies increased by increasing the volume of acetonitrile at first, and then decreased with further increase of the acetonitrile volume; this phenomenon may be attributed to the fact that at a low volume of acetonitrile, a cloudy state is not well formed. Based on the experimental results, 1.0 mL acetonitrile was chosen for the subsequent study.

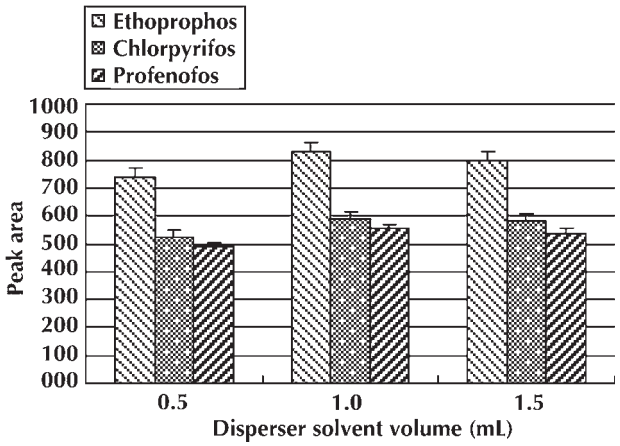

Figure 4. Effect of the disperser solvent volume on DLLME. Extraction conditions: water sample volume, 5.0 mL; extraction solvent (chlorobenzene) volume, 20.0 μL; extraction time, 1 min; and without salt addition. The concentration of each OPPs was 5 ng/mL.

Effect of salt concentration

The effect of the salt addition on the extraction was evaluated with the sodium chloride concentration ranging from 0 to 5 % (w/v). Figure 5 shows that the increase of the sodium chloride concentration leads to a decrease of the extraction efficiency. The phenomenon may be attributed to the salt concentration increasing, which may have caused the chlorobenzene solubility in the water to decrease, thus the volume of the sedimented phase increased, which led to the decrease of the extraction efficiency. Therefore, no salt was added for further experiments.

Effect of extraction time

In DLLME, the extraction time is defined as the time interval between the addition of the mixture of the dispersive solvent (acetonitrile) and the extraction solvent (chlorobenzene) to the sample but before centrifugation. The effect of the extraction time was investigated over the time range between 1 and

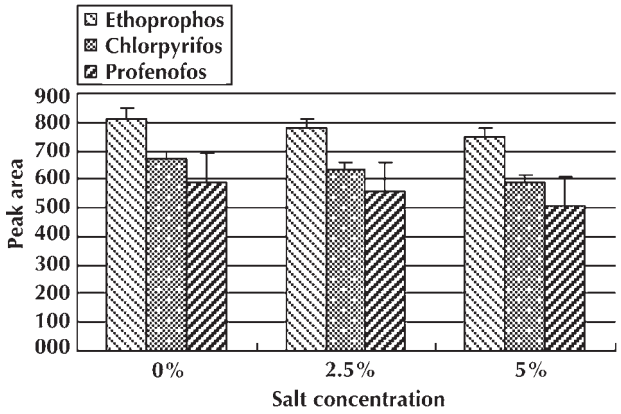

Figure 5. The effect of the salt concentration on DLLME. Extraction conditions: water sample volume, 5.0 mL; extraction solvent (chlorobenzene) volume, 20.0 μL; disperser solvent (acetonitrile) volume, 1.0 mL; extraction time, 1 min. The concentration of each OPP was 5 ng/mL.

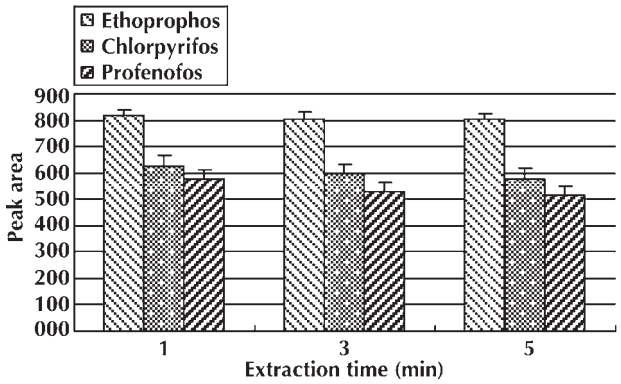

Figure 6. The effect of the extraction time on DLLME. Extraction conditions: water sample volume, 5.0 mL; extraction solvent (chlorobenzene) volume, 20.0 μL; disperser solvent (acetonitrile) volume, 1.0 mL; without salt addition. The concentration of each OPP was 5 ng/mL.

5 min. As demonstrated in Figure 6, there was no significant difference in the analytical responses when the extraction time was changed. It could be explained that after the formation of a cloudy state of the solution, the surface area between the extraction solvent (chlorobenzene) and the water sample is infinitely large. Thereby, it was fast for the transition of the analytes from the water sample to the extraction solvent, and equilibrium was achieved quickly. This is one of the remarkable advantages of a DLLME technique. So, at last, the extraction time was fixed at 1 min.

In general, the following experiment factors were used in the DLLME procedure were: 20 μL chlorobenzene as the extraction solvent, 1.0 mL acetonitrile as the disperser solvent, no addition of salt, and the extraction time was 1 min.

Quantitative analysis

Under the optimum conditions, the proposed method was applied to a series of samples containing each of the OPPs at five concentration levels in order to obtain the respective calibration curves. Linearity was obtained by five points in the concentration range of 2.5–1500 μg/kg, and three replicates were used for each point. The correlation coefficients (R) ranged from 0.9987 to 0.9997. The repeatability, expressed as relative standard deviations (RSDs) for the three replicate analyses, was tested by spiking the soil samples at a concentration level of 5 μg/kg. The RSDs ($n = 3$) varied between 2.0% and 6.6%. The limits of detection (LODs), based on a signal-to-noise ratio (S/N) of 3, ranged from 200 to 500 pg/g. The results are summarized in Table I.

Table I
Analytical Performance Data for OPPs by the DLLME Method

OPPs	RSDs (%) (n = 3)	Linearity (μg/kg)	R	LODs (pg/g)
Ethoprophos	2.0	2.5–1500	0.9997	500
Chlorpyrifos	6.6	2.5–1500	0.9987	200
Profenofos	4.2	2.5–1500	0.9992	500

Table II
Analytical Results in Soil Samples

OPPs	Added (μg/kg)	Found (μg/kg)	R* (%)	RSDs (%)
Soil samples A1 (n = 3)				
Ethoprophos	0	N.D.†		
	10	10.4	104.0	3.4
	20	19.8	98.8	2.8
	50	44.0	87.9	3.7
Chlorpyrifos	0	N.D.†		
	10	10.8	108.0	4.5
	20	18.1	90.5	5.2
	50	44.1	88.2	7.1
Profenofos	0	N.D.†		
	10	10.4	104.3	2.8
	20	18.1	90.5	3.6
	50	46.3	92.6	5.4
Soil samples A2 (n = 3)				
Ethoprophos	0	N.D.†		
	10	10.2	102.0	2.8
	20	19.3	96.7	3.2
	50	44.2	88.3	4.1
Chlorpyrifos	0	N.D.†		
	10	10.8	108.0	5.6
	20	18.5	92.5	5.4
	50	43.7	87.4	4.2
Profenofos	0	N.D.†		
	10	10.6	106.4	3.2
	20	18.2	91.2	2.1
	50	47.2	94.3	4.7
Soil samples A3 (n = 3)				
Ethoprophos	0	N.D.†		
	10	10.7	107.2	3.2
	20	18.6	93.2	4.7
	50	43.8	87.6	5.8
Chlorpyrifos	0	N.D.†		
	10	10.7	107.1	7.6
	20	18.2	91.2	5.2
	50	43.4	86.7	4.1
Profenofos	0	N.D.†		
	10	9.8	98.2	3.8
	20	19.5	97.3	6.6
	50	43.6	87.2	5.2

* R = recovery of the method.
† N.D. = Not Detected

Real soil sample analysis

In order to investigate the developed method, the proposed method was applied to the analysis of OPPs in real soil samples (S1, S2, and S3) As a result, the three types of the target analytes were not found in the real samples. In order

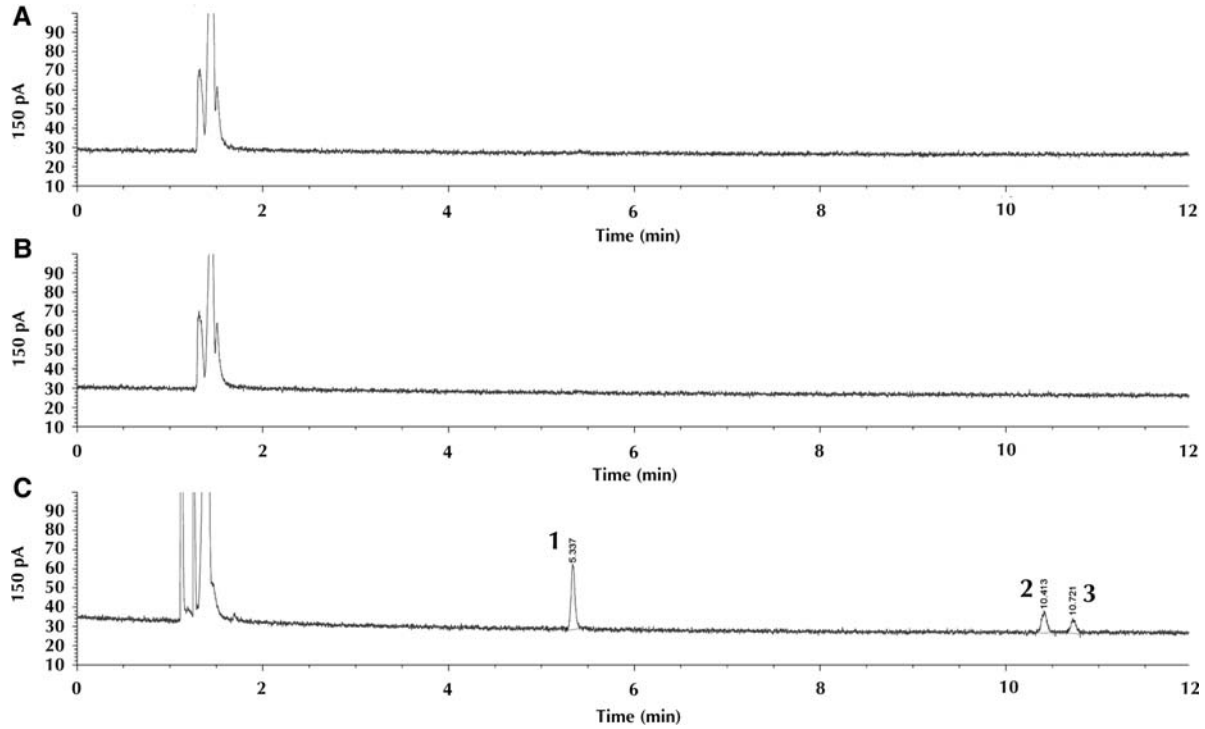

Figure 7. Chromatogram of the control soil (A), the real soil sample (S1) (B), and the spiked soil sample (C). Peak identification: 1, ethoprophos; 2, chlorpyrifos; 3, profenofos.

Table III
Comparison of DLLME with other Methods for Determination of OPPs in Soil

Methods	LODs (pg/g)	RSDs (%)	Volume of organic solvent required (mL)	References
SPE–GC–NPD	2970–9490	4.0–20.0	30.0	29
MAME–HPLC	200–95000	0.3–2.6	10.0	30
SPME–GC–FPD	500	1.95–12.2	–	31
DLLME–GC–FPD	200–500	2.0–6.6	<2.0 (1 + 0.02)	This work

to assess the matrix effect on the developed method, a 20.0-g soil sample, which was free of OPPs, was accurately weighed and put into a 100 mL centrifuge tube. The individual stock standard solutions (see the Reagents and materials section) were added to the tube, and the soil sample was spiked with each OPP at three levels of 10.0, 20.0, and 50.0 μg/kg. Then, the mixture was air-dried at room temperature to obtain the spiked soil sample and was analyzed using the proposed method. The results are summarized in Table II. The recoveries ranged from 87.9% to 108.0%, 87.4% to 108.0%, and 86.7% to 107.2%, with RSDs varying from 2.8% to 7.1%, 2.1% to 5.6%, and 3.2% to 7.6%, respectively. These results demonstrate that the soil matrix in the present context had little effect on DLLME. Figure 7 shows the chromatograms of the control soil, the real soil sample, and the spiked soil sample.

Comparison of the DLLME with other sample preparation techniques

A comparison between the DLLME method and other methods has been performed. Table III shows the LODs, the RSDs, and the volume of the organic solvent required in the SPE–GC–NPD (29), microwave assisted micellar extraction–HPLC (MAME–HPLC) (30), SPME–GC–FPD (31), and DLLME–GC–FPD (the proposed method) methods for the extraction and determination of OPPs in soil samples. From Table III, it is obvious that the LODs and the volumes of the organic solvent required in both SPE–GC–NPD and MAME–HPLC were higher than that with the method developed herein. The RSDs for MAME–HPLC are lower than the represented method, and the RSDs for both SPE–GC–NPD and SPME–GC–FPD are higher than the DLLME–GC–FPD method. All of these results indicate that DLLME is a simple, rapid, and environmentally friendly method.

Conclusion

A simple, rapid, and sensitive DLLME method combined with GC–FPD has been developed for the determination of OPPs in soil samples. Compared with conventional methods, DLLME provides good repeatability, recovery, and has the advantage of simplicity, fastness, and lower consumption of organic solvents.

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