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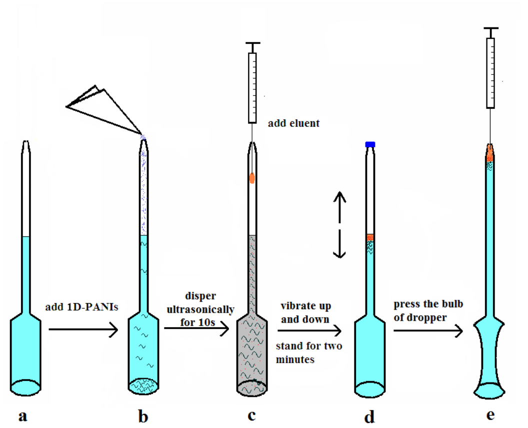
Graphical Abstract

Highlights

1D-PANIs has good dispersibility and permeability.

A plastic dropper was acted as both the extraction and preconcentration device.

The proposed method is simple, inexpensive and highly efficient.



A novel dispersive micro-solid phase extraction method combined with gas chromatography for analysis of organochlorine pesticides in aqueous samples

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Abstract:

A novel dispersive micro-solid phase extraction (D-μ-SPE) method was presented in this paper. The most attractive feature of this method is taking full advantage of a plastic dropper and nanoscale one-dimensional polyaniline (1D-PANI). The plastic dropper employed as both the extraction and preconcentration device. All procedures needed in the common μ-SPE were performed in a plastic dropper without any additional devices, such as centrifuge, magnetic field and pressure blowing concentrator. So the operating steps were simplified greatly. 1D-PANIs was used as the sorbent. The huge surface and interconnected net-work structure of 1D-PANIs endows it high dispersive adsorbability and good permeability for the adsorbed analytes to be eluated. To test the feasibility of the proposed method, eight organochlorine pesticides (OCPs) were selected as the model analytes for D-μ-SPE of OCPs in water samples. A series of extraction parameters have been investigated systematically. Under optimized conditions, the method showed the linear correlation coefficients (r) were better than 0.9971 and the limits of detection (LODs) for eight OCPs ranged from 0.0121 to 0.0468 μg L^{-1}. The intra- and inter-day relative standard deviations (RSDs) were less than 11.9%. The recoveries of OCPs for three spiked aqueous samples ranged from 73.6 to 107.0%. The novel D-μ-SPE is promising to be an alternative sample preparation method for extracting apolar analytes in complex sample matrices because of the simplicity, low cost and high extraction efficiency.

Keywords: Dispersive micro-solid phase extraction; Plastic dropper; One-dimensional polyaniline; Organochlorine pesticides; Gas chromatography.

1. Introduction:

Sample preparation is an important step in trace analysis. The major problem encountered is the separation of pollutants from matrix components. Owing to the low concentration level of pollutants, inefficient extractions always cause loss of analytes and make the analytes difficult to be determined. Hence, the development of efficient extraction and preconcentration steps prior to accurate determination of trace level of compounds has been explored in considerable depth over recent decades.

Generally, liquid-liquid extraction (LLE) [1] and solid-phase extraction (SPE) [2,3] are commonly used steps in extraction and preconcentration of compounds from various samples. SPE has distinguished from many other extraction techniques due to the advantages such as lower cost, higher enrichment factor and less consumption of organic solvents [4]. Although SPE is being applied broadly, it suffers from some shortcomings such as solvent loss, large secondary wastes, a long procedure, and a need for complex equipment. Dispersive micro-solid phase extraction (D-µ-SPE) is categorized as a SPE technique. The D-µ-SPE exhibits some advantages over traditional SPE, such as convenience for efficiency of recovery and reduced solvent consumption [5,6]. Moreover, it is simple, economic and easy to perform [7,8]. Various sorbents can be employed in D-µ-SPE. Compared to traditional SPE sorbents, nanomaterials possess large surface area and short diffusion route, which may result in high extraction efficiency and rapid extraction dynamics. Hence, nanomaterial-based D-µ-SPE as a novel SPE method aroused more and more concern of researchers [9,10]. The nano-sorbent used in D-μ-SPE have been extended to various forms of carbon [11] and conductive polymers (CPs) [12.13], etc. Conductive polymers (CPs) are organic materials that possess an extended conjugated-system associated with the polymer backbone, and have been known to have great application potential in electroluminescent devices, electromagnetic shielding, sensors, corrosion prevention, etc. [12,14-18]. Recent researches suggest CPs are also promising in separation science owing to their versatile properties such as hydrophobicity, large-conjugated structure, polar functional groups, ion exchange property, and so on [12,19-21]. In a previous work, various forms of CP nanomaterials, including zero-dimensional (0D) CPs nanoparticles and one-dimensional (1D) CPs (eg. Nanofiber, nanotube, nanowire) were prepared and investigated as the sorbents in D-μ-SPE [6,13,19-21]. It was found that 0D nanoparticles tended to agglomerate closely after D-μ-SPE because of their high surface energy and solvophobic property [14,22], which probably discounted the extraction efficiency. Furthermore, it is difficult to eluate the target analytes from the tightly packed nanoparticles. 1D-CPs are generally nano-scaled in diameter with lengths over several microns, and still remain the advantage of high surface area. Although 1D-CPs also tend to agglomerate in many solvents, the resulting interconnected network-like structure can offer better permeability in comparison with fine powders and tightly packed nanoparticles [23,24], and may obtain better extraction efficiency than 0D-CPs as the sorbents.

In this work, 1D-PANI was chosen as the sorbent, and eight organic chloride pesticides (OCPs) were selected as model analytes. A novel D-μ-SPE method was developed in a plastic dropper which was acted as both extraction and preconcentration devices. No complex equipments, such as centrifuge, magnetic field and pressure blowing concentrator, were needed. 1D-PANIs was dispersed to extract OCPs in water loaded in a plastic dropper under ultrasonic radiation. After extraction, 1D-PANIs could be agglomerated with the addition of the eluent (n-hexane) which owns lower density than water. The agglomerated 1D-PANI located between the aqueous phase and organic phase (n-hexane) at the narrow end of the plastic dropper. The plastic dropper was vibrated up and down for several seconds and stand for a while, and then the eluent floated again on the gathered 1D-PANIs. The eluent was pressed up to the tip end of the plastic dropper and withdrawn to be analyzed by gas chromatography (GC). Some parameters which influenced the extraction efficiency were investigated. Hence, a 1D-PANI based D-μ-SPE was developed and applied for monitoring eight OCPs in some environmental water samples. Neither centrifugation nor magnetic separation was needed. The novel D-μ-SPE is promising to be an alternative sample preparation method for extracting apolar analytes in complex sample matrices because of the simplicity, low cost and short sample preparation time.

2. Experimental

2.1 Instruments

Chromatographic analysis was carried out on an Agilent 6890N GC (Agilent Technologies, USA) with a micro-cell electron capture detector (μ-ECD). Analytes were separated by a DB-17 fused silica capillary column (30m×0.25mm I.D., 0.25 μm film thickness, J & W Scientific, Folsom, CA, USA). The column oven temperature was initially set at 150 ◦C, held on 1 min, and then raised to 280 ◦C at 8 ◦C min^{-1} and hold on 8 min. The ECD temperature was set at 300 ◦C. The inlet was set at 280 ◦C, in splitless mode. Nitrogen (purity 99.9995%) was used as carrier gas at the flow rate of 0.5 mL min^{-1} and make up gas at 60 mL min^{-1}. Ultrasonic instrument KQ-100DE was purchased from Kunshan Ultrasonic Instrument (Jiangsu, China).

The 1D-PANIs were characterized by JEOL JSM-6500F scanning electron microscope (SEM, Jeol, Japan).

2.2 Reagents and materials

Aniline and ammonium persulfate ($(NH_4)_2S_2O_8$) were purchased from Sinopharm Chemical Reagent (Shanghai, China) and were used directly without further purification. N-hexane (Pesticide analysis grade) was ordered from Tedia (Fair Lawn, New Jersey, USA). Organochlorine pesticides α, β, γ and δ-HCH; p, p'-DDE; p, p'-DDD; p, p'-DDT; o, p'-DDT was purchased from Sigma-Aldirich (St. louis, MO, USA). Sodium chloride from Zhanyun Chemical Co., Ltd. (Shanghai, China) was used in the experiment. Ultrapure water was purified on a Mill-Q water purification system (Millipore Corporation, Billerica, MA, USA).

The stock solutions containing 20 μg mL^{-1} of OCPs were prepared in HPLC grade methanol. A series of standard solutions were daily prepared by appropriate dilution from the stock solution with ultrapure water, and all of which were stored at 4 ◦C in a refrigerator.

2.3 Sample preparation

Danjiang Kou water samples were collected from Danjiang Kou reservoir (Danjiang Kou, China). Ponding water samples were collected from a vegetable plot (Wuhan, China). Lake water samples were collected from South Lake (Wuhan, China), and all of them were kept at 4 ◦C. These real water samples were filtered through a 0.45 μm polyether sulfone membrane which was purchased from Wuhan Shenshi Chemical Industry Co. Ltd (Wuhan, China) prior to analysis.

2.5 Proposed D-μ-SPE procedure

Preparation and characterization of 1D-PANIs are described in the Supplementary Information (SI) [14,25,26]. The proposed D-μ-SPE procedure is roughly illustrated by Fig. 1. Typically, 3.0 mg 1D-PANIs powder used as the sorbent was added to 6.5 mL aqueous samples spiked with variable known amounts of OCPs in a 3 mL plastic dropper (containing 15% NaCl). The mixture was sonicated for about 10 seconds to form a homogeneous dispersion solution due to the high dispersity of nanoscale 1D-PANIs, and then 1D-PANIs was agglomerated after adding 65 µL n-hexane as the eluent. The eluent floated up on the gathered 1D-PANIs because the density of eluent is lower than water. Vibrated the plastic dropper up and down adequately, and then let it stand for two minutes. The eluent refloated up on the surface of 1D-PANIs, ascending at the tip of the plastic dropper by pressing the bulb end of the plastic dropper. 1 µL was withdrawn by a microsyringe for GC analysis.

3. Results and discussion

3.1 Application to the proposed D-µ-SPE

Due to the large surface area and high affinity towards many organic compounds, 1D-PANIs have been recently exploited as the SPE sorbents [24]. In the present case, the time-consuming procedures, such as centrifugation, elution and even magnetic separation were left out. A plastic dropper were used as a water sample container, and the high dispersive adsorption capacity and good permeability of interconnected network-like structure of the 1D-PANIs (Fig. 1s, see SI) were taken full advantage. Here, eight OCPs (α-HCH, β-HCH, γ-HCH, δ-HCH, P,P'-DDE, P,P'-DDD, O,P'-DDT, P,P'-DDT) were chosen as model compounds to verify the feasibility of proposed D-µ-SPE method. The parameters that might affect the performance of the extraction, such as sample volume, 1D-PANIs amount, extraction time (see SI), ionic strength (see SI), and desorption conditions, etc. were investigated as follows.

3.1.1. Effect of sample volume

It is evident that an increase in sample volume enhances the amount of the target analytes adsorbed onto the sorbents and transferred to the eluent, which improves the sensitivity and extraction efficiency. Firstly, different volumes of plastic dropper should be considered in our study because it influenced the sample volume. The results showed that the water sample in 1 mL plastic dropper is too small to bring about low extraction efficiency. 5 mL plastic dropper is so big that 1D-PANIs can not gathered with a certain thickness at the narrow end. Hence, the eluent can not form a drop on the gathered 1D-PANIs. The enrichment effect decreased greatly. Only 3 mL plastic dropper meet the above experiment requirements well. Hence, 3 mL plastic dropper was selected as the extraction device. The influence of sample volume on the extraction efficiency was studied in the range of 4.5-6.5 mL. As shown in fig.2s (see SI). The results demonstrated that the analytical signal increases with the sample volume in the range of 4.5-6.5 mL. This may be because increasing sample volume leads to the increase of analytical signals. However, the 3 mL plastic dropper can not hold more water. Consequently, 6.5 mL water sample was selected as the optimal volume of sample.

3.1.2 Sorbent amount

To achieve a high recovery, different amounts of 1D-PANIs ranging from 1 to

5 mg were applied to extract OCPs in water samples (Fig.3s, see SI). The result shows that the recovery increased with the increase of the 1D-PANIs mass from 1 to 3 mg, and then decreased with the increase of 1D-PANI mass from 4 to 5 mg. The reason is that the amount of 1D-PANIs is less than 3mg, less target analytes would be adsorbed by 1D-PANIs and further eluated by the eluent (n-hexane). Hence the extraction efficiency decreased. If the amount of 1D-PANIs is more than 3mg, owing to the narrow neck of the dropper, 1D-PANIs would stack much higher, and the eluent (n-hexane) could not permeate 1D-PANIs to eluate the target analytes adsorbed by 1D-PANIs well. So the extraction efficiency decreased. Thus, 3 mg 1D-PANIs was selected and employed in the following experiment.

3.1.3 Desorption conditions

The desorption time was optimized by increasing the vibrating time from 10s to 60s, and then letting it stand for 2 mins. The result indicated that 30s vibrating time and two mins were enough to elute the extracted OCPs from the 1D-PANIs sorbent. Selecting an appropriate eluent is essential for D-μ-SPE. It should have low solubility in water, lower density than water, high affinity for the analytes, and good chromatographic behavior. Five solvents with these properties were tested: n-hexane, cyclohexane, n-octane, o-xylene and p-xylene. As shown in Fig.5s (see SI), n-hexane got the best extraction efficiency, followed by cyclohexane, p-xylene, n-octane and o-xylene. It may be because the solubilities of the target analytes in n-hexane is the biggest among the selected eluents. Hence, n-hexane was selected as the optimal eluent in the following experiments.

After selecting n-hexane as the eluent, its volume should be optimized. At its low volume, n-hexane can not eluate analytes from the sorbent completely. While, at its high volume, the concentration of analytes eluated by n-hexane decreased, which will result in a reduced extraction efficiency. To optimize the volume of acetonitrile, the effect of its volume on the extraction efficiency was investigated in the range of 55-100 μL. As shown in Fig. 6s (see SI), extraction efficiency increased with the increase of n-hexane volume from 55 to 65 μL, and decreased with the increase of n-hexane volume up to 100 μL. On the basis of these results, 65 μL was chosen as the optimal volume of the desorption solvent.

3.2 Analytical performance

To evaluate the proposed method, experiments with regard to the linearity, limit of detection (LOD) and limit of quantification (LOQ), precision were performed.

The calibration was constructed by plotting peak area versus concentration. As shown in Table 1, satisfactory correlation coefficients (R^2) ranging from 0.9971 to 0.9993 are obtained for OCPs in the concentration range of 0.05-50 μg L^{-1} for α-HCH, β-HCH and γ-HCH, 0.1-100 μg L^{-1} for δ-HCH and p,p'-DDT, 0.15-100 μg L^{-1} for p,p'-DDE and o,p'-DDT, 0.2-100.μg L^{-1} for p,p'-DDD. The LOD and LOQ are considered as the analyte's minimum concentration that can be identified and quantified by the method, and they are calculated at a concentration at which signal-to-noise ratios are equal to 3 and 10, respectively. As shown in Table 1, the LODs and LOQs for eight OCPs are found to be 0.0074-0.0468 μg L^{-1} and 0.0244-0.1544 μg L^{-1}, respectively. Precision was evaluated by measuring intra- and interday relative standard divations (RSDs). The results obtained are shown in Table 1. RSDs of intra- and interday ranging from 0.6 to 6.6% and from 4.2 to 11.9% are obtained, respectively.

3.3 Comparison of the proposed method with other published methods

The proposed method was compared with C_{18} based SPE (C_{18}-SPE), polydimethylsiloxane/divinylbenzene based solid phase microextraction (PDMS/DVB -SPME), graphene oxide based SPE (GO-SPE), Electrodeposited polyaniline based solid-phase microextraction (ELC-PANI-SPME), dual stir bar sorptive extraction (SBSE) and directly suspended droplet microextraction (DSDME) method. And the results are shown in Table 2. It is obvious that the LODs of the proposed method are lower than that of C_{18}-SPE and DSDME. The sample volume is smaller and the extraction time is shorter than all the other mentioned methods. Furthermore, all procedures of the proposed method can be performed in a plastic dropper, without additional centrifuge and pressure blowing concentrator, so the cost is low. The high dispersity and good permeability of 1D-PANIs made the extraction and elution steps easy, so the sample preparation time is short. The extraction recovery is high because of no solvent loss. The proposed method is promising to be an alternative of D-μ-SPE method for extracting apolar analytes in complex sample matrices because of high extraction efficiency, low cost and short sample preparation time.

3.4 Application to real water samples

The proposed method was applied to determine the α, β, γ and δ-HCH; p, p'-DDE; p, p'-DDD; p, p'-DDT; o, p'-DDT OCPs in three kinds of real water samples including Danjiang Kou water, ponding water and lake water from South Lake of Wuhan, China. The water samples were filtered before analysis and the subsequent results are shown in Table 3. As recorded in this table, 0.056 μg L^{-1} β-HCH and 0.187 μg L^{-1} δ-HCH were detected in the Danjiang Kou water, 0.012 μg L^{-1} γ-HCH, 0.151 μg L^{-1} β-HCH and 0.128 μg L^{-1} δ-HCH were detected in the Lake water but no analytes were found in ponding water. In order to evaluate the feasibility of the improved method in real samples, they were spiked with three different kinds of concentrations of the target analytes, including 0.2 μg L^{-1}, 1.0 μg L^{-1} and 10.0 μg L^{-1}. The result demonstrated good recoveries ranging from 73.6% to 107.0%. The chromatograms of the blank and spiked South Lake water using the proposed D-μ-SPE method are shown in Fig. 2.

4. Conclusions

In summary, 1D-PANIs was synthesized by oxidative polymerization method.

The interconnected network-like structure endowed the nano-material with good adsorbability and permeability. A plastic dropper was employed as both the extraction and preconcentration device. The complex equipment, such as a centrifuge or a pressure blowing concentrator was not needed. The study demonstrated that the proposed 1D-PANI-based D-μ-SPE was simple, rapid, and effective method for sample preparation. Furthermore, the work would considerably expand the application of 1D-CPs in sample preparation,

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Figure captions

Fig.1. Schematic procedure of the proposed D-μ-SPE: (a) 6.5 mL water sample were added in a 3 mL plastic dropper. (b) 3 mg 1D-PANIs was added into the plastic dropper and dispersed ultrasonically for 10 seconds (c) 65 μL n-hexane was injected into 6.5 mL water sample with a microsyringe and the plastic dropper was vibrated up and down 30s (d) 1D-PANIs was agglomerated and the eluent (n-hexane) floated up on it by letting the plastic dropper stand for a several minutes. (e) The eluent was ascended to the tip of the plastic dropper by pressing the bulb of the plastic dropper and was withdrawn by a microsyringe for analysis by GC.

Fig.2. Chromatograms of eight OCPs from blank (a) and spiked South Lake water (b) extracted by the proposed D-μ-SPE method. The sample solution was spiked at

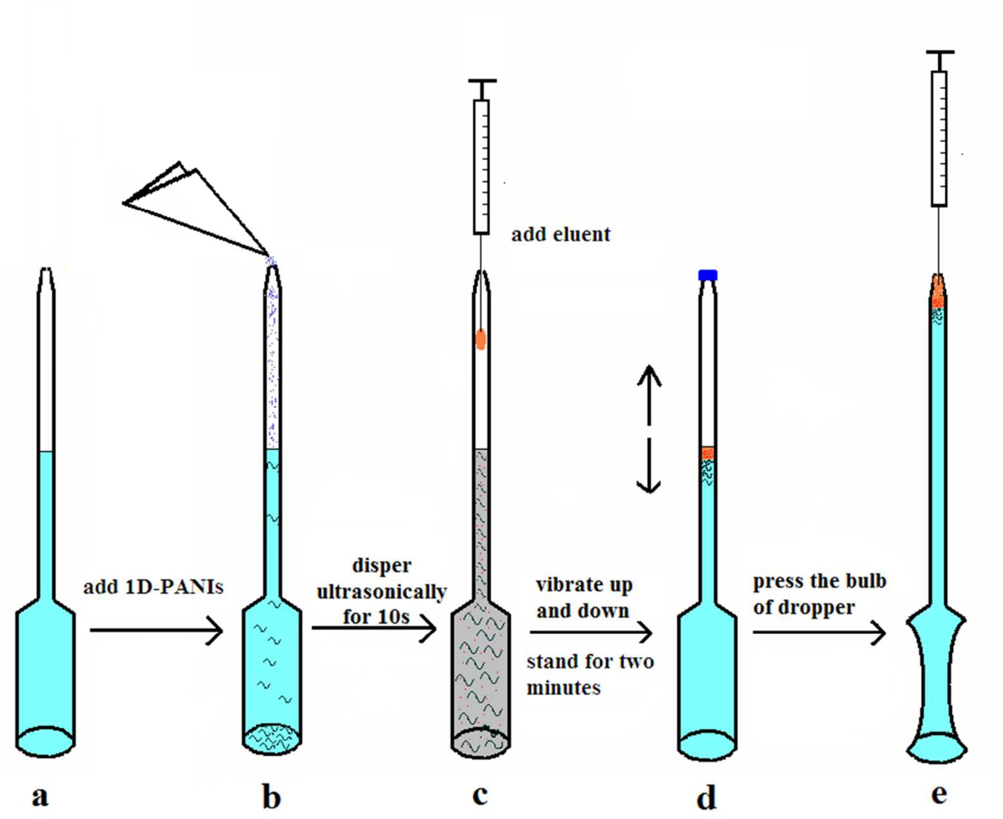
0.5 μg L^{-1} for eight OCPs. Peaks: (1) α-HCH; (2) γ-HCH; (3) β-HCH; (4) δ-HCH; (5) p,p′-DDE; (6) p,p′-DDD; (7) o,p′-DDT; (8) p,p′-DDT

Table captions

Table 1 Analytical performance data for eight OCPs by the proposed D-μ-SPE method

Table 2 Comparison of the proposed D-μ-SPE method with other published methods

Table 3 Relative recoveries of eight OCPs from three spiked environmental water sample


add 1D-PANIs
disper ultrasonically for 10s
add eluent
vibrate up and down
stand for two minutes
press the bulb of dropper
a
b
c
d
e

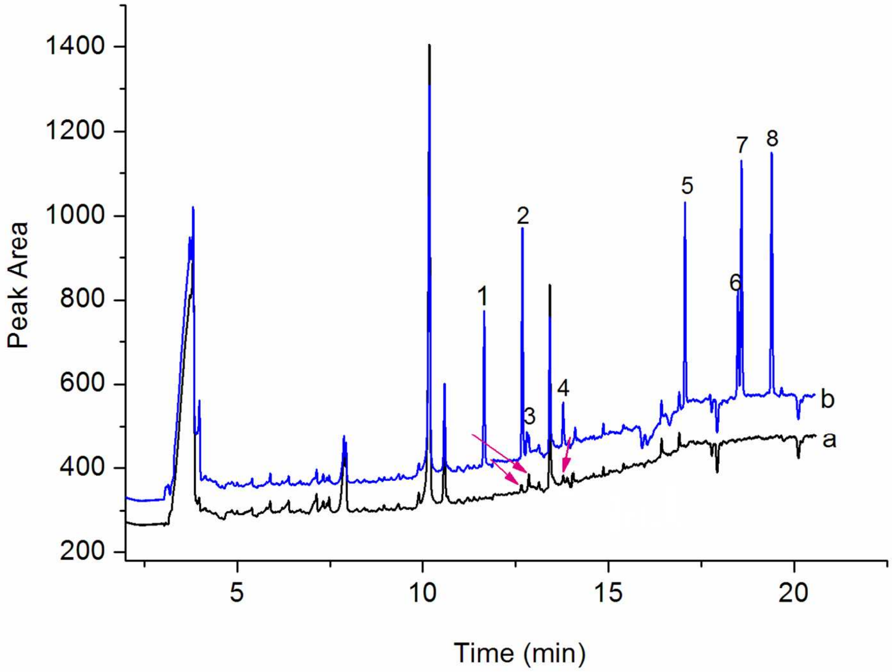


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Table 1 Analytical performance data for eight OCPs by the proposed D-μ-SPE method

Analyte	Linear range (μg L^{-1})	R^2	LOD[a] (μg L^{-1})	LOQ[b] (μg L^{-1})	RSD (%)	
					Intra-day	Inter-day
α-HCH	0.05-50	0.9992	0.0126	0.0416	6.6	11.9
γ-HCH	0.05-50	0.9981	0.0074	0.0244	1.5	4.2
β-HCH	0.05-50	0.9981	0.0121	0.0399	0.6	5.6
§-HCH	0.1-100	0.9971	0.0174	0.0574	5.2	6.2
p,p′-DDE	0.15-100	0.9988	0.0315	0.1040	6.5	8.5
p,p′-DDD	0.2-100	0.9996	0.0468	0.1544	3.8	5.3
o,p′-DDT	0.15-100	0.9989	0.0306	0.1009	2.0	8.3
p,p′-DDT	0.1-100	0.9993	0.0260	0.0858	1.3	6.6

[a]Limit of detection, S/N = 3; [b]Limit of quantification, S/N = 10.

Table 2 Comparison of the proposed D-μ-SPE method with other published methods

Analytical method	Sample volume (mL)	Extraction time (min)	Correlation coefficient	LOD (μg L^{-1})	Detector	Reference
C18-SPE	2000	>60	>0.999	0.2-40	GC-ECD	20
PDMS/DVB	18	>50	0.996-0.999	0.0038-0.011	GC–MS	6
GO-SPE	200	>96	0.982-0.999	0.0015-0.0094	GC–MS	21
ELC-PANI-SPME	10	>46	0.979-0.999	0.0001-0.0016	GC-ECD	13
SBSE-TD-LTM	20	>60	0.993-0.999	0.0014-0.006	GC–MS	22
DSDME	5	15	0.993-0.999	0.04-0.1	GC–ECD	23
D-μ-SPE	6.5	3	0.997-0.999	0.0074-0.0468	GC-ECD	This method

Table 3 Relative recoveries of eight OCPs from three spiked environmental water sample

	Danjiangkou water (%±RSD, n=3)				Ponding water (%±RSD, n=3)				Lake water (%±RSD, n=3)			
	0	$0.2\ \mu gL^{-1}$	$1.0\ \mu gL^{-1}$	$10\ \mu gL^{-1}$	0	$0.2\ \mu gL^{-1}$	$1.0\ \mu gL^{-1}$	$10\ \mu gL^{-1}$	0	$0.2\ \mu gL^{-1}$	$1.0\ \mu gL^{-1}$	$10\ \mu gL^{-1}$
α-HCH	ND[a]	90.0±4.8	94.0±3.1	91.6±3.4	ND[a]	85.8±5.2	99.6±6.3	94.3±4.1	ND[a]	84.7±8.9	81.4±5.2	99.5±4.3
γ-HCH	ND[a]	95.1±5.6	98.3±3.3	89.8±2.9	ND[a]	88.8±4.5	107.0±4.9	86.7±3.5	0.012	83.9±7.4	89.7±5.6	93.9±4.9
β-HCH	0.056	76.6±5.1	83.7±7.6	103.3±4.8	ND[a]	84.1±6.0	82.9±3.7	81.4±4.9	0.151	86.9±5.3	86.6±4.1	87.4±3.9
§-HCH	0.187	73.6±2.0	106.0±3.8	92.7±3.3	ND[a]	90.4±5.2	81.1±4.1	92.4±46	0.128	79.5±5.7	94.6±2.1	88.6±4.8
p,p′-DDE	ND[a]	104.0±5.3	96.0±3.2	86.5±4.6	ND[a]	99.6±4.9	94.1±3.8	81.3±6.6	ND[a]	103.4±6.0	90.1±7.2	93.3±5.1
p,p′-DDD	ND[a]	100.9±5.1	91.8±5.8	86.2±6.6	ND[a]	85.2±7.8	80.7±5.8	99.1±8.1	ND[a]	87.6±8.3	95.4±7.2	90.4±5.9
o,p′-DDT	ND[a]	98.6±5.6	86.6±7.2	83.3±4.3	ND[a]	105.9±10.2	93.0±8.9	79.9±7.5	ND[a]	106.1±11.3	94.2±10.5	90.3±9.9
p,p′-DDT	ND[a]	90.2±6.1	88.7±7.7	85.3±8.2	ND[a]	91.5±5.3	80.1±8.0	82.4±7.6	ND[a]	98.9±8.4	83.8±7.3	91.2±9.6

[a] ND: not detected;