

Determination of Organophosphorus Pesticides in Underground Water by SPE-GC-MS

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Abstract

A rapid and effective method is developed for the determination of organophosphorus pesticides (dichlorvos, methyl parathion, malathion, and parathion) in underground water by solid-phase extraction (SPE)-gas chromatography-mass spectrometry. Some important extraction parameters including types of SPE adsorbents, elution solvents, and injection volume of water samples are optimized. The use of Cleanert-PEP polymer SPE column improved higher extraction efficiencies than the C18 SPE column commonly used. Water samples are extracted using Cleanert-PEP as SPE adsorbent and ethyl acetate as elution solvent. Precision values expressed as relative standard deviation for 1 µg/L of spiked water sample are in the range of 1.6–4.0%. Dichlorvos, methyl parathion, malathion, and parathion are linear in the range of 0.1–1.0 µg/L ($r^2 = 0.9976$), 0.1–2.0 µg/L ($r^2 = 0.9883$), 0.1–2.0 µg/L ($r^2 = 0.9798$), and 0.055–1.1 µg/L ($r^2 = 0.9790$), respectively. The limits of detection for spiked water samples are in the range of 4–10 ng/L. The optimized method is applied to the determination of underground water samples. Recoveries are between 59.5% and 94.6% for spiked underground water samples. The benefit of the method developed is rapid, simple, and has good repeatability.

Introduction

As many of the organochlorine pesticides became banned in the 1970s, the agrochemical industry turned to the less persistent, but more acutely toxic, organophosphorus pesticide (OPP) compounds to control insect pests. Nowadays, OPPs are the class of agricultural insecticides most widely used in the world. Their extensive use, especially for crop protection, implies an environmental risk, which has risen to an increasing social concern with respect to the presence of OPPs in a wide range of surface and ground waters, drinking waters, fruits, vegetables, and foodstuffs in general (1–3).

Determination of OPPs in environmental water samples usually requires the application of sample preparation procedures to extract the analytes from the aqueous solution and bring them to

a suitable concentration level prior to final gas chromatographic (GC) analysis. Liquid-liquid extraction (LLE) is still the most common sample preparation approach. It is, however, a time- and labor-intensive procedure and requires large amounts of high-purity solvents that are expensive and potentially toxic. In the past few years, simple and miniaturized sample preparation techniques have been reported as alternatives to conventional sample preparation procedures. These include solid-phase extraction (SPE) (4), solid-phase microextraction (SPME) (5), single-drop microextraction (6), dispersive liquid-liquid microextraction (7), etc. SPME is a solvent-free extraction technique. However, SPME fibers are comparatively expensive and have a limited lifetime, as they tend to degrade with repeated usage (8). Single-drop microextraction has been demonstrated to be a simple, inexpensive, and fast sample preparation procedure. However, drop stability and unsuitability for complex samples often have been encountered (9). Nowadays, another alternative sample pretreatment technique, SPE, is more and more widely used in environmental analysis due to many advantages, such as wide availability of selective sorbents, lower consumption of organic solvents, cost, and time of analysis, and it is easy to be automatically controlled using commercial auto-SPE instruments (10). C18 phase is the most widely used SPE cartridge, which has been applied to the sample preparation of OPPs in different matrices, such as water (11–12), animal matrices (13), and eggs (14). However, the recoveries of pesticides were not satisfactory in some cases and, thus, improvements are still needed. Cleanert-PEP extraction material is a kind of polymer which has both hydrophilic and hydrophobic groups. So, the Cleanert-PEP extraction cartridge is suitable for extraction of both polar and non-polar compounds. It also has some other advantages over C18 material, such as a wider pH range from 1 to 14. These characteristics of Cleanert-PEP determine that it may have a potential application in the extraction of some pesticides.

On the other hand, the detection of extracted OPPs can be carried out by using different GC detectors [e.g., flame photometric detector (FPD) (15), nitrogen-phosphorus detector (NPD) (16), and electron capture detector (ECD) (17)]. However, to use mass spectrometry (MS) detection is even more advantageous because it can further assess peak identity (18–25).

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The aim of this work was to develop a rapid and efficient method to analyze four OPPs (dichlorvos, methyl parathion, malathion, and parathion) in underground water. GC–MS was used to provide structural information in full scan mode and high sensitivity for quantification in selected ion monitoring (SIM) mode. The GC–MS run time was only ~ 10 min after separation experiment optimization. SPE was used to pre-concentrate the water samples. The polymer material Cleanert-PEP was used as SPE sorbent to enrich the four selected OPPs. The extraction efficiencies of the SPE process developed were compared using Cleanert-PEP polymer and two classical C18 cartridges (LC-18 and ODS) as the SPE matrix during control

experiments. The use of Cleanert-PEP polymer resulted in higher extraction efficiencies (larger peak areas) than the C18 SPE column commonly used. The elution solvents (methanol, acetone, and ethyl acetate) were also optimized. Validation parameters such as linearity, precision, and detection limits (LODs) were determined. The method was successfully applied in the analysis of OPPs in underground water samples.

Compared with published papers on the determination of OPPs in water, the method we developed shows that the chromatogram run is faster than other published methods, and has low solvent consumption, good repeatability, and easy peak identification.

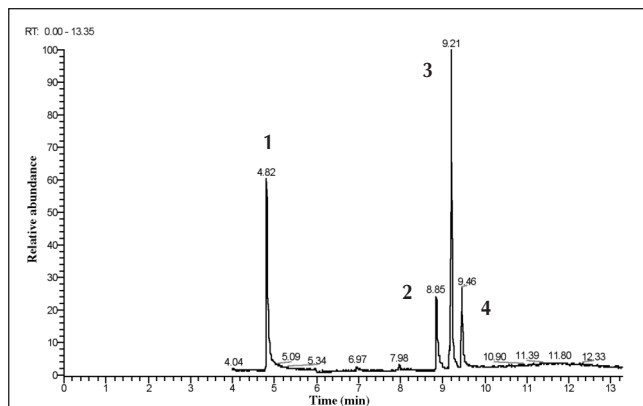


Figure 1. Total ion chromatogram (TIC) of the four OPPs. Experimental conditions: DB-5MS fused-silica column (30 m × 0.25 mm; 0.25 μm); Carrier gas (99.999% Helium) flow rate: 1.0 mL/min; Temperature program: $T_0 = 50^\circ\text{C}$; $T_0 - T_1$, $30^\circ\text{C}/\text{min}$, $T_1 = 150^\circ\text{C}$ (hold, 1 min); $T_1 - T_2$, $30^\circ\text{C}/\text{min}$, $T_2 = 210^\circ\text{C}$; $T_2 - T_3$, $10^\circ\text{C}/\text{min}$, $T_3 = 250^\circ\text{C}$ (hold, 3 min); Injection: splitless mode at 250°C ; Injection volume: 1.0 μL; Solvent delay: 4.00 min; EI, 70 eV; MSD transfer-line temperature: 280°C ; Ion source temperature: 230°C ; Mass range: m/z 50–650. Peak identification: 1, dichlorvos; 2, methyl parathion; 3, malathion; 4, parathion.

Experimental

Reagents, standards, and samples

The individual OPP standards including dichlorvos, methyl parathion, malathion, and parathion were from Institute for Reference Material of SEPA (Beijing, China). Stock solutions of each pesticide were 200 mg/L in chloroform, which was used for MS qualitative analysis. The concentration of four OPPs in stock mixture solutions was, respectively, 100 mg/L for dichlorvos, methyl parathion, and malathion, and 55 mg/L for parathion in chloroform, which was also purchased from the Institute for Reference Material of SEPA. All solutions were stored in a freezer and in the dark before use. All solvents, including methanol, acetone, hexane, and ethyl acetate were of HPLC grade and purchased from Tianjin Kermel Chemical Co. (China). A model Synergy 185 ultrapure water system (Millipore, Milford, MA) was used to purify water.

The underground water sample was collected from Qingdao. The sample was filtered with a 0.45-μm membrane before analysis. The SPE sorbents were disposable extraction columns, Supelclean LC-18 (250 mg/2 mL, Supelco, Bellefonte, PA), ODS (250 mg/2 mL, Agela Technologies, China), Cleanert-PEP (200 mg/3 mL, Agela Technologies).

Instrumentation

Analyses were performed on a Thermo Finnigan Trace GC (Thermo Electron Co., Waltham, MA) equipped with an autosampler. A Thermo Finnigan Automass quadrupole (Thermo Electron) MS was used for detection. The operation was in electronic impact (EI) ionization mode. A 30 m × 0.25 mm i.d., 0.25 μm film thickness, DB-5MS (5% phenyl–methylsiloxane) fused-silica column was used. Helium (99.999%) was the carrier gas, at a flow rate of 1.0 mL/min. The temperature program for the chromatographic run, after optimization, was the following: $T_0 = 50^\circ\text{C}$; $T_0 - T_1$, $30^\circ\text{C}/\text{min}$, $T_1 = 150^\circ\text{C}$ (hold, 1 min); $T_1 - T_2$, $30^\circ\text{C}/\text{min}$, $T_2 = 210^\circ\text{C}$; $T_2 - T_3$, $10^\circ\text{C}/\text{min}$, $T_3 = 250^\circ\text{C}$ (hold, 3 min). The injection was set on a splitless mode at 250°C . The injection volume was 1.0 μL. The solvent

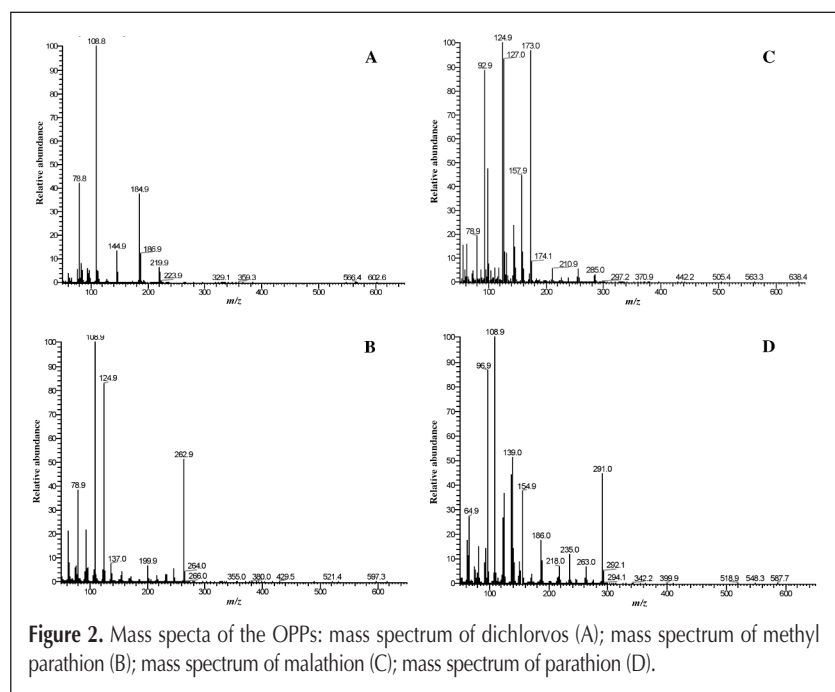


Figure 2. Mass spectra of the OPPs: mass spectrum of dichlorvos (A); mass spectrum of methyl parathion (B); mass spectrum of malathion (C); mass spectrum of parathion (D).

delay was 4.00 min and total run time was ~ 10.00 min.

EI ionization was performed at electron energy of 70 eV. The MSD transfer-line and ion source temperatures were 280°C and 230°C, respectively. A mass range from m/z 50–650 was recorded in the full-scan mode. The MSD was programmed in its SIM mode to respond to the four analytes at their corresponding GC retention times. The appropriate m/z values selected for each analyte and their corresponding group start times are given in Table I.

SPE procedure

The SPE cartridge was first conditioned with 5 mL ethyl acetate to remove air and leach impurities, then with 5 mL ultra-pure water to equilibrate the phase. Next, a 500-mL water sample was loaded by a vacuum pump. Water was then removed, maintaining vacuum for 25 min. Analytes were eluted from SPE sorbents by 2 mL of ethyl acetate. The solution was then transferred to double layer silicone–teflon septum vials for the auto-sampler and analyzed by GC–MS.

Results and Discussion

Chromatographic separation

Under the optimized GC–MS conditions, a baseline separation for the four OPPs was obtained. A typical chromatogram is shown in Figure 1. The identification of OPPs was made on the basis of standard solution retention times and mass spectra of the four OPPs. Figure 2 shows the mass spectra of the four OPP compounds in this study.

Calibration

Calibration curves were obtained preparing six level concentrations for each analyte (0.01, 0.05, 0.10, 0.50, 1.00, and 2.00

Table I. List of Ions and Time Windows used for SIM EI–MS Detection

Compound	Starting time/min	m/z
Dichlorvos	4.0	109, 79, 185, 220
Methyl parathion	8.0	109, 263, 125
Malathion	9.0	125, 93, 173, 127, 285
Parathion	9.35	109, 125, 155, 139, 291

Table II. Retention Times and Regression Results for the Analytes

Analyte	Retention time (min)	Regression equation*	r^2	Linear range (mg/L)
Dichlorvos	4.82	$y = 1 \times 10^7 x + 129629$	0.9967	0.01–2.00
Methyl parathion	8.85	$y = 1 \times 10^7 x - 636386$	0.9820	0.01–2.00
Malathion	9.21	$y = 1 \times 10^7 x + 2863160$	0.9928	0.01–2.00
Parathion	9.46	$y = 1 \times 10^7 x + 83557$	0.9900	0.0055–1.10

* x = concentration (mg/L); y = area. Calibration results are obtained referring to the selective ions listed.

mg/L) except for of parathion, for which concentrations were 0.0055, 0.0275, 0.055 0.275, 0.55, and 1.1 mg/L. A mixture containing each analyte at the specified concentration was injected. Detection was performed referring to the selective ions listed in Table I. The results obtained for the regression are collected in Table II.

Comparison of different extraction phases

In order to optimize the extraction steps, the type of sorbent was considered first. 500 mL of water sample spiked with 1 $\mu\text{g/L}$ of each analyte was used for different phases. For each sorbent, ethyl acetate was used both for activation and for the recovery of the analyte sorbed, according to the procedure detailed in the “Experimental” section. The results obtained are shown in Figure 3. It can be seen that Cleanert-PEP sorbent obtained the largest peak areas for the four OPPs, meaning the best extraction efficiencies. It can be explained by the following reasons. Cleanert-PEP is a kind of polymeric sorbent; besides the advantage of a broader pH range stability (pH limit range is 1–14) than C_{18} sorbent, it has a both hydrophilic and hydrophobic surface. For some polar analytes, such as OPPs, a higher recovery can be found with Cleanert-PEP than with C_{18} . So the Cleanert-PEP phase was chosen for further investigation and optimization.

Effect of the solvents

The conditioning and eluting steps are crucial in determining the efficacy of analyte recovery. The effect of solvents at different polarity (methanol, acetone, and ethyl acetate) was evaluated according to peak areas. Operatively, the Cleanert-PEP phase was conditioned with solvent of 5 mL each, then the analytes were eluted with 2 mL solvent. The results obtained are shown in Figure 4. It can be seen that the best elution result was obtained by using ethyl acetate.

Breakthrough curve

To obtain reliable analytical results and a high concentration factor, it is very important to get satisfactory recoveries for all analytes in as large volume of sample solutions as possible. So, it is necessary to obtain the breakthrough volumes in the SPE. In

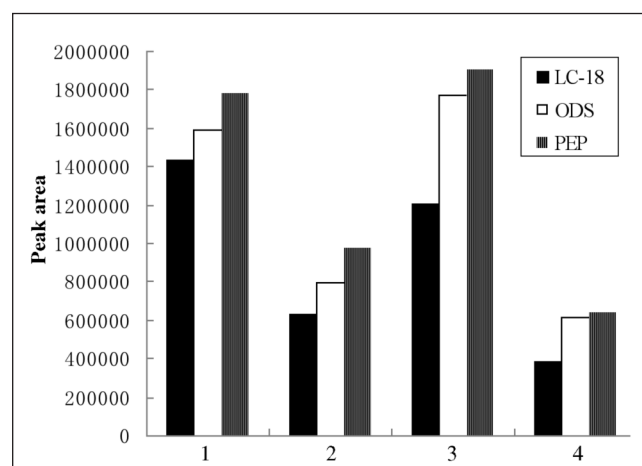


Figure 3. Peak areas from 500 mL water sample spiked with 1 $\mu\text{g/L}$ of each analyte using different SPE phases: 1, dichlorvos; 2, methyl parathion; 3, malathion; 4, parathion. Elute solvent, 2 mL ethyl acetate.

order to determine the breakthrough volumes, different volumes (50, 100, 200, 300, 400, and 500 mL) of pure water were spiked with 100 μL 5 mg/L of dichlorvos, methyl parathion, malathion, and parathion. Following the experimental procedure, the peak areas of four analytes at different volumes were obtained. The effects of sample volumes on the peak areas of four analytes are shown in Figure 5. The breakthrough curve shows that the water sample volume below 500 mL cannot cause breakthrough by using Cleanert-PEP sorbent. Therefore, in the analyses of spiked and real water samples, a sample volume of 500 mL was selected.

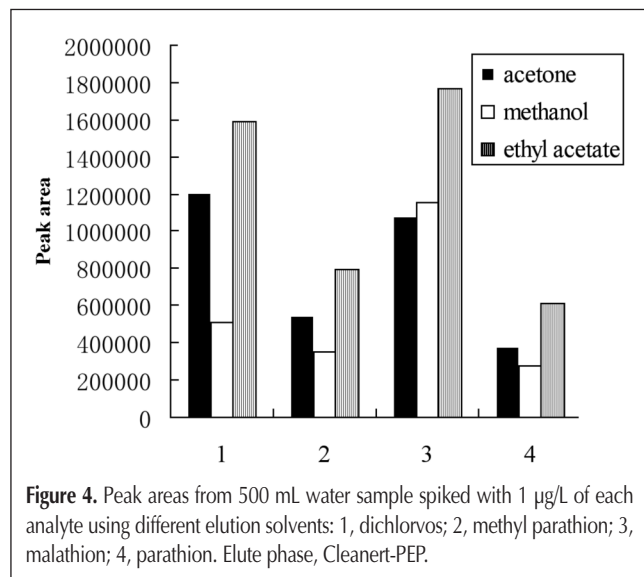


Figure 4. Peak areas from 500 mL water sample spiked with 1 $\mu\text{g/L}$ of each analyte using different elution solvents: 1, dichlorvos; 2, methyl parathion; 3, malathion; 4, parathion. Elute phase, Cleanert-PEP.

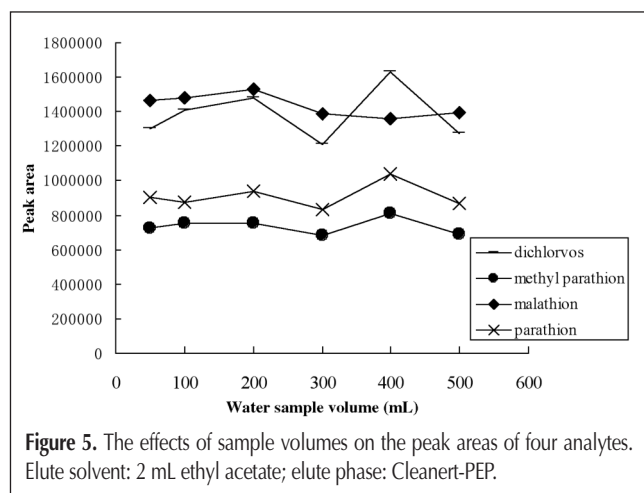


Figure 5. The effects of sample volumes on the peak areas of four analytes. Elute solvent: 2 mL ethyl acetate; elute phase: Cleanert-PEP.

Compound	Linear range (mg/L)	r^2	LOD (ng/L)
Dichlorvos	0.1–1.0	0.9976	4
Methyl parathion	0.1–2.0	0.9883	10
Malathion	0.1–2.0	0.9798	4
Parathion	0.055–1.1	0.9790	5.5

Analytical performance and application

Under the selected conditions (conditioning of the Cleanert-PEP sorbent with 5 mL of ethyl acetate, rinsing with 5 mL ultra-pure water, sample loading volume 500 mL at 4 mL/min flow rate, elution with 2 mL ethyl acetate at 1 mL/min flow rate), the analytical performance of the proposed method was assessed with standard solutions and spiked underground water samples.

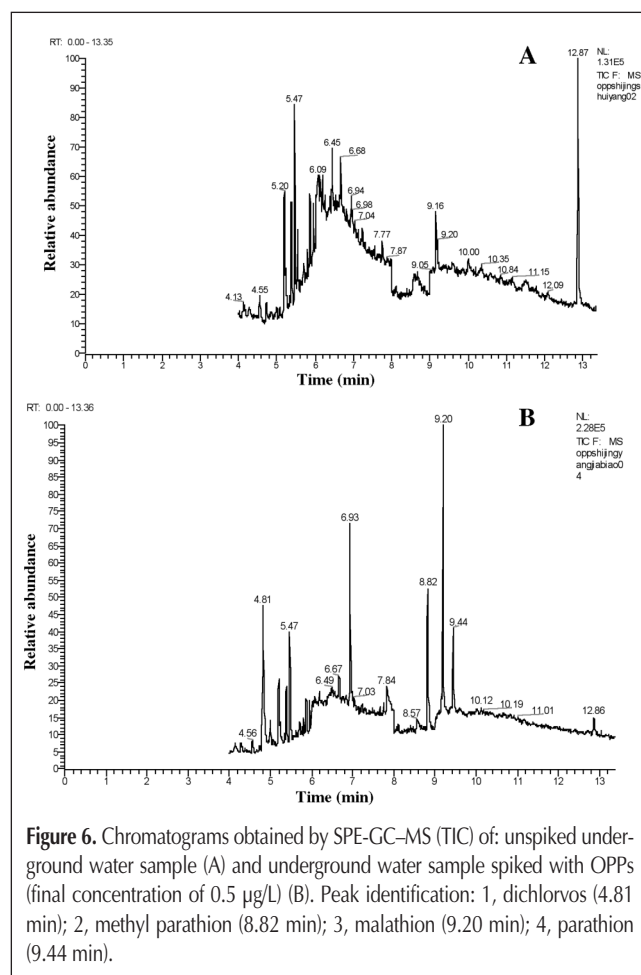


Figure 6. Chromatograms obtained by SPE-GC-MS (TIC) of: unspiked underground water sample (A) and underground water sample spiked with OPPs (final concentration of 0.5 $\mu\text{g/L}$) (B). Peak identification: 1, dichlorvos (4.81 min); 2, methyl parathion (8.82 min); 3, malathion (9.20 min); 4, parathion (9.44 min).

Table IV. Determination and Recoveries of Four Analytes in Spiked Water Samples*

Compound	Added (mg/L)	Found (mg/L)	Recovery (%)
Dichlorvos	0.5	0.304	60.8
	1.0	0.665	66.5
	1.5	1.419	94.6
Methyl parathion	0.5	0.359	71.8
	1.0	0.634	63.4
	1.5	1.165	77.7
Malathion	0.5	0.333	66.6
	1.0	0.622	62.2
	1.5	1.307	87.1
Parathion	0.275	0.207	75.3
	0.55	0.327	59.5
	0.825	0.562	68.1

* Mean for five determinations.

	This study	Ref. 11	Ref. 26	Ref. 19	Ref. 20	Ref. 27
Pretreatment method	Cleanert-PEP SPE	C ₁₈ SPE	molecularly imprinted SPE	BN-LPME	SPME	single drop microextraction
Total run time of the chromatogram (min)	10	30	18	18.5	30	30
Extraction solvents	2 mL ethyl acetate	4 mL dichloromethane	2 mL CH ₂ Cl ₂ /MeOH	5 mL toluene-hexane	solvent free	0.9 mL carbon tetrachloride
Detector	MS	ECD	NPD	MS	MS	FPD
LOD (ng/L)	4–10, 10 ng/L for methyl parathion, 4 ng/L for malathion	1–4	10–32	0.3–11.4, 11.4 ng/L for methyl parathion	5 ng/L for malathion	3 ng/L for methyl parathion, 5 ng/L for malathion
Recoveries (%)	59.5–94.6	79–129	79.3–93.5	73–102	71–114	91–104
RSD%	1.6–4.0	3–26	2.3–5.5	≤12%	6–29	1.1–8.6
Advantages	rapid, low solvent consumption, good repeatability, easy to identify peak	low detection limits	selective	low solvent consumption inexpensive, easy to identify peak	solvent free, easy to identify peak	simple, inexpensive
Disadvantages	solvent usage	toxic solvent usage	toxic solvent usage		bad repeatability, expensive SPME fibers	drop instability

The results obtained with spiked standard solutions are given in Table III. Linear relationships have been found between peak area and the concentration of OPPs in the 0.055–1.0 µg/L range for parathion, and 0.1–2.0 µg/L for methyl parathion and malathion, 0.1–1.0 µg/L for dichlorvos. LODs for spiked OPPs in aqueous solution were in the range of 4–10 ng/L. The RSD ($n = 5$) for 1.0 µg/L spiked OPP aqueous solution was determined between 1.6% (dichlorvos) and 4.0% (malathion).

The proposed analytical method has been applied to the analysis of underground water sample. Figure 6A shows the chromatogram obtained for the water from Qingdao underground. No OPPs were detected in the real samples. Therefore, to assess matrix effects, OPPs were spiked to real samples at 0.5 µg/L, 1.0 µg/L, and 1.5 µg/L. Figure 6B shows the chromatogram obtained for the real water sample added in 0.5 µg/L of OPPs. Relative recoveries were calculated to evaluate the effect of the matrix. It is observed from Table IV that the recoveries are in the range of 59.5%–94.6% for the spiked water samples.

In order to compare this study with other methods for determination of OPPs in published papers, some parameters, advantages, and disadvantages of different methods are summarized in Table V.

Conclusions

It is confirmed that SPE using Cleanert-PEP cartridge is an

effective technique for the preconcentration of several OPPs in water samples at very low concentration levels. The technique is rapid, simple, and economical, with good repeatability. The combination of SPE with GC–MS enables selective and sensitive analysis of OPPs at very low levels in water samples, and easy to identify chromatographic peaks.

The comparison of this study with other methods to determination of OPPs in published papers illustrates their advantages and drawbacks. In this paper, the chromatogram run is faster than in other published methods. Cleanert-PEP SPE phase was more effective than C₁₈ SPE phase for the four selected OPPs analytes. Less solvent was consumed than other SPE methods, and the solvent was less toxic. Compared with single drop microextraction, the method appeared more stable. And the method is costs less than SPME. After optimization, it can be said that the method provided similar detection limits (at the very low ppb or ppt levels) with other reported methods. Moreover, the linearity, precision, and accuracy ranges were comparable.

Acknowledgments

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