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Dispersive Microextraction Based on "Magnetic Water" Coupled to Gas Chromatography/Mass Spectrometry for the Fast Determination of Organophosphorus Pesticides in Cold-Pressed Vegetable Oils

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ABSTRACT: This article presents a novel application of dispersive microextraction based on "magnetic water" (m-water) for the purification of organophosphorus pesticides (methamidophos, omethoate, monocrotophos) from cold-pressed vegetable oils. In the present study, a trace amount of water (extractant) was adsorbed on bare Fe_3O_4 by hydrophilic interaction to form m-water. Rapid extraction can be achieved while the m-water is dispersed in the sample solution with the aid of a vigorous vortex. After extraction, the analyte-adsorbed m-water can be readily isolated from the sample solution by a magnet, which could greatly simplify the operation and reduce the whole pretreatment time. Several parameters affecting the extraction efficiency were investigated, and under the optimized conditions, a simple and effective method for pesticide analysis was established by coupling with gas chromatography/mass spectrometry (GC/MS). The linearity range of the proposed method was 2−100 ng/g with satisfactory correlation coefficients (R) of 0.9997−0.9998, and the limits of quantification (LOQ) for the target compounds were in the range of 0.70−1.27 ng/g. In addition, the reproducibility was obtained by evaluating the intra- and interday precisions with relative standard deviations (RSDs) less than 7.2% and 6.5%, respectively. Finally, the established "magnetic water" microextraction method was successfully applied for the determination of pesticide residues in several kinds of cold-pressed vegetable oils.

KEYWORDS: *"magnetic water", organophosphorus pesticides, cold pressed vegetable oil, GC/MS*

INTRODUCTION

Vegetable oils are essential consumer products in daily life. In the increased demand for "natural" vegetable fats, people search for products other than those produced by extracting with organic solvents or those undergoing subsequent chemical and physical refining processes.[1] Over the past few years, with the development of cold-pressing technology, original cold-pressed vegetable oil has been preferred by more and more consumers due to its rich source of unsaturated fatty acids which can prevent or retard the development of diet-related lifestyle diseases such as obesity, coronary heart disease, and hypertension.[2] However, the pesticide residues derived from oilseeds seem to be some of the main drawbacks of cold-pressed vegetable oils.[3] Especially the organophosphorus pesticides, which are extensively used for agricultural activities, were found to exist in cold-pressed vegetable oil in high concentrations.[4] Therefore, the concentration of organophosphorus pesticide residues in vegetable oils should be monitored strictly to ensure food safety.

It is well-known that the high fat content may cause the main difficulty in the analysis of residual compounds with low concentration in vegetable oil matrices.[5] Even with the advent of advanced hyphenated techniques based on mass spectrometry, these complex fatty matrices usually require extensive sample extraction and purification.[6] Consequently, the separation of pesticide residues from vegetable oils is usually a laborious and time-consuming process. The current reported methods on determination of pesticide residues in vegetable oils always involve the use of one or a combination of some of the following techniques for both the preconcentration of the analytes and removal of interfering substances: liquid−liquid extraction (LLE), solid-phase extraction (SPE), gel-permeation chromatography (GPC), matrix solid-phase dispersion (MSPD), etc.[6] The main drawbacks of LLE are the time involved and requirement of large amounts of organic solvent, which often leads to the formation of emulsions.[7,8] More importantly, it is very difficult to avoid the coextraction of fatty substances; therefore, sequential cleanup procedures (low-temperature fat precipitation,[9−11] column chromatography cleaning,[12] SPE,[13,14] GPC,[15,16] MSPD[17,18]) are necessary. Although a single SPE[19,20] or tandem SPE[21,22] for separation of pesticides from vegetable oils after dilution uses much less organic solvent than LLE, the invariable packing of sorbent materials into cartridges and column conditioning are always tedious stages.[23] In addition, the evaporation of the eluate and reconstitution of the residue also takes a great deal of time. Solid phase microextraction (SPME) is used for pesticide analysis in vegetable oils by the mode of headspace.[24,25] It is solvent free or uses less organic solvent. However, due to the limited interface between the samples and the extractants, a considerable extraction time (more than 60 min) is required to obtain satisfactory extraction efficiency. Thus, a simple, rapid, and effective method for the analysis of pesticides in vegetable oils is also desirable.

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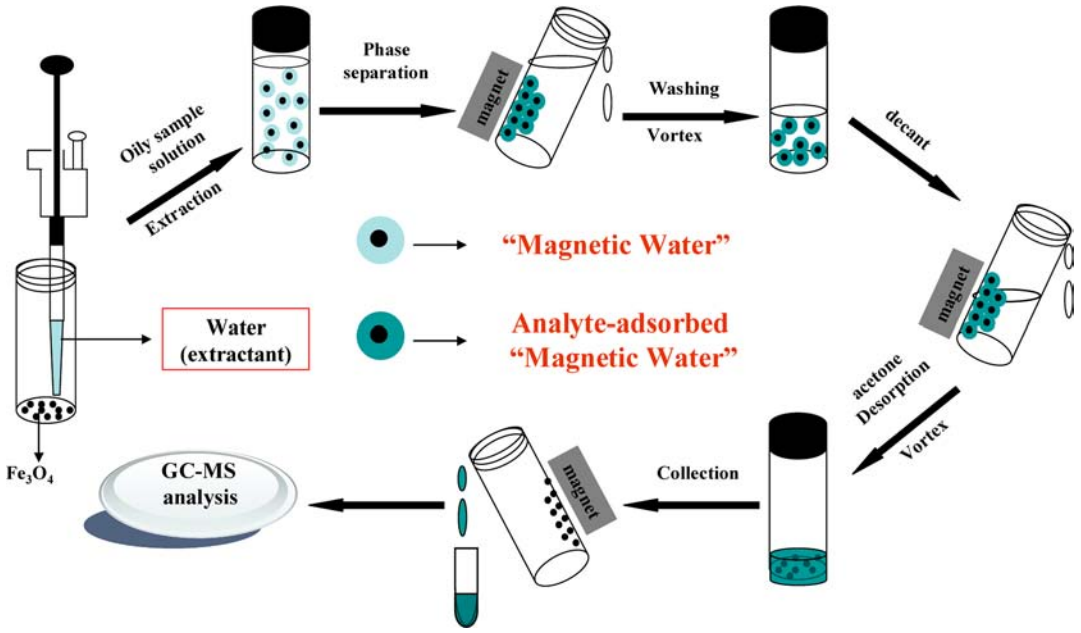

Figure 1. Extraction procedure of pesticides from cold-pressed vegetable oils.

Dispersive liquid–liquid microextraction (DLLME), as a miniature sample preparation approach, emerged in 2006.[26] It had shown very competitive features such as high recovery and enrichment factors, simplicity, and time savings in comparison with classic liquid-phase microextraction (LPME). In this technique, an appropriate mixture of extraction solvent and disperser solvent is injected into the aqueous sample to form an emulsified solution. Since the extractant is highly dispersed in the aqueous phase, the contact surface between phases is markedly increased; therefore, extraction can be achieved within a few seconds. However, there is some inconvenience in retrieving the extractant. Apart from the mandatory centrifugation, some additional processing steps, including refrigeration of the organic solvent, manual retrieval of the extractant, and use of surfactants or some special apparatus such as conical bottom test tubes, may be required.[27]

In recent years, magnetic solid-phase extraction (MSPE) has attracted much attention in sample preparation.[28−31] It is a relatively new mode of extraction technique based on the use of a magnetic or magnetizable sorbent, which can be collected easily by application of an external magnet, greatly simplifying the phase separation. In the current study, we reported a novel dispersive microextraction technique by combining the advantages of DLLME and MSPE. In this new technique, a trace amount of water (extractant) was coated on the surface of bare Fe_3O_4 by hydrophilic physical adsorption to form "magnetic water". With the aid of a vigorous vortex, rapid extraction can be achieved while the "magnetic water" is dispersed in the sample solution. The Fe_3O_4 replaced the disperser solvent in DLLME and served as the supporter of water. After extraction, the "magnetic water" can be collected readily by application of an external magnet, avoiding conventional centrifugation for phase separation, which simplifies the operation and reduces the whole pretreatment time. In addition, the economical water is used as the extractant, which is more environmentally friendly than the halogenated hydrocarbons in classic DLLME. This novel method might be applicable to the extraction of hydrophilic analytes such as polar small organic molecules and metal ions from a hydrophobic sample matrix, including edible fats and oils, fatty foods, and biological samples with high amounts of lipids, and the efficiency of this technique has been proved by extraction of 3-monochloropropane-1,2-diol from edible oils.[32] Herein, we expand this strategy to the dispersive microextraction of organophosphorus pesticides from cold-pressed vegetable oils. As far as we know, this was the first time that DLLME and magnetic separation has been introduced in the purification of pesticides from oils. By coupling with gas chromatography/mass spectrometry (GC/MS), a rapid, simple, and effective method for the determination of three kinds of organophosphorus pesticides (methamidophos, omethoate, monocrotophos) in cold-pressed vegetable oils was established.

EXPERIMENTAL SECTION

Chemicals and Materials. Ethylene glycol (EG), ethanol, acetic acid, acetone, anhydrous magnesium sulfate, ethylenediamine (ED), ferric trichloride hexahydrate ($FeCl_3{\cdot}6H_2O$), *n*-hexane, disodium hydrogen phosphate, and sodium acetate (NaAc) were purchased from Sinopharm Chemical Reagent (Shanghai, China). Octadecyltrimethoxysilane (OTMS) was purchased from the Chemical Plant of Wuhan University (Wuhan, China). Acetone (HPLC grade) and *n*-hexane (HPLC grade) were purchased from Mallinckrodt Baker Inc. (Phillipsburg, NJ 08865, USA). Methanol (HPLC grade) was obtained from Tedia Company Inc. (Fairfield, OH 45014, USA). Purified water was obtained with a Millipore Milli-Q apparatus (Bedford, MA, USA).

Standard solutions of the organophosphorus pesticides methamidophos (100 μg/mL in acetone), omethoate (100 μg/mL in acetone), and monocrotophos (100 μg/mL in acetone) were provided by the Agro-Environmental Protection Institute, Ministry of Agriculture (Tianjin, China). *N*-Methylaniline was used as an internal standard (IS, 95%), supplied by Tingxin Chemical Plant (Shanghai, China), and D-sorbitol (≥99.5%, HPLC) employed as an analyte protectant was supplied by Aladdin (Shanghai, China). The pesticide stock solutions and the IS stock solution were prepared at a concentration of 1 μg/mL with *n*-hexane (HPLC grade) and acetone (HPLC grade), respectively, and stored at −20 °C in darkness. With the stock solution, the sample solution was spiked to the desired concentration for the following experiments. The analyte protectant stock solution was prepared in methanol/water (97/3, v/v) with a concentration of 10 mg/mL and

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was directly added to pesticide extracts, yielding final concentrations of 1 mg/mL.

Sample Preparation. Oil samples were prepared by spiking the analytes at a known concentration (5 ng/mL) to study the extraction performance under different conditions.

Several kinds of cold-pressed vegetable oils were purchased from local markets in Wuhan (China) and stored at room temperature. One refined maize oil sample which was checked to be free of any of the three kinds of organophosphorus pesticides was used as a blank oil for calibration and validation purposes. The analytes were directly spiked into 1 g oil samples over a range of 2−100 ng/g. After they were mixed evenly, the samples were diluted to 10 mL with *n*-hexane.

Synthesis of Fe_3O_4 Magnetic Nanoparticles. Fe_3O_4 magnetite nanoparticles were synthesized via a solvothermal process according to previously reported methods.[28] Briefly, $FeCl_3{\cdot}6H_2O$ (5.0 g) was dissolved in EG (100 mL), and then NaAc (15.0 g) and ED (50 mL) were added to the solution. After vigorous stirring for 30 min, the homogeneous mixture was sealed in a Teflon-lined stainless-steel autoclave (200 mL). The autoclave was heated to 200 °C, maintained for 8 h, and cooled to room temperature. The product was magnetically collected, washed with water/ethanol several times, and vacuum-dried at 60 °C for 6 h.

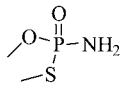
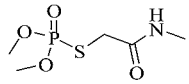
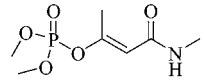
Hydrophobic Modification of Glass Vial Inner Surface. In order to avoid adsorption of the Fe_3O_4 on the glass wall, the glass vial was pretreated by a hydrophobic modification as reported by Gong et al.[33] The pretreatment of the glass vial inner surface involved two steps. In the first step, the 15 mL glass vials were cleaned in an ultrasonication bath of acetone for 15 min followed by rinsing with purified water to remove the surface contamination and then dried with a stream of nitrogen at room temperature. Second, the acidic OTMS and ethanol mixture (1/19, v/v, pH 5−5.5) was added into the clean glass vials and heated to 45 °C for 24 h. The resultant vials were washed with ethanol and purified water several times and dried with a stream of nitrogen.

Extraction Procedure. The extraction procedure of pesticides from cold-pressed vegetable oils is depicted in Figure 1. Briefly, Fe_3O_4 magnetic nanoparticles (20 mg) were added into the modified 15 mL glass vial and then 40 μL of extractant (water) was added by a syringe and soaked by the magnetic nanoparticles. Then, 10 mL of a 0.1 g/mL oily sample solution was added and the mixture was vortexed vigorously for 5 min. In the process, the added extractant was broken up into numerous fine droplets with Fe_3O_4 as cores forming "magnetic water" (m-water), which dispersed in the sample solution to achieve rapid extraction. Subsequently, a magnet was applied to rapidly collect the m-water to the vial bottom, and the supernatant was discarded. After washing with 1 mL of *n*-hexane (30s vortex), the analyte-adsorbed m-water was desorbed by 150 μL of acetone with 5 min of vortexing. The desorption solution was separated from Fe_3O_4 by a magnet and collected in a vial. After dehydration with anhydrous magnesium sulfate (30 mg) and addition of analyte protectant (10 μg), 1 μL of the desorption solution was injected in splitless mode into the GC/MS for analysis.

GC/MS Analysis. The GC/MS analysis was performed on a Shimadzu GC/MS QP2010plus instrument which was equipped with an AOC-20i+s autosampler (Kyoto, Japan). The GC separation was achieved on an Rxi-5 ms column (30 m × 0.25 mm × 0.25 μm) purchased from Restek (Bellefonte, USA). Initially, the oven temperature was held at 70 °C for 2 min and then increased to 180 °C at a rate of 10 °C/min. Subsequently, it was increased to 260 °C at a rate of 20 °C/min. Finally it was held at 260 °C for another 5 min. The solvent cut time was 5.0 min. The injection volume was 1.0 μL in splitless mode. Helium (purity ≥99.999%) was used as the carrier gas at a flow rate of 0.99 mL/min. The temperatures of the injection port, detector, and interface were held at 200, 200, and 260 °C, respectively. The selective ion monitoring (SIM) mode was adopted for the quantitative analysis, and qualitative and quantitative information on the target ions for each pesticide is given in Table 1.

In order to minimize the peak distortion and compensate matrix-induced chromatographic response enhancement effect, which always adversely affected accurate quantitation of polar pesticide in GC analysis,[34−40] D-sorbitol (1 mg/mL) was added into the desorption solution; the benefits of the D-sorbitol addition are shown in Figure 2.

Table 1. Chemical Structure, Retention Time, Molecular Weight, and Target Ions for the GC/MS Analysis of the Target Compounds

Analytes	Chemical structure	t_R (min)	Molecular weight	Quantifier (m/z)	Qualifier (m/z)
Methamidophos		7.9	141	94	141 95
Omethoate		12.7	213	156	110 109
Monocrotophos		13.7	223	127	192 97

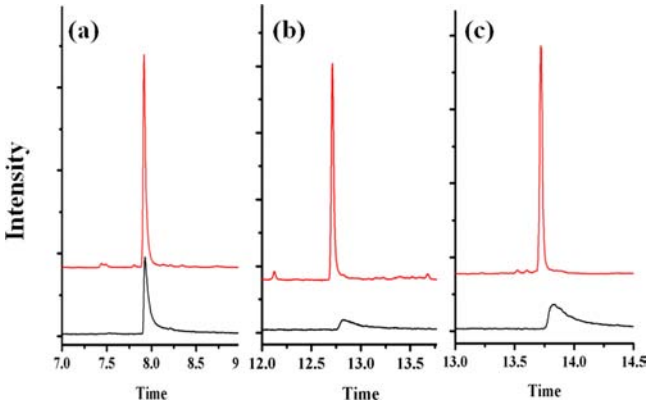


Figure 2. Effect of the addition of D-sorbitol (1 mg/mL, red line) on the peak shape, intensity, and retention time of the target pesticides in standard solution at a concentration of 100 ng/mL (black line, without addition): (a) methamidophos; (b) omethoate; (c) monocrotophos.

As can be seen, the addition of D-sorbitol in a pesticide standard solution allowed enhancement of the chromatographic response and significantly improved the peak shape of the target compounds (omethoate, monocrotophos), increasing the sensitivity of the chromatographic analysis.

RESULTS AND DISCUSSION

Extraction Optimization. In classical DLLME, the extraction solvent is dispersed into the sample solution to form fine droplets with the assistance of a disperser solvent, and then the extraction solvent is isolated by centrifugation. Up to now, DLLME has been demonstrated to be suitable for the analysis of aqueous samples.

In our proposed microextraction method, "magnetic water" was utilized as an extractant to extract the polar analytes from cold-pressed vegetable oils. The "magnetic water" was dispersed in an oily sample solution by vortexing and then collected by a magnet. Thanks to its water-immiscible properties, vegetable oil can be dissolved in nonpolar solvents such as hexane, from which the polar analytes can easily be extracted by "magnetic water". In addition, it may be expected that the extraction efficiency and selectivity of the "magnetic water" are able to be regulated by mixing the water with hexane-immiscible polar solvents such as methanol or by using buffer solution as the extractant.

Effect of the Methanol Content in the Extractant. The effect of adding methanol into the extractant was investigated by increasing the volume ratio of methanol from 0 to 100%. The result is depicted in Figure 3. As can be seen, when the

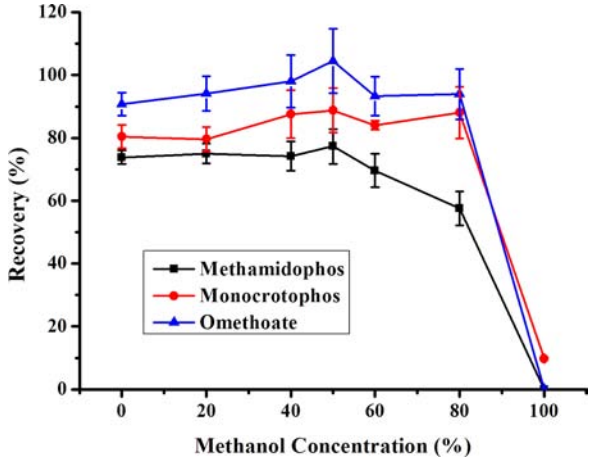


Figure 3. Effect of methanol content in the extractant on extraction efficiency with a concentration of 5 ng/mL of each pesticide in oily sample solutions.

methanol was increased from 0 to 50%, no significant increase in recoveries was observed. An excess of methanol dramatically decreases the extraction efficiency, which may be ascribed to the fact that the excess methanol increases the dissolution of extractant in the sample solution, leading to less retrieval of the pesticide-adsorbed extractant; thus, poor recoveries were obtained. Therefore, no methanol was added in the following experiments.

Effect of the Extractant pH. The pH optimization was performed by using 20 mM phosphate buffer solution as the extractant, in which the pH was adjusted from 5.0−9.0. As shown in Figure 4, the highest extraction efficiencies for the

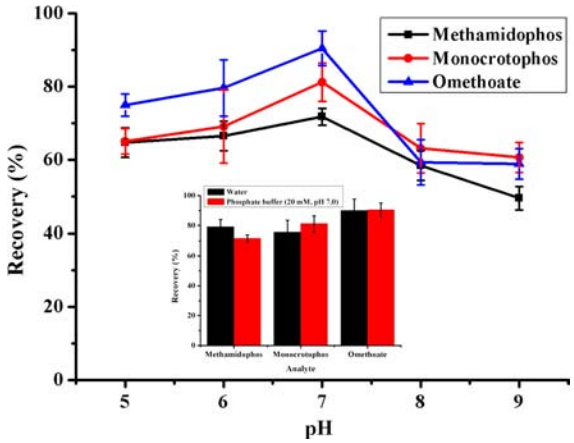


Figure 4. Effect of extractant pH on extraction efficiency with a concentration of 5 ng/mL of each pesticide in oily sample solutions.

analytes were obtained at pH 7. With subacidic or alkaline extractants, lower recoveries was found, which may be attributed to the partial decomposition of the target pesticides. A comparison between the water and phosphate buffer (20 mM, pH 7.0) used as extractant was also performed. The experimental result suggests that there was no significant pH effect on extraction efficiencies. Considering the simplification of the method, further experiments were conducted with water as extractant.

Effect of the Volume of Extractant. To ensure sufficient recoveries of the target analytes, the amount of extractant should be carefully taken into account. Figure 5 shows the

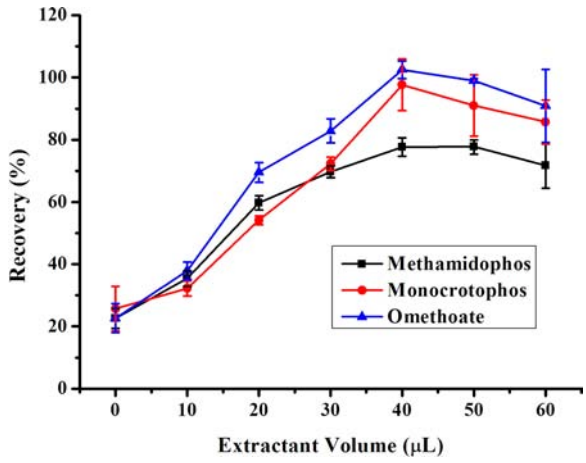


Figure 5. Effect of extractant volume on extraction efficiency with a concentration of 5 ng/mL of each pesticide in oily sample solutions.

effect of extractant amount on extraction efficiency by increasing the extractant volume from 0 to 60 μL (in the case of 0 μL, 20 mg of MNPs was used as sorbent). The result indicates that the recoveries were enhanced as the extractant volume increased from 0 to 40 μL; however, the larger volume of extractant gave reduced recoveries and increased the deviation. The same phenomenon was observed in our previous study,[32] and it can be explained as follows: when a given amount of Fe_3O_4 (20 mg) was utilized, the greatest amount of extractant that could be adsorbed on the material was under the limit. Therefore, in the case of a larger volume, part of the analyte-adsorbed extractant might be separated away from the supporter (Fe_3O_4) by a vigorous vortex during the extraction stage, which failed to be retrieved by a magnetic field. Consequently, 40 μL of extractant was selected for the following analysis.

Effect of the Volume of Desorption Solvent. The volume of the desorption solvent is vital for the desorption efficiency; therefore, the optimum desorption volume should be carefully evaluated. In the present study, acetone was selected as the desorption solvent, and the influence of the acetone volume on recoveries was investigated in the range 100−500 μL. The results showed that there was no significant change in the recoveries when the volume of acetone was varied. In addition, with an increase of desorption solvent, the enrichment factors for the analytes decreased due to dilution effects (Figure 6). Although the use of less desorption solvent would lead to higher enrichment, after dehydration with anhydrous magnesium sulfate, the collection of the desorption solvent was an obstacle if less than 150 μL of acetone was used. Therefore, 150 μL was selected as the compromise desorption volume, at which point the enrichment factors were calculated to be 38, 65, and 75 times for methamidopho, monocrotophos, and omethoate, respectively.

Effect of Extraction and Desorption Time. The effect of both extraction and desorption time was examined in the range 1−10 min. The results indicated that as the extraction time

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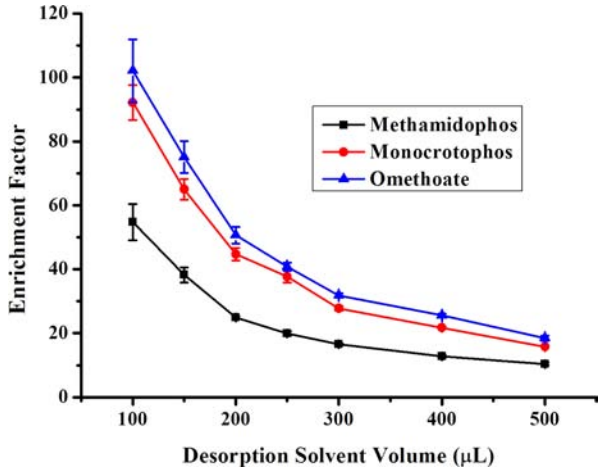

Figure 6. Effect of desorption volume on enrichment factors with a concentration of 5 ng/mL of each pesticide in oily sample solutions.

increased from 1 to 5 min the extraction efficiency increased but the prolonged vortex time did not provide a significant increase in the extraction efficiency. A similar situation was found for the desorption time. Therefore, both the extraction and desorption times were fixed at 5 min.

Validation of the Method. Under the optimal conditions mentioned above, the target pesticides were quantitatively analyzed using *N*-methylaniline as IS. A total ion chromatogram of the oily sample solution (0.1g/mL) spiked at 10 ng/mL of three organophosphorus pesticides and then extracted by "magnetic water" is shown in Figure 7. The linearity was

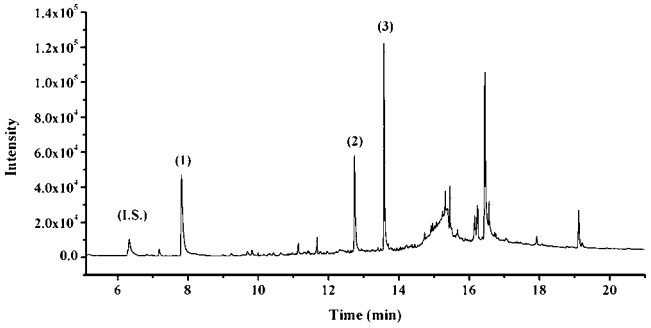

Figure 7. Total ion chromatogram of the oily sample solution (0.1 g/mL) spiked at 10 ng/mL of three organophosphorus pesticides and then extracted by "magnetic water". Peak identification: (1) methamidophos; (2) omethoate; (3) monocrotophos.

studied using blank refined maize oil samples spiked with different concentrations ranging from 2 to 100 ng/g. For the construction of the calibration curve, triplicate measurements were performed, and the calibration curve was generated by plotting the mean peak area ratio versus sample concentration. The data for linearity and sensitivity characteristics are given in Table 2. As shown in Table 2, satisfactory correlation coefficients (R) for the three compounds were obtained, ranging from 0.9997 to 0.9998. The sensitivity of the method was established by examining the LOD and LOQ. LOD was defined as the lowest detectable concentration with a signal-to-noise ratio of at least 3, and the LOQ was defined as the lowest quantifiable concentration with a signal-to-noise ratio of at least 10. The LOD and LOQ data were in the ranges 0.21−0.38 and 0.70−1.27 ng/g, respectively.

Table 2. Linear Range, Regression Data, Limit of Detection (LOD), and Limit of Quantification (LOQ) for the Determination of Organophosphorus Pesticides in Oil Samples

		regression line			
analyte	linear range (ng/g)	linear equation	R	LOD (ng/g)	LOQ (ng/g)
methamidophos	2−100	$Y = -0.03756 + 0.03944X$	0.9997	0.38	1.27
monocrotophos	2−100	$Y = 0.13714 + 0.06176X$	0.9998	0.21	0.70
omethoate	2−100	$Y = -0.03157 + 0.02698X$	0.9997	0.33	1.09

The reproducibility of the method was determined by the intra- and interday precisions. The intra- and interday relative standard deviations (RSDs) were calculated with the pesticides spiked at three different concentrations. Six parallel extractions of a sample solution over 1 day gave the intraday RSDs, and the interday RSDs were determined by extracting sample solutions that had been independently prepared for a continuous 3 days. The results showed that the intra- and interday RSDs were less than 7.2% and 6.5%, respectively (Table 3), illustrating that satisfactory reproducibility was achieved by the method.

Table 3. Method Precisions at Three Different Concentrations for the Determination of Organophosphorus Pesticides in Oil Samples

	intraday precision (RSD%, $n = 6$)			interday precision (RSD%, $n = 3$)		
analyte	low (5 ng/g)	medium (20 ng/g)	high (100 ng/g)	low (5 ng/g)	medium (20 ng/g)	high (100 ng/g)
methamidophos	3.4	4.2	6.5	3.0	2.8	5.8
monocrotophos	2.4	4.5	7.2	5.9	4.7	5.9
omethoate	4.1	4.8	4.7	3.7	6.5	6.0

Analysis of Real Samples. To demonstrate the applicability of the method, several kinds of cold-pressed vegetable oils, including three olive oils, flaxseed oil, tea-seed oil, colleseed oil, walnut oil, and coconut oil, were analyzed. All of these samples were analyzed in triplicate, and the results are outlined in Table 4. The recoveries were obtained by comparing the amounts of analytes calculated from the calibration curve with the corresponding spiked analyte amounts. As shown in Table 4, the recoveries of the target pesticides from various real samples were in the range of 76.0−135.9%, with RSDs of less than 11.6% indicating that the accuracy of the present method was acceptable. Additionally, in the analysis, there no positive samples were found.

A comparative study of our developed method for pesticide analysis in oil matrices to previously reported methods was performed, and the results are presented in Table 5. Obviously, the developed dispersive microextraction based on "magnetic water" was more convenient and rapid than other methods. The extraction stage can be accomplished by a 5 min simple vortex, and the cleanup needs only a 30 s vortex. Additionally, the extractant can be retrieved readily by a magnet, avoiding time-consuming centrifugation, and the desorption solution was directly supplied to instrument without tedious concentration. Moreover, this was the first time that magnetic separation was applied to extraction of pesticides from oils,

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Table 4. Recoveries and Precision of the Target Pesticides in Several Real Samples[a]

	recovery (%) (RSD%), n = 3)							
analyte	olive oil I	olive oil II	olive oil III	flaxseed oil	tea-seed oil	colleseed oil	walnut oil	coconut oil
methamidophos	135.9 (4.5)	108.2 (5.2)	110.5 (1.2)	95.6 (0.8)	87.9 (2.7)	94.0 (10.8)	78.1 (0.3)	80.8 (2.0)
monocrotophos	110.7 (2.9)	110.7 (5.2)	92.1 (2.4)	92.9 (7.0)	91.5 (1.8)	93.9 (3.2)	97.9 (3.9)	97.2 (5.9)
omethoate	133.4 (2.3)	118.9 (1.9)	114.2 (2.3)	98.6 (5.3)	94.4 (1.3)	76.0 (11.6)	93.1 (2.0)	106.8 (5.3)

[a]The concentrations of the spiked pesticides were 10 ng/g.

Table 5. Comparison of Sample Preparation Procedures and Recoveries among Different Methods

matrix	extraction	extraction time (min)	cleanup	entire pretreatment time	determination	recovery (%) (RSD%)	ref
olive oil	LLE (acetonitrile)	30	no cleanup	>60 min	GC-NPD	74−118 (1−16)	8
soybean oil, peanut oil, and sesame oil	LLE (acetonitrile)	>10	low temperature fat precipitation (overnight)	>12 h	GC-FPD	51.3−112.4 (<14.9)	11
virgin olive oil	LLE (acetonitrile)	>10	tandem-SPE (ENVI-Carb and Diol cartridges)	>60 min	GC-NPD or GC-ECD	70.9−107.4 (2.4−12)	13
food commodities	LLE (MeOH/H_2O (80/20, v/v) 0.1% HCOOH)	>10	SPE (OASIS HLB cartridges)	>2 h	LC-MS/MS	70−110 (≤15)	14
olive oil	LLE (acetonitrile)	>10	DSPE or MSPD	>60 min	LC−TOF-MS or GC-MS	70−130	18
virgin olive oils	SPE (CNTs)	8	3 mL of hexane	>20 min	GC-MS	79−105 (≤12.5)	19
vegetable oils	SPE (alumina)	>10	SPE (C18)	>40 min	GC-MS	91−104 (2−10)	22
olive oil	HS-SPME (PDMS)	60	no cleanup	>60 min	GC-FTD	80−106 (1.6−12.0)	25
cold-pressed vegetable oils	dispersive microextraction ("magnetic water")	5	30 s vortex	<15 min	GC-MS	76.0−135.9 (1.2−11.6)	this work

which greatly enhances the simplicity of operation and reduce the entire pretreatment time.

In conclusion, the proposed dispersive microextraction based on "magnetic water" was proven to be a simple and effective method for the determination of organophosphorus pesticides in cold-pressed vegetable oils by coupling with GC/MS. With a vigorous vortex, the "magnetic water" was dispersed in the sample solution to achieve rapid extraction, and after extraction, it can be conveniently isolated from the oily sample solution by application of a magnetic field. The whole pretreatment process was accomplished by a simple vortex within 15 min, which is more time-saving than most of the reported methods. Under the optimal extraction conditions, the limits of detection were as low as the subnanogram per gram range for organophosphorus pesticides with high polarity. Good linearity and reproducibility were also achieved. The results demonstrated that the established pesticide analysis method is suitable for routine determinations. Taken together, the dispersive microextraction technique based on "magnetic water" possesses great potential in sample preparation due to its good extraction abilities and convenient construction methods, and it expands the applicability of microextraction methods in complex sample matrixes such as oils.

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Notes

The authors declare no competing financial interest.

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