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Multiwalled Carbon Nanotubes as Matrix Solid-Phase Dispersion Extraction Absorbents To Determine 31 Pesticides in Agriculture Samples by Gas Chromatography−Mass Spectrometry

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A matrix solid-phase dispersion extraction (MSPDE) method was developed to extract 31 pesticides from agriculture samples using multiwalled carbon nanotubes (MWCNTs) as adsorbent prior to gas chromatography−mass spectrometry (GC−MS) determination. The comparisons of MWCNTs with C_{18} and diatomite were studied in the MSPD procedure. The results showed that the extracts obtained by using MWCNTs were cleaner than those obtained by using C_{18} and diatomite. Using the developed method, recoveries ranged from 74.2 to 104.2% with relative standard deviations (RSD) ranging from 3.1 to 8.8% for the apple matrix, and 71.5−113.3% with RSD ranging from 3.2 to 9.7% for the potato matrix. The limits of detection (LODs), calculated as 3 times the background noise, ranged from 0.1 to 3.1 μg kg^{-1} for the apple matrix and 0.1 to 4.0 μg kg^{-1} for the potato matrix. The proposed MSPDE method was used to analyze real samples obtained in a local market, the results were approximation to those obtained using accelerated solvent extraction (ASE) method, and prometryn, isocarbophos and methidathion were detected at levels below the maximum residue limits (MRLs) allowed by the Chinese Government.

KEYWORDS: Multiresidue; pesticides; multiwalled carbon nanotubes; matrix solid-phase dispersion extraction; gas chromatography−mass spectrometry; agriculture sample

INTRODUCTION

Today, more than 500 compounds have been registered worldwide as pesticides or metabolites of pesticides (*1*). It is well-known that pesticides have brought enormous benefits in terms of increasing agricultural production and quality. However, most pesticides fail to degrade in the natural environment, and pesticide residues in food commodities, water and soil have caused many environmental and food safety problems.

In this connection, monitoring pesticide multiresidues is one of the most important aspects in minimizing potential hazards to human health from food contamination. Nowadays, multiresidue determination methods capable of simultaneously determining more than one residue in a simple analysis have been developed (*2*−*15*). As we know, sample pretreatment is one of the most important steps in compound residues analysis. Before the residues in samples are determined, extraction and purification are required. Recently, some new techniques such as microwave-assisted extraction (MAE) (*16*, *17*), supercritical-fluid extraction (SFE) (*18*, *19*), accelerated solvent extraction (ASE) (*20*), matrix solid-phase dispersion extraction (MSPDE) (*21*), solid-phase extraction (SPE), solid-phase microextraction (SPME) (*22*), and stir-bar sorptive extraction (SBSE) (*23*) were developed. Among these pretreatment methods, MSPDE has been applied to extract and purify drug residues in animal tissue samples (*21*), and it has been used in particular applications as an analytical process for the preparation, extraction and fractionation of solid, semisolid and/or highly viscous biological samples, such as apple (*24*), apple juice (*3*), tomato juice (*25*), fruits and vegetables (*26*−*28*), tea (*5*), tobacco (*29*), milk (*30*), olive oil (*31*), honey (*32*), fish (*33*), soil (*34*), and so on.

MSPDE is an SPE-based strategy in which a fine dispersion of the matrix is mixed with absorbent material (silica, alumina, C_{18}, poly(propylene) tubes, etc.) with a mortar and pestle. After blending, this material is packed into a glass column where the analytes are eluted by a relatively small volume of a suitable eluting solvent. This step can be accomplished together with a "co-column" cleanup to achieve a further degree of matrix removal. The co-column material (Florisil or silica, for example) is packed into the bottom of the same column of the absorbent, cleaning the sample as it elutes from the MSPDE absorbent−matrix mixture. Therefore, extraction and cleanup can be

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completed in one step. At the same time, MSPDE reduces analysis time and the amount of solvents needed.

For instrumental analysis, GC with electron-capture detection (ECD), nitrogen−phosphorus detection (NPD), flame photometric detection (FPD), mass spectrometry (MS) and high-performance liquid chromatography (HPLC) with diode-array detection (DAD), fluorescence detection (FLD) and MS are used most frequently. Generally, GC and GC−MS are used as analytical instruments to screen pesticide multiresidues, and sometimes, LC (*35*), LC−MS (*36*), LC−MS−MS (*37*) and CE (*38, 39*) are used to analyze some decomposed compounds such as carbamate pesticides, glyphosate, carbaryl, and simazine.

This work focused on the development and evaluation of a simple analysis strategy based on MSPDE using multiwalled carbon nanotubes (MWCNTs) as absorbent material and acetone and hexane (1:1, v/v) as eluting solvent, with a cleanup process performed in the elution step using Florisil, and analyzed by GC−MS. The analytical parameters such as recovery, linearity, detection limits and reproducibility were studied in detail. To our knowledge, there have been no reports on the application of MWCNTs as an MSPDE absorbent material to extract pesticides in vegetable and fruit samples.

EXPERIMENTAL PROCEDURES

Chemicals and Reagents. Pesticide analytical standards and internal standards were purchased from Riedel-de-Haën (Seelze, Germany) and Dr. Ehrenstorfer (Augsburg, Germany). HPLC grade acetone, hexane and ethyl acetate were purchased from Merck (Darmstadt, Germany). Individual stock standard solutions of pesticides were prepared by dissolving 4−10 mg of each compound in 5 mL of acetone and were stored in glass-stoppered flasks at −20 °C. Mixed compound calibration solutions in acetone were prepared from the stock solutions with concentrations disregarding their GC−MS sensitivities (**Table 1**) and used as spiking solutions. Hexachlorobenzene and bis-(2-ethylhexyl) phthalate were used as internal standards (10 mg L^{-1}) to compensate for sample and injection volume changes. These internal standards were added to the vial prior to GC−MS analysis. Multiwalled carbon nanotubes (40−60 nm i.d., 40−300 m^2 g^{-1}) were obtained from Nanotech Part Co. (Shenzhen, China). Diatomite was obtained from Shanghai Chemical Reagent Research Institute (Shanghai, China). C_{18} were obtained from UCT Corporation.

Instruments and Apparatus. Analyses were performed with a Shimadzu (Tokyo, Japan) QP2010 gas chromatography−mass spectrometry system equipped with a Shimadzu AOC-20i autosampler and a DB-5 ms fused silica capillary column of dimensions 30 m × 0.25 mm i.d. × 0.25 μm film thickness (J&W Scientific, Folsom, CA). Ultrapure helium (99.999%) was passed through a molecular sieve trap and an oxygen trap prior to use as the carrier gas at a constant flow-rate of 1 mL min^{-1}. Samples (1 μL) were injected in splitless mode, and the sampling time was 1.0 min. The injector and the interface temperatures were 280 and 220 °C, respectively. The column oven temperature program was used as follows: initial temperature 120 °C, increased to 160 °C at a rate of 18 °C min^{-1}, and increased to 200 °C at 3 °C min^{-1}, and held for 2 min, and then increased to 290 °C at 7 °C min^{-1}, and eventually held for 5 min. Mass spectrometry was conducted in EI mode at 70 eV, and the ion source temperature was set at 200 °C. Analysis were performed by selective ion monitoring (SIM) mode, and each compound was quantified based on peak area using one target ion and two or three qualifier ions. The parameters for qualitative and quantitative analyses were shown in **Table 1**. Pesticides were identified by the retention times and full scan spectra of the standards. Quantification was based on SIM for the target ion of each analyte.

Identification and Quantification of Pesticides in Samples. Matrix-matched calibration curves were prepared by adding mixed compound calibration solutions at six different concentrations to blank samples to produce a final concentration of 20, 100, 200, 500, 1000, 2000 μg kg^{-1} (*p,p′*-DDD was 10, 50, 100, 250, 500, 1000 μg kg^{-1}; heptachlor, endrin and cypermethrin were 40, 200, 400, 1000, 2000, 4000 μg kg^{-1}; folpet and endosulfan (II) were 60, 300, 600, 1500, 3000, 6000 μg kg^{-1}).

Table 1. Peak Number, Group, Retention Times, Target Ions, and Confirmation Ions of Pesticides

peak no.	pesticides	group	retention time (min)	target ions (*m/z*)	Q1 (*m/z*)	Q2 (*m/z*)
I.S.1	hexachlorobenzene	1	9.058	284	286	282
1	atrazine	1	9.895	200	92	68
2	lindane	1	10.274	111	109	181
3	diazinon	1	10.789	137	179	152
4	chlorthalonil	1	10.924	266	264	268
5	iprobenfos	1	11.930	91	204	123
6	parathion-methyl	2	13.210	109	125	263
7	heptachlor	2	13.560	100	65	272
8	fenchlorphos	2	13.736	285	125	287
9	prometryn	2	13.868	241	184	68
10	fenitrothion	2	14.486	125	109	277
11	malathion	2	15.054	127	125	93
12	chlorpyifos	2	15.314	97	199	198
13	parathion	2	15.730	109	97	291
14	isocarbafos	2	15.951	136	121	120
15	bromophos-methyl	2	16.431	331	329	125
16	phenthoate	3	18.203	121	125	93
17	procymidone	3	18.349	96	67	68
18	folpet	3	18.468	104	76	130
19	methidathion	3	18.922	145	85	93
20	butachlor	3	19.579	160	176	188
21	*p,p′*-DDE	3	20.808	246	248	318
22	endrin	4	21.766	81	67	79
23	endosulfan (II)	4	22.248	195	237	159
24	*p,p′*-DDD	4	22.590	235	237	165
25	ethion	4	22.696	231	125	153
26	carbofenothion	4	23.642	121	153	125
27	*p,p′*-DDT	4	24.017	235	237	165
28	methoxychlor	5	25.989	227	228	113
29	fenpropathrin	5	26.137	55	125	181
I.S.2	bis-(2-ethylhexyl)phthalate	5	26.730	149	57	167
30	cypermethrin[a]	5	30.101	163	91	181
	cypermethrin[a]	5	30.296	163	91	181
	cypermethrin[a]	5	30.362	163	91	181
	cypermethrin[a]	5	30.427	163	91	181
31	fenvalerate[a]	5	31.565	125	167	225
	fenvalerate[a]	5	31.930	125	167	225

[a] Isomeric compounds.

31 pesticides were divided into 5 groups according to their retention times, and the groups are listed in **Table 1**. To quantify precisely 31 pesticides,two internal standards were added. Groups 1 and 2 were quantified using hexachlorobenzene (I.S.1), and groups 3, 4 and 5 were quantified using bis-(2-ethylhexyl)phthalate (I.S.2). Quantification was based on the peak area ratio of the target ion of pesticide and internal standard.

Sample Preparation. Apple and potato used as blank samples and spiked ones were produced by organic farming without the use of pesticides, and obtained from a local market. The developed procedure was also applied to the analysis of real samples obtained at random from the local market. The samples were immediately stored in polyethylene bags for transport to the laboratory. Samples were stored at 4 °C. The sample was chopped into small pieces and homogenized in a food processor (Taurus, Berlin, Germany). The homogenized samples were placed into a sealed glass beaker and then stored at −20 °C before analysis.

MSPDE Procedure. A two gram homogenized sample was transferred into a glass mortar, where it was fortified homogeneously with the working standard solution. After the mixture was gently blended in the mortar for 30 min and left to stand at room temperature for 1 h, 0.6 g of MWCNTs (40−60 nm i.d., 40−300 m^2 g^{-1}) was added into the mortar and the mixture was gently blended with a pestle. The mixture was introduced into a glass syringe barrel containing 0.5 g of silanized glass-wool at the bottom, and filled (from bottom to top) with 2 g of anhydrous sodium sulfate (which had been dried at 120 °C overnight) and 1.5 g of Florisil (to aid cleanup). Next, the syringe barrel was compressed with a glass bar until it reached a volume of approximately 7 mL. The mixture was eluted with 15 mL (5 + 5 + 5

Table 2. Comparative Study of MWCNTs, C_{18} and Diatomite in the MSPDE Procedure in Spiked Samples ($n = 3$)

	mean recovery (%) ± RSD (%)						
	apple			potato			
pesticides	MWCNTs	C_{18}	diatomite	MWCNTs	C_{18}	diatomite	spiked level (μg kg^{-1})
lindane	85.0 ± 3.8	100.9 ± 6.2	90.4 ± 4.3	83.2 ± 5.8	74.7 ± 4.3	72.3 ± 4.9	100
diazinon	83.6 ± 3.4	81.8 ± 4.1	85.8 ± 5.0	76.2 ± 4.1	84.6 ± 4.4	98.2 ± 5.5	100
chlorthalonil	88.4 ± 4.8	95.2 ± 5.4	82.9 ± 7.0	71.5 ± 5.5	76.0 ± 3.9	76.2 ± 4.6	100
iprobenfos	91.4 ± 6.3	95.6 ± 5.1	100.7 ± 7.4	95.0 ± 5.0	98.0 ± 4.9	95.9 ± 5.8	100
parathion-methyl	104.2 ± 8.1	100.1 ± 7.4	108.7 ± 7.7	91.7 ± 6.2	87.4 ± 4.5	96.9 ± 5.3	100
heptachlor	94.5 ± 4.6	80.2 ± 5.7	67.9 ± 4.4	94.2 ± 6.5	89.9 ± 4.9	71.7 ± 5.8	200
fenchlorphos	90.0 ± 4.2	83.9 ± 3.9	80.4 ± 5.3	71.6 ± 4.7	85.1 ± 4.4	82.8 ± 5.0	100
prometryn	86.9 ± 5.6	90.3 ± 4.2	113.8 ± 8.1	93.4 ± 6.4	85.6 ± 5.2	106.0 ± 6.9	100
fenitrothion	87.6 ± 5.0	100.6 ± 6.2	80.8 ± 5.4	94.8 ± 4.8	95.2 ± 5.1	87.7 ± 5.0	100
malathion	95.0 ± 6.7	88.1 ± 7.6	86.3 ± 7.0	98.5 ± 5.1	99.3 ± 3.8	79.2 ± 4.1	100
chlorpyifos	101.5 ± 4.5	92.3 ± 3.2	71.7 ± 6.1	82.5 ± 3.8	93.2 ± 3.6	85.9 ± 4.8	100
parathion	92.3 ± 4.1	84.5 ± 4.6	93.2 ± 5.1	110.6 ± 7.1	101.4 ± 6.7	94.6 ± 3.8	100
isocarbafos	93.1 ± 4.0	92.2 ± 5.4	89.7 ± 4.1	101.9 ± 7.7	106.9 ± 7.3	94.2 ± 6.4	100
bromophos-methyl	80.8 ± 3.8	79.6 ± 5.2	90.9 ± 4.7	71.8 ± 4.6	84.3 ± 4.9	89.4 ± 3.8	100
phenthoate	95.0 ± 6.1	91.3 ± 5.6	72.3 ± 5.8	113.1 ± 9.7	95.5 ± 5.3	87.8 ± 4.9	100
procymidone	74.2 ± 3.2	76.6 ± 3.8	74.3 ± 4.0	78.8 ± 3.3	75.4 ± 4.1	85.3 ± 3.6	100
folpet	89.1 ± 3.1	93.3 ± 3.2	85.0 ± 3.8	90.2 ± 5.0	91.7 ± 4.3	81.8 ± 4.1	300
methidathion	93.3 ± 3.7	89.1 ± 3.1	90.3 ± 3.5	96.2 ± 4.5	99.1 ± 4.9	96.9 ± 4.4	100
butachlor	95.2 ± 3.6	78.4 ± 5.2	85.3 ± 4.3	78.7 ± 3.5	91.1 ± 5.1	92.1 ± 4.2	100
p,p′-DDE	81.8 ± 3.7	72.9 ± 4.5	79.8 ± 5.1	76.5 ± 4.8	86.6 ± 4.4	74.6 ± 3.9	100
endrin	103.9 ± 8.8	89.0 ± 5.1	92.9 ± 5.3	90.0 ± 4.7	82.6 ± 4.0	82.3 ± 5.2	200
endosulfan (II)	93.1 ± 4.7	80.5 ± 6.3	84.0 ± 5.2	84.17 ± 3.2	88.9 ± 3.7	89.7 ± 4.4	300
p,p′-DDD	82.2 ± 6.5	86.7 ± 4.5	85.5 ± 3.8	89.07 ± 5.2	87.0 ± 5.1	92.3 ± 4.7	50
ethion	93.1 ± 5.0	78.5 ± 4.4	88.7 ± 4.2	113.3 ± 6.5	91.2 ± 4.3	83.3 ± 5.8	100
carbofenothion	95.9 ± 3.2	102.6 ± 5.8	80.3 ± 3.6	102.3 ± 7.3	91.7 ± 6.2	80.1 ± 5.5	100
p,p′-DDT	83.7 ± 5.1	80.2 ± 4.5	73.0 ± 4.8	82.2 ± 3.3	89.1 ± 3.6	78.8 ± 4.2	100
methoxychlor	97.5 ± 5.4	92.7 ± 4.5	75.2 ± 6.1	96.1 ± 3.8	101.0 ± 6.9	77.0 ± 4.7	100
fenpropathrin	97.7 ± 4.1	101.9 ± 7.4	90.3 ± 5.1	94.3 ± 4.6	96.4 ± 3.4	85.7 ± 3.8	100
cypermethrin[a]	95.2 ± 5.6	98.9 ± 4.8	79.0 ± 3.9	98.4 ± 4.1	97.0 ± 5.0	83.6 ± 4.6	200
fenvalerate[a]	87.5 ± 5.6	81.8 ± 4.2	89.4 ± 5.3	93.4 ± 3.6	77.2 ± 3.7	82.7 ± 4.2	100

[a] Calculation of the general amount of the isomers.

mL) of acetone and hexane (1:1, v/v), previously used in washing the mortar and pestle. Elution was made using a SPE vacuum manifold with a flow rate of 1 mL min^{-1}. The eluent was collected into a tube and concentrated to 0.9 mL under a gentle stream of nitrogen. 0.1 mL of internal standards solution was added to 0.9 mL of the above eluent.

ASE Procedure. ASE was performed using an ASE 300 accelerated solvent extractor (Dionex, Sunnyvale, CA) equipped with 11 mL stainless-steel extraction cells. The extraction cell was closed at one end, with a frit and an end cap, and a cellulose filter was placed at the bottom of the extraction cell to prevent cell frit blockage. Two grams of Florisil was placed on top of the filter, and 2 g of sample and 4 g of diatomite were mixed and placed on top of the Florisil. The second filter was covered on sample/diatomite mixture, and the extraction cell was closed with a frit and an end cap. The samples were extracted as follows: extraction solvent, 2 × 5 mL of acetone and hexane (1:1, v/v); temperature, 120 °C; pressure, 10 MPa; extraction time, 2 × 5 min. After static extraction, the raw extract was treated with 2 g of anhydrous sodium sulfate. The clean extract was transferred into 100 mL pear-shaped flasks and concentrated to about 2 mL by means of a rotary evaporator (Büchi, Flawil, Switzerland). The residue was further reduced in volume to 0.9 mL by blowing the residue with a nitrogen stream. 0.1 mL of internal standards solution was added to 0.9 mL of the above residue.

RESULTS AND DISCUSSION

Comparison of Absorbents in MSPDE Procedure. In the preliminary experiments, some parameters such as the amount of absorbent, the eluent, the amount of eluent, the cleanup method and so on were optimized. The amount of MWCNTs, C_{18} and diatomite are 0.6 g, 2 g and 2 g, respectively. The eluent is 15 mL of acetone and hexane (1:1, v/v). Although some MSPDE extracts are clean enough to be directly subjected to instrumental analysis (*3*), a cleanup step is often required in some complex matrices. In this study, 1.5 g of Florisil at the bottom of the glass syringe barrel was used for cleanup.

Many types of absorbents such as aluminum oxide, Florisil, C_8, C_{18} and diatomite were used in the MSPDE procedure (*3, 40*). MWCNTs are a kind of new carbon-based nanomaterial. In theory, MWCNTs can have excellent adsorption ability owing to their extremely large surface area and structural characteristics. It is believed that the reasons for its adsorption may be primarily due to their dramatically hydrophobic surface (*41*) and unique structure with internal tube cavity (*42*). Many results of previous studies have demonstrated that MWCNTs have a unique feature of notable enrichment efficiency. Some reports have described using MWCNTs to extract pesticides (*43, 44*) and herbicides (*45*) in water. In this experiment, MWCNTs have been used as an absorbent material in MSPDE processes, and the performances of MWCNTs, C_{18} and diatomite were compared.

Spiked samples (the spiked levels are listed in **Table 2**) were used to study the recoveries obtained by different absorbents. The recoveries of the pesticides except for heptachlor obtained using MWCNTs, C_{18} and diatomite are above 70%. However, the extracts obtained by using MWCNTs are cleaner than those obtained by using C_{18} and diatomite. The results showed that MWCNTs are an accepted absorbent material to extract pesticides from the MSPDE process with a minimal amount of consumption (0.6 g per extraction).

Analytical Performance of MSPDE. To investigate the accuracy of the developed method, 2 g blank samples were spiked with the working solution to provide samples containing selected pesticides at levels ranging from 50 to 300 μg kg^{-1} (**Table 2**). The spiked level was chosen because it was close to the China MRLs for these pesticides in fruit and vegetables. Every spiked level was replicated 3 times. The recoveries shown

Table 3. Linearity, Correlation Coefficients, LODs and LOQs ($n = 6$) of the Developed Method

		correlation coefficients (R^2)		LOD (μg kg^{-1})		LOQ (μg kg^{-1})	
pesticides	linearity (μg kg^{-1})	apple	potato	apple	potato	apple	potato
atrazine	20−2000	0.9959	0.9985	0.4	0.3	1.3	1.0
lindane	20−2000	0.9930	0.9981	0.6	0.7	2.0	2.3
diazinon	20−2000	0.9966	0.9931	3.1	3.3	10.1	11.0
chlorthalonil	20−2000	0.9910	0.9970	0.6	0.6	2.0	2.0
iprobenfos	20−2000	0.9968	0.9976	0.4	0.4	1.3	1.3
parathion-methyl	20−2000	0.9872	0.9818	0.7	0.9	2.3	3.0
heptachlor	40−4000	0.9990	0.9985	0.4	0.4	1.3	1.3
fenchlorphos	20−2000	0.9935	0.9980	0.4	0.4	1.3	1.3
prometryn	20−2000	0.9977	0.9991	0.5	0.5	1.7	1.7
fenitrothion	20−2000	0.9945	0.9969	1.0	1.0	3.3	3.3
malathion	20−2000	0.9982	0.9987	0.9	1.0	3.0	3.3
chlorpyifos	20−2000	0.9982	0.9995	1.0	1.0	3.3	3.3
parathion	20−2000	0.9980	0.9813	1.0	1.0	3.3	3.3
isocarbafos	20−2000	0.9978	0.9988	1.1	1.2	3.7	4.0
bromophos-methyl	20−2000	0.9875	0.9953	0.6	0.7	2.0	2.3
phenthoate	20−2000	0.9973	0.9920	3.0	4.0	9.9	13.3
procymidone	20−2000	0.9982	0.9790	0.3	0.3	1.0	1.0
folpet	60−6000	0.9962	0.9915	2.0	2.0	6.6	6.7
methidathion	20−2000	0.9971	0.9990	0.2	0.2	0.7	0.7
butachlor	20−2000	0.9962	0.9956	0.4	0.4	1.3	1.3
p,p′-DDE	20−2000	0.9988	0.9916	0.3	0.5	1.0	1.7
endrin	40−4000	0.9984	0.9907	1.0	1.2	3.3	4.0
endosulfan (II)	60−6000	0.9993	0.9989	2.0	2.0	6.6	6.6
p,p′-DDD	10−1000	0.9927	0.9973	0.1	0.1	0.3	0.3
ethion	20−2000	0.9956	0.9874	0.5	0.7	1.7	2.4
carbofenothion	20−2000	0.9975	0.9943	0.9	1.0	3.0	3.3
p,p′-DDT	20−2000	0.9994	0.9989	0.5	0.6	1.7	2.0
methoxychlor	20−2000	0.9990	0.9976	0.4	0.6	1.4	2.0
fenpropathrin	20−2000	0.9913	0.9911	3.0	3.0	9.9	9.9
cypermethrin[a]	40−4000	0.9962	0.9876	1.2	1.5	4.0	5.0
fenvalerate[a]	20−2000	0.9932	0.9913	0.8	1.0	2.7	3.3

[a] Calculation of the general amount of the isomers.

Table 4. Concentrations of Market Sample Analyses (μg kg^{-1}, $n = 3$)

	mean ± SD				
	apple		potato		
pesticides	MSPD	ASE	MSPD	ASE	MRLs (*46*)
prometryn	ND[a]	ND	65.2 ± 5.2	54.0 ± 4.4	−
isocarbafos	ND	ND	54.2 ± 4.1	47.7 ± 3.9	100
methidathion	115.2 ± 7.3	126.4 ± 9.8	ND	ND	2000

[a] Not detected.

in **Table 2** are in the range of 74.2−104.2% for the apple sample with an RSD of less than 8.8%, and 71.5−113.3% for the potato sample with an RSD of less than 9.7%.

Linear ranges were achieved by determining a series of standard solutions at different concentrations and summed up in **Table 3**. The correlation coefficients (R^2) of the calibration curve were higher than 0.98 (**Table 3**).

Blank samples were used to determine the detection and quantification limits for each pesticide. LODs were established by considering a value 3 times the background noise of the blank sample at the retention time of each pesticide, and the limits of quantification (LOQs) were calculated by considering a value 10 times that of the background noise. **Table 3** shows the LODs and LOQs for each pesticide. The LODs were in the range of 0.1−3.1 μg kg^{-1} for the apple sample and 0.1−4.0 μg kg^{-1} for the potato sample. The LODs achieved with the proposed method are similar to those previously obtained by other authors for pesticides in fruit juices (*3*).

Application to Real Samples. The method described in this paper was applied to the analysis of pesticides in apple and potato samples obtained from a local market, and the results are listed in **Table 4**. As shown in **Table 4**, prometryn and

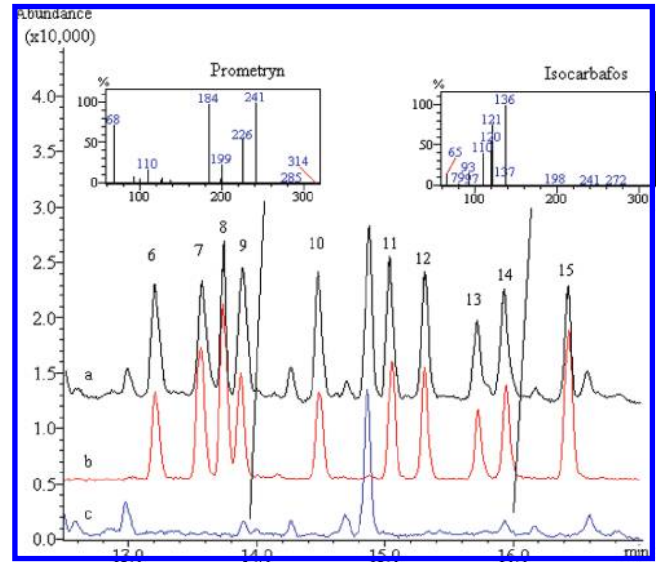

Figure 1. Chromatograms obtained by the developed method in a potato matrix (trace a, blank sample spiked at 500 μg kg^{-1} level; trace b, standard solvent at 500 μg kg^{-1} level; trace c, real sample). For peak identification see **Table 1**.

isocarbophos were detected in the potato sample (**Figure 1**), and only methidathion was detected in the apple sample (**Figure 2**), but the pesticides identified in the samples were at levels below the maximum residue limits (MRLs) allowed by the Chinese Government (*46*).

ASE, an automated, fast pretreatment technique that is included as a standard method by the United States Environmental Protection Agency (US EPA) (*47*), was used to verify

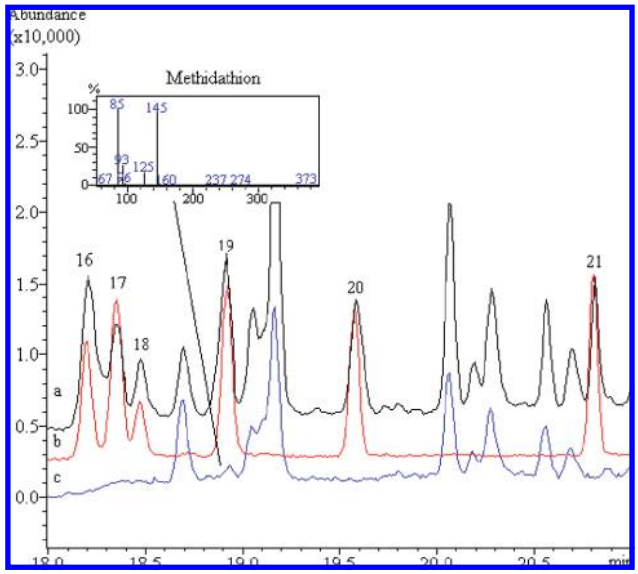

Figure 2. Chromatograms obtained by the developed method in an apple matrix (trace a, blank sample spiked at 500 μg kg^{-1} level; trace b, standard solvent at 500 μg kg^{-1} level; trace c, real sample). For peak identification see **Table 1**.

the results obtained by the developed method. From **Table 4**, we can see that the results obtained by ASE and MSPD are similar. The results showed that the developed method was available to determine pesticides in apple and potato samples. The advantages of the present MSPD method are its simplicity, speediness and the economical consumption rate of only 0.6 g of MWCNTs adsorbent per extraction.

ABBREVIATIONS USED

MSPDE, matrix solid-phase dispersion extraction; GC−MS, gas chromatography−mass spectrometry; MWCNTs, multiwalled carbon nanotubes; RSD, relative standard deviations; LODs, limits of detection; MRLs, maximum residue limits; SPE, solid-phase extraction; SPME, solid-phase microextraction; SBSE, stir-bar sorptive extraction; HPLC, high-performance liquid chromatography; ASE, accelerated solvent extraction; SFE, supercritical-fluid extraction; MAE, microwave-assisted extraction; I.S.2, bis-(2-ethylhexyl)phthalate; I.S.1, hexachlorobenzene; LOQs, limits of quantification.

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