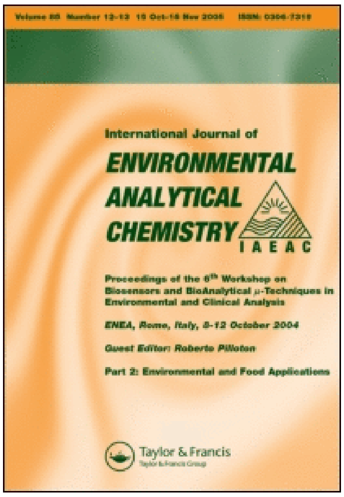

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MULTI-RESIDUE PESTICIDE ANALYSIS IN SOIL BY SOLID-PHASE DISK EXTRACTION AND GAS CHROMATOGRAPHY/ION-TRAP MASS SPECTROMETRY

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A rapid and reproducible multi-residue analysis was developed for the simultaneous determination of 46 pesticides belonging to triazines, organophosphorus and organochlorine compounds, carbamates, anilides, anilines, and amides in various soil samples. Soil samples including its natural water contents were extracted with a mixture of methanol/water (3/1, v/v). The aqueous methanol extracts were directly transferred to an extraction reservoir containing 1 L of reagent water and subjected to clean-up and enrichment by an SPE membrane workstation on Empore C_{18} disks. The analytes were eluated, concentrated and analyzed without additional treatment by gas chromatography/ion-trap mass spectrometry (GC-ITDMS). Recoveries of the analytes using this procedure ranged from 65 to 102% measured at 20–200 μg/kg spiked levels for 41 pesticides tested. With 10 g of soil sample, the detection limits were between 0.5 and 25 μg/kg. The disk SPE procedure was compared to the soxhlet extraction, and comparable recoveries and precisions were demonstrated for most of the pesticides studied.

KEY WORDS: Pesticides, solid-phase extraction disk, gas chromatography, ion-trap detection, soil analysis.

INTRODUCTION

The determination of pesticide residues in soil and sediment samples is necessary for solving various environmental and biological problems. The accuracy and precision of analysis are dependent on both sample preparation and instrumental performance. Traditional analytical methods for pesticides contained in soils mostly include solvent extraction such as soxhlet extraction, preconcentration and clean-up procedures[1, 2], which can make pesticide determination a time consuming and laborious process involving consumption of large volumes of organic solvents. During the last several years, extraction with supercritical fluids (SFE) has received considerable attention as a sample preparation technique for the isolation of analytes from soil, sediment and other environmental samples[3-5]. SFE offers several significant advantages over the conventional soxhlet extraction procedure typically employed for soil analysis. It drastically reduces the volume of solvent required for extraction and provides good recoveries with short extraction times. A limit of this technique is that the solid matrix samples need to be dried prior to SFE because residue water can cause restrictor plugging due to ice formation during extraction and lead to erratic flows[6,7]. Losses of analytes can occur during the drying procedure through volatilization and degradation. Another limitation of SFE technique is that the sophistication and cost of the SFE system make this method less acceptable for routine applications in government laboratories at present.

The trend in pesticide analysis in recent years has been to substitute liquid-liquid extraction with solid-phase extraction (SPE) using a suitable sorbent prepacked in cartridges or embedded in disks. The reasons for this are the better extraction efficiency, the easy, fast, reduced use of solvents and the potential for automation. This technique has become popular in the multi-residue analysis of pesticides in water[8-10]. Although only a few examples of SPE application for soil were reported, with a limited number of analytes, the potential of SPE for soil has been demonstrated[11-15]. In this study, a systematic investigation was carried out applying this technique to the extraction of 46 pesticides from various soil samples. These 46 compounds comprise a majority of the most commonly used and important pesticides in the mediterranean region[16], belonging to triazines, organophosphorus and organochlorine compounds, carbamates, anilides, anilines and amides. The method is based on C_{18} disk SPE followed by GC-MS with ion-trap detection. The main advantages of using SPE disks over SPE cartridges are the higher sampling flow-rate permission and the fact that they are less susceptible to clogging problems from particulate contained in aqueous samples, owing to the use of smaller and embedded silica particles, and due to the fact that they have a high cross-sectional area. The extraction performance using C_{18} SPE disks was compared to the soxhlet extraction for these pesticides from fortified soil samples.

EXPERIMENTAL

Reagents and materials

Pesticide-grade methanol, ethyl acetate, hexane and acetone were obtained from Merck (Darmstadt, Germany). Reagent-grade water was prepared by ultrafiltration with a Milli-Q System (Millipore, Bedford, MA, USA). Pesticide standards were obtained from Supelco (Bellefonte, PA, USA) and Riedel-de-Haën (Seelze-Hannover, Germany). Table 1 lists the 46 pesticides investigated in this study. Stock standard solutions of each pesticide at 1 mg/mL were prepared in methanol. Composite working standard solutions were prepared by dilution with acetone.

Empore SPE disks (C_{18}- and C_8-bonded silica, 47 mm diameter, containing about 500 mg of adsorbent) were obtained from J. T. Baker (Phillipsburg, NJ). Prior to use, each SPE disk was washed sequentially with 10 mL of ethyl acetate, 10 mL of methanol, and 10 mL of reagent-grade water.

Apparatus

The SPE procedure was performed with an SPC DISC 6 (Stepbio, Bologna, Italy) SPE membrane workstation equipped with a Unijet II vacuum pump. With this SPE

Table 1 Nomenclature, solubility in water and $\log K_{oc}$[a] of pesticides selected for this study.

No.	*Common name*	*CAS RN*[b]	*Activity*[c]	*Solubility (mg/L)*[17]	*$\log K_{oc}$*[18,19]
1	Dichlorvos	62-73-7	I	10000	—
2	Dichlobenil	1194-65-6	H	21.2	2.60
3	EPTC	759-94-4	H	344	2.30
4	Butylate	2008-41-5	H	46	2.60
5	Vernolate	1929-77-7	H	108	2.41
6	Pebulate	1114-71-2	H	60	2.63
7	Molinate	2212-67-1	H	970	2.28
8	Propachlor	1918-16-7	H	613	2.62
9	Propoxur	114-26-1	I	1800	1.48
10	Ethoprop	13194-48-4	N, I	750	1.85
11	Cycloate	1134-23-2	H	95	2.63
12	Trifluralin	1582-09-8	H	0.3	4.37
13	Benfluralin	1861-40-1	H	0.1	4.26
14	Bendiocarb	22781-23-3	I	40	2.76
15	Phorate	298-02-2	I, A	22	2.82
16	Carbofuran	1563-66-2	I, A, N	351	1.34
17	Simazine	122-34-9	H	6.2	2.37
18	Atrazine	1912-24-9	H	33	2.46
19	Propazine	139-40-2	H	8.6	2.44
20	Profluralin	26399-36-0	H	0.1	2.46
21	Terbutylazine	5915-41-3	H	8.5	—
22	Propyzamide	23950-58-5	H	15	2.54
23	Diazinon	333-41-5	I	60	2.36
24	Terbacil	5902-51-2	H	710	1.92
25	Propanil	709-98-8	H	200	2.17
26	Metribuzin	21087-64-9	H	1220	2.21
27	Methyl parathion	298-00-0	I, A	60	3.71
28	Alachor	15972-60-8	H	240	2.23
29	Heptachlor	76-44-8	I	0.06	—
30	Ethofumesate	26225-79-6	H	50	2.53
31	Linuron	330-55-2	H	75	2.60
32	Malathion	121-75-5	I, A	130	3.26
33	Metolachlor	51218-45-2	H	530	2.30
34	Aldrin	309-00-2	I	0.05	—
35	Flurochloridone	61213-25-0	H	28	—
36	Diphenamid	957-51-7	H	260	2.30
37	Isopropalin	33820-53-0	H	0.1	4.0
38	Pendimethalin	40487-42-1	H	0.275	3.70
39	Procymidone	32809-16-8	F	4.5	—
40	Napropamide	15299-99-7	H	74	2.85
41	Oxadiazon	19666-30-9	H	0.7	3.51
42	Oxyfluorfen	42874-03-3	H	0.1	5.0
43	Flamprop-methyl	52756-25-9	H	35	—
44	Ethion	563-12-2	A	1.1	4.43
45	Hexazinone	51235-04-2	H	33000	1.73
46	Diclofop-methyl	51338-27-3	H	3	4.2

[a] $\log K_{oc}$, log organic carbon partition coefficient. [b] CAS RN, Chemical Abstracts Service Registry Numbers. [c] I, insecticide; H, herbicide; N, nematicide; A, acaricide; F, fungicide.

workstation, simultaneous extraction of six samples can be semiautomatically performed. Determinations of pesticides were performed with a Varian 3400 gas chromatograph coupled to a Finnigan Mat ion-trap detector mass spectrometer (GC-ITDMS). A 30 m × 0.25 mm i.d. fused silica capillary column with a 0.25 μm bonded phase of

DB-5 (J & W Scientific, Folsom, CA, USA) was used for GC. The injector temperature was 200°C and a splitless injection of 1 μL sample volume was performed. The GC oven was held at 50°C for 1 min and programmed to 130°C at 30°C/min, and then from 130 to 270°C at 5°C/min. Carrier gas was helium at 12 psi. The transfer line was maintained at 220°C, and the mass spectrometer was scanned from m/z 50 to 350 nm.

Soil sample preparation

The uncontaminated clay-loam soil (1.1% organic carbon content and 12.1% water content) collected locally (Florence, Italy) was sieved to remove plant materials and large particles. For SPE experiments, the soil samples (10 g) were not dried and fortified with 100 μL of spiking solution in acetone containing 200–2000 ng of each pesticide. For soxhlet extraction experiments, the soils were air-dried prior to spiking. Spiked samples were kept for 24 h at room temperature before SPE and soxhlet extraction.

Soil extraction procedures

SPE procedure 10 g of spiked clay-loam soil sample were added to 5 mL of reagent-grade water, and equilibrated for 1 h by shaking with a mechanical shaker. After addition of 15 mL of methanol, the mixture was extracted by sonication at 60°C for 15 min. The mixture was subsequently shaken for another 15 min with a mechanical shaker at room temperature. The resulting suspension was centrifuged and the clear supernatant was transferred directly into a 1-L filtration reservoir containing 1 L reagent-grade water. Another 15 mL of methanol was added to the soil sample and the extraction procedure was repeated. The second supernatant was also transferred into the filtration reservoir and 20 μL of surrogate standards, 1-chloronaphthalene and l-chloroantracene (100 ng/μL each) were added. The water containing soil extracts was acidified to $pH < 3$ with 6 M HCl and then passed through the preconditioned SPE disk at a flow-rate of about 50 mL/min. After the sample had been extracted, the disk was dried by air suction for 15–30 min. The adsorbed pesticides were eluated with 2 × 5 mL of ethyl acetate. The extract was concentrated on a Univapo 100 H concentration workstation (Stepbio, Bologna, Italy) to 0.5 mL for GC-ITDMS analysis.

Soxhlet extraction 10 g of spiked clay-loam soil were extracted with 200 mL of a n-hexane and acetone mixture (1/1, v/ v) for 24 h. The extracts were dried in a anhydrous Na_2SO_4 column. After addition of 20 μL of surrogate standard, the dried extract was evaporated to 5 mL with a vacuum rotary evaporator and then concentrated to 0.5 mL on Univapo 100 H concentration workstation. No further clean-up steps were performed prior to GC-ITDMS analysis.

RESULTS AND DISCUSSION

Disk solid-phase extraction

Because the aim of this study was to test the applicability of the disk SPE in soil analysis of pesticides, the capacity of the C_{18} and C_8 SPE disks for the pesticides studied and the extraction efficiency of the disk SPE procedure as described in the experimental section were examined first. The capacity of the SPE disks was determined by spiking 1-L of reagent-grade water with 2 µg of each pesticide. Methanol (30 mL, equivalent to approximately 40 mL of aqueous methanolic soil extracts) was added prior to disk SPE. Figure 1 shows the mean recoveries obtained from five determinations in the extraction of pesticides from reagent-grade water and clay-loam soil samples. It can be observed that good mean recoveries (more than 80%) can be obtained for 40 analytes using C_{18} SPE disks from 1-L reagent-grade water. The reason for the low recovery (54%) of phorate is not yet clear. In the case of the C_8 disk SPE some pesticides, such as dichlorbenil, propachlor, propoxur, bendiocarb, carbofuran, terbacil, metribuzin and hexazinon, have extremely low recoveries. These compounds exhibit relatively high water solubility (Table 1), which shows that the C_{18} SPE disk is more adequate for medium polar compounds than the C_8 SPE disk. These results are consistent with those of other studies[10,20,21]. The results reported in Figure 1 indicate that although the recovery data for all pesticides from clay-loam soil were lower than those from reagent-grade water, 41 pesticides studied gave recoveries of more than 65% from clay-loam soil by C_{18} disk SPE procedure, indicating that the disk SPE procedure is capable of yielding acceptable results. The recoveries for dichlorvos, heptachlor, aldrin and diclofop-methyl from clay-loam soil were extremely low (less than 60%). This may be caused by the evaporation (for dichlorvos) or oxidation (for heptachlor, aldrin and diclofop-methyl) during the disk drying period[7], because we found that the C_{18} SPE disks that had been used for soil extracts required longer air drying time (15–30 min) than disks for reagent-grade water (10 min).

Since the methanol/water mix was used for soil extraction, it is possible that the presence of 3% methanol could affect the extraction efficiency on C_{18} SPE disks for the selected pesticides[14], which exhibit a wide level of water solubility (Table 1).To

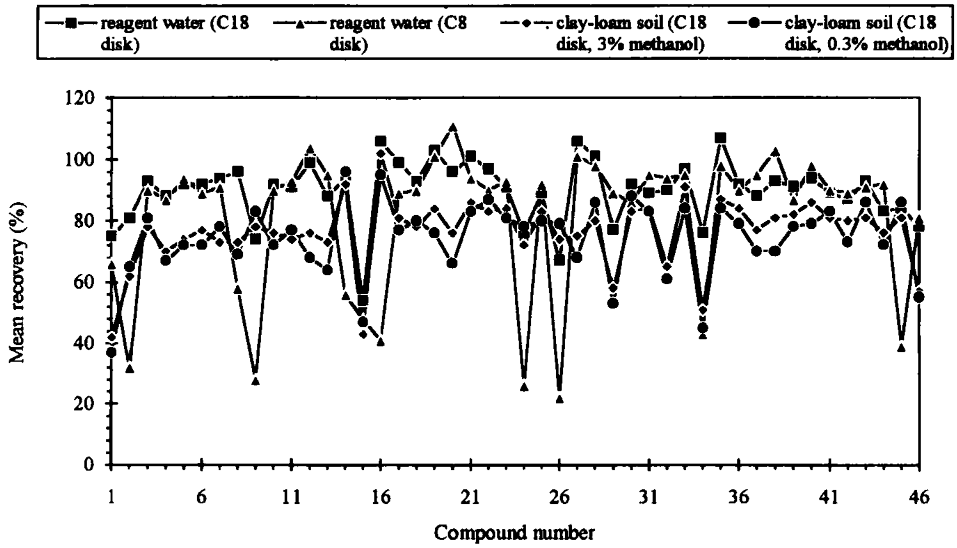

Figure 1 Mean Recovery of pesticides studied from fortified reagent-grade water (2 µg/L) and clay-loam soil (200 µg/kg) samples with disk SPE procedure.

investigate whether the presence of methanol yielded a significant effect on the recovery on C_{18} SPE disks, the soil extracts obtained with methanol/water mix extraction were reduced to 10 mL (containing less than 3 ml of methanol) with a vacuum rotary evaporator and then diluted in 1-L reagent-grade water for disk SPE. The results are also shown in Figure 1. As seen from Figure 1, the removal of methanol from soil extracts prior to SPE did not result in increasing recoveries for all pesticides studied. On the contrary, the recoveries of most pesticides, especially trifluralin, benfluralin, profluralin, methyl parathion, isopropalin and oxyfluorfen, were slightly lower than the values obtained when the soil extracts were directly diluted in 1-L reagent-grade water followed by disk SPE. This may be because the presence of methanol allows a better disk extraction as previously reported[20–22], and reduces the losses of analytes due to adsorption onto the reservoir wall during SPE.

Comparison of disk SPE and soxhlet extraction

Table 2 shows the mean recoveries and precisions of the pesticides studied from fortified clay-loam soil samples with C_{18} disk SPE procedure and soxhlet extraction. The spike level for the experiments comparing recoveries in Table 2 was 200 μg/kg of each pesticide. It was found that the mean recoveries for 31 pesticides studied were not significantly different between two extraction procedures. The low recoveries of dichlorvos, phorate, heptachlor, aldrin and diclofop-methyl obtained from the disk SPE procedure, as explained before, are attributed to their lower affinity for the C_{18} SPE disk or the losses during disk drying periods. The soxhlet extraction gave higher mean recoveries compared with those obtained from the disk SPE procedure for trifluralin, benfluralin, profluralin, malathion, flurochloridone, isopropalin, pendimethalin, oxyfluorfen and diclofop-methyl. A possible explanation of this may be that the procedure of soxhlet extraction with the mixed solvents hexane/acetone (1/1) yields a more efficient extraction for high hydrophobic pesticides ($\log K_{OC} > 3.5$) than the procedure using mixed solvent methanol/water (3/1) and disk SPE.

Figure 2 shows ITD chromatograms obtained after extraction of 10 g spiked and non spiked clay-loam soil samples using C_{18} disk SPE procedure, and of 10 g non spiked clay-loam soil sample using soxhlet extraction procedure. The blanks show that the C_{18} disk SPE procedure gives a final extract with much lower interferences than that obtained by soxhlet extraction procedure. This fact is more likely to be responsible for the lower coefficient of variation obtained by disk SPE procedure than by soxhlet extraction. In fact, at the beginning of the study, the extracts obtained by both procedures were also analyzed by electron capture detector (ECD) and we found that the ECD chromatograms of extracts obtained by the soxhlet extraction contained many background or interfering peaks which made quantification by ECD impossible for many pesticides; whereas in many instances, additional clean-up was not necessarily needed for determination by ECD of the extracts obtained by disk SPE procedure.

Recovery experiments at low spiking levels, 20 μg/kg of each pesticide, were also carried out using C_{18} disk SPE procedure to check the effect of sample concentration. With the exception of dichlorvos and phorate, which could not be determined due to their high method detection limits, there was no significant reduction of recovery and repeatability found for other pesticides studied.

Table 2 Mean recovery (R %) and precision (RSD %) of the pesticides studied from spiked soil sample with C_{18} disk SPE and soxhlet extraction.

Compound	*C_{18} disk SPE*				*Soxhlet extraction*	
	200 μg/kg (n=5)		*20 μg/kg (n=4)*		*200 μg/kg (n=5)*	
	R %	*RSD %*	*R %*	*RSD %*	*R %*	*RSD %*
Dichlorvos	42	16.2	nd	—	61	19.1
Dichlobenil	65	8.5	67	10.8	71	14.3
EPTC	78	6.4	69	7.2	74	8.3
Butylate	70	8.6	66	5.9	76	7.7
Vernolate	74	6.8	72	8.3	72	9.6
Pebulate	76	6.9	67	13.0	78	11.0
Molinate	73	8.1	75	8.0	76	9.5
Propachlor	73	4.3	68	5.6	86	6.3
Propoxur	78	9.7	82	8.0	71	10.9
Ethoprop	74	2.7	68	5.9	75	8.6
Cycloate	76	5.6	66	10.4	78	9.4
Trifluralin	76	4.1	78	3.8	88	6.6
Benfluralin	73	7.8	75	5.3	87	5.2
Bendiocarb	92	9.3	101	11.1	104	13.2
Phorate	43	8.8	nd	—	79	8.7
Carbofuran	102	9.1	96	10.4	102	11.4
Simazine	81	5.9	82	8.5	86	7.0
Atrazine	78	7.4	84	6.0	83	10.8
Propazine	84	6.0	80	8.8	86	8.7
Profluralin	76	5.3	70	5.7	91	6.2
Terbutylazine	81	7.8	86	7.3	89	9.0
Propyzamide	83	10.9	90	13.8	113	16.3
Diazinon	84	5.1	80	4.9	90	9.3
Terbacil	72	8.0	80	9.8	77	11.2
Propanil	80	10.3	73	12.3	86	13.2
Metribuzin	74	7.7	66	6.8	74	10.1
Methyl parathion	75	11.0	69	13.6	62	12.0
Alachlor	80	7.3	77	6.5	82	8.7
Heptachlor	58	11.3	54	12.5	78	9.8
Ethofumesate	83	6.0	76	5.3	89	6.7
Linuron	84	8.7	83	7.6	83	12.1
Malathion	65	6.2	69	11.8	75	8.6
Metolachlor	91	4.4	83	5.6	93	6.4
Aldrin	51	7.9	43	9.6	81	6.2
Flurochloridone	87	7.2	82	5.7	103	13.4
Diphenamid	84	9.3	86	10.5	83	8.2
Isopropalin	76	3.9	73	5.7	92	9.4
Pendimethalin	78	2.5	75	4.7	88	6.4
Procymidone	82	4.9	77	7.8	90	8.7
Napropamide	86	12.5	93	13.6	105	17.2
Oxadiazon	81	8.8	76	9.0	92	9.8
Oxyfluorfen	80	5.0	76	7.9	97	6.4
Flamprop-methyl	81	3.5	88	4.5	83	10.2
Ethion	76	5.3	72	8.3	84	12.6
Hexazinone	81	9.9	76	11.5	62	12.4
Diclofop-methyl	57	9.3	51	11.4	71	9.7

nd, not detectable.

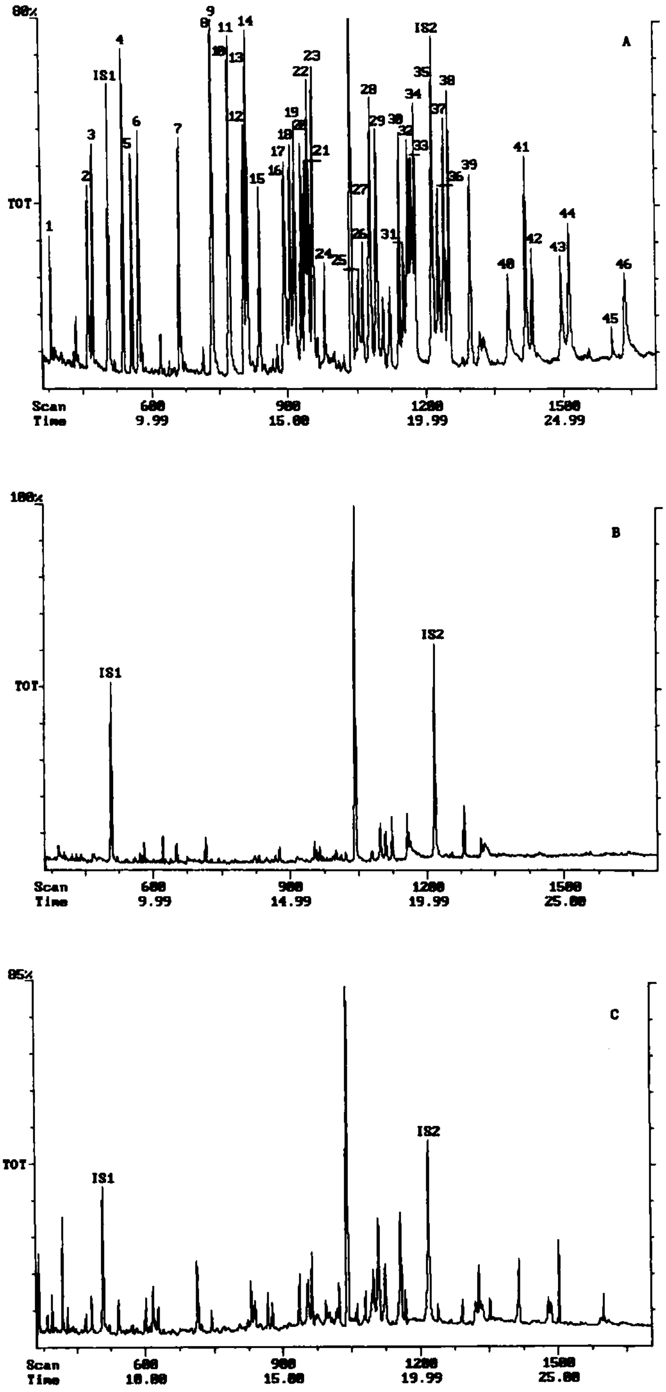

Figure 2 ITD chromatograms of extracts obtained from: A) clay-loam soil spiked with 200 μg/kg of each of pesticide and B) clay-loam soil, nonspiked with C_{18} disk SPE procedure, and C) clay-loam soil, nonspiked with soxhlet extraction. For peak numbers, see Table 1; IS1 = 1-chloronaphthalene; IS2 = 1-chloroantracene.

Disk SPE of pesticides from different soil samples

To assess the effect of the soil matrix on the recovery and precision of the disk SPE method for pesticides studied, sand-loam soil, agricultural soil, river sediment and sand containing different amounts of organic matter, were spiked with 46 pesticides at 200 μg/kg and extracted with C_{18} disk SPE procedure as stated in the experimental section. The sand-loam soil had organic carbon content of 0.8%. The agricultural soil was a dark top field soil containing 4.2% organic carbon content. River sediment was collected from the Arno River in Florence and centrifuged at 2000 rpm before use. The river sediment prepared contained 1.3% organic carbon. The mean recoveries and relative standard deviations (n=4) obtained for each soil sample and pesticide are shown in Figure 3. It was found that the recoveries from sand were comparable to those obtained from reagent-grade water (Table 2) for most of the pesticides, the only exception being the dichlorvos, for which the recovery was much lower (27%) than either from reagent-grade water (75%) or from clay-loam soil (42%), probably because of losses during spiking and the 24 h equilibration period. In sand-loam soil and river sediment the mean recoveries and relative standard deviations for all pesticides are similar to those obtained from clay-loam soil (Table 2), except for dichlobenil (54%), methyl parathion (66%), malathion (51%), ethion (62%) and diclofop-methyl (44%), whose recoveries were found to be lower in river sediment. In agricultural soil, propachlor, diazinon and some more hydrophobic pesticides (trifluralin, benfluralin, profluralin, methyl parathion, pendimethalin and oxyfluorfen) exhibited much lower recoveries (41–72%) compared with those from clay-loam soil (73–84%). These results indicate that in some cases the soil matrix seems to have an appreciable effect on the recoveries of the disk SPE procedure for

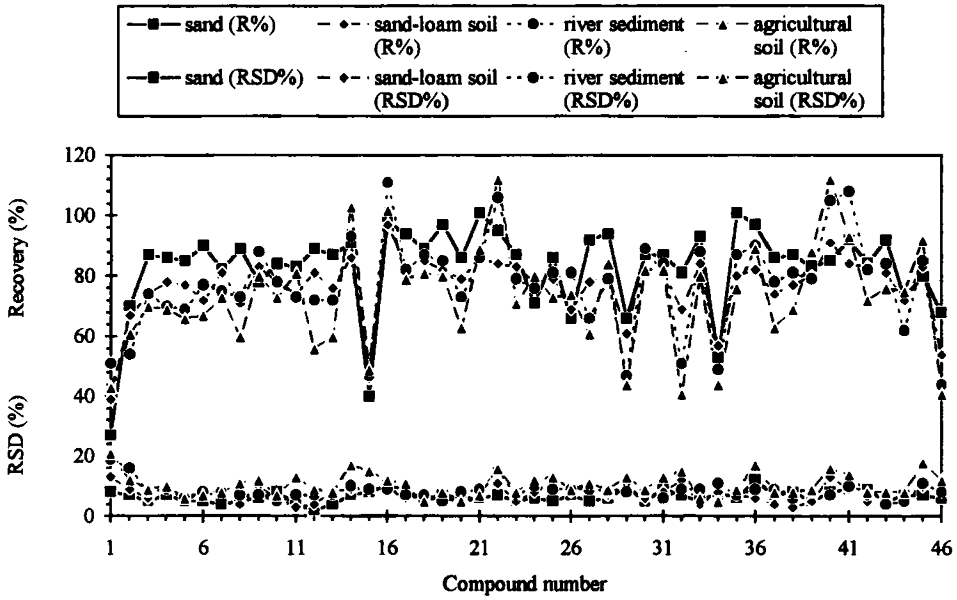

Figure 3 Mean recovery (R %) and precision (RSD %) of pesticides studied from fortified soil, river sediment and sand sample with C_{18} disk SPE procedure.

pesticides, especially for high hydrophobic compounds. Recently, Albanis and Hela[10] also reported that recoveries of some pesticides with C_{18} SPE disks were found to be significantly lower from surface natural waters (rivers, lakes and sea) than distilled and underground water.

GC-ITDMS analysis

In multi-residue procedures for complex environmental samples, mass spectrometry is always the preferred confirmation technique for the identification of the analytes. In this study, soil sample extracts were analyzed by GC with ion-trap detector mass spectrometry (ITDMS). ITDMS was shown to have comparable sensitivity and specificity to those obtained by quadrupole or magnetic MS, while its relatively low cost and ease of use make this technique more adequate for routine analysis[23,24]. Table 3 shows the retention times, ions used for quantitation, the calibration curves, and the method detection limits (MDLs) of the pesticides investigated. The calibration curves were drawn against l-chloronaphthalene (IS1) and 1-chloroantracene (IS2) (2 μg each for 10 g of spiked clay-loam soil) as internal standards (IS1 for compounds 1 to 19, IS2 for compounds 20 to 46, for compound numbers, see Table 1). All pesticides showed linearity in the range of 10–400 μg/kg except for dichlorvos and phorate, which were linear in the range of 40–400 μg/kg. The MDLs were calculated for a 10 g clay-loam soil sample spiked at the 20 μg/kg level and using a signal-to-noise ratio of 5; they range from 0.5 to 25 μg/kg.

Figure 4 shows an ITD chromatogram of a field-contaminated soil sample extract obtained by C_{18} disk SPE procedure. 26 ± 2.4 μg/kg of alachlor, 43 ± 3.1 μg/kg of

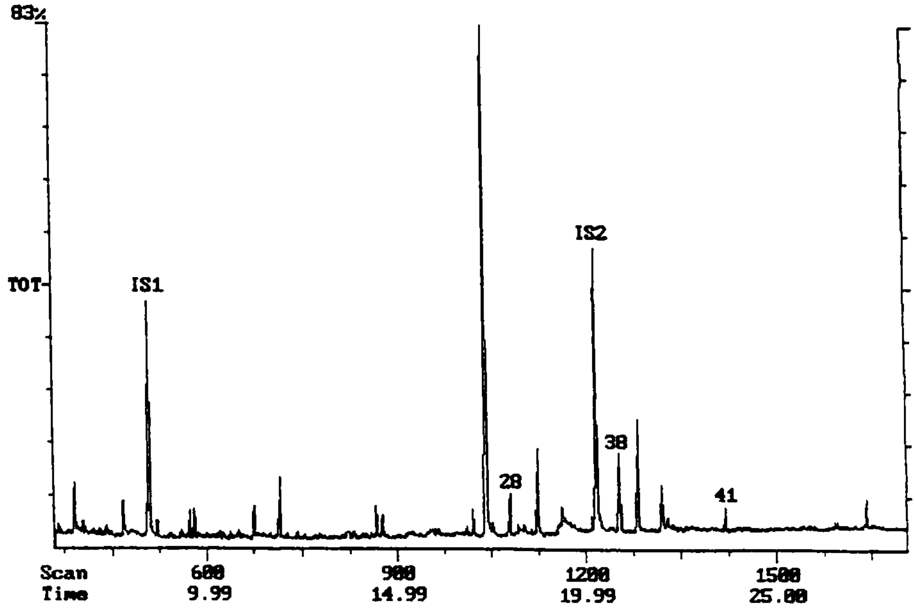

Figure 4 ITD chromatogram of a field-contaminated soil extract obtained by C_{18} disk SPE procedure. For peak numbers, see Table 1.

Table 3 GC retention times (RT), quantitation ions, calibration curves and method detection limit for pesticides studied in soil samples with disk SPE procedure and GC-ITDMS.

Compound	*RT (min)*	*Quant. ions*	*Equation*[a]	R^2	*Detection limit (µg/kg)*
Dichlorvos	6.33	109	$y = 0.0016x + 0.0143$	0.986	25
Dichlobenil	7.70	171/173	$y = 0.0044x + 0.0094$	0.990	2.5
EPTC	7.88	128	$y = 0.0056x - 0.0074$	0.996	1
Butylate	8.99	146	$y = 0.0051x - 0.0082$	0.999	1
Vernolate	9.31	128	$y = 0.0054x - 0.0149$	0.997	2
Pebulate	9.54	128	$y = 0.0061x + 0.0154$	0.997	2
Molinate	11.08	126	$y = 0.0089x + 0.0093$	0.999	0.5
Propachlor	12.26	120	$y = 0.0062x - 0.0241$	0.993	2
Propoxur	12.28	110	$y = 0.0085x - 0.0233$	0.990	2
Ethoprop	12.83	158	$y = 0.0072x + 0.0167$	0.998	5
Cycloate	12.88	154	$y = 0.0027x - 0.0084$	0.995	0.5
Trifluralin	13.39	306	$y = 0.0045x - 0.0127$	0.994	1
Benfluralin	13.51	292	$y = 0.0062x - 0.0166$	0.999	1
Bendiocarb	13.55	151	$y = 0.0051x - 0.0124$	0.994	2
Phorate	13.98	75	$y = 0.0021x + 0.0189$	0.992	25
Carbofuran	14.89	164	$y = 0.0066x - 0.0211$	0.997	2
Simazine	14.94	201	$y = 0.0028x - 0.0144$	0.996	2
Atrazine	15.13	200	$y = 0.0049x - 0.0175$	0.999	1
Propazine	15.28	214	$y = 0.0032x - 0.0097$	0.996	2
Profluralin	15.53	318	$y = 0.0032x - 0.0171$	0.998	1
Terbutylazine	15.66	214	$y = 0.0043x - 0.0118$	0.999	2
Propyzamide	15.78	173/175	$y = 0.0050x - 0.0241$	0.992	1
Diazinon	15.96	304	$y = 0.0021x + 0.0083$	0.993	3
Terbacil	16.34	160/161	$y = 0.0030x - 0.0188$	0.995	6
Propanil	17.56	161/163	$y = 0.0015x - 0.0283$	0.990	5
Metribuzin	17.73	198	$y = 0.0025x - 0.0211$	0.996	3
Methyl parathion	17.96	263	$y = 0.0014x - 0.0144$	0.984	6
Alachlor	18.03	188	$y = 0.029x - 0.0178$	0.999	2
Heptachlor	18.24	272/274	$y = 0.0014x - 0.0127$	0.994	4
Ethofumesate	19.09	207	$y = 0.0046x - 0.0194$	0.998	1
Linuron	19.18	248	$y = 0.0013x + 0.0097$	0.991	5
Malathion	19.41	173	$y = 0.0034x - 0.0219$	0.997	7
Metolachlor	19.51	162	$y = 0.0071x - 0.0311$	1.000	1
Adrin	19.64	263/265	$y = 0.0010x - 0.0122$	0.993	3
Flurochloridone	20.26	311/313	$y = 0.0028x + 0.0217$	0.997	4
Diphenamid	20.50	167	$y = 0.0033x - 0.0281$	0.994	3
Isopropalin	20.71	280	$y = 0.0047x - 0.0241$	0.998	1
Pendimethalin	20.90	252	$y = 0.0031x - 0.0191$	0.999	2
Procymidone	21.66	96	$y = 0.0034x - 0.0262$	0.995	1
Napropamide	22.99	271	$y = 0.0016x - 0.0255$	0.993	4
Oxadiazon	23.63	258	$y = 0.0026x - 0.0188$	0.999	2
Oxyfluorfen	23.86	252	$y = 0.0019x + 0.0116$	0.993	4
Flamprop-methyl	24.93	105	$y = 0.0074x - 0.0384$	0.998	4
Ethion	25.23	231	$y = 0.0047x - 0.00245$	0.996	2
Hexazinone	26.78	171	$y = 0.0020x + 0.0191$	0.986	8
Diclofop-methyl	27.26	340	$y = 0.0019x - 0.0244$	0.992	5

[a] Peak area ratio (y = area analyte/area internal standard) *versus* spiked analyte concentration (x, µg/kg). Five plots with different concentration (ranged from 10 to 400 µg/kg) of each pesticide were used.

pendimethalin and 8.2 ± 1.4 μg/kg of oxadiazon were detected in this soil. The results are calculated from four determinations. This illustrates that this method can be used to determine pesticide residues in soil samples such as the chromatogram with few coextractive interference peaks and the concentrations determined with better precision.

CONCLUSIONS

The study presented here demonstrates that utilizing disk SPE resulted in a reproducible and accurate multi-residue method for the trace analysis of pesticides from different soil samples. Before C_{18} disk SPE, there is no need to eliminate the methanol from the soil extracts obtained with mixed solvent methanol/water, so the sample preparation time can be drastically reduced. Compared to the soxhlet extraction method, for most of the pesticides studied the disk SPE procedure provided comparable recoveries but with the major advantages of short sample preparation times, a minor use of solvent and less interference in the GC-ITDMS traces.

The combination of disk SPE with GC-ITDMS achieves method detection limits in the range of 0.5–25 μg/kg for the analysis of pesticides belonging to different chemical classes. No additional sample clean-up steps are needed. The disk SPE procedure can be performed automatically and simultaneously. Therefore, this method appears to be ideal for the routine analysis of large numbers of soil samples for numerous pesticides.

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