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Comparison of octadecylsilica and graphitized carbon black as materials for solid-phase extraction of fungicide and insecticide residues from fruit and vegetables

C.M. Torres, Y. Picó*, J. Mañes

Laboratori de Bromatologia i Toxicologia, Facultat de Farmàcia, Universitat de València, Av. Vicent Andrés Estellés s/n, 46100 Burjassot (València), Spain

Abstract

Methods for the determination of thirteen fungicide and insecticide residues by solid-phase extraction with C_{18} and graphitized carbon black (GCB) were evaluated. The extraction of the residues was achieved by using matrix solid-phase dispersion (MSPD) and more conventional polar solvent extraction followed by liquid–solid phase partitioning. Determination was carried out by capillary gas chromatography with electron-capture and mass spectrometry detectors. The recoveries were determined by fortifying six different crops (apples, oranges, pears, tomatoes, lettuces and paprikas) with the pesticides studied (bromopropylate, chlorpyrifos methyl, cypermethryn, deltamethryn, fenarimol, fenvalerate, imazalil, lindane, permethryn, phentoate, procymidone, propiconazole and vinclozoline). Although, the data showed that the two extraction methods and both sorbents were able to isolate the pesticide residues from fruit and vegetables, the best results were obtained using MSPD with C_{18} which gave recoveries ranging from 70 to 105% and practical detection limits between 5.0 and 50.0 μg/kg for all the compounds. Ten of these pesticides have been detected in samples taken from Valencia markets, at levels of 0.02–20.50 mg/kg using the described methodology. © 1997 Elsevier Science B.V.

Keywords: Extraction methods; Fruits; Vegetables; Food analysis; Pesticides

1. Introduction

The current developments of analytical technologies to detect pesticide residues in fruit and vegetables, and to offer options for the improvement of their analytical capability have been recently summarized [1,2]. In these studies, main attention has been paid to simplification, miniaturization and improvement of the sample extraction and clean-up methods with universal microextraction procedures [3,4], solid-phase extraction (SPE) and/or solid-phase clean-up (SPC) on cartridges to replace liquid–liquid extraction (LLE) [5–8], matrix-solid phase dispersion (MSPD) [9–11] and selective extraction with supercritical fluid (SFE) [12–14]. Moreover, maximizing the number of analytes to be determined with given resources is considered the best practical approach in a monitoring program [15–19].

In two previous publications, we have discussed the ability of MSPD using octadecylsilica (C_{18}) for the extraction of some organochlorine and organophosphorus pesticides in oranges [20] and in a wide range of fruit and vegetables [21]. The latter study demonstrated that the extracts obtained can be properly analyzed employing capillary GC with

*Corresponding author.

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specific detection methods such as electron-capture (ECD), nitrogen–phosphorus (NPD), flame photometric (FPD; P and S modes) and mass spectrometric (MS) detection [scan or selected ion monitoring (SIM) modes] [21].

In this study, MSPD is checked for the determination of thirteen pesticides with different chemical structures which are currently applied to horticultural crops (including pyrethroid insecticides and nitrogen heterocyclic fungicides), and their performance is contrasted with other approaches. The second objective is carried out in two ways. The first one is to compare two extraction methods based on solid-phase extraction, such as MSPD, and polar solvent extraction followed by liquid–solid phase partitioning, in order to assess if they could completely and advantageously replace liquid–liquid extraction methods. The second one is to evaluate the abilities of the graphitized carbon black (GCB) and C_{18} in quantitatively extracting the selected compounds from fruit and vegetables.

2. Experimental

2.1. Materials

Bromopropylate, chlorpyrifos methyl, cypermethryn, deltamethryn, fenarimol, fenvalerate, imazalil, lindane, permethryn, phentoate, procymidone, propiconazole and vinclozoline were purchased from Dr. Ehrenstorfer Laboratory (Promochem, Wesel, Germany). Individual standard solutions were prepared by dissolving 100 mg of each compound in 100 ml of ethyl acetate. A stock solution of the thirteen pesticides was prepared at concentrations of 0.1 μg/ml for chlorpyrifos-methyl, 0.2 μg/ml for vinclozoline, 2 μg/ml for cypermethryn and permethyrn and 1 μg/ml for the others in ethyl acetate. This solution was stored for three months at 4°C and during this period, degradation or losses of the compounds were not observed. This solution was conveniently diluted to calculate the detection limits.

All the solvents used were of pesticide grade, ethyl acetate was obtained from Scharlau (Barcelona, Spain), methanol and acetone from Merck (Darmstadt, Germany) and dichloromethane from Promochem.

The sorbent materials used in these investigations were octadecylsilica MFE C_{18} with a particle diameter of approximately 50 μm and a pore diameter of 60 Å supplied by Análisis Vínicos (Tomelloso, Spain), and GCB Carbograph with a total surface area of 100 m^2/g and particle size in the range of 37–150 μm by Alltech Associates (Lancashire, UK). The silica was silica gel 60 (particle diameter in the range of 40–63 μm) with a surface area of 500 m^2/g and pore diameter of 60 Å were from Scharlau.

Sep-Pak cartridges contain 500 mg of C_{18} from Millipore (Milford, MA, USA) with particle size of 80 μm and pore size of 125 Å.

2.2. Extraction procedures

A representative portion of sample (200 g of the whole fruit or vegetable) was prepared using a food processor and mixed thoroughly, according to the Directive 79/700/CEE [22].

For the preparation of fortified samples, 500 μl of stock solution were added to 0.5 g of sample. Then they were allowed to stand at room temperature for 3 h. The spiking level was chosen because it was nearest of the European Union MRLs for these pesticides in fruit and vegetables.

2.2.1. Matrix solid-phase dispersion procedure

A sample of 0.5 g was placed into a glass mortar (50 ml capacity) and gently blended with 0.5 g of C_{18} or GCB depending of the material that will be tested. C_{18} was used without previous treatment and GCB was washed with 10 ml of dichloromethane–methanol (80:20, v/v). This solvent mixture removed any interfering compounds from the GCB material [23].

The homogenized sample was introduced onto a 100×9 mm I.D. glass column containing 0.5 g of silica. A 10 ml volume of ethyl acetate for C_{18} or toluene for GCB were added to the column and the sample was allowed to elute dropwise by applying a slight vacuum. The eluent was collected into a graduated conical tube (15 ml) and concentrated under a nitrogen stream to 0.5 ml.

2.2.2. Liquid–solid phase partitioning

A sample of 0.5 g was weighed into a blender cup

and 10 ml of acetone–water (1:1, v/v) were added. The sample was mixed thoroughly for 15 min by sonication. The homogenized sample was filtered through a Büchner. Then, 50 ml of distilled water was added to the filtrate and it was passed through a C_{18} or Carbograph column.

When C_{18} is used, the 500 mg disposable cartridge was previously conditioned with 5 ml of methanol and 5 ml of water. The C_{18} SPE cartridge was eluted with 10 ml of ethyl acetate, and the eluent was concentrated to 0.5 ml as in the previous procedure.

Carbograph (500 mg) was transferred to a 100 mm×9 mm I.D. glass column fitted with a coarse frit (number 3), and covered with a plug of silanized glass wool. It was pre-treated following the procedure reported elsewhere for water samples [23]. The adsorbed residues were eluted with 10 ml of toluene. The extract was concentrated to 0.5 ml.

In all the cases 1 μl samples were injected into the gas chromatograph.

2.3. Gas chromatographic analysis

The gas chromatographic analyses were carried out on two systems: (1) a Konik 3000 gas chromatograph (Barcelona, Spain) equipped with an ECD and a data station Konikrom Chromatographic System. (2) A Fisons Instruments Serie 8000 gas chromatograph coupled to a mass spectrometer detector Trio-1000 via direct capillary interface. The instrument was linked to a work station LAB-BASE and National Bureau of Standards (NBS) spectra library.

A DB-5 capillary column of 30 m×0.25 mm I.D. with 0.25 μm film thickness (J and W Scientific, Folsom, CA, USA) was used with both gas chromatographs.

Injections were performed with the column oven at 50°C in the splitless mode (splitless time 0.7 min). This temperature was maintained for 1 min and then programmed at 30°C/min to 200°C, held for 2 min and at 4°C/min to 280°C and held for 7 min. The carried gas was helium in both systems, at a flow-rate of 1 ml/min.

For GC–ECD, the temperatures of the injector and detector were 280°C and 300°C, respectively.

The mass spectrometer was operated in the electron impact ionization (EI) mode with temperatures as follows: transfer line 200°C, ion source 250°C and analyzer 320°C. The screening analysis was performed in the SIM mode, monitoring one or two characteristic ions for each compound. In some experiments and for confirmation purposes, more characteristic ions for each compound or the scan acquisition mode (m/z 50–450) were used.

3. Results and discussion

Table 1 shows the recoveries achieved using the MSPD and the liquid–solid phase partitioning method using C_{18} from samples of oranges, apples, pears, lettuces, paprika and tomatoes. The recoveries of the different pesticides in the six studied crops were 70–105% using MSPD and 52–92% by liquid–solid phase partitioning. These results show clearly lower efficiency when the second procedure is employed.

Nitrogen heterocyclic fungicides such as fenarimol, imazalil, procymidone, propiconazole or vinclozoline as well as classical organophosphorus (chlorpyrifos methyl and phentoate) and organohalogenated (lindane and bromopropylate) insecticides gave slightly better recoveries than pyrethroid (cypermethryn, deltamethryn, fenvalerate and permethryn) insecticides. The effect of the eluting solvent using MSPD with Florisil has been studied by Ling and Huan [11] for pyrethryns, and the results demonstrated that better recoveries were obtained with acetone–hexane mixtures than with ethyl acetate. However, ethyl acetate is also recommended as elution solvent [17,18] because it allows good recoveries in a wide range of other permitted pesticides.

The lower recoveries of pyrethroid insecticides are more pronounced when liquid–solid phase partitioning is employed. An improvement of the SPE efficiency of pyrethryns from water, if an organic modifier was added to the water sample before SPE has been reported [24]. In this case, the small percentage of acetone (ca. 5%) that contains the extract, which passes though the cartridge, has the advantageous effect of the modifier. Another reason is that pyrethroids are strongly retained on reversed-phase materials and they could be only partially eluted with the ethyl acetate [24].

Fig. 1 illustrates typical ECD and MS chromatograms of the unfortified and a fortified paprika

Table 1
Percentage of pesticides recovered from C_{18} sorbent material using MSPD and liquid–solid phase partitioning (LSPP)

Pesticide	Peak No.	Recovery±R.S.D.[a] (%)											
		Paprika		Lettuce		Tomato		Orange		Apple		Pear	
		MSPD	LSPP	MSPD	LSPP	MSPD	LSPP	MSPD	LSPP	MSPD	LSPP	MSPD	LSPP
Bromopropylate	9	85±3	57±4	94±3	60±3	98±8	70±3	92±7	70±9	91±3	64±2	97±5	77±4
Chlorpyriphos methyl	2	78±4	52±6	103±4	56±3	103±8	71±5	97±6	75±5	84±5	63±5	91±3	77±3
Cypermethryn I	13	87±3	64±5	78±2	58±4	94±6	54±5	77±6	58±4	93±4	59±5	91±4	67±5
Cypermethryn II	14	86±2	64±6	70±5	57±7	86±7	52±6	75±4	52±2	96±3	57±4	86±5	62±4
Cypermethryn III	15	81±3	68±3	74±3	60±3	79±5	56±4	72±3	50±8	94±5	50±8	83±5	68±5
Cypermethryn IV	16	79±6	62±6	73±3	58±2	78±7	57±3	70±5	53±2	85±6	53±6	80±2	57±2
Deltamethryn	19	83±4	63±6	72±4	57±4	85±7	60±7	76±7	58±6	103±2	62±2	83±2	58±5
Fenarimol	10	83±5	58±4	74±6	59±2	86±9	75±9	78±8	66±3	81±4	67±3	95±4	68±8
Fenvalerate I	17	100±6	69±6	80±5	57±1	71±2	59±6	102±5	68±2	93±3	54±7	78±5	65±5
Fenvalerate II	18	81±4	67±6	85±2	60±4	75±3	60±5	76±4	92±4	93±5	65±5	82±6	58±6
Imazalil	6	79±4	64±5	71±2	58±5	74±7	56±4	74±3	66±5	95±8	65±6	85±2	50±4
Lindane	1	96±6	62±3	100±5	62±4	82±9	66±8	100±2	64±6	93±7	72±4	95±5	71±7
Permethryn I	11	92±7	68±7	105±5	61±3	89±5	68±5	91±4	64±2	91±6	65±2	94±4	62±7
Permethryn II	12	80±4	57±5	96±8	73±4	88±6	50±6	77±6	90±9	87±5	66±3	97±7	67±5
Phentoate	4	78±8	59±5	69±6	58±8	83±8	57±2	76±8	81±9	85±4	69±4	89±3	69±3
Procymidone	5	97±6	70±5	97±2	58±2	83±9	65±3	105±9	67±3	91±8	58±5	89±2	67±4
Propiconazole I	7	85±4	59±6	91±2	65±2	90±5	76±4	96±5	66±5	88±6	67±8	96±5	71±5
Propiconazole II	8	85±4	76±6	93±2	61±2	89±3	78±8	96±4	85±4	81±2	63±3	96±5	66±6
Vinclozoline	3	102±5	59±4	94±2	56±2	83±2	58±6	94±3	76±3	90±3	65±2	95±4	68±8

[a] $n=5$.

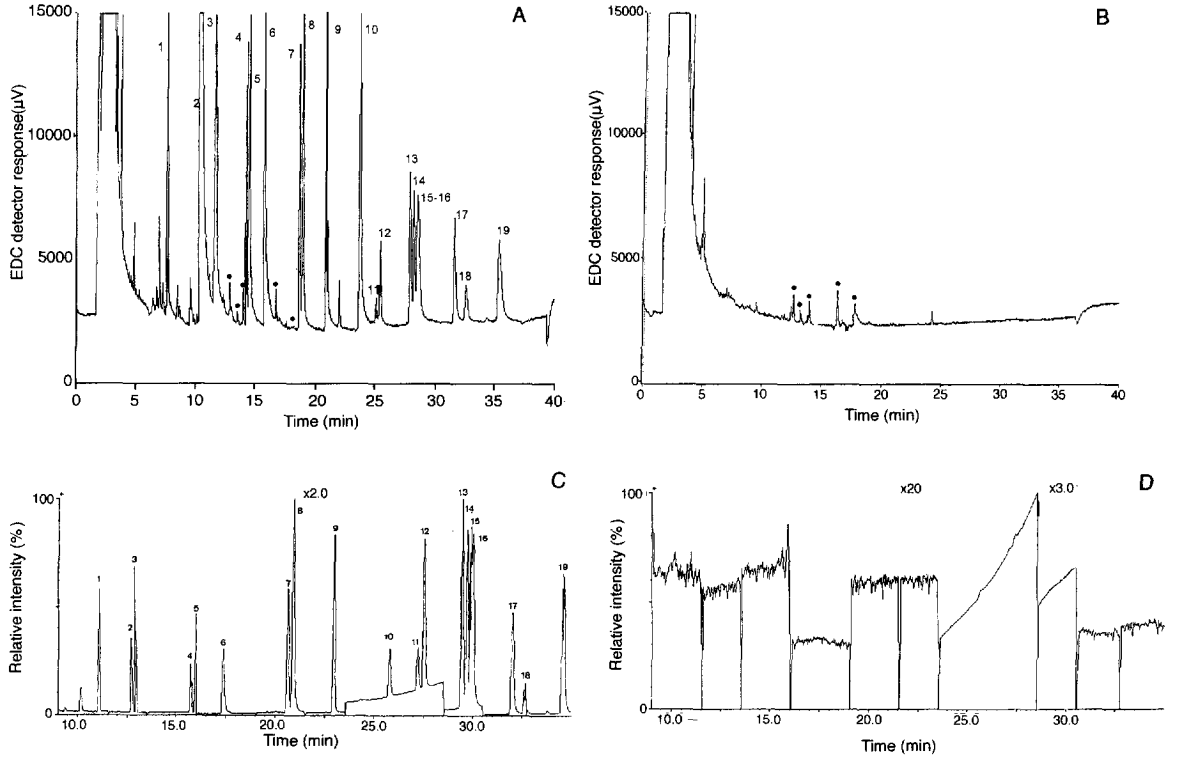

Fig. 1. GC analysis of paprika extracts obtained by MSPD with C_{18} with ECD (A) spiked sample with the 13 pesticides and (B) unspiked sample; and MS (C) spiked sample and (D) unspiked sample. For peak identification see Table 1. ● Unknown peaks.

Table 2
Percentage of pesticides recovered from GCB sorbent material using MSPD and liquid–solid phase partitioning (LSPP)

Pesticide	Recovery±R.S.D.[a] (%)											
	Paprika		Lettuce		Tomato		Orange		Apple		Pear	
	MSPD	LSPP	MSPD	LSPP	MSPD	LSPP	MSPD	LSPP	MSPD	LSPP	MSPD	LSPP
Bromopropylate	90±4	51±6	84±6	50±8	88±8	50±9	82±7	50±10	81±5	54±5	87±5	54±9
Chlorpyriphos methyl	72±4	62±6	63±5	56±8	73±4	61±6	77±4	55±7	74±4	53±7	81±3	57±4
Cypermethryn I	58±6	50±7	68±5	48±9	64±6	54±6	67±6	48±14	63±5	49±9	61±4	47±5
Cypermethryn II	59±8	51±5	60±4	57±5	56±7	52±7	65±7	52±9	56±7	57±7	66±5	52±6
Cypermethryn III	57±3	49±5	64±7	50±8	69±5	46±12	62±5	50±7	64±7	50±8	63±5	58±4
Cypermethryn IV	59±4	48±5	63±7	48±8	58±7	47±8	60±9	43±10	70±5	43±8	70±2	47±9
Deltamethryn	40±5	25±15	42±6	47±8	44±7	40±7	46±3	38±9	43±3	42±6	43±2	48±9
Fenarimol	107±6	57±7	84±7	59±6	92±9	55±9	88±5	56±5	81±2	57±9	75±5	58±5
Fenvalerate I	50±5	27±12	60±4	47±9	63±2	39±6	62±6	48±9	43±5	54±9	68±5	55±6
Fenvalerate II	52±8	30±18	65±5	40±5	65±3	40±7	56±3	42±3	53±4	45±8	52±6	48±7
Imazalil	105±9	62±5	91±5	58±8	94±7	56±14	94±4	56±9	95±9	55±8	85±8	50±9
Lindane	60±9	45±9	60±6	32±12	62±9	46±9	60±5	44±8	63±8	42±10	65±5	41±8
Permethryn I	56±8	27±12	55±7	31±11	59±6	38±7	61±9	36±10	65±7	35±9	64±4	42±10
Permethryn II	59±7	30±18	66±9	43±8	68±7	40±8	57±5	40±8	67±9	46±8	67±7	47±9
Phentoate	57±6	59±7	59±7	58±6	63±8	57±12	56±9	51±8	55±10	59±9	59±10	54±13
Procymidone	82±6	71±6	77±5	68±14	73±9	65±15	75±4	67±5	71±5	68±9	69±2	57±14
Propiconazole I	101±5	57±6	81±6	55±9	80±5	56±14	86±8	56±10	88±9	57±12	86±5	55±9
Propiconazole II	85±7	50±4	73±8	51±8	79±5	58±10	76±6	55±16	71±10	53±9	76±15	53±15
Vinclozoline	65±6	64±8	64±6	56±16	63±8	58±15	64±5	56±15	60±16	55±15	65±14	50±8

[a] $n=5$.

sample extracted by MSPD. Although no interfering peaks were observed on the chromatograms of the unspiked extracts obtained under the selected conditions (Fig. 1B and D), some matrix peaks are observed when they are analyzed with ECD. This has been reported in the previous study [21]. However, these peaks do not interfere with the selected pesticides.

The chromatograms of the spiked samples (Fig. 1A and C) demonstrated that the pesticides eluted separately with the selected column. Thus, permethryn, propiconazole and fenvalerate consist of two isomers (*cis*- and *trans*-) and cypermethryn a composite of four isomers (*trans*-D/*cis*-A/*cis*-B/ and *trans*-C), were eluted separately in their isomeric peaks.

Chromatograms obtained for the other matrices and by liquid–solid phase partitioning are similar to those reported in Fig. 1 for the MSPD procedure, showing a satisfactory clean-up of the sample extract.

The results obtained with GCB are given in Table 2. The mean recoveries of the different pesticides in the crops were 35–107% using MSPD and 25–72% by liquid–solid phase partitioning. Comparison of Tables 1 and 2 indicate that GCB retains stronger than C_{18} the studied compounds. In fact, the recommended eluent for GCB extractions are mixtures of dichloromethane–methanol but with them the pyrethroids were not recovered. However, toluene, which has stronger desorption capabilities and has been employed as eluent for carbon clean-up of extract that contain pyrethroids [25], obtained acceptable results. As it can be observed in Table 2, the lowest recoveries are reported for pyrethroids and this might be due to the anomalous behaviour

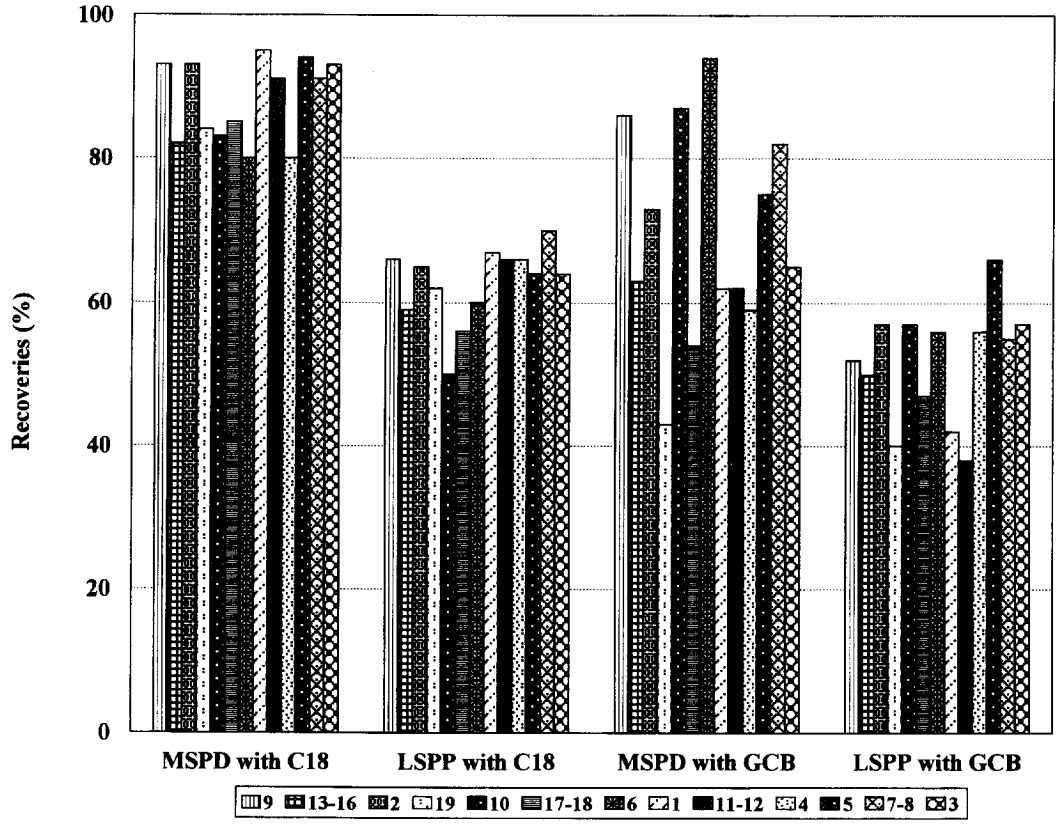

Fig. 2. Comparison of the recoveries obtained by the four extraction methods used in this study. For peak identification see Table 1.

Table 3
LODs, selected ions and MRLs legislated by the EU

Pesticide	LOD (mg/kg)		Selected ions *m/z*	MRLs (mg/kg)
	ECD	MS		
Bromopropylate	0.02	0.02	185, 341	1.00–3.00
Chlorpyrifos methyl	0.02	0.01	286	0.05–0.50
Cypermethryn	0.20	0.05	183, 207	0.50–2.00
Deltamethryn	0.05	0.02	181	0.05–0.50
Fenarimol	0.02	0.05	183, 207	0.02–0.20
Fenvalerate	0.02	0.05	274	0.05–0.50
Imazalil	0.05	0.02	167	0.05–2.00
Lindane	0.02	0.05	215	0.02–5.00
Permethryn	0.05	0.02	109, 181	0.50–2.00
Phentoate	0.05	0.02	183	0.50–2.00
Procymidone	0.02	0.02	283	0.02–5.00
Propiconazole	0.02	0.05	173, 259	0.05–0.20
Vinclozoline	0.02	0.01	212	0.05–5.00

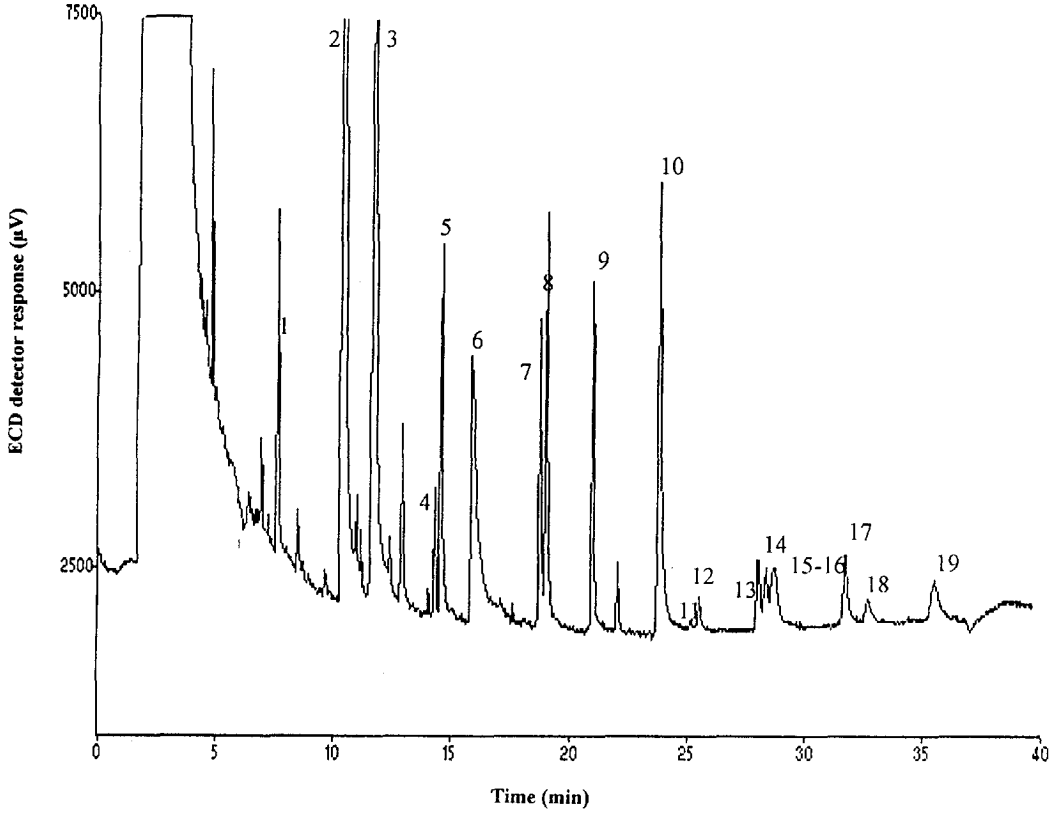

Fig. 3. ECD chromatograms obtained by liquid–solid phase partitioning with GCB of a lettuce sample spiked with the 13 pesticides at levels 10 times lower than in the previous chromatogramns. For peak identification see Table 1.

reported by different authors for these pesticides [11,24]. Further study is required to determine the reason for the poor recovery of pyrethroids.

Summarizing, recovery results for fruit and vegetables with the materials and methods employed are clearly represented (for fruit and vegetables) in Fig. 2. The high efficiency of MSPD with C_{18} for the larger part of compounds studied can be clearly observed, comparing the recovery data with those obtained with GCB. However, similar results are obtained for bromopropylate, fenarimol, imazalil, procymidone and propioconazole with both solid phases by MSPD extraction procedure. The recoveries of residues decrease if liquid–liquid partitioning is used, specially with the GCB.

The limits of detection (LODs) were calculated for the MSPD procedure with C_{18}, after the whole processing of fruit and vegetable samples by a conventional method (signal-to-noise ratio=3). They were obtained by measuring peak heights determined after the extraction spiked with a ten times diluted stock solution and are shown in Table 3. As can be observed, they were well bellow of the MRLs set by the EU. Fig. 3 shows an example of the lettuce

Table 4
Content of pesticide residues in fruit and vegetable samples expresed as mg/kg

Commodity	Sample	Pesticide residue	C_{18}		GCB	
			MSPD	LSPP	MSPD	LSPP
Paprika	1	Chlorpyrifos methyl	0.04	0.03	0.03	0.02
		Fenarimol	0.02	0.02	–	–
	2	Imazalil	4.00	2.60	4.10	2.00
		Bromopropilate	0.90	0.90	0.90	0.20
	4	Vinclozoline	0.20	0.20	0.20	0.10
		Imazalil	0.66	0.50	0.68	0.32
		Cypermethryn	14.0	10.1	8.20	7.50
	5	Permethryn	3.00	2.00	1.50	–
		Cypermethryn	20.0	10.2	10.2	7.00
	8	Cypermethryn	0.80	0.50	0.50	0.10
	9	Lindane	0.35	0.20	0.19	–
		Chlorpyrifos methyl	0.04	0.02	0.02	–
		Vinclozoline	9.60	4.60	8.20	4.00
		Propiconazole	0.20	0.10	0.20	0.08
		Fenarimol	0.09	0.05	0.005	–
		Cypermethryn	0.60	0.50	0.40	0.30
Lettuce	1	Lindane	0.04	–	–	–
	4	Fenarimol	0.08	0.05	0.07	–
Tomato	1	Lindane	0.33	0.25	0.18	0.10
		Propiconazole	0.20	–	–	–
	5	Fenarimol	0.05	–	0.03	–
Apple	3	Chlorpyrifos methyl	0.08	0.05	0.04	–
		Imazalil	0.50	0.27	0.45	0.19
	4	Vinclozoline	0.90	0.80	0.80	0.40
Pear	2	Vinclozoline	0.06	–	–	–
Orange	1	Fenarimol	0.02	–	–	–
	2	Chlorpyrifos methyl	0.90	0.80	0.70	–
		Imazalil	18.73	11.47	17.20	10.00
	4	Procymidone	0.64	0.39	0.60	0.27
		Cypermethryn	2.90	1.00	1.20	0.50

sample spiked with thirteen pesticides in the range of 10–200 mg/kg by means of liquid–solid phase partitioning with GCB, which provided the worst results. Table 3 and Fig. 3 indicate that LODs lower than MRLs can be expected even for the less efficient situation.

As the results demonstrate, the sample matrix does not influence the recoveries of pesticides significantly. The reason may be that the composition of crops studied is very similar, lipid and protein content range between traces 0.3% and 0.4–1.5%, respectively [26]. Main differences between the composition of fruit and vegetables were found in the carbohydrate and water content which were 9–12% and 86–89% for fruit and 1–4% and 94–95% for vegetables [26]. Moreover, water content and texture of plant material may vary depending on the varieties and cultivate areas, as well as on maturity of the crops. Because of this, the variability of the same fruit or vegetable composition is great at the same time as the differences between them are not sufficient to have incidence on the procedure extraction efficiency.

These methods were applied to the determination of the pesticides in fruit and vegetables obtained from a local market in different days. In Table 4, the residue data for the analysis of ten paprika samples and five samples of the other crops are summarized. Samples were analyzed by the four extraction methods.

Firstly, the identification of the compounds was performed by ECD comparing the retention times of the standards and the peaks. Peak confirmation is necessary because the chromatograms of real samples can present peaks corresponding to other contaminants or endogenous compounds which elute at the same retention times as the studied compounds. In order to confirm the pesticide identification, MS in the SIM mode, as reported in Table 3, is used.

Furthermore, the identity of each suspected pes-

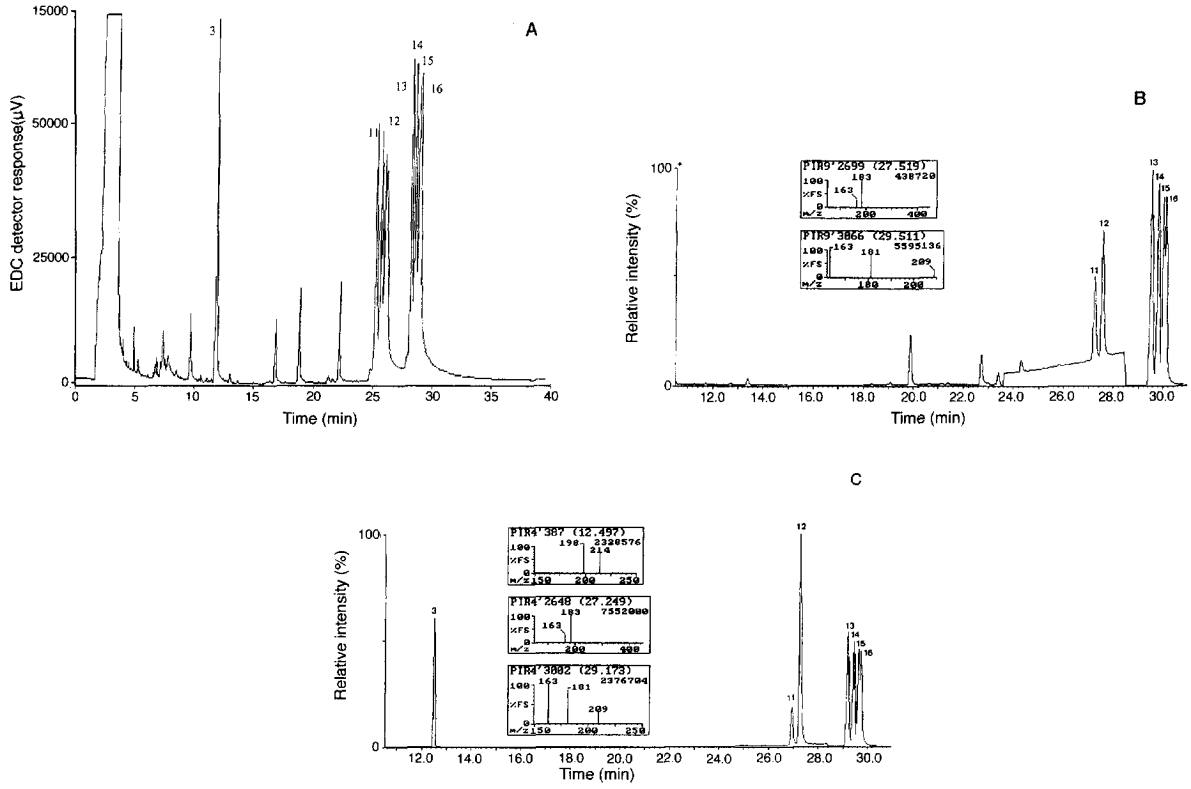

Fig. 4. Chromatograms obtained by MSPD with C_{18} of paprika sample. (A) ECD chromatogram, (B) MS-SIM chromatogram and (C) standard of the suspected compounds. For peak identification see Table 1.

ticide was studied by comparing a larger number of selected ions or, if the concentration found allows it, a full scan mass spectrum obtained, with those of the standards as recommended in the literature [17,25] for complex samples.

An example of the results for a real paprika and orange sample are presented in Figs. 4 and 5. Fig. 4A illustrates the ECD chromatogram. Permethryn and cypermethryn were safely detected by ECD, and vinclozoline also seems to be identified. Fig. 4B and C show the MS chromatograms obtained with the SIM program developed for this sample of it and a standard of similar concentration of the three compounds. Cypermethryn and permethryn were confirmed by two and three indicative ions, respectively, with their calibrated intensity rations. As can be observed, the identification of vinclozoline is erroneous.

Fig. 5A and B recognized in ECD and MS the presence of chlorpyrifos methyl and imazalil. Confirmation was performed by GC–MS in full scan spectrum mode. As expected, an automatic search in the NBS Pesticide Library gave positive results and the identification is unambiguous.

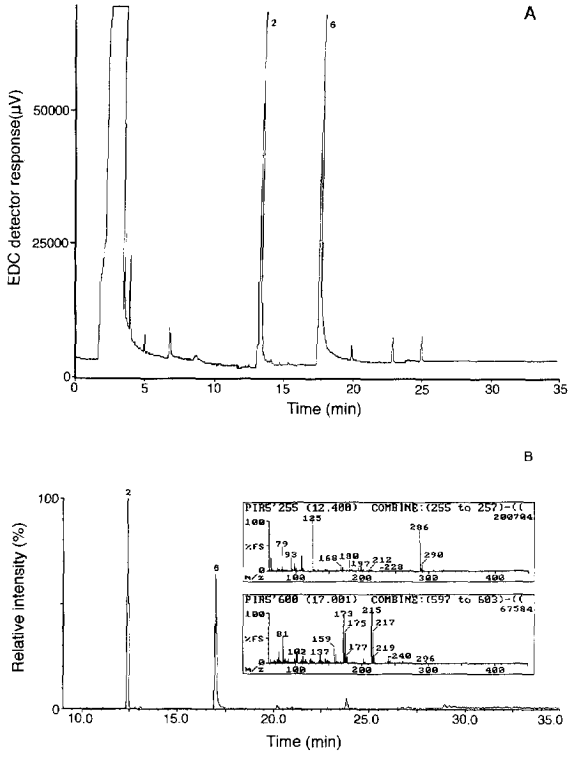

Fig. 5. Chromatograms obtained by MSPD with C_{18} of orange sample (A) ECD chromatogram and (B) MS-scan chromatogram. For peak identification see Table 1.

With regard to the results of the real samples, it is interesting to note the high levels found of imazalil and cypermethryn. Imazalil is used as post-harvest fungicide and its levels are high but still near to the MRLs. However, the levels of cypermethryn are extremely high (about ten times the MRLs) in two paprika samples, which are not fit for human consumption and should be withdrawn from trade. The results highlight the need to establish residue monitoring programs to guarantee the consumer's health.

4. Conclusions

This study has shown that, for extracting pyrethroid insecticides and other selected pesticides from fruit and vegetables, MSPD with two types of sorbents C_{18} and GCB is more effective than liquid–solid phase partitioning. In particular, C_{18} has a better extraction efficiency than that of GCB, which seems to over-retain non-polar compounds.

In order to obtain the highest efficiency, MSPD with C_{18} is the method of choice. The results showed good performance of the analytical protocol with fruits and vegetables. For the pesticides studied employing ECD and MS in the SIM mode, detection limits in the range of μg/kg are attainable. The MSPD method described is relatively simple, rapid and economical, and is suitable for multi-residue analysis for pyrethroid insecticides, fungicides and other chemical structures with insecticide activity.

Its application to real samples proves unmistakably the importance of the inclusion of the studied compounds in general multi-residue procedures to protect the consumer's health.

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