Semiautomatic method for the screening and determination of 23 organochlorine pesticides in horticultural samples by gas chromatography with electron-capture detection

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Abstract

A rapid, simple, efficient device for the extraction–preconcentration of 23 organochlorine pesticides currently applied to vegetables is proposed. Pesticide residues are extracted from chopped samples by using a mixture of distilled water and light petroleum (1:1, v/v). After phase separation, an aliquot of the organic layer is continuously evaporated to dryness under a N_2 stream as it is dropped into a glass tube containing distilled water. The aqueous phase, containing the analytes, is then passed through a miniaturized RP-C_{18} column for preconcentration, clean-up and subsequent elution with 150 µl of ethyl acetate. A volume of 1 µl of the extract containing pesticides is injected into the gas chromatograph, fitted with an electron-capture detector, for their selective determination. Limits of detection vary between 0.04 and 10 ng/ml, with linear ranges from 0.2 to 500 ng/ml; the average relative standard deviation at the low nanogram-per-millilitre level is 5.3%. The potential of the proposed method was realized by applying it to the screening/determination of organochlorine pesticides in horticultural commodities. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Public concern over pesticide residues has risen over the past decade to the point where it has become a significant food safety issue. This concern has materialized in the joint issuance by the European Union and the governments of its member countries of maximum recommended limits (MRLs) for pesticide residues in a variety of agricultural foods [1]. Analytical methods for pesticide residues are mainly used to control foods for human consumption (particularly fruits and vegetables, which usually receive direct applications of pesticides) [2]. Organochlorine pesticides (OCPs) are of special interest in this context as their high chemical stability results in their persistence and bioaccumulation in the environment and animal tissues [3]. Sensitive, rapid, reliable methods for the routine determination of OCP residues in fruit and vegetables are thus much needed. The high sensitivity required arises from the need to meet established MRLs which can be as low as 10 µg/kg depending on the particular pesticide and sample type [1].

The more frequently used methods for analysing

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OCP residues involve gas chromatographic separation and selective detection by electron-capture [4–9], electrolytic conductivity [9–11], atomic emission [9,12] detectors or mass spectrometry for confirmation of positives [4,13,14]. However, these detectors are inadequately selective in many cases and several extraction and clean-up steps are required to avoid deterioration of the chromatographic column. Methods involving sample preparation for OCP determination have been developed for different types of matrices. In most cases, the analytes are extracted by using large volumes of organic solvents such as ethyl acetate [4,7,8], acetone [5,10], 2-propanol–petroleum ether [6] or acetonitrile [9,11–14]. At present, multiresidue solvent extraction with ethyl acetate is superseding earlier extraction methods by virtue of its simplicity and expeditiousness, which result in decreased costs. However, this solvent also extracts a number of indigenous compounds present in most agricultural commodities [4]; in this regard, the use of solid-phase clean-up in combination with selective liquid–liquid back-extractions is recommended to diminish the presence of potential interferents in the final extract [4,6,9]. In any case, evaporation to dryness is needed to preconcentrate the analytes and make them compatible with the chromatographic system, taking into account that no losses are observed for these compounds.

The purpose of this work was to develop a simple, efficient one-step extraction method for the screening and determination of organochlorine pesticides in vegetables. After manual extraction of the chopped sample, the extract is cleaned-up, preconcentrated and eluted on a short RP-C_{18} column, all on-line; in this way, up to 23 OCP residues can be identified and determined. The high preconcentration factor achieved enables the determination of pesticide residues at their MRLs.

2. Experimental

2.1. Chemicals, standards and samples

All chemicals and sorbents were of analytical grade or better. The following organochlorine pesticides, Pestanal quality, were studied: aldrin, captan,

captafol, chlorbensid, chlordane, dichlofuanid, dicloran, dicofol, dieldrin, α- and β-endosulfan (3:1, w/w), endosulfan sulphate, endrin, hexachlorobenzene (HCB), heptachlor, iprodione, α-, β-, δ- and γ-hexachlorohexane (α-, β-, δ- and γ-HCH 1:1:1:1, w/w), lindane (γ-HCH), methoxychlor, procimidone, and vinclozolin, all of which were obtained from Riedel–de Haën (Seelze, Germany). 2,4-Dichlorophenol (internal standard), and RP-C_{18} HPLC sorbent were supplied by Sigma (Madrid, Spain). All other reagents and solvents [ethyl acetate, acetone, dichloromethane, light petroleum (b.p. 50–70°C), ethanol and sodium sulphate] were purchased from Merck (Darmstadt, Germany).

Stock standard solutions of the OCPs were prepared in acetone (except HCB, which was dissolved in dichloromethane), at concentrations of 5 mg/ml, and stored in glass stoppered bottles in the dark at 4°C.

Vegetables were purchased at a local market in Córdoba, Spain. Because legally tolerated limits of pesticide residues have been set for raw materials, samples were analysed unwashed and in the raw state [15].Sampling was done according to the protocol established by legislation [16]. Thus, a raw sample consisting of 10–20 units (ca. 1 kg) was initially selected and subsequently reduced to 3–5 units following the most appropriate procedure (mainly quartering). These units are then cut into slices about 1 cm thick and then chopped into smaller pieces to obtain the 5 g fractions required by the proposed method.

2.2. Apparatus

Experiments were carried out by using a Hewlett–Packard 5890A gas chromatograph equipped with a [63]Ni electron-capture detection (ECD) system. Chromatographic separation was achieved by using a fused-silica capillary column (30 m×0.25 mm I.D.) coated with 5% phenyl-methylpolysiloxane (film thickness 0.25 μm) (Supelco, Madrid, Spain). Peak areas were measured with a Hewlett–Packard 3392 A integrator. The injector and detector temperatures were kept at 225°C and 325°C throughout. The column temperature was raised from 120°C (hold 2 min) to 180°C (hold 4 min) at 8°C/min, then to

255°C (hold 10 min) at 8°C/min and finally to 270°C (hold 2 min) at 10°C/min.

Two Gilson Minipuls-2 peristaltic pumps fitted with poly(vinyl chloride) and Solvaflex pumping tubes for aqueous solutions and ethanol, respectively, were employed. Two Rheodyne 5041 injection valves, PTFE tubing and commercially available connectors were also used. The sorbent column was prepared by packing a commercial Omnifit glass column (2 cm×2.5 mm I.D.) with ca. 40 mg of RP-C$_{18}$ sorbent material; small cotton beads were used on the ends to prevent material losses. The sorbent column was conditioned with distilled water for 3 min prior retention. An Omnifit 3303 PTFE filter furnished with a paper disk (Whatman No. 1) was used to filtrate the organic phase; the filter was modified by using circular channels in both ends to increase the chamber inner volume to 100 μl and the filtration area to ca. 3 cm^2. It was washed upstream with water after ca. 5 analyses.

2.3. Procedure

The flow system designed for the determination of OCPs is depicted in Fig. 1. An amount of 5.0 g of chopped sample was placed in a extraction funnel and 50 ml of the extractant (distilled water–light petroleum 1:1, v/v) were added. The mixture was mechanically shaken for ca. 10 min and allowed to settle for 2–3 min. Then, the organic phase, containing the analytes, was continuously aspirated for 5 min (5 ml) and filtered; the filtrate was collected in a 10 ml graduated glass tube containing 5 ml of distilled water and evaporated to dryness under a N$_2$ stream as it dropped into the tube; also, bubbling N$_2$ in the tube favoured homogenization of the solution. As P$_1$ was stopped and P$_2$ started, the aqueous solution was aspirated at a flow-rate of 0.5 ml/min and passed through the RP-C$_{18}$ sorbent column, located in the loop of an injection valve (IV$_1$). Simultaneously, the loop of the second injection
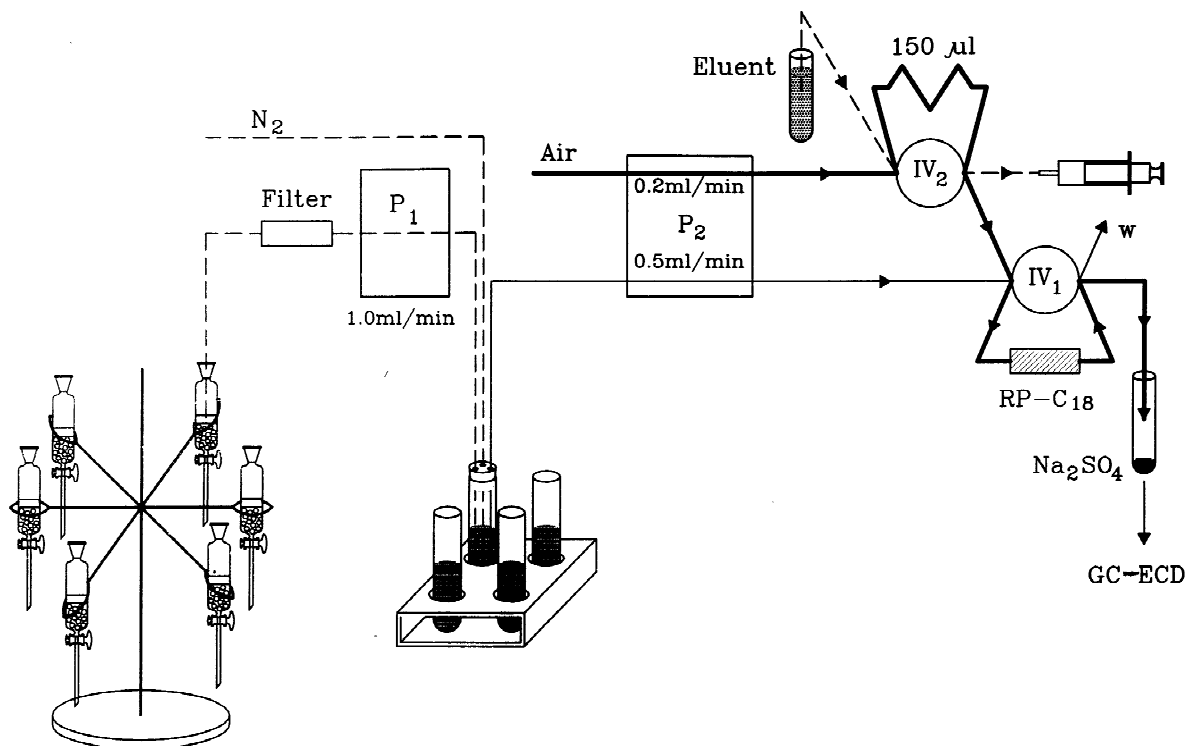

Fig. 1. Experimental set-up used for the screening and determination of OCPs in horticultural samples. P=peristaltic pump; IV=injection valve; W=waste; GC–ECD=gas chromatography–electron-capture detection.

valve (IV_2) was filled with eluent (ethyl acetate) containing the internal standard (1 μg/ml 2,4-dichlorophenol) by means of a syringe. On switching both injection valves, the loop contents were carried by an air stream at a flow-rate of 0.2 ml/min. The eluent was passed through the column and eluted analytes collected in a glass vial containing anhydrous sodium sulphate. A 1 μl aliquot of the dried solution was injected into the GC–ECD system for analysis. The organic phase remaining in the funnel can be sequentially aspirated into the flow system in order to perform replicate analyses per sample. After each sample, the sorbent column was washed with 3 ml of ethanol to remove potentially adsorbed interferents and then conditioned with 3 ml of water. To simplify tube changeover during the evaporation step (see Fig. 1), a cylindrical piece of PTFE tubing with three small holes for insertion of the three channels and a larger one to allow solvent evaporation was used. The tubes were washed with water between samples to avoid contamination.

3. Results and discussion

3.1. Clean-up and preconcentration device

Preliminary experiments were carried out in order to find the best sorbent and eluent for the solid-phase extraction (SPE) system. For this purpose, RP-C_{18}, Amberlite XAD-2, Florisil, silica gel, alumina, Li-Chrolut-EN and activated carbon were tested. First, the adsorption efficiency was examined by using columns packed with 70 mg of each sorbent material. The aqueous solution, containing ca. 0.3 μg/ml of OCPs, was aspirated at 0.5 ml/min through each column. Fractions of 1 ml sample were collected in glass vials before and after the sorbent column and extracted with 1 ml of ethyl acetate; after evaporation to dryness under N_2, the residue was redissolved in 200 μl of ethyl acetate, a 1 μl aliquot of the extract being analysed by GC. After each sample was processed, the column was rinsed with ethyl acetate and water for 1 min to remove potentially adsorbed analytes. High retention (>80%) was obtained in all instances; however, activated carbon, silica gel and RP-C_{18} exhibited the best sorption properties. Different eluents (ethyl acetate, *n*-hexane

and light petroleum) were evaluated with the three sorbents. Incomplete elution was obtained with activated carbon (<10%) and silica gel (<50%) whichever the solvent. RP-C_{18} was thus selected as it exhibited optimal sorption and desorption properties. Ethyl acetate was the best eluent (ca. 100% elution), if even surpassed *n*-hexane and light petroleum supplied with 2-propanol in order to increase their polarity. The amount of sorbent material was optimized by varying the length of the column (packed with 20–80 mg of RP-C_{18}). Chromatographic signals increased with increasing amount of sorbent up to 30 mg, beyond which they remained virtually constant. A working column packed with 40 mg RP-C_{18}, and ethyl acetate as eluent, were adopted for further experiments.

Optimization experiments were carried out by aspirating 5 ml of a standard solution containing 20–60 ng/ml of each OCP in distilled water, into the SPE system. The eluate from the sorbent column (200 μl) was collected in 5 ml glass vials containing anhydrous sodium sulphate and 1 μl fractions were injected into the chromatograph.

The influence of the sample pH was studied over the range 1–11, using aqueous standards adjusted with HNO_3 or NaOH solutions. Pesticides exhibited three distinct types of variation in this respect. Thus, lindane, α-, β- and δ-HCH, captafol, chlordane, dichlofuanid, dicloran, dicofol, endosulfan sulphate and methoxychlor were not affected by pH over the range studied. On the other hand, aldrin, chlorbensid, dieldrin, endrin, HCB and heptachlor were optimally retained under weakly alkaline conditions, whereas captan, α- and β-endosulfan, iprodione, procimidone and vinclozolin were best extracted in a weakly acidic medium. Some of these compounds, however, decompose in the alkaline medium [17] and give spurious results. For this reason, and taking into account the poor retention of some under acid conditions, the pesticides were prepared in distilled water prior to continuous SPE as a compromise.

The effect of the sample flow-rate through the column during the preconcentration step was studied between 0.3 and 0.9 ml/min. Signals remained almost constant throughout this range; exceptionally, the signals for chlorbensid and α- and β- endosulfan decreased above 0.6 ml/min. A flow-rate of 0.5 ml/min was selected for all OCPs. The effect of the

eluent (ethyl acetate) flow-rate was studied over the range 0.1–0.5 ml/min, using an air stream as carrier. Chlorbensid and dicloran elution was markedly affected by the eluent flow-rate; in fact, a very low flow-rate was required to ensure efficient elution, so 0.2 ml/min was chosen. The influence of the eluent volume was studied by changing the loop of IV_2. Obviously, as the eluent volume was increased, desorption was more efficient but also the analytes were more dilute. Because of these two opposing effects, the only way to correctly determine the most appropriate eluent volume was to dilute the extracts to a constant volume using the same solvent. Thus, the column effluent (between 50 and 500 μl of ethyl acetate) was always diluted to 500 μl with ethyl acetate. The desorption efficiency increased with increasing injected volume up to 150 μl and remained constant above this value. An ethyl acetate injected volume of 150 μl was selected as optimal. A second injection with the same eluent volume revealed the absence of carry-over; complete elution of analytes was thus obtained with a single injection of 150 μl of ethyl acetate.

3.2. Analytical figures of merit

All the pesticides studied exhibited good gas chromatographic properties and could be identified in a direct manner as they were well resolved under these chromatographic conditions. Analytical curves for standards of organochlorine pesticides were obtained by using the SPE system depicted in Fig. 1 and passing 5 ml of aqueous standards containing variable concentrations (0.1–500 ng/ml) of the pesticides through the sorbent column. The curves were constructed by plotting the analyte-to-I.S. peak area ratio against the analyte concentration. 2,4-Dichlorophenol was used as I.S. in preference to others because it was found to be compatible with the chromatographic behaviour of the analytes as well as with ECD; it was added to the eluent at a concentration of 1 μg/ml. The results obtained are listed in Table 1. All the OCPs tested fitted a straight line with a correlation coefficient of 0.990–0.999. Limits of detection, calculated on the basis of a signal/noise ratio of 3/1 are also given in Table 1. The lowest was that of dicloran (the most sensitive). For the other pesticides, they ranged from 0.2 to 0.5

ng/ml. The slighty broadened peak for iprodione resulted in the highest detection limit (10 ng/ml); in any case, its MRL in agricultural commodities ranges from 20 ng/ml to 10 μg/ml, so there should be no problem to detect it.

The within-day precision (repeatability), expressed as relative standard deviation, was calculated for 11 standards containing 20–60 ng/ml of each OCP in water. The precision obtained was acceptable for all the compounds, the average being 5.3%.

3.3. Screening and determination of OCPs in horticultural samples

The main purpose of this work was to develop an extraction procedure, as simple as possible, that would allow both quantitative extraction and preconcentration of OCPs from samples and clean extracts from a variety of horticultural commodities. In order to select the best possible extractant, different samples of 5.0 g of chopped lettuce (test sample) were spiked with 500 ng of the pesticides and allowed to stand overnight to simulate the weathering process. Then, 25 ml of extractant were added to each test sample and the mixture was mechanically shaken for 10 min. An aqueous medium of variable pH was initially tested for extraction prior to direct insertion into the manifold; the recoveries thus obtained were all below 40% (due to their poor solubilities in water). Therefore, acetone, acetonitrile, ethyl acetate and light petroleum were assayed as extractants because they are common organic solvents for these samples [4–14]. As the extract also contained other compounds present in the sample and the sorption of OCPs on the column was only achieved in aqueous media, several additional steps were required prior SPE preconcentration. Four 5 ml aliquots of the organic phases were evaporated to dryness under N_2 and the residue was redissolved in 5 ml of distilled water for continuous introduction into the SPE system. Although high recoveries were obtained in all cases, light petroleum diminished the presence of peaks due to the matrix; also, the time required for evaporation of the acetone or acetonitrile phases was too long, probably due to the presence of a large amount of co-extractives (mainly natural pigments), which resulted in dirtier chromatograms. Light petroleum as extractant is also advantageous

Table 1
Figures of merit for the determination of 23 organochlorine pesticides using an SPE system

Compound	Detection limit (ng/ml)	Regression equation[a]	Linear range (ng/ml)	RSD (%)
α-HCH	0.3	$y=5.8\times10^{-2}x+6\times10^{-3}$	1–200	5.2
HCB	0.4	$y=3.8\times10^{-2}x+7\times10^{-3}$	2–200	4.7
Dicloran	0.04	$y=2.3\times10^{-1}x+2\times10^{-2}$	0.2–100	4.7
β-HCH	0.4	$y=6.7\times10^{-2}x+2\times10^{-3}$	2–200	4.3
Lindane	0.2	$y=9.4\times10^{-2}x+7\times10^{-3}$	1–200	5.2
δ-HCH	0.2	$y=1.2\times10^{-1}x+3\times10^{-3}$	1–200	4.0
Vinclozolin	0.2	$y=1.2\times10^{-1}x+2\times10^{-3}$	1–200	5.8
Heptachlor	0.4	$y=3.3\times10^{-2}x+7\times10^{-3}$	2–200	5.4
Dichlofuanid	0.5	$y=6.1\times10^{-2}x+7\times10^{-3}$	2–200	5.9
Aldrin	0.2	$y=6.0\times10^{-2}x-2\times10^{-3}$	1–200	5.6
Dicofol	1.0	$y=1.1\times10^{-2}x+2\times10^{-3}$	5–400	4.3
Captan	0.3	$y=1.4\times10^{-1}x-4\times10^{-3}$	1–200	5.5
Procimidone	0.4	$y=6.2\times10^{-2}x+2\times10^{-3}$	2–200	6.0
Chlorbensid	1.0	$y=1.7\times10^{-2}x+2\times10^{-3}$	5–400	5.1
Chlordane	2.0	$y=5.0\times10^{-3}x+1\times10^{-4}$	10–500	5.2
α-Endosulfan	0.4	$y=3.4\times10^{-2}x+6\times10^{-3}$	2–200	5.4
Dieldrin	0.5	$y=2.3\times10^{-2}x-3\times10^{-3}$	2–200	5.7
Endrin	0.4	$y=2.5\times10^{-2}x-3\times10^{-3}$	2–200	5.9
β-Endosulfan	0.4	$y=2.6\times10^{-2}x+2\times10^{-3}$	2–200	6.0
Endosulfan sulphate	0.4	$y=6.8\times10^{-2}x-3\times10^{-3}$	2–200	5.6
Iprodione	10.0	$y=5.3\times10^{-2}x+2\times10^{-3}$	25–500	5.7
Captafol	0.5	$y=8.9\times10^{-2}x-4\times10^{-3}$	2–200	5.3
Methoxychlor	1.0	$y=1.0\times10^{-2}x+2\times10^{-3}$	5–400	5.1

[a] y, analyte-to-internal standard area ratio; x, concentration (ng/ml).

because it is compatible with the pumping tubes, so it allows the on-line aspiration and simultaneous filtration of the extract in order to prevent solid particles from entering the flow system and clogging the sorbent column. Careful examination of the results, in terms of relative standard deviation of the peak area for each pesticide, revealed that it was much higher than that for the standards. This can be ascribed to the presence of coextractives hindering the redissolution step.

From the previous method, two modifications were introduced in the extraction procedure. One was the use of a mixture of water and petroleum ether as extractant in order to remove potentially interfering water-soluble compounds; the other, avoiding redissolution of the dry residue. The finally adopted extractant was water–light petroleum (1:1, v/v) and the filtered organic phase was evaporated under a nitrogen stream as it dropped into a glass tube containing 5 ml of distilled water. Good precision was obtained by operating in this way so fortified samples were extracted and evaporated as

described above. Finally, the effect of the ratio of amount of sample to extractant volume (w/v) was optimized. For this purpose, different samples of 5.0 g of chopped lettuce were fortified with variable amounts of pesticides depending on the extractant volume, and allowed to stand overnight. Then the samples were extracted with 10, 20, 50 and 100 ml of water–light petroleum (1:1, v/v), respectively. A portion of 5 ml of the organic phase (always containing 500 ng of each OCP) was treated following the procedure described above. Satisfactory results were obtained in all cases, so the sample/extractant ratio can be varied between 2 and 20 ml of extractant per gram of sample with little difference. In order to obtain replicate results, a volume of 50 ml of extractant (ca. 25 ml of extract) was selected. In this way, amounts of 2.5 to 25 g of sample can be extracted with 50 ml of extractant. This operational sequence was the most efficient procedure, and was applied to the determination of OCPs in nine different horticultural commodities.

No samples containing pesticide residues at detect-

Table 2
Percent recovery ($\pm$SD) of organochlorine pesticides added to horticultural samples*

Commodity	Compound	Recovery (%)	Commodity	Compound	Recovery (%)
Onion	Dichlofuanid[c]	95±6	Tomato	Captan	64±3
	Dichloran	87±5		Chlordane	91±5
	Heptachlor	102±6		HCB	100±5
	Procimidone[a]	83±5		α-HCH	96±5
	Vinclozolin	93±6		β-HCH	85±4
				δ-HCH	103±5
Lettuce	Captan	75±4		Lindane	101±6
	Chlordane	92±5		Vinclozolin	93±6
	Dichloran	96±5			
	α-HCH	94±6	Spinach	Endrin	93±6
	β-HCH	93±4		α-Endosulfan[b]	88±6
	δ-HCH	93±5		β-Endosulfan	92±6
	Heptachlor	94±5		Endosulfan Sulphate	97±7
	Lindane	97±6		α-HCH	95±5
	Procimidone[a]	86±6		β-HCH	94±4
				δ-HCH	93±4
Carrot	Aldrin	104±6		Heptachlor	96±6
	Captan	70±4		Lindane	99±5
	Chlorbensid	96±5		Methoxychlor[c]	99±6
	Dicofol[c]	84±4		Vinclozolin	102±6
	Dieldrin	88±6			
	HCB	102±5	Potato	Aldrin	97±6
	Heptachlor	105±7		Chlorbensid	89±5
	Methoxychlor[c]	96±6		Chlordane	86±4
				Dicofol[c]	99±5
Green pepper	Aldrin	97±6		Dieldrin	95±6
	Chlorbensid	79±4		Endrin	100±6
	Dichloran	98±5		α-Endosulfan[b]	96±6
	Dicofol[c]	90±5		β-Endosulfan	102±6
	Dieldrin	97±6		Endosulfan Sulphate	103±7
	Endrin	91±6		HCB	99±5
	α-Endosulfan[b]	93±6		α-HCH	103±5
	β-Endosulfan	104±7		β-HCH	102±4
	Endosulfan Sulphate	96±6		δ-HCH	102±4
	Lindane	100±6		Lindane	103±5
	Procimidone[a]	99±6		Methoxychlor[c]	106±6
	Vinclozolin	93±7			
			Cucumber	Aldrin	112±7
Aubergine	Captafol[c]	81±6		Chlordane	109±6
	Captan	66±4		Dichloran	98±5
	Chlorbensid	91±5		Dieldrin	92±6
	Dicofol[c]	93±5		Endrin	103±6
	HCB	103±6		Lindane	97±6
	Iprodione[d]	94±6		Procimidone[a]	96±6
	Methoxychlor[c]	89±5		Vinclozolin	98±6

*Spiked level was 15 ng/g for all OCPs, except those with superscripts.
[a] (25 ng/g).
[b] (45 ng/g).
[c] (50 ng/g).
[d] (200 ng/g).

able concentrations could be found, so a recovery test was carried out. For this purpose, the analytes were added to each uncontaminated vegetable according to use and occurrence/appearance [15,18]. Since all the pesticides studied are administered by foliar application [18], most of their residues remain on plant surfaces. Therefore, in order to ensure acceptable simulation of the real situation, the fortification process was carried out as follows: 1 ml of acetone containing variable amounts of OCPs between 75 and 1000 ng was added to 5.0 g of chopped sample and allowed stand overnight at room temperature in a closed fume hood to avoid contamination. Each sample was spiked three times and then analysed in triplicate (n=9), using the proposed

method. The recoveries obtained (Table 2) ranged from 64 to 112% and are comparable to or better than those provided by existing methods for the determination of these compounds in horticultural samples. No interference from the matrices studied was observed, which testifies to the high selectivity of the proposed method. By way of example, Fig. 2 shows the gas chromatograms for a spinach sample unfortified and fortified with the OCPs listed in Table 2.

4. Conclusions

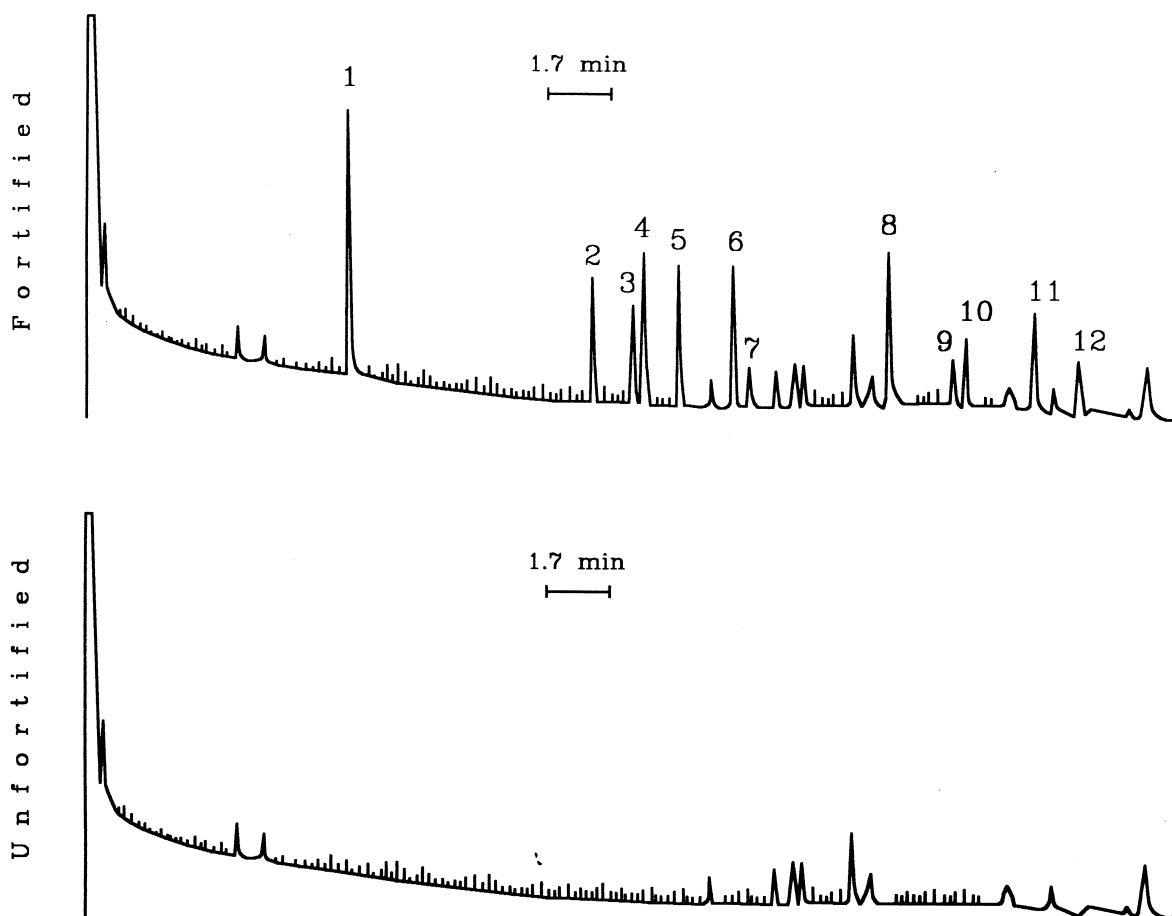A rapid, sensitive method involving semiautomatic

Fig. 2. Gas chromatograms for a 5.0 g sample of spinach unfortified and fortified with 11 OCPs at the concentrations listed in Table 2. 1=Internal standard, 2=α-HCH; 3=β-HCH; 4=lindane; 5=δ-HCH; 6=vinclozolin; 7=heptachlor; 8=α-endosulfan; 9=endrin; 10=β-endosulfan; 11=endosulfan sulphate and 12=methoxychlor.

sample treatment and low solvent consumption was developed and proved effective for the screening of the more commonly used OCPs in the matrices studied. An evaporation step is used to facilitate solvent changeover in order to make the analytes compatible with the SPE system. Liquid–liquid extraction, the most common choice in this context, cannot be used here because back-extraction of the pesticides from petroleum ether to aqueous phase is unfeasible at any pH. The proposed method is an effective alternative to more costly and time-consuming conventional methods, as well as to highly sophisticated clean-up procedures.

Acknowledgements

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