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Simultaneous analysis of 25 pesticides in crops using gas chromatography and their identification by gas chromatography–mass spectrometry

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ABSTRACT

The simultaneous analysis of 25 pesticides in soy beans and rices was performed by gas chromatography with dual electron-capture detection and nitrogen–phosphorus detection. The pesticides were extracted from the samples with solvent and the Bio-Beads S-X3 clean-up procedure was used. Recovery studies were performed at the 1-ppm level of pesticides added to each crop. Their recoveries ranged between 83 and 105% with coefficient of variations of 0.5–8.2%. The gas chromatographic properties of the 25 pesticides were also investigated. Conformation analysis was achieved by the retention time and characteristic fragment ions using the technique of gas chromatography–mass spectrometry–selected-ion monitoring.

INTRODUCTION

The monitoring of pesticides in crops is of importance in public health, because of the inherent toxicity of pesticides. Many analysts have contributed to the methodological development for analysis of pesticide residues in crops. Several chromatographic methods have been reported for the separation, detection and quantitative measurement of pesticides in food [1,2], water [3–5] and soil [6,7]. Published methods include those based on gas–liquid chromatography [8,9], gas chromatography (GC)–mass spectrometry (MS) [10–12], high-performance liquid chromatography (HPLC) [13,14] and liquid chromatography (LC)–MS [15–17].

GC methods have been based on the chemical structure of pesticides containing nitrogen, phosphorus or chlorine atoms, and so high sensitivity has been obtained with electron-capture detection (ECD) and nitrogen–phosphorus detection (NPD). LC systems have been applied to thermally unstable and non-volatile pesticides, which have proved to be difficult to quantify by GC. Many procedures for sample preparation prior to GC analysis have been reported using extraction by organic solvents [18,19], distillation systems [20,21] on column chromatography [22,23]. Recently, Bio-Beads have been widely used in column chromatography for the analysis of samples containing fat and oil [24,25]. Mattern *et al.* [26] described a GC–MS method for detection and quantitation of twelve pesticides in fruits and vegetables. And Roach and Carson [12] reported

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the MS behaviour of organopesticides in food using the collisionally activated decomposition mode.

In this paper, we describe a GC–ECD–NPD procedure for the simultaneous separation and determination of 25 pesticides regulated in our country [27]. Each pesticide was confirmed using GC–MS–selected-ion monitoring (SIM) mode.

EXPERIMENTAL

Chemicals

All reagents were of residual pesticide grade. Acetone, methanol, ethylacetate, hexane and methylene chloride purchased from J.T. Baker (Phillisburg, NJ, USA). Bio-Beads S-X3 (200–400 mesh) for chromatography was from Bio-Rad (Richmond, CA, USA). Purified water was

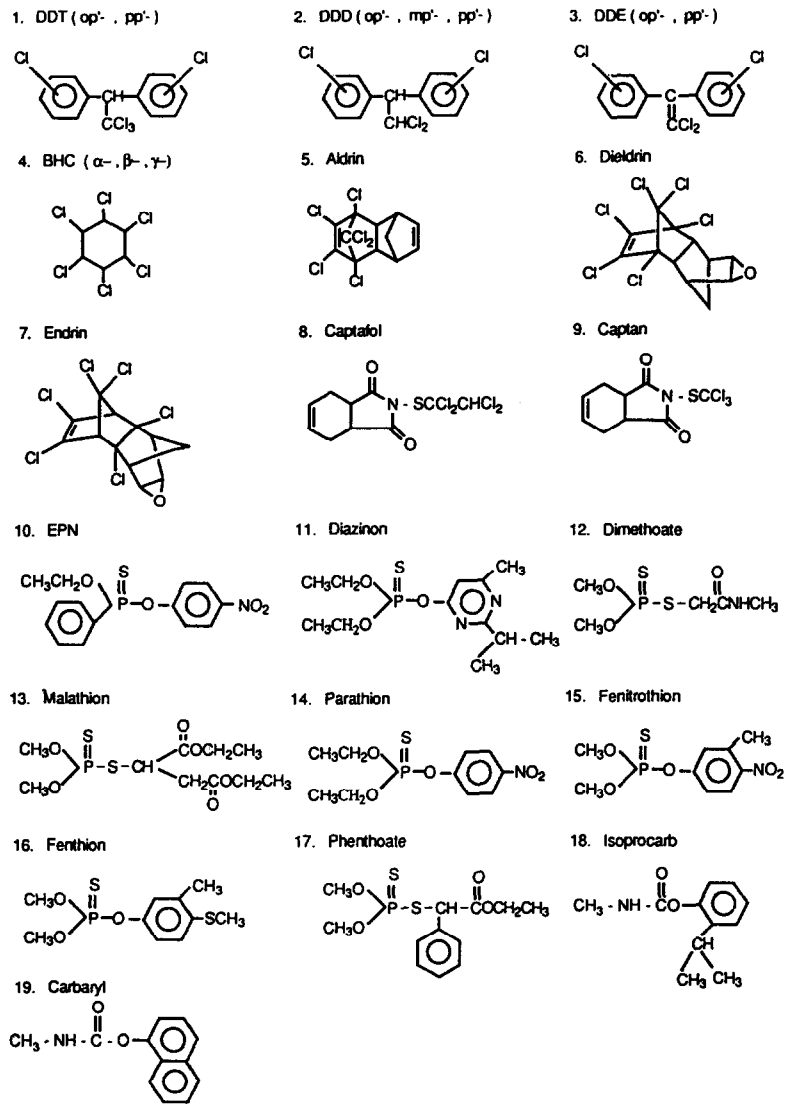

Fig. 1. Chemical structures of pesticides.

obtained with a Milli-Q system (Millipore, USA). Twenty-five pesticide standards were obtained from Chem. Service (West Chester, PA, USA) and from Aldrich (Milwaukee, WI, USA). Standard stock solutions in hexane and acetone were stored at 4°C. Triphenyl phosphate (TPP) and 24,-dichloronitrobenzene (DCNB) from Merck (Darmstadt, Germany) were used as internal standards and dissolved in hexane. The chemical structures of the pesticides tested in this study are shown in Fig. 1.

Gas chromatography

The gas chromatographic analysis was carried out on a Varian Vista 6000/6500 gas chromatograph (Sunnyvale, CA, USA) equipped with a dual nitrogen–phosphorus detector and ^{63}Ni electron-capture detector. A Varian Vista 402 chromatograph data system was used for the data processing. All extracts were injected onto an on-column capillary inlet designed for fused-silica columns. Separation was achieved with an HP-1 capillary column with cross-linked methylsilicone (SE-30, 50 m × 0.32 mm I.D., 0.32 μm film thickness). The capillary column was installed and connected to both detectors via the variable effluent splitter from Varian. The chromatographic conditions were as follows: detector temperature, 280°C, column temperature, 150°C at 6°C/min to 260°C, held for 10 min; carrier gas, nitrogen at a flow of 0.4 ml/min for ECD and 4.0 ml/min for NPD.

Gas chromatography–mass spectrometry

The Hewlett-Packard GC–MS system consisted of a Model 5890A gas chromatograph, a Model 5970B mass-selective detector, an HP 5970C MS Chemstation and an HP 7946 disc drive. A fused-silica capillary column coated with HP-1 cross-linked metylsilicone (SE-30, 25 m × 0.25 mm I.D., 0.17 μm film thickness) was also used. The GC temperature programme was as follows: initial temperature was 100°C, held for 4 min, increased by 8°C/min to 280°C, and held for 5 mins. Samples were injected in the split mode with a splitting ratio of 1:10. The carrier gas was helium (99.999%) at 0.9 ml/min. Injector temperature was 250°C, transfer line temperature was 270°C and ion source temperature was 200°C. The mass spectrometer was operated at 70 eV in the electron-impact (EI) mode using scan or SIM. The selected ion groups for the identification of 25 pesticides in SIM mode are listed in Table I. The dwell time for each ion was set at 50 ms.

Extraction and partitioning

Samples of 25 g were ground and extracted with a mixed solvent of 100 ml of acetone and 50 ml of methanol in a blender jar for 10 min at high speed. The mixture was filtered with suction through a 12-cm Büchner funnel. The filtrate was transferred to a 500-ml round-bottomed flask. The volume of this solution was reduced to about 100 ml by a rotary evaporator and then 50 ml of water and 30 ml of saturated sodium chloride solution added. To this mixture, 100 ml of methylene chloride were added, followed by vigorous shaking in a separatory funnel. The

TABLE I

FOUR ION GROUPS ACCORDING TO RETENTION TIME IN THE SIM MODE

Ion groups	Selected ions
Group A (6 min to 12.5 min)	
Isoprocarb	121, 136
BHC isomers	181, 183, 219
Dimethoate	93, 125
Diazinon	137, 179
Group B (12.5 min to 15 min)	
Carbaryl	144, 115
Fenitrothion	125, 109
Aldrin	66, 263
Malathion	125, 173
Fenthion	278
Parathion	291, 97
Captan	79, 149
Group C (15 min to 17.4 min)	
Phenthoate	274, 121
DDE isomer	246, 248
Endrin, dieldrin	261, 263, 265
DDD	235, 237
Group D (17.4 min to 22 min)	
DDT isomers	235, 237
Captafol	79, 311, 313
EPN	157

extracted organic phase was collected in a 200-ml round-bottomed flask. The aqueous phase was re-extracted with 50 ml of methylene chloride in the same way. The organic phase was combined with the first extract in a 200-ml round-bottomed flask. The organic phase was evaporated to dryness by a rotary evaporator.

Clean-up

Bio-Bead S-X3 was slurried into a 30 cm × 1 cm I.D. column to *ca.* 15 cm height and was washed with 5 ml of methylene chloride–cyclohexane (1:1). Extracted residue was dissolved in methylene chloride–cyclohexane (1:1) and then placed on the column. Methylene chloride–cyclohexane was used as eluent solvent at a flow-rate of 2 ml/min. The eluate was collected in two fractions: the first fraction (9 ml) containing lipids was discarded, while the second fraction (11 ml) was collected and then evaporated under a nitrogen stream. The dried residue was dissolved with 2 ml of hexane.

RESULTS AND DISCUSSION

Analysis by GC–NPD–ECD

GC with dual NPD and ECD in parallel is able to identify residual pesticides and achieve the simultaneous determination of compounds containing chlorine, phosphorus or nitrogen atoms. The GLC separation of 25 standard pesticides on an SE-30 fused-silica capillary column using dual

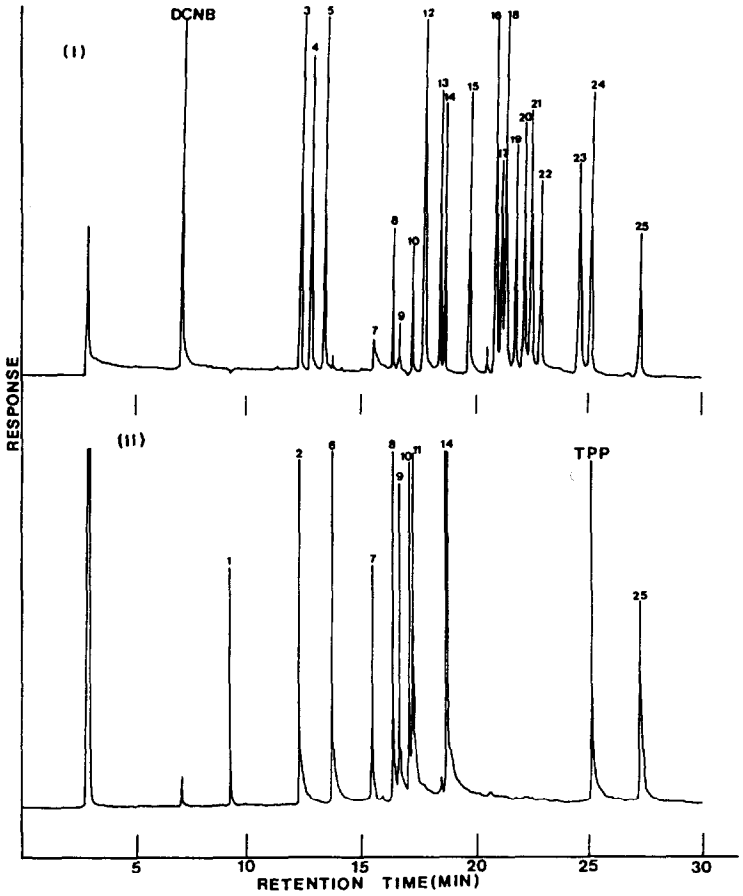

Fig. 2. Dual ECD (I) and NPD (II) chromatograms of 25 standard pesticides. Peaks: 1 = isoprocarb; 2 = dimethoate; 3 = α-BHC; 4 = β-BHC; 5 = γ-BHC; 6 = diazinon; 7 = carbaryl; 8 = fenitrothion; 9 = malathion; 10 = fenthion; 11 = parathion; 12 = aldrin; 13 = captan; 14 = phenthoate; 15 = *o,p'*-DDE; 16 = *p,p'*-DDE; 17 = *o,p'*-DDD; 18 = dieldrin; 19 = *m,p'*-DDD; 20 = endrin; 21 = *p,p'*-DDD; 22 = *o,p'*-DDT; 23 = *p,p'*-DDT; 24 = captafol; 25 = EPN.

NPD and ECD is shown in Fig. 2. As shown in Fig. 2, 25 pesticides were successfully separated within 30 min. Noticeably, each peak exhibited no significant peak tailing. Baseline separation was achieved for each pesticide in the standard mixture. In general, N-methylcarbamates are thermally unstable at the temperatures required for GC analysis. For example, carbaryl and isoprocarb underwent thermal decomposition and lost their carbamates in the hot insert liner, which contained glass beads or OV-101. Typically, 75% of carbaryl and 15% of isoprocarb were converted into naphthol and *o*-isopropylphenol, respectively. So it was difficult to quantify by GC with a hot packed injector. To circumvent this problem, we used the cold on-column injector instead of the hot packed injector in GC and used the split liner which contained only the silanized glass wool in GC–MS analysis.

The relative retention time (RRT) and relative molar response (RMR) of pesticide with respect to internal standard DCNB and TPP are listed in Table II. As indicated in Table II, excellent precision in RRT and RMR of each pesticide was observed. The retention times of dimethoate and α-BHC were very close (12.992 and 12.993 min, respectively). Nevertheless, these compounds could still be analysed, because dimethoate and α-benzene hexachloride (BHC) should be detected by NPD and ECD, respectively.

In the RMR study, captan and captafol

TABLE II

RELATIVE RETENTION TIME (RRT) AND RELATIVE MOLAR RESPONSE (RMR) OF PESTICIDES IN RICE AND SOY BEANS USING GC–NPD–ECD ($n = 3$)

Pesticide	ECD		NPD	
	RRT (R.S.D., %)	RMR (R.S.D., %)	RRT (R.S.D., %)	RMR (R.S.D, %)
DCNB (I.S.)[a]	1.000 (0.98)	1.00	–	–
Isoprocarb	–	–	0.356 (0.46)	0.13 (3.9)
Dimethoate	–	–	0.494 (0.15)	1.01 (4.6)
α-BHC	1.780 (0.18)	4.45 (4.8)	–	–
β-BHC	1.925 (0.13)	1.11 (4.5)	–	–
γ-BHC	1.945 (0.13)	4.09 (4.6)	–	–
Diazinon	–	–	0.527 (0.09)	1.92 (8.6)
Carbaryl	–	–	0.623 (0.06)	0.12 (4.4)
Fenitrothion	–	–	0.641 (0.03)	1.50 (2.0)
Malathion	–	–	0.648 (0.02)	1.26 (3.1)
Fenthion	–	–	0.666 (0.02)	1.22 (3.4)
Parathion	–	–	0.670 (0.02)	1.88 (6.1)
Aldrin	2.495 (0.03)	3.79 (4.1)	–	–
Captan	2.733 (0.02)	0.53 (6.4)	–	–
Phenthoate	–	–	0.730 (0.01)	0.80 (3.6)
o,p'-DDE	2.821 (0.01)	1.52 (3.6)	–	–
p,p'-DDE	2.995 (0.01)	2.64 (3.7)	–	–
o,p'-DDD	3.058 (0.01)	1.40 (3.9)	–	–
Dieldrin	3.011 (0.01)	3.69 (3.8)	–	–
m,p'-DDD	3.170 (0.01)	1.46 (4.0)	–	–
Endrin	3.208 (0.01)	2.28 (5.1)	–	–
p,p'-DDD	3.279 (0.01)	2.17 (3.9)	–	–
o,p'-DDT	3.306 (0.01)	1.35 (3.9)	–	–
p,p'-DDT	3.561 (0.01)	2.08 (3.8)	–	–
TPP(I.S.)[a]	–	–	1.000 (0.01)	1.00
Captafol	3.789 (0.01)	0.87 (6.5)	–	–
EPN	–	–	1.089 (0.02)	1.52 (0.7)

[a] Retention times of DCNB and TPP are 6.687 and 25.123 min, respectively.

showed a slightly lower response than other chlorinated pesticides. In particular, β-BHC of the BHC isomers showed a significantly lower response on ECD than α- or γ-BHC. It is suggested that the six chlorine atoms on the cyclohexane ring are located in an equatorial position in β-BHC, whereas in α- and γ-BHC three and four of the six chlorine atoms, respectively, are positioned axially. Presumably, the different response of BHC isomers on ECD is caused by the difference in stereochemical structure. DDE, DDD and DDT isomers also showed different responses depending on the position of the chlorine atoms on the benzene ring.

The NPD response of pesticides is also dependent on the structure and is particularly affected by substituents bonded at the nitrogen atom. Isoprocarb and carbaryl showed slightly lower sensitivity than other nitrogen-containing compounds because the nitrogen of carbamates bonded to a carbonyl group is known to be less effective in NPD response [28]. Although, of chlorinated pesticides, captan and captafol contain a nitrogen atom, these compounds exhibited very low sensitivity in the NPD chromatogram. This could be attributed to the fact that the nitrogen atom in captan and captafol is bonded to two carbonyl groups. Some pesticides, such as carbaryl, fenitrothion, malathion, fenthion, phenthoate and O-ethyl O,4-nitrophenyl phenylphosphonothioate (EPN), could be detected with both ECD and NPD. These results can be used to identify pesticide peaks.

Extraction and clean-up

It is necessary to pretreat the specimens in order to extract the pesticide of interest and to remove inferences from the fatty sample. Therefore, clean-up including solvent partitioning and column chromatography were required to remove the fatty materials.

In this study, methylene chloride was chosen in the solvent partitioning and Bio-Beads S-X3 was used for column chromatography. In general, Florisil clean-up in column chromatography is known to be unsuitable for the elution of polar pesticides and the removal of fatty materials. However, Bio-Bead S-X3 clean-up removes interfering lipids from the initial methylene chloride extract, so it is particularly valuable for the analysis of the residual pesticides in fatty samples. The methylene chloride extracts containing pesticides and lipids were chromatographed on a 15-cm Bio-Beads S-X3 column to determine the pesticide recovery. The elution curves of pesticides and rice oils with Bio-Beads S-X3 are shown in Fig. 3. The effluent from 11 to 20 ml was collected, concentrated and analysed for pesticide contents by gas chromatography. As shown in Fig. 3, more than 75% of lipid was removed through this column, whereas most pesticides were recovered.

Typical chromatograms obtained from the control rice and soy bean extracts using the methylene chloride partition and Bio-Beads S-X3 are shown in Fig 4. No interferences were detected in the dual chromatograms.

Recovery studies were performed three times at the 1-ppm (w/w) level for each pesticide spiked in rices and soy beans. These samples were prepared by adding 0.5 ml of 50 μg/ml pesticide stock solutions to 25 g of ground rices or by adding 0.1 ml of 50 μg/ml stock solution to 5 g of ground soy beans before extraction. The extracts were analysed as previously described. Fig. 5 shows the chromatograms obtained from the spiked rices and soy beans. The ratios of peak area obtained from extracted pesticides were compared with those of standard solutions containing the same concentration of pesticide and internal standards.

The recoveries of pesticide in crops are listed in Table III. Recoveries for rices were between

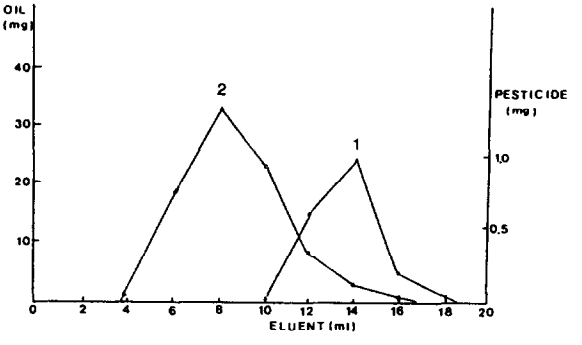

Fig. 3. Elution curves of (1) pesticides and (2) rice oil with a Bio-Beads S-X3 column.

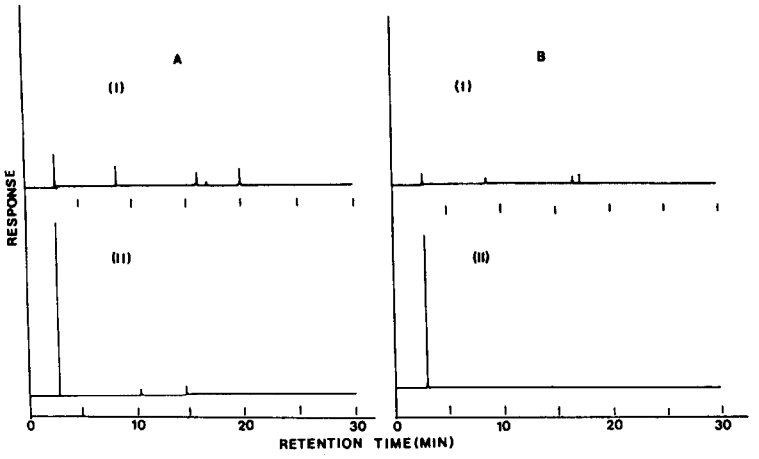

Fig. 4. Dual ECD (I) and NPD (II) chromatograms of (A) control rices and (B) control soy bean extract.

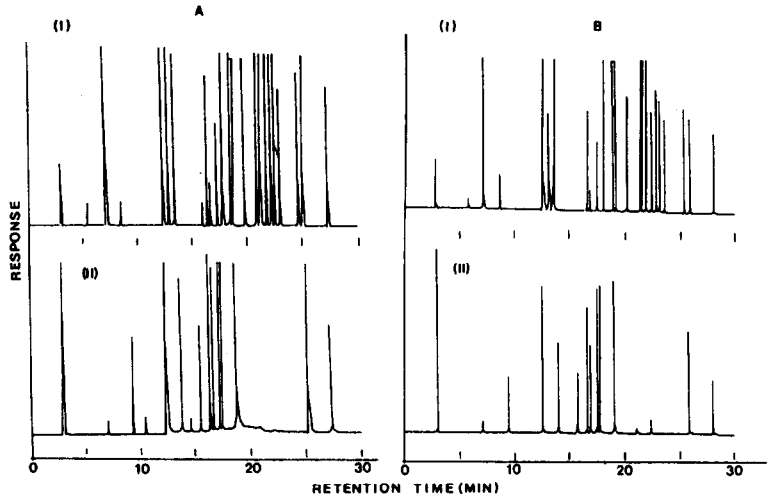

Fig. 5. Dual ECD (I) and NPD (II) chromatograms of (A) rice extract and (B) soy bean extract (peaks same as in Fig. 2).

83 and 105%, and the coefficients of variation were 0.5–7.2%, with an average of 94%, and for soy beans were between 63 and 102% with coefficients of variation of 0.9–8.2%, with an average of 88%.

The limits of detection of all pesticides in the crops tested are also listed in Table III. Of the 25 pesticides, isoprocarb and carbaryl had a limit of detection of 0.3 ppm in soy beans. The other pesticides had a limit of detection between 0.002 and 0.05 ppm in soy beans and rices.

In view of their recoveries and removal of interference peaks, methylene chloride partition and Bio-Beads S-X3 column clean-up was good for the reliable conformation and quantitation analysis of pesticides.

Analysis by GC–MS

In principle, the analysis of pesticides by GC–NPD–ECD may be falsified by a compound with the same retention time as one of the pesticides. In this case, the reliability of analysis can be greatly improved by GC–MS.

In Fig. 6, the total-ion chromatogram of the mixture of pesticides is shown, demonstrating good GC separation of 25 pesticides. Under the

TABLE III

RECOVERIES (%) AND LIMIT OF DETECTION OF PESTICIDES IN RICE AND SOY BEANS USING GC–NPD–ECD ($n = 3$)

R.S.D.s are given in parentheses.

Pesticide	Rice		Soy beans	
	Recovery	Limit of detection (ppm)	Recovery	Limit of detection (ppm)
Isoprocarb	95.4 (3.7)	0.05	81.8 (3.6)	0.3
Dimethoate	101.2 (2.8)	0.01	100.5 (2.1)	0.03
α-BHC	101.8 (2.7)	0.002	88.4 (1.4)	0.01
β-BHC	91.3 (0.8)	0.009	91.9 (1.8)	0.04
γ-BHC	95.6 (2.5)	0.002	96.2 (2.8)	0.01
Diazinon	83.4 (1.5)	0.01	62.7 (8.6)	0.05
Carbaryl	99.8 (2.6)	0.05	101.7 (4.4)	0.3
Fenitrothion	95.3 (2.2)	0.005	96.1 (3.3)	0.03
Malathion	91.4 (3.8)	0.02	79.5 (7.2)	0.08
Fenthion	89.6 (4.1)	0.008	98.7 (3.0)	0.04
Parathion	86.8 (1.2)	0.007	91.3 (1.2)	0.04
Aldrin	87.4 (4.3)	0.006	84.8 (2.0)	0.03
Captan	84.9 (3.7)	0.02	85.2 (0.6)	0.07
Phenthoate	100.4 (4.6)	0.03	86.1 (3.6)	0.1
o,p'-DDE	99.6 (7.2)	0.007	89.7 (4.4)	0.04
p,p'-DDE	97.6 (2.7)	0.007	84.3 (0.9)	0.04
o,p'-DDD	97.0 (5.0)	0.01	91.2 (1.9)	0.05
Dieldrin	96.7 (3.3)	0.006	89.2 (1.5)	0.03
m,p'-DDD	97.4 (2.6)	0.01	91.9 (3.2)	0.05
Endrin	99.1 (2.4)	0.01	91.7 (2.3)	0.05
p,p'-DDD	97.3 (2.6)	0.01	90.2 (3.2)	0.05
o,p'-DDT	92.9 (0.5)	0.01	90.1 (8.2)	0.05
p,p'-DDT	91.7 (2.2)	0.01	87.4 (1.6)	0.05
Captafol	83.4 (0.7)	0.03	77.2 (1.6)	0.1
EPN	96.2 (1.8)	0.02	91.2 (1.0)	0.08

GC–MS conditions specified in the experimental section, the mass spectra of pesticides were obtained in the electron-impact mode. Table IV summarizes the retention times, the molecular weights, base peak and characteristic ions of the mass spectra. For organochlorinated pesticides, their mass fragment [M] ions are accompanied by [M + 2] and/or [M + 4] ions, because of the isotopic effect of chlorine. For example, the isomers of DDD and DDT yielded a base peak m/z 235 from the loss of the $-CHCl_2$ and $-CCl_3$ group, respectively, and this fragment is accompanied by two isotopic peaks, m/z 237 and m/z 239. Of the pesticides containing six chlorine atoms, BHC isomers, aldrin, endrin and dieldrin show a weak intensity of molecular ion. The fragmentation of these compounds exhibited the loss of HCl and Cl in stepwise pattern from the molecular ion. In particular, aldrin, endrin and dieldrin containing a cyclohexene ring produced the ion cluster m/z 261, 263 and 265 by the retro-Diels–Alder (RDA) fragment. Captan and captafol showed the very weak intensity of molecular ion and also produced the base peak, m/z 79 (cyclohexadiene) by the RDA fragment.

For organophosphorus pesticides, the typical fragmentation patterns of phosphorus groups are explained in most part by Fig. 7. This fragmentation patterns are in good agreement with those represented by Pritchard [29]. These fragments appeared with strong intensity in the mass spectra of organophosphorus pesticides. In the case

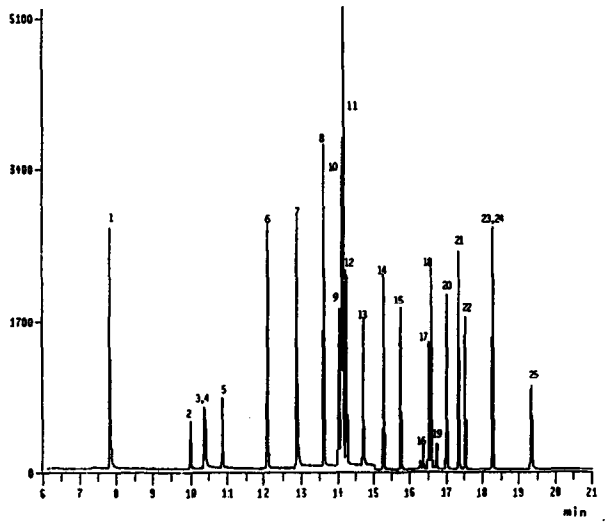

Fig. 6. Total-ion chromatogram of standard pesticides using SIM mode. Peaks: 1 = isoprocarb; 2 = α-BHC; 3 = dimethoate; 4 = β-BHC; 5 = γ-BHC; 6 = diazinon; 7 = carbaryl; 8 = fenitrothion; 9 = aldrin; 10 = malathion; 11 = fenthion; 12 = parathion; 13 = captan; 14 = phenthoate; 15 = *o,p'*-DDE; 16 = dieldrin; 17 = *p,p'*-DDE; 18 = *o,p'*-DDD; 19 = endrin; 20 = *m,p'*-DDD; 21 = *p,p'*-DDD; 22 = *o,p'*-DDT; 23 = *p,p'*-DDT; 24 = captafol; 25 = EPN. *y*-Axis: abundance; *x*-axis: retention time (min).

of N-methylcarbamate pesticides, isoprocarb and carbaryl, the base peak of carbaryl was produced by the loss of N-methyl carbamate group from the molecular ion and that of isoprocarb was formed by the loss of the methyl group from ($M-O=C=N=CH_3$) ion. On the basis of this fragment information, various pesticides could be identified and complementary structural information would be obtained.

In this study, the determination of the pesticides at trace level in crops was achieved by GC–MS using selected-ion monitoring (SIM) model with two or three ions. The SIM mode may be used to improve the detection limit by producing the strongest intensity and to improve the specificity for the compound of interest by reducing the interference peaks. As shown in Fig. 6, although some pesticides were co-eluted, they could still be analysed because of the specificity of SIM, as typically demonstrated in Fig. 8 for β-BHC (*m/z* 181 or 183) and dimethoate (*m/z* 93) co-eluting at 10.5 min and *p,p*-DDT (*m/z* 235) and captafol (*m/z* 79) at 18.4 min. The ion *m/z* 93 instead of *m/z* 87 for dimethoate was selected to obtain the precise analysis by SIM mode because the ion *m/z* 87 also appeared in the mass spectrum of β-BHC.

The detection limits of some pesticides were around 10 ng as an injection amount in the scan mode. However, the detection limits in the SIM mode using only the base peak of each pesticide were about 0.05 ng, except for dieldrin and endrin, whose detection limits were about 0.2 ng

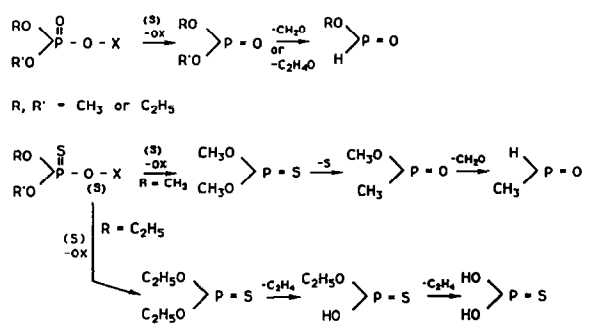

Fig. 7. Basic fragmentation patterns of organophosphorus compounds.

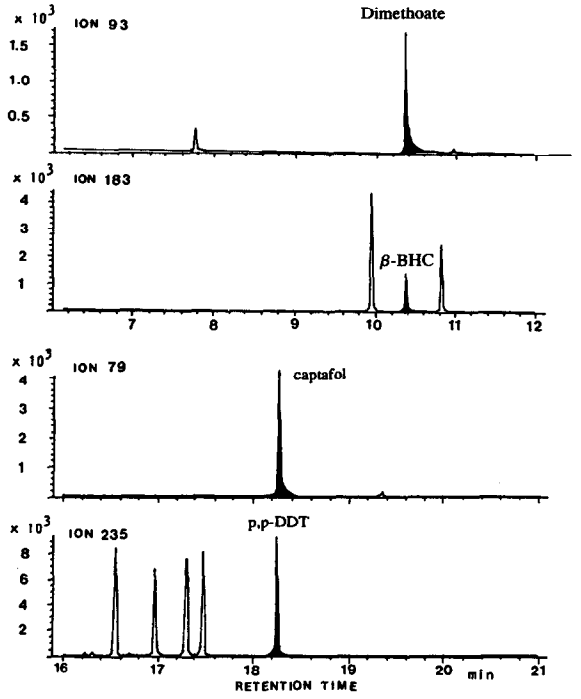

Fig. 8. Selected-ion chromatograms of some co-eluting pesticides. *y*-Axis: abundance.

TABLE IV

RETENTION TIMES (t_R) AND CHARACTERISTIC MASS FRAGMENT IONS FOR PESTICIDES

Relative abundance (%) is given in parentheses.

Compound	t_R (min)	Molecular mass mass	Mass fragment ion (m/z)					
Isoprocarb	7.929	193	121 (100)	136 (57)	91 (17)	77 (11)	193 (2)	
α-BHC	10.119	291	181 (100)	183 (94)	217 (52)	219 (74)	109 (60)	111 (57)
Dimethoate	10.518	229	87 (100)	93 (77)	125 (43)	63 (17)	79 (16)	229 (12)
β-BHC	10.520	291	183 (100)	181 (95)	217 (44)	219 (65)	109 (36)	111 (40)
γ-BHC	10.989	291	181 (100)	183 (94)	109 (92)	111 (91)	217 (52)	219 (62)
Diazinon	12.289	304	137 (100)	179 (74)	152 (56)	93 (44)	66 (28)	304 (21)
Carbaryl	13.021	201	144 (100)	115 (48)	89 (12)	63 (6)	201 (5)	
Fenitrothion	13.747	277	125 (100)	109 (93)	277 (34)	93 (31)	79 (28)	
Aldrin	14.175	365	66 (100)	261 (40)	263 (58)	265 (54)	91 (38)	
Malathion	14.225	330	125 (100)	93 (76)	173 (57)	158 (42)	99 (32)	79 (18)
Fenthion	14.287	278	278 (100)	109 (92)	125 (86)	93 (51)	169 (40)	79 (10)
Parathion	14.369	291	109 (100)	97 (93)	139 (41)	153 (34)	291 (32)	
Captan	14.830	300	79 (100)	149 (26)	117 (20)	119 (19)	77 (14)	
Phenthoate	15.432	320	125 (100)	93 (76)	121 (64)	274 (55)	246 (24)	
o,p'-DDE	15.896	318	246 (100)	248 (72)	316 (45)	318 (55)	320 (48)	176 (38)
Dieldrin	16.509	380	79 (100)	261 (28)	263 (45)	265 (24)	279 (18)	
p,p'-DDE	16.673	316	246 (100)	248 (68)	316 (42)	318 (53)	320 (48)	176 (45)
o,p'-DDD	16.740	320	235 (100)	237 (59)	165 (38)	199 (13)	318 (5)	320 (6)
Endrin	16.899	380	81 (100)	261 (41)	263 (59)	265 (38)	289 (25)	
m,p'-DDD	17.154	320	235 (100)	237 (71)	165 (48)	199 (15)	318 (4)	320 (5)
p,p'-DDD	17.491	320	235 (100)	237 (59)	165 (42)	199 (18)	318 (2)	320 (3)
o,p'-DDT	17.665	354	235 (100)	237 (58)	165 (38)	199 (12)	136 (7)	
p,p'-DDT	18.425	354	235 (100)	237 (70)	165 (31)	199 (9)	136 (5)	
Captafol	18.426	349	79 (100)	311 (18)	313 (23)	183 (10)	149 (7)	
EPN	19.491	323	157 (100)	169 (51)	141 (32)	185 (27)	63 (25)	323 (15)

at a signal-to-nose ratio of 5. But the detection limits by GC–ECD, for dieldrin and endrin, were noticeably lower than those by SIM. The base peak m/z 79 of dieldrin and m/z 81 of endrin could not be distinguished at times between 15 and 17.4 min (group C) in the SIM mode because these ions were subject to interference from fatty species likely to be present in the sample matrix. The ion cluster m/z 261, 263 and 265, instead of m/z 79 and 81, could be monitored to enhance specificity for endrin and dieldrin but with a reduction in sensitivity. For most pesticides, the detection limits with the GC–MS–SIM method were similar to those with GC–NPD–ECD. However, the GC–MS–SIM method provided much higher sensitivity for carbamates, which was shown by the low sensitivity of the NPD response. The detection limits using SIM were seven times lower for isoprocarb and 12.5 times lower for carbaryl than those using NPD. In many cases of GC analysis, the detection limits could also be decreased by adjusting the sample volume and splitless mode.

CONCLUSIONS

The screening of 25 pesticides in rice and soy beans with GC–NPD–ECD has been achieved within 30 min using an SE-30 capillary column. For the simultaneous determination of 25 pesticides, the solvent partition and Bio-Beads S-X3 column method appears to be suitable for removal of the interferences from the fatty matrix components. The present method for the analysis of various pesticides in the fatty crops gave good recoveries with reasonable precision and seemed to be suitable for multiresidue analysis. Each pesticide was identified by its retention time and characteristic mass fragment ions using GC–MS–SIM. The GC–MS–SIM was proved to be a reliable means of identification and confirmation of a variety of pesticide residues. Although the response of dual detection alone does not give enough evidence of the presence of the pesticides, the appearance of two or three ions at a specific retention time using the GC–MS–SIM technique can be a good evidence that a specific pesticide is present.

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