

Study of multiresidue analytical method for organonitrogen and organophosphorus pesticides in soil and water

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Abstract—A gas chromatographic method without derivatization was developed for the residue analysis of 10 organonitrogen and 9 organophosphorus pesticides in soil and water. The samples were blended or shaken with acetone for extraction. The extracts were cleaned up by coagulation, then, re-extracted with three 50 ml portions of dichloromethane. The final residue was detected by gas chromatography equipped with NPD. All of the 19 pesticides were completely separated at a constant temperature. The method described above was applicable to the simultaneous determination of 10 organonitrogen and 9 organophosphorus pesticides in soil and water with the satisfactory recovery (from 82.42% to 103.57%), coefficient of variance (from 0.17% to 12.57%) and limit of detection (from 0.0006 ppm to 0.058 ppm).

Keywords: organonitrogen; organophosphorus pesticides; multiresidue; gas chromatography.

INTRODUCTION

Since organonitrogen and organophosphorus pesticides has begin widely used for the control of insects and nematodes, the development of analytical method for determining their residues in environment is necessitated. Several multiresidue analytical methods have been developed for the simultaneous determination of pesticides in various substrates (Cabris, 1979; Hollond, 1983; Ripley, 1983; War, 1985; Huang, 1988; Zhang, 1988; Huang, 1988; Qian, 1985; Huang, 1989). However, only a few attempts have been made on the methods for the simultaneous detection of organonitrogen and organophosphorus pesticides using gas chromatography. A gas chromatographic method without derivatization for 10 organonitrogen and 9 organophosphorus pesticides is presented in paper. In this experiment only water and soil samples were used, however other substrates could also be analysed by using this method with little modification.

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MATERIALS AND METHODS

Reagents

All reagents and solvents were analytical grade. The solvents were redistilled before use. The coagulation solution was prepared as follows.

Coagulating solution: 20 g ammonium chloride and 40 ml phosphoric acid (85%) were dissolved in 360 ml distilled water, and diluted 5 times with distilled water. The pH of the solution was adjusted to 4 before use.

Pesticides used in the present study are listed as follows:

- Mevinphos: 2-methoxy-carbonyl-1-methylvinyl dimethyl phosphate (90% pure);
- Parathion: o, o-diethyl o-4-nitrophenyl phosphorothioate (99% pure);
- Phorate: o, o-diethyl s-ethylthiomethyl phosphorothioate (98% pure);
- Methidathion: s-2, 3-dihydro-5-methoxy-2-oxo-1, 3, 4-thiadiazol-3-methyl-o, o-dimethyl phosphorodithioate (99.6% pure);
- Bromophos: o, o-dimethyl o-(4-bromo-2, 5-dichloro-phenyl) phosphorothioate (99% pure);
- Optunul: o-methyl-o (2-isopropoxycarbonylphenyl) phosphoro-imidate (99% pure);
- Kitasine: o, o-diethyl-s-benzylthiophosphate (99% pure);
- Phenthoate: s-a-ethoxycarbonylbenzyl o, o-dimethyl phosphorodithioate (99% pure);
- Diazinon: o, o-diethyl o-(2-isopropyl-4-methyl-6-pyrimidinyl)-thionophosphate (98% pure);
- Pirimiphos-methyl: o-[2-(diethylamino)-6-methyl-4-pyrimidinyl]-o, o-dimethyl phosphorothioate (99% pure);
- Diuron: 3-(3, 4-dichlorophenyl)-1, 1-dimethylurea (99% pure);
- MTMC: m-Tolyl-N-methylcarbamate (98% pure);
- Isoproc carb: 2-(1-methylethyl) phenyl methylcarbamate (99% pure);
- ENT-25500: 3-isopropylphenyl methylcarbamate (95% pure);
- BPMC: 2-(1-methylpropyl)phenyl methylcarbamate (99% pure),
- Carbofuran: 2, 3-dihydro-2, 2-dimethylbenzofuran-7-methylcarbamate (99% pure);
- Chlorothalonil: 3, 4, 5, 6-tetrachloroisophthalonitrile (99% pure);
- Carbaryl: 1-naphthalenyl methylcarbamate (99% pure);
- Sumilex: N-(3, 5-dichlorophenyl)-1, 2-dimethylcyclopropane-1, 2-dicarboximide (99% pure).

All pesticide standards were dissolved in acetone to yield a mixed standard solution. Their concentrations are as follows:

Mevinphos was 0.001 mg/ml; parathion 0.0014 mg/ml; phorate 0.0024 mg/ml; methidathion 0.0012 mg/ml; bromophos 0.0012 mg/ml; optunul 0.0012 mg/ml; kitasine 0.0009 mg/ml; phenthoate 0.0014 mg/ml; diazinon 0.0017 mg/ml; pirimiphos-methyl 0.0009 mg/ml; diuron 0.048 mg/ml; MTMC 0.027 mg/ml; isoproc carb 0.027 mg/ml; ENT-25500 0.064 mg/ml; BPMC 0.040 mg/ml; carbofuran 0.104 mg/ml; chlorothalonil 0.080 mg/ml; carbaryl 0.160 mg/ml and sumilex 0.190 mg/ml.

Fortification of water and soil

100 ml of field water was fortified with 2 ml of mixed-standard solution to yield the water sample suitable for our study.

20g of air-dried loam soil was fortified with 2 ml of mixed-standard solution to yield the soil sample for the present experiments.

Extraction and clean up

1. Water sample

Add 1 g of Celite 545, 18 ml of coagulating solution, 50 ml of acetone and 100 ml of water fortified with pesticides into a 250 ml separatory funnel. Shake the funnel for 2 minutes, then filter the water to another 250 ml separatory funnel through a filter paper. Add 5 g of sodium chloride to the second funnel. Extract the sample three times each with 50 ml of dichloromethane. Combine the extracts and dry the organic phase by passing the solution through a 3 ml bed of anhydrous sodium sulfate, then add 1 ml of ethyl acetate to the filtrate. Transfer the extracts to a rotary evaporator and concentrate to 1-2 ml. Dissolve the residue in acetone and make the total volume 5 ml for detection.

2. Soil sample

Add water to 20 g of soil fortified with pesticides to yield a system containing 20 g of water. Shake the soil with 100 ml of acetone: water (4:1, V/V) for 1 hour on a shaking machine. Filter the slurry through a coarse sintered glass funnel containing 1 cm of Celite 545 under reduced pressure. Take an aliquot of 50 ml filtrate for further extraction. The following procedure was just the same as that for water sample except treating the soil sample twice (Junshi, 1978).

Gas chromatography

The pesticides in acetone extracts were analyzed by using a Perkin-Elmer Sigma 2 GC equipped with a Nitrogen-Phosphorus Flame Ionization Detector. The conditions of gas chromatography are as follows:

Chromatographic column: id 2 mm \times 1 m glass column packed with 5% OV-17 on Chrom Q, 80-100 mesh (Cassil, 1969; Riva, 1969; Cook, 1969).

Temperatures: injector, 230 °C; detector, 250°C; column, 200 °C.

Gas flow rates: N₂, 37ml/min; H₂, 4.5 ml/min; air, 65 ml/min. 2 μ l of mixed-standard solution of sample was injected into the column of gas chromatography. Peak heights were used for calculating the concentration of pesticides.

RESULTS AND DISCUSSIONS

Separation of the pesticides by gas chromatography

In order to know the separation of the pesticides by gas chromatography and the recoveries of the pesticides through the processed of the method, 2 ml of the mixed standard solution was added to 50 ml of acetone. The following experiment steps were the same as that for the treatment of water sample. After determination, the separation of the pesticides is shown in Fig. 1.

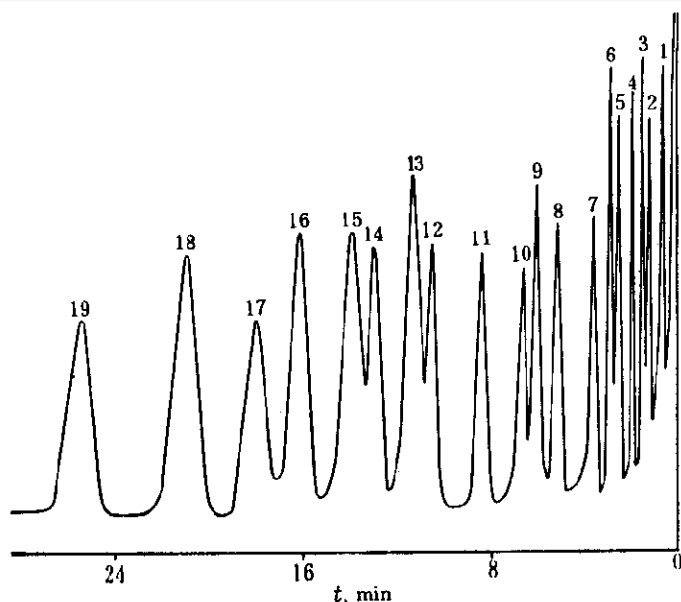


Fig. 1 Chromatogram of 19 pesticides

- (1) Diuron (2) Mevinphos (3) MTMC (4) Isoproc carb (5) BPMC (6) ENT-25500 (7) Phorate (8) Diazinon (9) Carbofuran (10) Kitazine (11) Chlorothalonil (12) Pirimiphos-methyl (13) Carbaryl (14) Parathion (15) Bromophos (16) Optunul (17) Sumilex (18) Phenthoate (19) Methidathion

Table 1 The recoveries of the preliminary test

Compound	Fortified level, ppm	Range of recoveries, %	Recovery \pm SD, %	C.V., %
Diuron	1.350	91.43-94.28	92.38 \pm 1.65	1.79
Mevinphos	0.061	95.00-100.00	97.22 \pm 2.55	2.63
MTMC	0.900	96.77-96.88	96.5 \pm 0.47	0.49
Isoproc carb	0.900	90.91-96.36	93.94 \pm 2.78	2.95
BPMC	1.150	92.45-96.43	95.10 \pm 2.30	2.42
ENT-25500	1.800	93.10-96.55	94.83 \pm 1.73	1.82
Phorate	0.120	91.42-97.44	94.38 \pm 3.01	3.19
Diazinon	0.087	97.31-98.13	97.84 \pm 0.46	0.47
Carbofuran	2.950	90.47-95.23	92.06 \pm 2.75	2.99
Kitazine	0.044	91.52-101.69	96.04 \pm 5.18	5.39
Chlorothalonil	2.300	93.90-97.20	97.03 \pm 3.05	3.14
Pirimiphos-methyl	0.044	92.59-100.00	97.53 \pm 4.28	4.39
Carbaryl	4.600	98.21-103.52	101.19 \pm 2.73	2.69
Parathion	0.070	92.86-96.43	94.63 \pm 1.79	1.89
Bromophos	0.061	94.59-102.71	98.50 \pm 4.07	4.13
Optunul	0.061	96.55-103.45	100.15 \pm 3.46	3.63
Sumilex	5.500	91.05-97.39	93.52 \pm 3.40	3.64
Phenthoate	0.070	96.00-102.00	99.00 \pm 3.00	3.03
Methidathion	0.061	90.00-100.00	94.44 \pm 5.09	5.39

After comparing with the standard solution, the preliminary recoveries are shown in Table 1, where the value of recovery is the average of three replicated trials. The preliminary recovery of each pesticide showed good indication of the method used.

Recoveries of 19 pesticides in water and soil

The recoveries of the fortified pesticides at three concentrations in water and soil are shown in Table 2 and 3. At both the lower and higher levels, the method gave satisfactory recovery, which mostly surpassed 90%. The calculated minimum detectable concentrations were 0.0006-0.058 ppm, the results are shown in Table 4. The method proved to be applicable to multiresidue analysis of the pesticides used in the present study in water and soil.

Table 2 Recoveries of 19 fortified pesticides in water

Compound	Fortified level, ppm	Recovery \pm SD, %	Compound	Fortified level, ppm	Recovery \pm SD, %
Diuron	0.5400	96.00 \pm 4.00	Chlorothalonil	0.9200	97.92 \pm 9.08
	0.1080	94.73 \pm 1.06		0.1840	93.66 \pm 4.30
	0.0540	103.57 \pm 3.57		0.0920	92.90 \pm 3.35
Mevinphos	0.0240	96.80 \pm 4.21	Pirimiphos-methyl	0.0170	88.43 \pm 5.35
	0.0043	99.30 \pm 5.24		0.0034	93.58 \pm 1.84
	0.0024	96.33 \pm 2.98		0.0017	94.68 \pm 6.46
MTMC	0.3600	97.09 \pm 5.34	Carbaryl	1.8400	96.20 \pm 7.53
	0.0720	100.71 \pm 4.34		0.3680	91.99 \pm 5.27
	0.0360	94.61 \pm 0.72		0.1840	95.96 \pm 7.98
Isoproc carb	0.3600	100.57 \pm 7.78	Parathion	0.0280	90.10 \pm 6.32
	0.0720	93.33 \pm 3.06		0.0056	96.53 \pm 3.18
	0.0360	96.59 \pm 3.74		0.0028	97.50 \pm 2.54
BPMC	0.4600	98.81 \pm 8.23	Bromophos	0.0240	94.52 \pm 2.79
	0.0920	90.00 \pm 2.00		0.0048	93.37 \pm 4.00
	0.0460	92.33 \pm 5.87		0.0024	94.48 \pm 1.92
ENT-25500	0.7200	100.57 \pm 4.34	Optunul	0.0240	90.53 \pm 3.90
	0.1440	91.43 \pm 4.33		0.0048	88.88 \pm 2.79
	0.0720	95.21 \pm 2.52		0.0024	84.18 \pm 0.74
Phorate	0.0480	96.08 \pm 8.20	Sumilex	2.2000	93.86 \pm 4.08
	0.0096	84.32 \pm 1.96		0.4400	95.06 \pm 2.14
	0.0048	85.99 \pm 2.45		0.2200	95.32 \pm 0.78
Diazinon	0.0350	93.91 \pm 2.35	Phenthoate	0.0280	94.76 \pm 5.04
	0.0070	94.41 \pm 1.90		0.0056	88.49 \pm 5.76
	0.0035	92.02 \pm 9.42		0.0028	94.04 \pm 5.75
Carbofuran	1.1800	91.01 \pm 5.96	Methidathion	0.0240	90.47 \pm 7.43
	0.2360	92.57 \pm 1.58		0.0048	90.62 \pm 5.69
	0.1180	94.35 \pm 7.90		0.0024	82.42 \pm 1.05
Kitazine	0.0170	90.29 \pm 5.20			
	0.0034	96.82 \pm 1.08			
	0.0017	94.21 \pm 11.39			

Table 3 Recoveries of 19 fortified pesticides in soil

Compound	Fortified level, ppm	Recovery \pm SD, %	Compound	Fortified level, ppm	Recovery \pm SD, %
Diuron	2.700	99.03 \pm 0.96	Chlorothalonil	4.600	90.59 \pm 0.47
	0.540	96.72 \pm 7.27		0.920	91.16 \pm 5.14
	0.270	94.42 \pm 5.06		0.460	89.04 \pm 2.98
Mevinphos	0.122	100.29 \pm 2.76	Pirimiphos-methyl	0.087	98.51 \pm 1.05
	0.024	91.16 \pm 7.01		0.017	89.44 \pm 9.70
	0.012	96.20 \pm 2.51		0.009	90.19 \pm 4.50
MTMC	1.800	98.44 \pm 1.58	Carbaryl	9.200	97.12 \pm 0.99
	0.360	86.47 \pm 3.35		1.840	95.77 \pm 0.84
	0.180	90.49 \pm 6.33		0.920	90.47 \pm 4.37
Isoproc carb	1.800	100.12 \pm 1.87	Parathion	0.139	97.75 \pm 1.30
	0.360	88.55 \pm 3.36		0.028	95.07 \pm 6.10
	0.180	92.76 \pm 1.51		0.014	91.40 \pm 2.85
BPMC	2.300	99.20 \pm 1.35	Bromophos	0.122	97.94 \pm 0.66
	0.460	95.26 \pm 6.21		0.024	94.35 \pm 7.13
	0.230	94.82 \pm 0.16		0.012	92.16 \pm 3.93
ENT-25500	3.600	100.01 \pm 1.37	Optunul	0.122	99.66 \pm 1.04
	0.720	100.27 \pm 7.53		0.024	92.72 \pm 10.50
	0.360	97.50 \pm 2.50		0.012	92.50 \pm 2.50
Phorate	0.243	96.71 \pm 4.71	Sumilex	11.00	94.18 \pm 3.63
	0.049	91.61 \pm 6.06		2.200	92.90 \pm 0.73
	0.024	96.02 \pm 2.36		1.100	91.67 \pm 2.81
Diazinon	0.174	99.40 \pm 2.71	Phenthoate	0.139	91.30 \pm 3.02
	0.035	88.06 \pm 8.83		0.028	96.02 \pm 4.91
	0.017	98.33 \pm 7.22		0.014	94.84 \pm 2.34
Carbofuran	5.900	92.56 \pm 4.37	Methidathion	0.122	99.64 \pm 2.16
	1.180	91.63 \pm 11.52		0.122	94.67 \pm 1.58
	0.590	99.99 \pm 7.53		0.012	93.53 \pm 3.23
Kitazine	0.087	99.70 \pm 2.58			
	0.017	95.23 \pm 7.61			
	0.009	100.05 \pm 2.68			

Table 4 The calculated minimum detectable concentrations in soil and water

Compound	MDC in water, ppm	MDC in soil, ppm
Diuron	0.0039	0.0154
Mevinphos	0.0018	0.0076
MTMC	0.0030	0.0120
Isoprocarb	0.0031	0.0124
BPMC	0.0037	0.0148
ENT-25500	0.0058	0.0232
Phorate	0.0003	0.0012
Dazinon	0.0003	0.0013
Carbofuran	0.0118	0.0472
Kitazine	0.0002	0.0580
Chlorothalonil	0.0096	0.0383
Carbaryl	0.0121	0.0480
Parathion	0.0003	0.0010
Bromophos	0.0002	0.0006
Optunul	0.0002	0.0008
Sumilex	0.0152	0.0162
Phenthoate	0.0002	0.0006
Methidathion	0.0003	0.0010

* MDC: the calculated minimum detectable concentration

CONCLUSIONS

Although some previously published methods are capable for determining organonitrogen and organophosphorus pesticides in various substrates (Huang, 1989; Zhang, 1988), it has been found that many of them have practical difficulties and shortcoming. On the basis of previous research, a new method was developed in our laboratory. Using this method 10 organonitrogen and 9 organophosphorus pesticides could be successfully determined at a single temperature without derivatization, this method was easy, fast and inexpensive.

In the method, coagulation was used for removing the impurity in the sample. Before clean up, evaporating most part of the acetone in extracts was beneficial to coagulation. For getting better recoveries of pesticides used in the present study, it was found that the pH of coagulating solution should be adjusted to 4.

Organonitrogen and some of organophosphorus pesticides are sensitive to high temperatures. When the extracts were concentrated in a rotary evaporator, dryness must be avoided. These pesticides are also easy to decompose under common gas chromatographic conditions, so, the temperature of the glass column should be below 200°C and the length of the column should be 1 m.

The method used here is also applicable to multiresidue analysis of 19 pesticides in other substrates, such as food, fruit and vegetables. It will be published later.

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REFERENCES

- Cabria, P., *et al.*, J. Chromatogr., 1979, 176: 437
- Cassil, C. C., Stanovick, R. P. and Cassil, C. C., J. Agr. Rev., 1969, 26: 63
- Cook, R. F., R. P. Stanovick and C. C. Cassil., J. Agr. Fd. Chem., 1969, 17: 277
- Hollond, P. T. and Meghle, T. K., J. Assoc. Off. Chem., 1983, 66: 1003
- Huang Shizhong and Tian Shuxian, J. Environ. Chem., 1988, 7(2): 37
- Huang Shizhong and Zhang Junting, J. Agr. Environ. Prote., 1988, 7(4): 43
- Huang Shizhong and Zhang Junting, J. Environ. Chem., 1989, 8(3): 45
- Huang Shizhong and Zhang Junting, Acta Scientiae Circumstantiae, 1989, 9(2): 225
- Junshi Miyamoto, Yoshiyuki Takimoto, J. Pesticide Sic., 1978, 3: 119
- Qian Chuanfan and Min Jiuxue, J. Environ. Sci., 1985, 6(1): 68
- Ripley, B. D. and Braun, H. E., J. Assoc. Off. Chem., 1983, 66: 1084
- Riva, M. and A. Carisano., J. Chromatog., 1969, 42: 464
- Wan Qinshun and He Shuiji, Journal Pesticide, 1985, 5: 9
- Zhang Qiao and Li Weige, J. Environ. Sci., 1988, 9(1): 47
- Zhang Qiao and Huang Shizhong *et al.*, Acta Scientiae Circumstantiae, 1988, 8(3): 67