

Multi-Pesticide Residue Method for Organopesticide Analysis

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Pesticide residues were extracted with 70% acetone and transferred to dichloromethane. Extracts were applied to open-column chromatography with florisil and alumina-N. The final extract was analyzed by gas chromatography with electron-capture detector(GC/ECD) and nitrogen-phosphorus detector(GC/NPD). Recoveries of the 17 organochlorine pesticides were ranged from 60.8 to 84.9% and those of 15 organophosphate pesticides, from 70.5% to 100.0%(except phosmet and azinphos-methyl). The minimum detectable levels of this analytical method were low(0.021~0.058mg/kg).

Key words : Organochlorine and organophosphate pesticide, florisil, alumina-N, gas chromatography, GC/ECD, GC/NPD

1. Introduction

Agricultural chemicals (pesticides) were classified into organochlorine, organophosphorus, and carbamate pesticide which included insecticides, disinfectants, fumigants, rodenticides, fungicides, and herbicides. They were known to act selectively to specific organisms and remove it, but they might induce harm for man. The residual property and chronic toxicity of pesticide were known and it brought about the problem of residual pesticide (Office, 1971; Pyysalo, 1983; Woodwell, 1967). Pesticides could be deposited in the environment and many living organisms involving human would be threatened. Residual pesticides are found in soil, food, and drinking water. In this aspect, not only the design of new pesticides which did not induce environmental problems but also the development of the precise

analytical method to detect the pesticides were demanded(Edwards, 1971; Hassall, 1982). The multi-pesticide residue method was an efficient way to screen a large number of pesticide samples in a relatively short time period(Joe, 1988; Luke et al., 1995; Mills et al., 1963). The instruments used in the analysis of pesticides are GC, HPLC, HPTLC, GC-MS and LC-MS(Grob, 1985; Lee et al., 1984; Willet et al., 1987). Analyses of synthetic organochlorine and organophosphorus pesticides by multi-residue method have been reviewed(Kim et al., 1996; Lee et al., 1997; Jennings, 1987; Mark et al., 1991; Stoherr, 1971). We proposed another multi-residue method for the analysis of organochlorine and organophosphorus pesticide, based on the modification methods of Kim et al.'s one(1996) and Lee et al.'s one(1997) in this paper.

2. Materials and Methods

2.1 Analytical reagents

Florisil (60-100 mesh) and alumina-N were purchased from Sigma Chemical Co. and used after activation in 130°C dry oven for 24h(for florisil). Methanol, acetone, hexane, and dichloromethane were used for the sample preparation of residual organopesticide, and special grade anhydrous sodium sulfate, benzene, and diethyl ether were used. 32 Standards for the organopesticides were obtained from Dr. Ehrenstorfer GmbH Co.

2.2 Preparation of analytical sample and analytical method for multi-pesticide

Organopesticide samples 10 - 20 g and 70% acetone 100ml were mixed for 10 min and filtered with Whatman No. 4 filter paper. This solution was evaporated and the residual solution (water layer) was extracted with dichloromethane 100 ml and was shaken for 10 min. The organic layer(lower layer) was filtered with Whatman No. 1PS filter paper, added anhydrous sodium sulfate, and filtered. This filtrate was evaporated and dichloromethane 10 ml were added. This solution was purified by open-column

chromatography. The packing material for analytical column was anhydrous sodium sulfate, alumina-N, and florisil. Analytical column(20 cm x 11 mm, id) was prepared. A small plug of cotton was placed at the bottom of the column and added 1 cm layer of anhydrous Na₂SO₄. Alumina-N 5 g and florisil 5 g were introduced into the column and tapped with 1 cm layer of anhydrous Na₂SO₄. The column was prewashed with ether : benzene(2:8) 20 ml, acetone 20 ml, and methanol 20 ml. The concentrated sample extract was loaded to the column. The pesticide samples was eluted with following elution solvents ; ether : benzene (2:8) 10 ml, hexane : benzene (1:1) 30 ml, dichloromethane 20 ml, acetone 20 ml, and methanol 20 ml. The eluate was collected in a 250 ml round-bottomed flask. Carefully the eluate was evaporated to dryness with rotary evaporator at 40°C and redissolved the residue in the proper volume of acetone, and then 1 µl of that was injected to GC/ECD and GC/NPD.

2.3 Analytical conditions for organochlorine and organophosphorus pesticide by gas chromatography

The organopesticides were analyzed und-

Table 1. Analysis condition of GC/ECD and GC/NPD for detecting residual organopesticide

column	GC/ECD	GC/NPD
	Ultra-2 (5% phenyl-methyl silicone) 50m x 0.32 mm x 0.17 µm	
flow	N ₂ 1.0 ml/min	N ₂ 1.6 ml/min
split ratio	1:90	1:8
injection Temp.	280 °C	280 °C
detection Temp.	300 °C	280 °C
initial Temp.	120 °C hold for 1 min	120 °C hold for 1 min
rate	5 °C/min	5 °C/min
final Temp.	190 °C hold for 19 min	200 °C hold for 6 min
rate A	5 °C/min	5 °C/min
final Temp. A	220 °C hold for 5 min	230 °C hold for 2 min
rate B	5 °C/min	10 °C/min
final Temp. B	280 °C hold for 8 min	300 °C hold for 3 min

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Table 2. Retention time, recovery, and detection limit of multi-pesticidee

Pesticide	Retention time (min)	Recovery (%)	Detection Limit (mg/kg)
α-BHC	8.810	64.3	0.047
β-BHC	9.716	84.9	0.036
γ-BHC	10.016	74.4	0.041
δ-BHC	11.008	81.4	0.039
chlorpyrifos	16.853	76.9	0.041
chlorfenvinfos	21.213	80.9	0.041
α-endosulfan	24.151	68.0	0.038
dieldrin	26.763	72.5	0.028
DDE	26.984	64.5	0.030
endrin	28.529	75.6	0.035
β-endosulfan	29.207	77.9	0.032
DDD	30.380	77.4	0.034
endosulfan sulfate	33.016	80.3	0.033
DDT	33.351	74.4	0.036
bromopropylate	38.188	71.8	0.047
tetradifen	39.892	84.2	0.028
cyhalothrin	42.277	60.8	0.050
permithrin	44.134, 44.539	80.4	0.037
cyfluthrin	45.830, 46.081,	75.8	0.052
	46.264, 46.273		
cypermethrin	46.582, 46.839,	76.9	0.058
	47.010, 47.138		
flucythrinate	47.538, 47.643	78.3	0.051
fenvalerate	48.867, 49.463	74.5	0.047
fluvalinate	49.483, 49.702	79.5	0.038
diltamethrin	51.058	61.0	0.035
ethroprophos	9.395	70.5	0.038
thiamethon	11.197	78.4	0.035
diazinon	12.809	81.5	0.028
etrimphos	13.506	79.1	0.036
parathion-methyl	15.191	80.6	0.037
fenitrothion	16.849	80.3	0.034
pirimifos-methyl	16.979	80.1	0.028
malathion	17.589	72.9	0.029
fenthion	18.188	82.6	0.031
parathion	18.402	79.4	0.028
phenthoate	22.122	100.0	0.021
methidathion	23.107	84.8	0.030
phosmet	33.378	48.9	-
EPN	33.743	73.7	0.032
azinphos-methyl	35.909	48.5	-

er the detection condition of GC/ECD and GC/NPD(HP 5890 Series II Plus) as shown in Table 1(Jennings, 1987; Willet, 1987).

3. Results and Discussion

The recoveries and detection limits by

gas chromatographic analysis in this study for multi-pesticides were shown in Table 2 and Fig. 1, 2, 3, and 4. In the pre-experiment, the recoveries of multi-pesticides were bad when florasil was used as the column packing material(Lee et al., 1997). But the analytical method used in

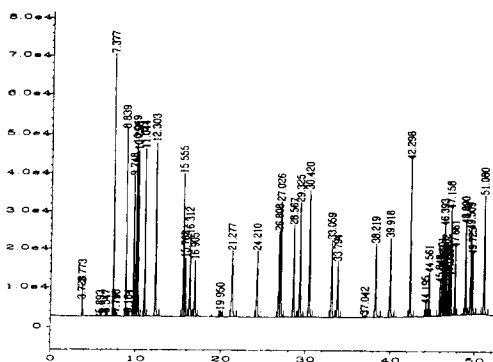


Fig. 1. GC/ECD analysis of organochlorine pesticide.

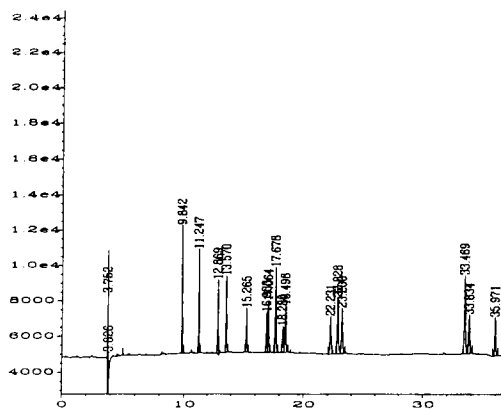


Fig. 2. GC/NPD analysis of organophosphorus pesticide.

this study was shown the best result because 32 kinds of organomulti-pesticides were detected sharply and the recoveries of the 17 organochlorine pesticides were ranged from 60.8 to 84.9% and those of 15 organophosphorus pesticides, from 70.5% to 100.0%(except phosmet and azinphos-methyl). The minimum detectable levels of this analytical method were low. The major advantage of this method was that cleanup procedure was no longer the rate determining step in the overall procedure because the next sample was undergoing cleanup during GC analysis. The analytical method in this paper could be applied to determine the multi-pesticides simultaneously. We proposed

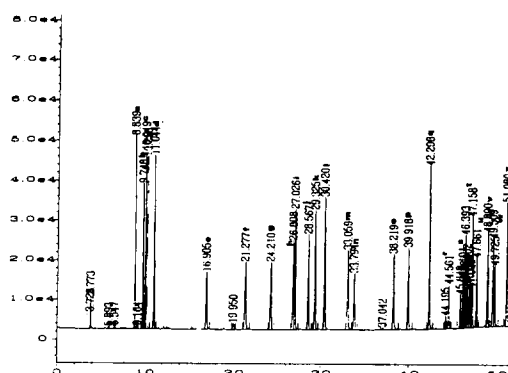


Fig. 3. Recoveries of organochlorine pesticides.

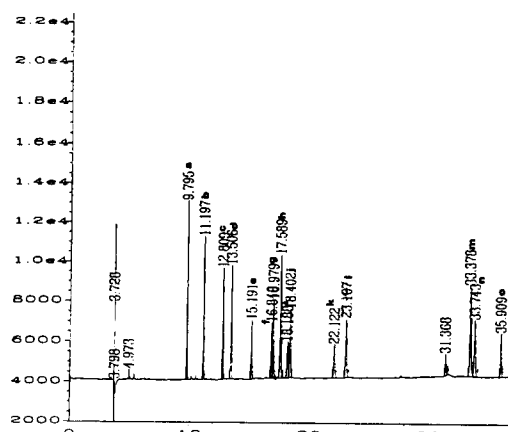


Fig. 4. Recoveries of organophosphorus pesticides.

this method for the analysis of multi-pesticides because the recovery was good and the detection limit was low.

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유기농약 분석을 위한 Multi-Pesticide Residue Method

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농약 잔류물을 70% acetone으로 추출한 다음 dichloromethane 층으로 옮겨 추출물을 florisil과 alumina-N으로 충전시켜 column chromatography를 행하였다. 마지막 추출물을 electron-capture detector(GC/ECD)와 nitrogen-phosphorus detector(GC/NPD)를 가진 GC로 분석하였다. 분석 결과 17 가지의 유기염소계 농약과 15 가지의 유기인계 농약의 회수율이 각각 60.8 에서 84.9%와 70.5에서 100.0%의 범위이었으며(phosmet와 azinphos-methyl은 제외) 본 분석 방법의 최소 검출 준위도 낮았다(0.021~0.058mg/kg).