

## Study on the Development of Analytical Method (Multi-Pesticide Residue Method) for the Organophosphate Pesticides

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Organophosphate pesticides were extracted with 70% acetone and then transferred to dichloromethane. Extracts were applied to open-column chromatography with florisil. The final extract was analyzed by gas chromatography with nitrogen-phosphorus detector(GC/NPD). Recoveries of the 18 organophosphate pesticides were ranged from 88.7% to 100.0% for the narrow-bore capillary GC(Ultra-2). The minimum detectable level of this analytical method was 0.019 - 0.035 mg/kg. Sample throughput(extraction, open-column chromatography, and GC analysis) was decreased considerably (8h per sample).

Key words : organophosphate pesticides, florisil, gas chromatography, GC/NPD

### 1. Introduction

Many pesticides have played an important role in removing harmful insects and in increasing the productivity of crops. But 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). Residual pesticides are found in soil, food, and drinking water. In this aspect, not only the design of new pesticides which do not induce environmental problems but also the development of the precise analytical method to detect the pesticides is demanded (Edwards, 1971; Hassall, 1982; Kanazawa, 1981).

The multi-pesticides residual method is 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 analyses of pesticides are GC, HPLC, HPTLC, and the combination methods, GC-MS and LC-MS(Grob, 1985; Lee et al., 1984; Willet et al., 1987). Analytical method for organochloride pesticides by multi-residual gas chromatography has already been reported (Kim et al., 1996; Jennings, 1987; Mark et al., 1991; Stoherr, 1971). We report a multi-residual method using narrow-bore column for the analysis of organophosphate pesticides and propose

another analytical method for the organochloride pesticides, based on the further modification method of Kim et al.'s one(1996). Florisil was used as the column packing material in this analytical method.

## 2. Materials and Methods

### 2.1 Analytical reagents

Packing material of column, florisil (60 - 100 mesh) was purchased from Sigma Chemical Co. and used after activation in 130°C dry oven overnight. Methanol, acetone, hexane, and dichloromethane were used for the sample preparation of residual organophosphate pesticides, and special grade anhydrous sodium sulfate, benzene, and diethyl ether were used. 18 Standards for the organophosphate pesticides were obtained from Dr. Ehrenstorfer GmbH Co.

### 2.2 Preparation of analytical sample

70% Acetone 100 ml were added to organophosphate pesticide samples 10 - 20 g and were shaken for 20 min. This solution was evaporated and the residual solution (water layer) was extracted with dichloromethane 100 ml, twice and was shaken for 5 - 10 min. The organic layer was filtered with Whatman No. 19S filter paper and was added anhydrous sodium sulfate. Above mixture was evaporated and dichloromethane 10 ml were added to the residual solution. This solution was purified by open-column chromatography. The packing material for analytical column was anhydrous sodium sulfate and florisil. The residual solution was added to column and was eluted with elution solvents ; ether : benzene (2:8) solution, hexane : benzene (1:1) solution, dichloromethane, acetone, and methanol. The eluted material was evaporated to mess up with acetone and 1 µl

Table 1. Condition of GC/NPD for detecting residual organophosphate pesticides

Column	Ultra-2 (5% phenyl-methyl silicone) 50m x 0.32 mm x 0.17 µm
Flow	N <sub>2</sub> 1.6 ml/min
Split ratio	1 : 8
injection Temp.	280 °C
detection Temp.	280 °C
initial Temp.	150 °C hold for 1 min
rate	5 °C/min
final Temp.	190 °C hold for 13 min
rate A	5 °C/min
final Temp. A	230 °C hold for 4 min
rate B	10 °C/min
final Temp. B	300 °C hold for 2 min

of that was injected to GC/NPD.

### 2.3 Analytical conditions for the organophosphate pesticides by gas chromatography

The organophosphate pesticides were analyzed under the detection condition of GC/NPD(HP 5890 Series II Plus) as shown in Table 1(Jennings, 1987; Willet, 1987).

### 2.4 Analytical method for organophosphate pesticides

Florisil column(20 cm x 11 mm, id) was prepared. A small plug of cotton was placed at the bottom of the column and added a 1 cm layer of anhydrous Na<sub>2</sub>SO<sub>4</sub>. Activated florisil 10 g were introduced into the column and tapped with a 1 cm layer of anhydrous Na<sub>2</sub>SO<sub>4</sub>. The column was prewashed with ether : benzene(2:8) 20 ml, acetone 20 ml, and methanol 20 ml. The concentrated sample extract was transferred to the column. The round-bottomed flask was rinsed twice with CH<sub>2</sub>Cl<sub>2</sub> 20 ml, transferred washes into the column, and allowed it to pass through the column.

Then the organophosphate pesticides were eluted with ether : benzene (2:8) 20

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**Table 2. Retention time, recovery, and detection limit of organophosphate pesticides**

Pesticide	Retention time (min)	Recovery (%)	Detection Limit (mg/kg)
Ethrophosphos	12.411	100.0	0.034
Dimethoate	14.258	95.8	0.024
Diazinon	15.773	98.2	0.031
Etrimfos	16.322	95.4	0.024
Parathion-methyl	17.450	92.3	0.031
Fenitrothion	18.634	90.4	0.025
Pirimifos-methyl	18.786	93.2	0.027
Malathion	19.208	100.0	0.023
Fenthion	19.543	64.0	0.028
Parathion	19.682	90.4	0.034
Phenthoate	22.153	92.3	0.019
Chinomethionat	22.485	96.1	0.031
Methidathion	22.892	96.4	0.026
Fensulfothion	28.195	92.3	0.035
Phosmet	33.775	95.9	0.021
EPN	34.112	88.7	0.026
Azinphos-methyl	36.204	96.3	0.028
Phosalone	36.350	97.4	0.026

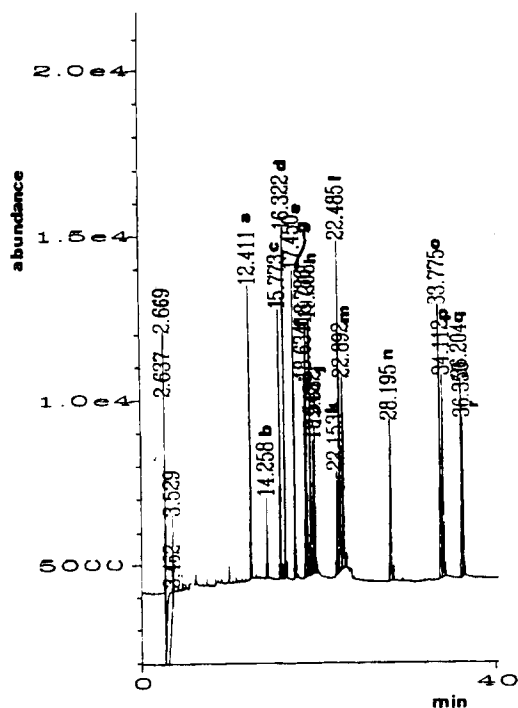


Fig 1. GC/NPD analysis of organo phosphate pesticides.

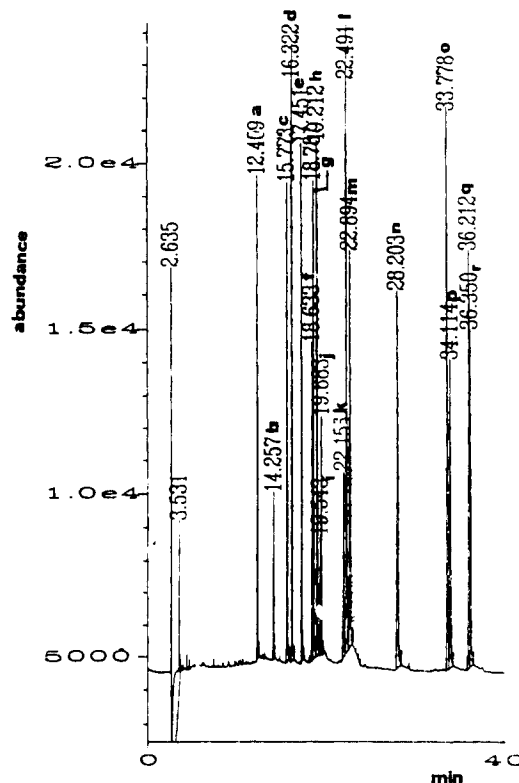


Fig 2. Recoveries of 18 residual organo phosphate pesticides.

ml, hexane : benzene (1:1) 30 ml, 40% hexane-saturated benzene 20 ml, and acetone 30ml diluent, collected the eluate in a 150 ml round-bottomed flask. Care-

fully the eluate was evaporated to dryness

with rotary evaporator at 40°C and redissolved the residue in the proper volume of hexane for GC analysis (Grob, 1985; Lee et al., 1984).

### 3. Results and Discussion

The results of gas chromatographic analysis for 18 kinds of organophosphate pesticides were shown in Table 2 and Fig. 1, 2 when florisil was used as the packing material. In the pre-experiment, the recovery of organophosphate pesticides was bad when florisil, silica, and alumina were used together as the column packing material, but good when florisil only (Kim et al., 1996). This analytical method was the best because 18 kinds of organophosphate pesticides were detected sharply and the recoveries of the organophosphates were ranged from 88.7 to 100.0% except fenthion. The minimum detectable level of this analytical method was 0.019 - 0.035 mg/kg. Sample throughput (extraction, open-column chromatography, and GC analysis) was decreased considerably (8h per sample, much shorter than 24h by general analytical method). Therefore we could save time and the analytical procedure could be completed by only one analytical condition.

Sample preparation, analyte isolation, and sample cleanup are becoming the major limiting procedures in the analysis of the residual organophosphate pesticides. The major advantage of this method is that cleanup is no longer the rate determining step in the overall procedures because the next sample is undergoing cleanup during GC analysis. The total cleanup procedure is executed within 60 min, which coincides with the time method for GC separation of the pesticides (Kanazawa, 1981).

The analytical method in this study can be applied to determine the 18 organophosphate pesticides simultaneously. We proposed this method for the analysis of organophosphate pesticides because the recovery was good and the detection limit was low.

### Conclusion

1. 18 Kinds of the residual organophosphate pesticides were detected sharply and showed high sensitivity using florisil as the column packing material by GC/NPD.
2. Sample throughput such as extraction, florisil cleanup, and on-line GC analysis was decreased considerably (8h per sample) with this method.
3. Recoveries of the 18 organophosphate pesticides were good (88.7 - 100.0%) and the detection limit was low (0.019 - 0.035 mg/kg). Therefore, the proposed analytical method in this study can be applied for the simultaneous determination of 18 organophosphate pesticides in samples.

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## 유기인제 농약 분석 방법 (Multi-Pesticide Residue Method) 개발에 관한 연구

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유기인제 농약을 70% acetone으로 추출한 다음 dichloromethane 층으로 옮겨 추출물을 florisil로 충전된 open-column에서 chromatography를 행하였다. 마지막 추출물을 nitrogen-phosphorus detector(GC/NPD)을 가진 GC로 분석하였다. Narrow-bore capillary GC(Ultra-2)에 대해 18 가지의 유기인제 농약의 회수율이 88.7%에서 100.0% 에 달하였다. 본 분석 방법의 최소 검출 준위는 0.019 - 0.035 mg/kg 이었으며 sample throughput(추출, open-column chromatography 및 GC 분석)도 상당히 개선되었다(sample 당 8시간).