한국환경과학회지 제5권(제5호), 561~567, 1996
J. of the Korean Environmental Sciences Society

Study on the Development of Simultaneous Analytical Method for the Residual Organic Chloride Pesticides by Gas Chromatography

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(Manuscript received 18 July 1996)

A method for the simultaneous analysis of 31 residual organic chloride pesticides was studied using gas chromatography. Prepared analytical samples were injected to gas chromatography (HP 5890 Series II plus) on the Ultra-2 column with ECD. The packing materials for column were changed as the following reagents ; florisil and alumina N. The residual solution was loaded to column and was eluted with elution solvents ; ether : benzene (2 : 8) solution, hexane : benzene (1 : 1) solution, dichloromethane, acetone, and methanol.

The analytical results showed that 6 kinds of organic chlorides were not detected when florisil (first condition) was used as the column packing material. The nondetected 6 kinds of organic chlorides in the first analytical condition were detected and the recoveries of thrin-pesticides were increased, in particular, captan and captafol, but the recoveries of benzene hexachloride compounds were decreased when dichloromethane and methanol were added as elution solvents (packing material was florisil as in the first condition). The recoveries of dichlorfluanid, chlorofenvinfos, folpet, and dicofol were increased and that of aldrin was increased, but those of captan and captafol were not good when alumina N was used as the packing material.

To detect simultaneously thrin-pesticides, captan, and captafol, florisil and alumina N were used as the packing materials. The elution result showed that captan and captafol were not detected. This was because the column was activated insufficiently. The analytical method was the best (31 kinds of organic chlorides in the residual pesticides were detected sharply and showed high sensitivity) when the column (packing materials were florisil and alumina N, together) was fully activated and the impurities were removed using various elution solvents.
Key words : organic chlorides, residual pesticides, gas chromatography, florisil, alumina N

1. INTRODUCTION

Removal of harmful insects by pesticides has played an important role in the aspect of decreasing the disease and increasing the productivity of crops. But a few pesticides were very toxic so that those killed healthful insects as well as harmful ones. Nowadays their residual property and chronic toxicity were known and brought about the problem of residual pesticide. So the use of organic chloride pesticides such as DDT and BHC was prohibited. Also insects showed a good adaptation ability for a new environment and could resist for a few drugs. Therefore, we must develop pesticides which do not make happen environmental problems. Pesticides can be deposited in the environment and threaten many living organisms involving human life. Residual pesticides are found in soil, food, and drinking water. Eventhough above problems exist, the comsumptions of pesticides are increased gradually. Today, the FDA of USA suggests the limit amount for almost all of pesticides. In this respect, not only the design of new pesticides but also the development of the precise analytical method is demanded.

The analyses of pesticides were generally carried out by Gas Chromatography (GC), High Performance Liquid Chromatography (HPLC), and High Performance Thin Layer Chromatography (HPTLC),

the identification and quantitative analysis were done by mass spectrometry (MS). The combination methods such as GC-MS and LC-MS were also used. In the case of analyzing residual pesticides, the multi-residual method (MRM) is used. The essence for MRM analysis is finding out the optimal separation condition to separate samples effectively on GC.

We conducted this study to develop a new simultaneous analytical method for the residual organic chloride pesticides using gas chromatography.

2. Materials and Methods

2.1 Reagents

Packing materials of column, alumina N and florisil (60~100 mesh) were purchased from Sigma Chemical Co. Methanol, acetone, hexane, and dichloromethane were used for the analysis of residual agricultural chemicals, and anhydrous sodium sulfate, benzene, and ether were special grade reagents. Standards for the organic chlorides were obtained from Dr. Ehrenstorfer Gmbh Co. 31 kinds of these standards were dissolved in n-hexane to concentration of 1~7 ppm. These stock solutions were used as the working solutions.

2.2 Preparation of analytical samples

100 ml of 70 % acetone were added to 20~30 g of sample of organic chlorides and were stirred for 20 min. This solution was filtered with Whatman No. 4 filter paper and the filtrate was evaporated. The residual solution (water layer) was extracted with 100 ml of dichloromethane, twice and was shaked 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 10 ml of dichloromethane was added to the residual solution. This solution was purified by column chromatography. The packing material for analytical column was anhydrous sodium sulfate, florisil, and alumina N. 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 n-hexane and 1 μl of that was injected to GC/ECD.

2.3 Analytical conditions for the residual organic chloride pesticides by gas chromatography

Condition of detection by GC/ECD for the residual organic chloride pesticides were shown in Table 1 and the condition of analysis by GC/ECD, Table 2.

Table 1. Condition of GC/ECD for detecting residual organic chloride pesticides

Column	Ultra-2 (5% phenyl-methyl silicone) 50 m×0.32 mm×0.17 μm
Flow	1 ml/min
Carrier gas	N_2

Table 2. Condition of analysis by GC/ECD

injection Temp.	280℃
detection Temp.	300℃
initial Temp.	170℃
rate a	5℃/min
final Temp. a	220℃
final time a	19 min
rate b	10℃/min
final Temp. b	285℃
final time b	10 min

2.4 Analytical methods for the organic chlorides

The packing material and the elution solvent were changed and then the elution patterns were compared. First, florisil was used as the packing material, second, florisil was the packing material as in the first condition, but dichloromethane and methanol was added as the elution solvent, third, alumina N was used as the packing material, and the last, florisil and alumina N were used simultaneously as the packing materials.

3. Results and Discussion

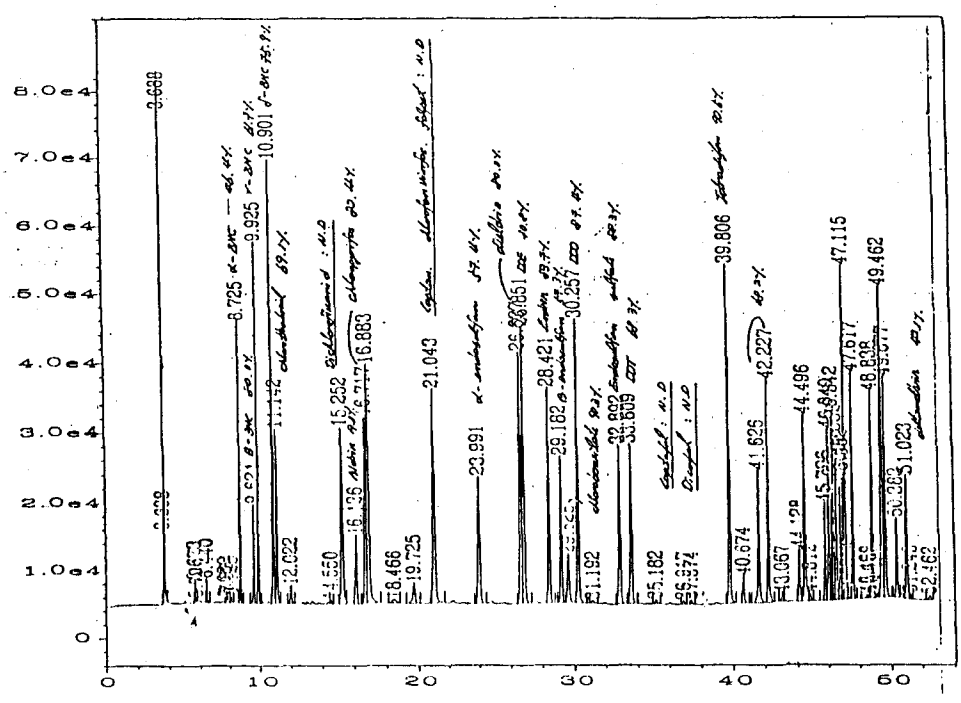

Fig. 1. Gas chromatogram for the residual organic chloride pesticides. The organic chloride standard mixtures were separated on a 50 m×0.32 mm column packed with *florisil* on Ultra-2.

3.1 Analytical result when only florisil was used

The result of gas chromatographic analysis for 31 kinds of organic chloride pesticides was shown in Fig. 1 when florisil (first condition) was used as the packing material. Fig. 1 showed that 6 kinds of organic chlorides (dichlorfluanid, captan, chlorofenvinfos, folpet, captafol, and dicofol) were not detected in above condition.

To compensate for this disadvantage and to obtain good recoveries for pesticides, dichloromethane and methanol were added as elution solvents (packing material was florisil as in the first condition). The result showed that the nondetected 6 kinds of organic chlorides in the first analytical condition were detected and the recoveries of thrin-pesticides were increased, in particular, captan and captafol. But the recoveries of BHC (benzene hexachloride) compounds were decreased (Fig. 2).

3.2 Analytical result when only alumina N was used

The result of gas chromatographic analysis for the organic chloride pesticides was shown in Fig. 3 when alumina N was used as the column packing material. Fig. 3 showed that the recoveries of dichlorfluanid, chlorofenvinfos, folpet, and dicofol were increased and that of aldrin was increased. But those of captan and captafol were not good.

3.3 Analytical result when florisil and alumina N were used together

To detect thrin-pesticides, captan, and captafol simultaneously, florisil and alumina N were used together as the packing materials and n-hexane was packed. The elution result showed that captan and captafol were not detected (Fig. 4). This was because the column was not activated sufficiently. Therefore the column was fully activated as the following process and analyzed. The column was eluted with 50 ml of ether : benzene (2 : 8), 20 ml of acetone, and 20 ml of methanol to remove the im-

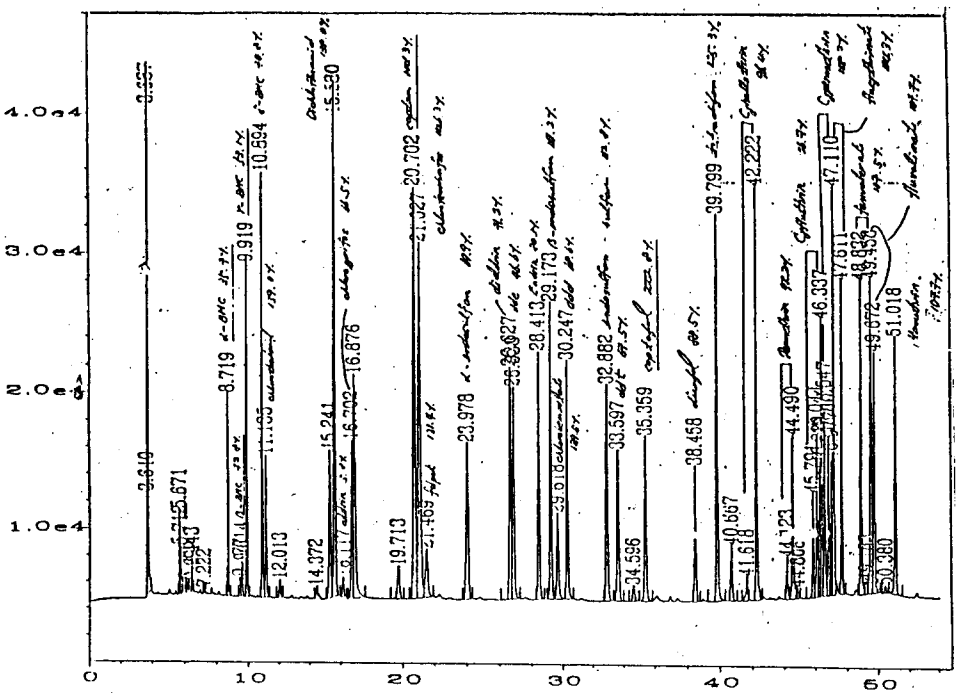

Fig. 2. Gas chromatogram for the residual organic chloride pesticides when dichloromethane and methanol were added as elution solvents.
The organic chloride standard mixtures were separated on a 50 m×0.32 mm column packed with *florisil* on Ultra-2.

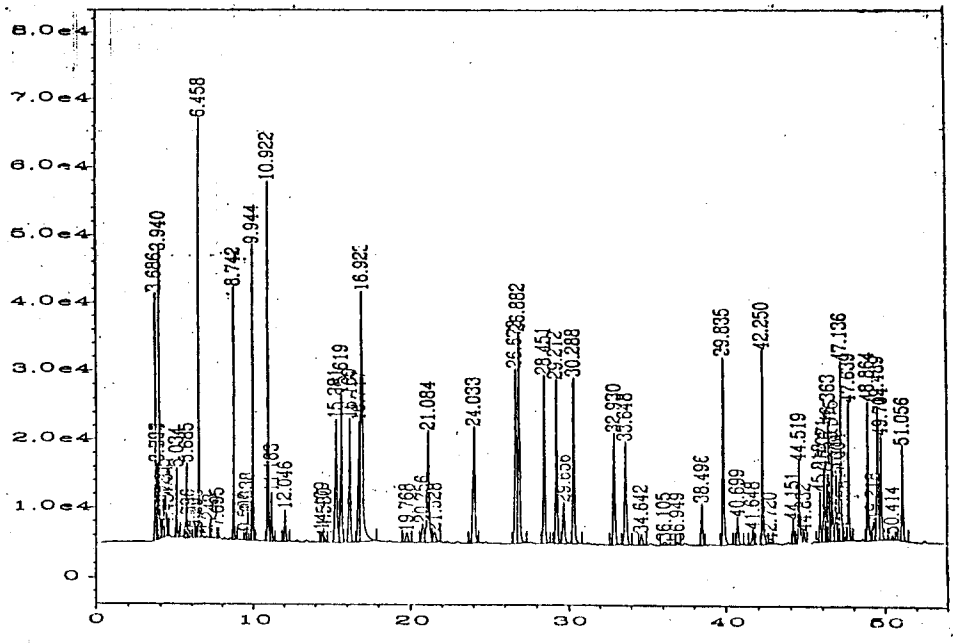

Fig. 3. Gas chromatogram for the residual organic chloride pesticides.
The standard mixtures were separated on a 50 m×0.32 mm column packed with *alumina N* on Ultra-2.

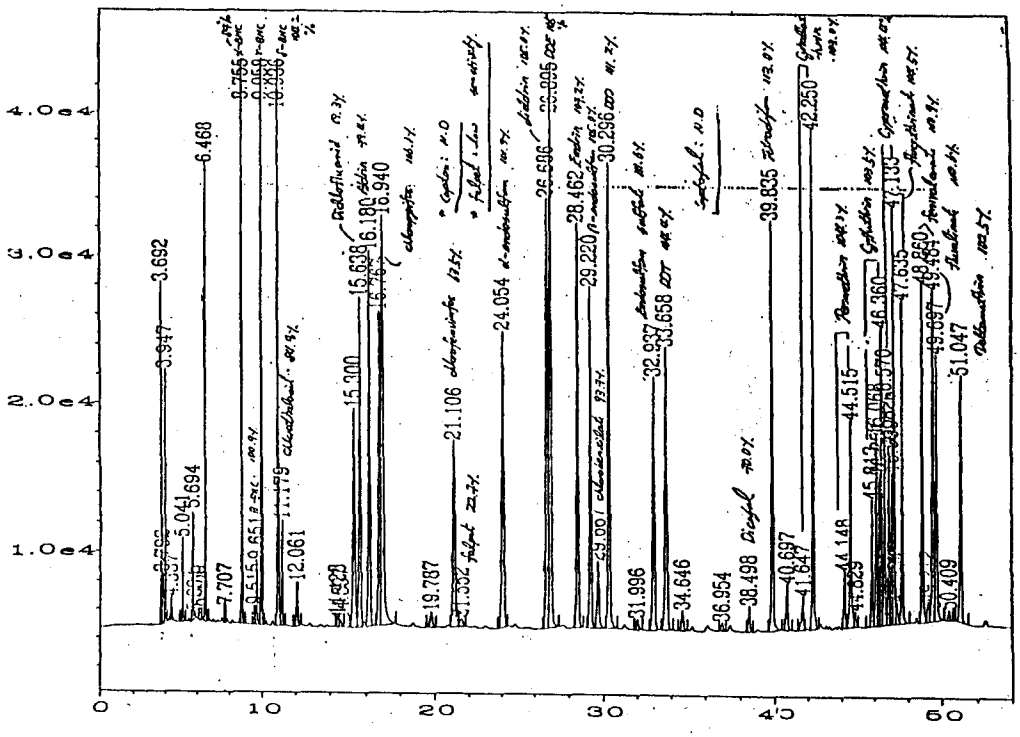

Fig. 4. Gas chromatogram for the residual organic chloride pesticides (not fully activated column).
The standard mixtures were separated on a 50 m×0.32 mm column packed with *florisil* and *alumina N* on Ultra-2.

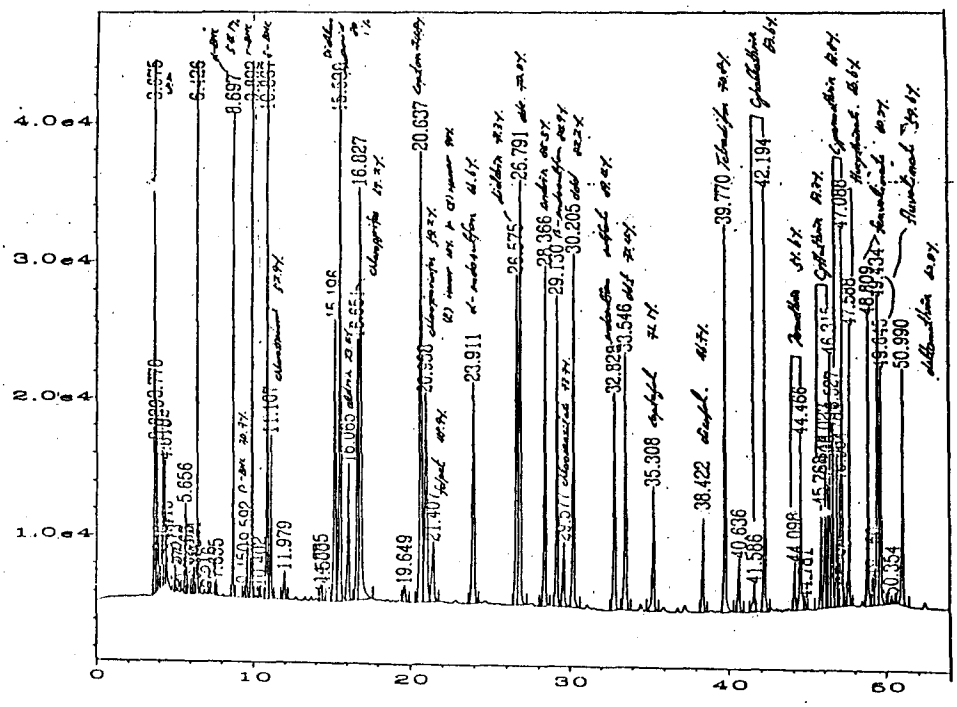

Fig. 5. Gas chromatogram for the residual organic chloride pesticides (fully activated column).
The standard mixtures were separated on a 50 m×0.32 mm column packed with *florisil* and *alumina N* on Ultra-2.

purities of the packing material and to activate the column. The residual solution was added to the column and was eluted with the elution solvents. The analytical result was shown in Fig. 5. This analytical method offered the best result because 31 kinds of organic chloride pesticides were detected sharply and showed high sensitivity.

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기체 크로마토그래피를 이용한 유기 염소계 잔류 농약 동시 분석 방법 개발에 관한 연구

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(1996년 7월 18일 접수)

31 종류의 유기 염소계 잔류 농약을 동시에 분석하는 기체 크로마토그래피 방법을 개발하기 위하여 본 연구를 수행하였다. 준비된 분석 시료를 ECD (electron capture detector)로 Ultra-2 column의 GC (gas chromatography)에 주입하였다. Column 충진 물질을 florisil 과 alumina N으로 변화시키면서 잔류 용액을 column에 loading하고 용출 용매로는 ether : benzene (2 : 8) solution, hexane : benzene (1 : 1) solution, dichloromethane, acetone 및 methanol을 사용하였다.

분석 결과 column 충진 물질로 florisil을 사용하였을때 (첫째 조건) 6종류의 유기 염소 (dichlorfluanid, captan, chlorofenvinfos, folpet, captafol과 dicofol)가 검출되지 않았다. 이 조건에서 dichloromethane과 methanol을 용출 용매로 첨가하였을때는 (둘째 조건) 첫째 분석 조건하에서 검출되지 않았던 6종류의 유기 염소가 검출되었고 thrin계 pesticides, 특히 captan과 captafol의 recovery가 증가하였다 (첫째 조건에서와 마찬가지로 충진 물질로 florisil을 사용). 그러나 BHC (benzene hexachloride) 화합물의 recovery는 감소하였다. 한편 alumina N을 column 충진 물질로 사용하였을 경우에는 dichlorfluanid, chlorofenvinfos, folpet 및 dicofol의 recovery가 증가하였으며 aldrin도 그러하였다. 하지만 captan과 captafol은 그렇지 못하였다.

Thrin계 pesticides, captan 및 captafol을 동시에 검출하기 위하여 florisil과 alumina N을 충진 물질로 동시에 사용하고 n-hexane을 충진시켜 용출시킨 결과, captan과 captafol이 검출되지 않았는데 이는 column이 충분히 활성화되지 않았기 때문이라고 생각된다. Column (florisil과 alumina N을 충진 물질로 동시 사용)을 충분히 활성화시키고 여러가지 용출 용매를 사용하여 불순물을 제거하였을때 분석 결과가 가장 우수하였다 (31 종류의 유기 염소계 잔류 농약이 sharp하게 검출되었고 높은 감도를 나타내었다).