## Determination of Aldrin and Dieldrin in Soil by Mass Chromatography<sup>\*</sup>

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Quantitative analyses of aldrin and dieldrin were carried out by mass chromatography. The m/z 66 and 79 fragment ions of aldrin and dieldrin and the m/z 81 ion of the heptachlor epoxide as internal standard were selected for the measurements. The method is free from sample related interferences. Recoveries of aldrin and dieldrin which had been added to the soil were approximately 90%, and the limit of detection was 5 ng for these compounds. The mass chromatographic method was applied for field soil samples.

### INTRODUCTION

Aldrin (1,2,3,4,10,10-hexachloro-1,4,4a,5,8, 8a-hexahydro-exo-1,4-endo-5,8-dimethanonaphthalene) and dieldrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-exo-1,4endo-5,8-dimethanonaphthalene), chlorinated cyclodienes, had been widely used for the control of a range of soil pests. Many reports on organochlorine pesticide residues in field soil and crops have been published.<sup>1-8)</sup> The contamination of livestock products and cow's milk by these insecticides has caused toxicity to men, and the use of these compounds has therefore been controlled in Japan. However, aldrin is transformed to dieldrin, and dieldrin persists in soil for more than 18 months,<sup>3)</sup> thus these compounds can still be detected in soil.<sup>6)</sup> A suitable analytical method is required for the determination of aldrin and dieldrin residues in soil.

Several analytical methods have been reported to determine these compounds.<sup>9-17)</sup> Gas chromatography equipped with an electron capture detector (GC-ECD) is highly sensitive, but this method requires a complicated cleanup procedure to remove interferences in the sample that produce peaks having the same retention times on the gas chromatogram.

Mass spectrometric analyses have been developed for the identification of compounds in biological and biomedical fluids.<sup>18–26)</sup> We have reported previously on analysis of organophosphorus pesticides by mass chromatography (MC).<sup>27)</sup> This mass chromatographic method enabled the simultaneous determination of many compounds.

In this paper, the method was successfully applied to the determination of aldrin and dieldrin residues in field soils.

### EXPERIMENTAL

### 1. Chemicals and Reagents

Aldrin, dieldrin and heptachlor epoxide were purchased from Wako Pure Chemicals Ind., Ltd., Osaka, Japan. These chemicals were dissolved in acetone. Florisil (60–100 mesh) was also obtained from Floridin Co., Tallahassee, Florida, U.S.A.

### 2. Physico-Chemical Properties of Soil

Yamagata upland soil (alluvial) was used and its physico-chemical properties were as follows: texture; clay loam, clay content;

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22.9%, clay mineral; montmorillonite, total carbon content; 2.53% and C.E.C.; 21.3 mEq/100 g dry soil.

### 3. Gas Liquid Chromatography (glc)

A Shimadzu GC-4BM instrument equipped with electron capture detector was used. The glass column (50 cm  $\times$  3 mm i.d.) was packed with 5% OV-17 on Gas chrom Q, 60–80 mesh. The carrier gas was nitrogen (40 ml/min). The temperature of the column oven, detection and injection were 160°C, 275°C and 275°C, respectively.

# 4. Gas Chromatography-Mass Spectrometry (GC-MS)

A Shimadzu LKB 9000 GC-MS-computer system was used with 1% OV-1 on Chromosorb WHP (60–80 mesh) column (50 cm × 3 mm i.d.) and helium (30 ml/min) as the carrier gas. Conditions were as follows: ionizing energy; 70 eV, column temperature; 190°C, sample port temperature; 255°C, separator temperature; 240°C, temperature of ion source; 270°C and scan interval; 4 sec.

# 5. Determination of Aldrin and Dieldrin in Field Soils

A mixture of 100 g of soil sample and 200 ml of acetone was shaken for 30 min at room temperature and filtered. The filtrate was added with 500 ml of 1% sodium chloride solution, and extracted twice with 150 ml of *n*-hexane. The organic phase was dried over anhydrous sodium sulfate, and evaporated to dryness at 40°C *in vacuo*. One ml of internal standard solution, heptachlor epoxide in *n*hexane (10 ng/ $\mu$ l), was added to the residue. After suitable dilution, a 3- $\mu$ l aliquot of the acetone solution was taken for analysis by mass chromatography.

Gas chromatographic determinations of aldrin and dieldrin are shown in Fig. 1.

### 6. Recoveries from Fortified Soil

From a standard solution containing 1,000 ng/ $\mu$ l or 100 ng/ $\mu$ l aldrin or dieldrin in *n*-hexane, l ml was added to 100-g of soil sample. After a few minutes of shaking, the treated soils were extracted following the procedure as described above.



Fig. 1 Procedure for determination of chlorinated pesticide from soil.

### 7. Calibration Curves

The calibration curves for the determination of aldrin and dieldrin by mass chromatography were prepared by plotting the ratio of the peak areas of aldrin  $(m/z \ 66)$  or dieldrin  $(m/z \ 79)$  to that of the internal standard, heptachlor epoxide  $(m/z \ 81)$ , against the ratio of the weight of aldrin or dieldrin to that of heptachlor epoxide.

### **RESULTS AND DISCUSSION**

In order to minimize the interfering compounds, the requirement in mass chromatographic determination is the use of stronger fragment ions with higher mass range. However, mass fragmentation patterns of aldrin, dieldrin and heptachlor epoxide were characterized by their base peaks, m/z 66, 79 and 81, respectively (Figs. 2–4). These base peaks are fragment ions with low mass range, but were free from interfering peaks in soils used in the experiments. Therefore, quantitative determination of aldrin and dieldrin by GC-MS was carried out by monitoring of these fragment ions. Heptachlor epoxide was used as an internal standard.

As shown in Fig. 5, the calibration curves of both chlorinated cyclodienes were linear. The recoveries of aldrin and dieldrin fortified with 10 ppm and 1 ppm in soil were calculated from



Fig. 2 Mass spectrum of aldrin.



Fig. 3 Mass spectrum of dieldrin.



Fig. 4 Mass spectrum of heptachlor epoxide.

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Fig. 6 Total ion monitor chromatogram (A) and mass chromatogram (B) of aldrin and dieldrin in soil.

Amount added (ppm)		Amount found (ppm)		Recovery $\binom{0}{70}$	
Aldrin	Dieldrin	Aldrin	Dieldrin	Aldrin	Dieldrin
10	10	10.2	10.1	102	101
		10.3	9.6	103	96
1	1	0.80	0.84	80	84
		0.76	0.94	76	94
mean±SD				$90\pm14$	$94\pm7$

Table 1 Recovery of aldrin and dieldrin from soil.

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	GC-MS		GC-ECD	
	Aldrin (ppm)	Dieldrin (ppm)	Aldrin (ppm)	Dieldrin (ppm)
Yamagata I (1973) <sup>a)</sup>	< 0.008 < 0.008	0.049 0.048	< 0.01 < 0.01	0.04 0.04
Yamagata II (1973)	< 0.008 < 0.008	0.115 0.085	< 0.01 < 0.01	0.06 0.06
Kanagawa (1973)	< 0.02 < 0.02	$0.115 \\ 0.111$		

Table 2 Residue levels of aldrin and dieldrin in field soil.

<sup>a)</sup> sampling year.

the curves, and approximately 90% was obtained (Table 1). The results of recoveries indicate that it is possible to quantitatively analyze chlorinated pesticides in soil using mass chromatography.

A mass chromatogram (total ion monitor: A) in field soil is shown in Fig. 6. The large peak at 4.2 min of retention time was similar to the retention time of aldrin. But this peak seems to be an interfering peak, because it was not present in the base peak of aldrin  $(m/z \ 66)$  on the mass chromatogram. Thus, this mass chromatographic method selectively determined the compounds in crude extracts which received no purification other than the extraction shown Fig. 1.

Residue levels of aldrin and dieldrin determined by mass chromatography are listed in Table 2 in comparison with those determined by GC-ECD. The results by the mass chromatographic method were in good agreement with those determined by GC-ECD.

Minimum detectable amounts by this mass chromatographic method were 5 ng, 5 ng and 10 ng for aldrin, dieldrin and heptachlor epoxide, respectively.

The method using mass chromatography was simple, rapid and selective for determination of these insecticides in soil.

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### 要 約

マスクロマトグラフィーによる土壌中の有機塩 素系農薬アルドリンおよびディルドリンの定量 法

小林裕子, 佐藤 清, 保野修身, 後藤真康 有機塩素系農薬, アルドリンおよびディルドリンの mass chromatography (MC) による定量法について検討 した.定量に用いたフラグメント・イオンはアルドリン, ディルドリンの base peak である *m*/*z* 66, *m*/*z* 79 であ り, ヘプタクロル・エポキシド (*m*/*z* 81, base peak) を 内部標準物質として使用した.この方法により, 精製操 作をほとんど行なわなくても天然物による妨害をうけず に,選択的な定量が可能である.土壌での添加回収率は 90%,最小検出量は5 ng であった.