Introduction

For the residue trials of Sumithrin [3-Phenoxybenzyl (1R)-cis, trans-chrysanthemate] in field, an analytical method has been developed to determine Sumithrin residue in soil.

Materials and methods

1. Materials

(1) Reagents

acetone, methyl alcohol, dichloromethane, ethyl acetate and hexane (n-hexane)
: residue analytical grade, Kanto Chemical Co., Inc.

Sodium chloride : pure grade, Wako Pure Chemical Industries, Ltd.

Anhydrous sodium sulfate : pure grade, Kanto Chemical Co.,Inc.

Hyflo Super-Cel : Johns Manvilles Corp.

Florisil PR : residue analytical grade, Floridin Co.,Ltd.

(2) Analytical standard

Sumithrin: Purity 97%, Sumitomo Chemical Co., Ltd.

(3) Apparatus

Mechanical shaker: KM-VD, Iwaki Co.

Rotary vacuum evaporator: Type N-1, Tokyo Rika Kikai Co., Ltd.

Gas chromatograph equipped with mass spectrometric detector (GC-MS) : Finnigan 4000 system, Finnigan Mat Co., Ltd.

2. Methods

(1) Soil sample preparation

Soil samples were passed through 5 mm sieves.
The water content of the sample was determined by drying under 130°C for 5 hours.

(2) Extraction

After shaking 20 g (dry weight) of the sample with 30 ml of methyl alcohol for 10 minutes, the mixture was filtered

under suction through Hyflo Super-cel (ca. 1 cm thickness) on a Kiriyama funnel (equivalent to Buchner funnel). The residue was rinsed with 10 ml of methyl alcohol by portions. The residue was re-extracted by shaking with 30 ml of methyl alcohol for 10 minutes as described above.

The filtrates were transferred into a separatory funnel and shaken with 80 ml of 10 % aqueous sodium chloride solution and 40 ml of dichloromethane for 10 minutes. The lower dichloromethane layer was drained and passed through ca. 50 g of anhydrous sodium sulfate in a filter funnel.

The remaining aqueous layer was shaken with 30 ml of dichloromethane for 5 minutes. The dichloromethane layer was drained and passed through the above filter funnel. The anhydrous sodium sulfate in the funnel was rinsed with 15 ml of dichloromethane.

The dried dichloromethane layers were concentrated to dryness with a rotary vacuum evaporator below 40°C (See Note 1).

(3) Florisil PR column chromatography (See Note 2)

The activated 15 g of florisil PR (activated overnight 130°C) was suspended in a mixed solvent (hexane/ethyl acetate=20/1, v/v). The suspended florisil PR was transferred into a glass column (18 mm in diameter). After tapping the side of the column to make uniform packing of florisil PR, 1 g of anhydrous sodium sulfate was putted on the top of the packed florisil PR.

The concentrated residue obtained by the extraction was transferred quantitatively to the column with four 3 ml portions of the mixed solvent, and each portions was drained to the top of the column. The compound was eluted with the same mixed solvent and 50 ml of eluate was collected after discarding the initial 20 ml (See Note 2).

The collected eluate was concentrated to dryness with rotary vacuum evaporator below 40°C (See Note 1). The obtained residue was dissolved in acetone for GC-MS.

(4) Preparation of standard solution

After weighing 20.00 mg of Sumithrin, it was added into 20 ml of a volumetric flask and diluted to the mark with acetone (1000 µg/ml standard solution; stock solution). This solution was used to prepare standard solutions with suitable concentration by diluting with acetone. Working standard solution was 2.0 µg/ml for GC-MS determination.

(5) Determination

a) GC-MS conditions

Apparatus:	Finnigan 4000 GC-MS system equipped with PROMIN ®
Column:	5% Silicone SE-30 on Chromosorb W AW DMCS, 60 - 80 mesh, i.d. 2 mm x L. 1.1 m
Temperature:	Column; 245°C
	Injection; 270°C
	Transferline; 230°C
	Separator; 280°C
	Ion source; 250°C
Carrier (He):	20 ml/minute
Electron energy:	30 eV
Emission current:	0.15 mA
Scan time:	3 second
Setting mass number:	m/e 350 (M^+)
Chart speed:	10 mm/minute

b) Calibration curve

The acetone solutions of Sumithrin with its concentration ranging from 0.2 µg/ml to 3.0 µg/ml were prepared and 2 µl each of the solutions was injected into the GC-MS. The peak height versus the amount of Sumithrin injected showed linear response in the range of 0.4 ng to 6 ng under the above operating conditions, where the retention time of Sumithrin was 3 minutes.

c) Determination

The obtained residue in section 2 (3) was dissolved in acetone to give a concentration of Sumithrin approximately equivalent to the working standard (2.0 µg/ml). Control sample and lower residue level (less than 10 times of minimum detectable concentration) sample were dissolved in 1.0 ml of acetone. An aliquot (2 µl) of the diluted solution was injected to the GC-MS. The Sumithrin peak height was compared with that of the working standard injected under the same conditions.

Note

1. After evaporating the solvent, the concentrating has to be stopped soon to prevent the loss of Sumithrin.

2. The recovery of Sumithrin from column chromatography has to be checked for each of activated florisil PR. A chromatography column is prepared as described in Section 2 (3). Ten ml of the working standard solution is pipetted into a round bottomed flask and concentrated to dryness with a rotary vacuum evaporator below 40°C. The concentrated residue is transferred to the column and chromatographed as described above. The obtained residue is dissolved in 10 ml of acetone and determined by GC-MS. If the recovery is less than 90 %, the eluting fraction of Sumithrin has to be reconfirmed.

3. The acceptable S/N (signal/noise) ratio for minimum detectable amount is more than 10 for quantitative analysis.

4. Calculation

Concentration of Sumithrin (ppm)

$$= \frac{Sa/St * A * B}{W}$$

Sa : Peak height (Sample)
St : Peak height (Standard)
A : Concentration of standard (ug/ml)
B : Dilution volume (ml)
W : Weight of sample (g)