PIPERONYL BUTOXIDE

33

33/LN/(M)/-

Applicability to

Permethrin/Piperonyl butoxide LN

Studies for Applicability of
Provisional Extension CIPAC Method to
Permethrin/Piperonyl butoxide LN

by
Makiko Mukumoto
Sumitomo Chemical Co., Ltd.
Organic Synthesis Research Laboratory
1-98, Kasugade-naka 3-chome, Konohanaku, Osaka
JAPAN

1. INTRODUCTION

The CIPAC 33/LN/(M)/3 is the provisional extension method of CIPAC 32+33+345/TK/(M)/3 for the determination of the content of piperonyl butoxide in polyethylene matrix.
This method is applicable for permethrin/piperonyl butoxide LN.
This report was prepared to demonstrate the validity of this method for permethrin/piperonyl butoxide LN.

2. METHOD DESCRIPTION

DETERMINATION OF PIPERONYL BUTOXIDE IN POLYETHYLENE MATRIX BY GC-FID 33/LN/(M)/-

1 Sampling. Take at least 500 g.

2 Identity tests
GLC. Use the GLC method below. The relative retention time of piperonyl butoxide with respect to the internal standard should not deviate by more than 2% from that of the calibration solution.

3 Active ingredient
SCOPE The method is suitable for the determination of piperonyl butoxide in polyethylene matrix.

OUTLINE OF METHOD The sample is extracted by refluxing with xylene. The piperonyl butoxide content is determined by capillary gas chromatography using flame ionisation detection and internal standard.

REAGENTS
Xylene
Piperonyl butoxide standard of known purity. Store below 0°C.
Octadecane internal standard.
Internal standard solution. Weigh (to the nearest 0.1 mg) into a volumetric flask (50 ml) octadecane (0.4 g). Fill to the mark with xylene and mix well.
Calibration solutions. Allow piperonyl butoxide to equilibrate to ambient temperature. Then weigh (to the nearest 0.1 mg) into a volumetric flask (50 ml) 0.25 g. Fill to the mark with xylene and mix well. To pipette 0.50 ml, 1.50 ml, 2.00 ml, 3.00 ml and 4.00 ml of

this solution into 5 volumetric flasks (25 ml). Add 2 ml of internal standard solution and fill up each to the mark with xylene and mix well.

Five solutions are used as calibration solutions A(C_A), B(C_B), C(C_C), D(C_D), E(C_E).

Transfer 200 µl out of each flask into separate GC vials. Place the vial into the sample tray of GC apparatus.

Description of the calibration solutions:

- C_A: concentration of approximately 2.5 mg piperonyl butoxide in 25 ml xylene
- C_B: concentration of approximately 7.5 mg piperonyl butoxide in 25 ml xylene
- C_C: concentration of approximately 10.0 mg piperonyl butoxide in 25 ml xylene
- C_D: concentration of approximately 15.0 mg piperonyl butoxide in 25 ml xylene
- C_E: concentration of approximately 20.0 mg piperonyl butoxide in 25 ml xylene

APPARATUS

Gas chromatograph capable of operating over the range 180 to 250°C fitted with a flame ionisation detector, a split injector, and an autosampler

Capillary column fused silica, 30 m x 0.32 mm (i.d.) with 100% methyl polysiloxane, cross-linked, surface bonded stationary phase and 0.25 µm film thickness (Durabond-1 or equivalent)

Electronic integrator or data system

PROCEDURE

(a) Operating conditions (typical):

Column	Fused silica, 30 m x 0.32 mm (i.d.) with 100% methyl polysiloxane, cross-linked, surface bonded stationary phase and 0.25 µm film thickness (Durabond-1 or equivalent)
Injection system	
Injector	Split injection
Injector temperature	250°C
Sprit ratio	20:1
Purge flow	1 ml/min
Injection volume	1 µl

Detector system	
Type	Flame ionisation
Temperature	300°C
Oven temperatures	
Initial	180°C
Program	180°C hold for 11 min → 200°C at 10°C/min, hold for 8 min → 210°C at 10°C/min, hold for 18 min → 245°C at 30°C/min, hold for 4 min
Total run time	45 min
Gas flow rates	
Helium (carrier)	linear velocity: 39 cm/min at 180°C
Helium (make up)	30 ml/min
Hydrogen	40 ml/min
Air	400 ml/min
Total flow	35 ml/min
Retention times	octadecane: about 6 min piperonyl butoxide: about 23 min

(b) Preparation of sample. Cut the sample with scissors into 1 – 2 cm squares and thoroughly mixed. Weigh (to the nearest 0.1 mg) sufficient sample to contain 12.5 mg of piperonyl butoxide into a 250 ml reflux flask. Add 23 ml xylene and 2 ml internal standard solution. Reflux the sample about 30 minutes. Cool down the sample to room temperature. Filter the solution through a 0.45 µm Teflon filter membrane. Transfer into a separate GC vial.

(c) System equilibration. Inject into the gas chromatograph a 1 µl portion of the sample solution to condition the column and to check for the appropriate flow rates and integration events.

(d) Determination. Inject in duplicate into the gas chromatograph 1 µl portions of the calibration and sample solutions in the following sequence:

C_A, C_A, C_B, C_B, C_C, C_C, C_D, C_D, C_E, C_E, S_1, S_1, S_2, S_2, ···etc

(e) Calculation.

$$\text{Concentration} = R/w \text{ (g/kg)}$$

Where:

R = Piperonyl butoxide reading from the analysis in mg
w = mass of sample taken in g

3. METHOD ASSESSMENT

According to the CIPAC method extension guideline, the applicability of this method to permethrin/piperonyl butoxide LN was investigated.

The sample subjected to this assessment was Olyset plus. The nominal contents of permethrin and piperonyl butoxide in the test sample are 20 g/kg and 10 g/kg, respectively.

3.1 Specificity

The sample solution prepared without addition of the internal standard solution and the solutions of the blank formulation treated in the same way as a sample, the piperonyl butoxide standard, the permethrin standard and the internal standard were chromatographed. As shown in Figures 1 to 5, there was no significant interference.

3.2 Check of the acceptability range

Scope of the existing CIPAC method: 4 g/kg to 167 g/kg

Acceptability range: 2 g/kg to 334 g/kg

Piperonyl butoxide content in permethrin/piperonyl butoxide LN; 10 g/kg

The piperonyl butoxide content in permethrin/piperonyl butoxide LN is within the acceptability content range of the existing CIPAC method.

3.3 Precision

Six separate sub-samples from a sample of permethrin/piperonyl butoxide LN were analyzed in accordance with CIPAC 33/LN/(M)/3.
The repeatability of this method was satisfactory with the relative standard deviation (RSD) of 0.9% as shown in Table 1.

Table 1 Precision Test

No.	Concentration of piperonyl butoxide (g/kg)
1	9.5
2	9.4
3	9.5
4	9.5
5	9.3
6	9.4
Mean	9.4
%RSD	0.9

4. CONCLUSION

The shown data demonstrated the validity of CIPAC 33/LN/(M)/3 for permethrin/piperonyl butoxide LN.
Therefore, JAPAC proposes that the CIPAC 33/LN/(M)/3 is applicable to permethrin/piperonyl butoxide LN.

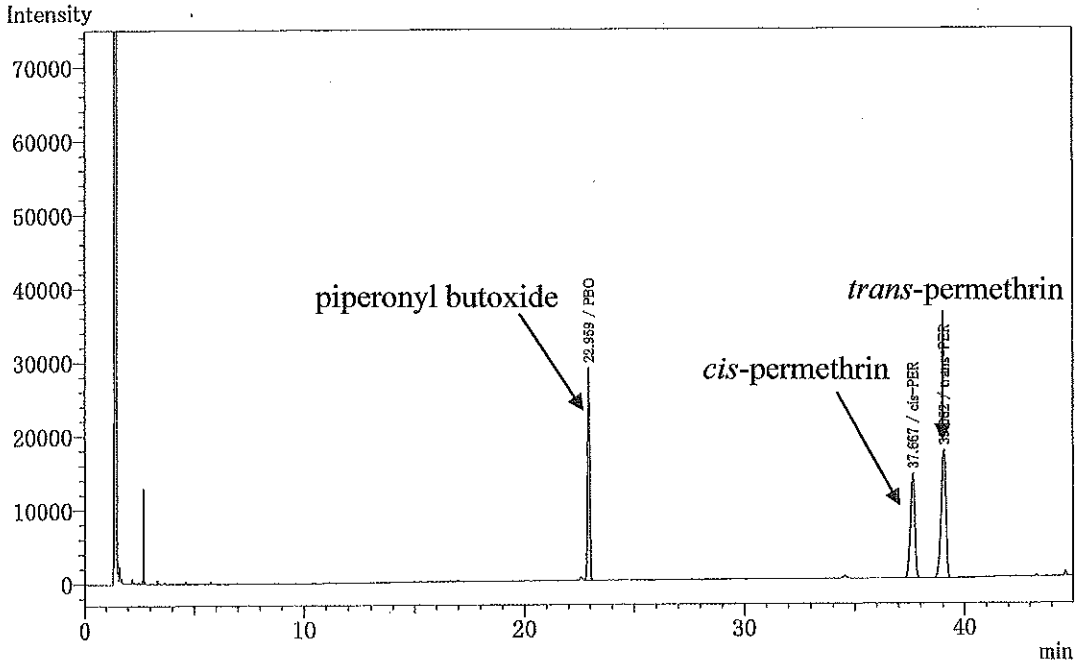

Fig 1 Gas chromatogram of permethrin/piperonyl butoxide LN, Olyset plus

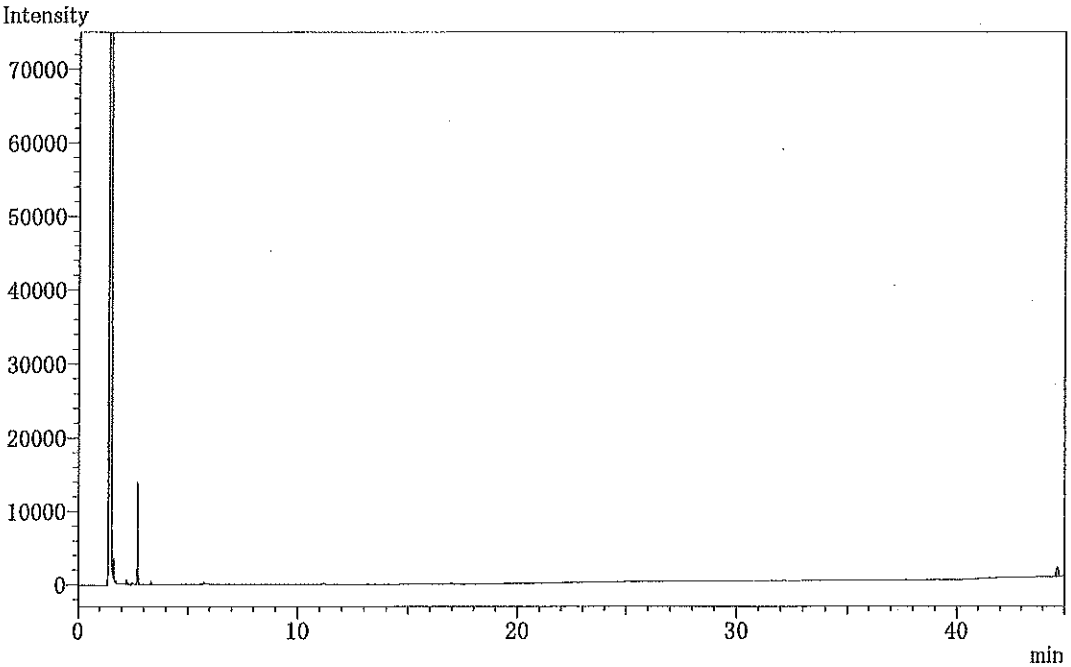

Fig 2 Gas chromatogram of blank formulation

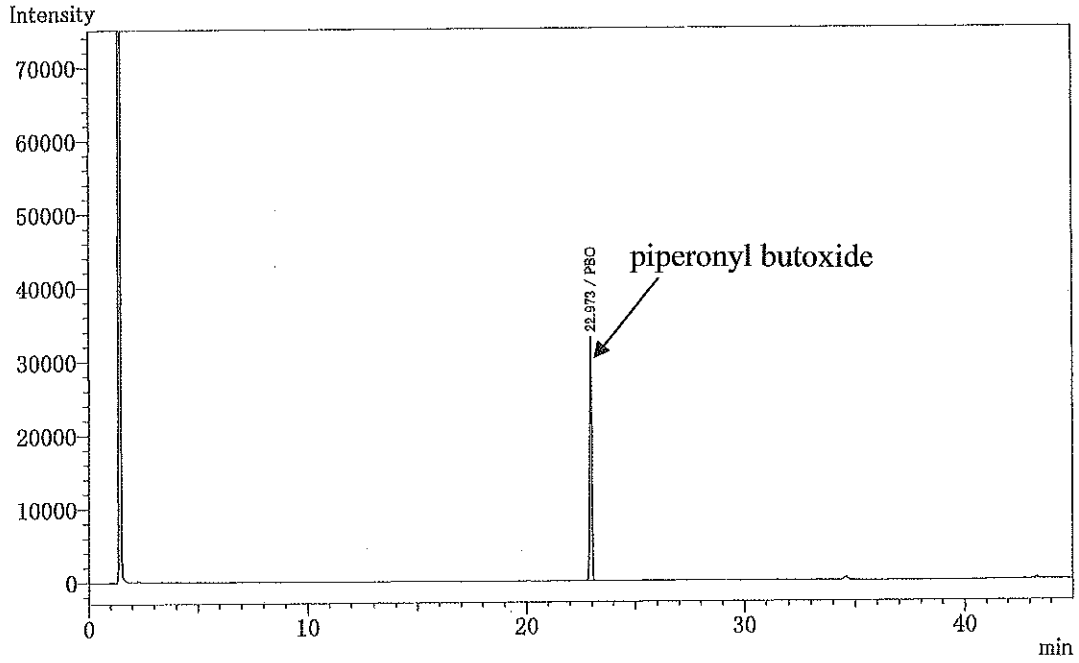

Fig 3 Gas chromatogram of piperonyl butoxide standard

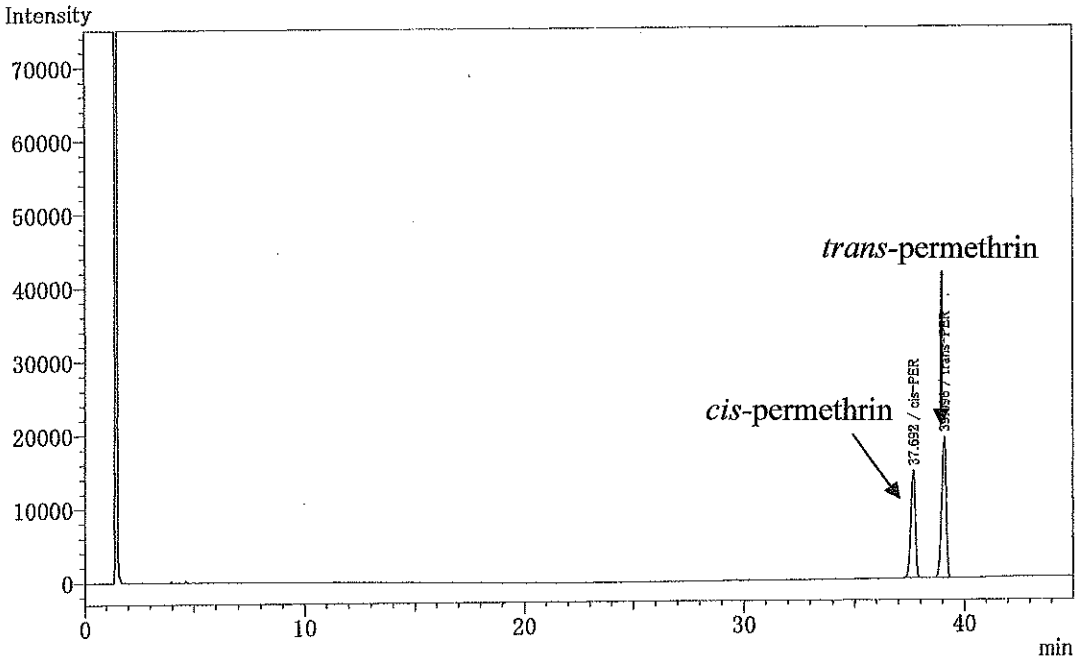

Fig 4 Gas chromatogram of permethrin standard

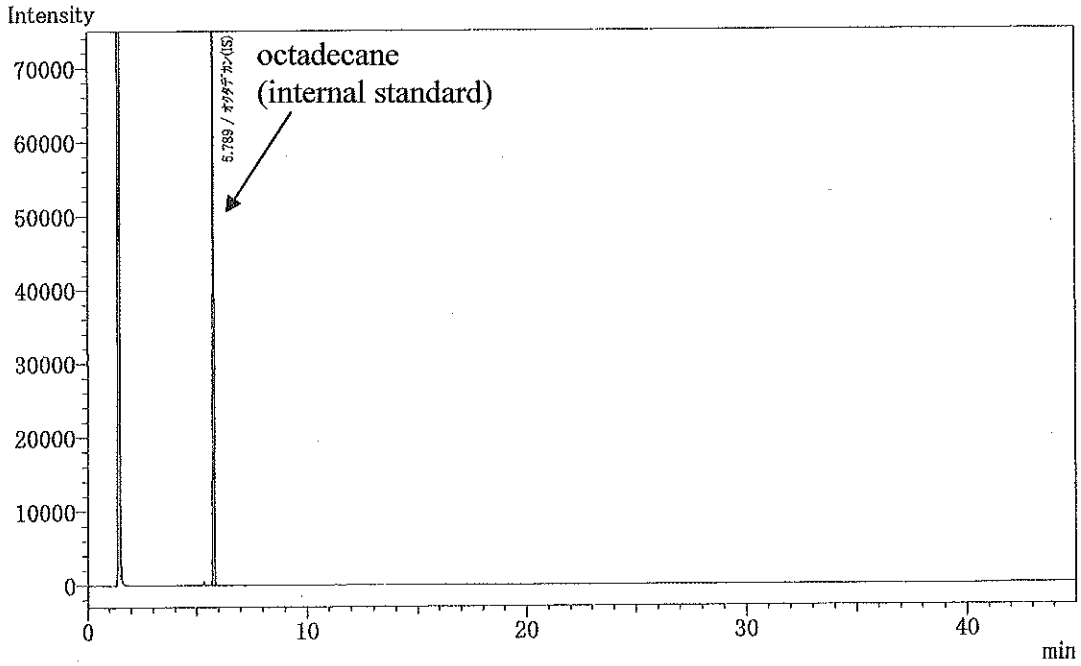

Fig 5 Gas chromatogram of internal standard