PIPERONYL BUTOXIDE

33

33/EW/M/-

Method Extension for

Metofluthrin/*d,d-trans*-Cyphenothrin/Piperonyl butoxide EW

Studies for Method Extension of Existing CIPAC Method
for Metofluthrin/*d,d-trans*-Cyphenothrin/Piperonyl butoxide EW

by
Makiko Mukumoto
Sumitomo Chemical Co., Ltd.
Environmental Health Science Laboratory
1-98, Kasugade-naka 3-chome, Konohanaku, Osaka
JAPAN

1. INTRODUCTION

The CIPAC 33/EW/M/3 is the extension method of CIPAC 32+33+345/TK/(M)/3 for the determination of the content of piperonyl butoxide in piperonyl butoxide oil in water emulsions (EW).
This method was extended for metofluthrin/*d,d-trans*-cyphenothrin/piperonyl butoxide EW with changing the internal standard.
This report was prepared to demonstrate the validity of the extension of the existing CIPAC 33/EW/M/3 for metofluthrin/*d,d-trans*-cyphenothrin/piperonyl butoxide EW.

2. METHOD DESCRIPTION

DETERMINATION OF PIPERONYL BUTOXIDE IN PIPERONYL BUTOXIDE OIL IN WATER EMULSIONS 33/EW/M/3

1 Sampling. Take at least 1 l.

2 Identity tests
2.1 GC. Use the GLC method below. The relative retention time obtained from the sample should not deviate by more than 1% from that of the standard under the same conditions.

2.2 GC-MS. (formulations with two or more active substances) Use a GC apparatus connected to a mass spectrometer with an electron impact ion source and separate the components by the GLC method below. Record the mass spectrum of the peak found at the retention time assigned to piperonyl butoxide. The mass spectrum should match that found from the standard.

3 Piperonyl butoxide
SCOPE The method is suitable for the determination of piperonyl butoxide formulations containing piperonyl butoxide as the only active ingredient and in mixtures with metofluthrin and *d,d-trans*-cyphenothrin.

OUTLINE OF METHOD Piperonyl butoxide is determined by capillary gas chromatography using flame ionisation detection and heptadecane as internal standard.

REAGENTS

Piperonyl butoxide standard of known purity. Store below 0°C.

Heptadecane internal standard.

Propan-2-ol

Internal standard solution. Weigh into a volumetric flask (1l) heptadecane (12.5 g). Fill to the mark with propan-2-ol 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 (100 ml) 0. 11 g piperonyl butoxide (*s* mg). Add by pipette internal standard solution (5.0 ml) and make up to volume with propan-2-ol. Mix well (Solution C). Keep tightly closed and store in the dark under refrigeration.

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	heptadecane: about 4 min
	piperonyl butoxide: about 23 min

(b) Preparation of sample. Thoroughly shake the sample container to homogenise the sample before use. Weigh (to the nearest 0.1 mg) into a volumetric flask (100 ml) sufficient sample (*w* mg) to contain 0.11 g piperonyl butoxide. Add by pipette internal standard solution (5.0 ml) and make up to volume with propan-2-ol. Mix wee (Solutions S).

(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:

$$C_1, C_2, S_1, S_2, C_3 \cdots \text{etc.}$$

Determine piperonyl butoxide to internal standard peak area ratio (*R* and *R'* for the sample and calibration solutions respectively). Average the ratios (*R'*) of the calibration solution injections bracketing the sample solution injections and the ratios (*R*) of the bracketed sample solution injections.

(e) Calculation.

$$\text{Piperonyl butoxide content} = \frac{R \times s \times P}{R' \times w} \text{ g/kg}$$

Where:

R = piperonyl butoxide to internal standard peak area ratio of the sample solution

R' = piperonyl butoxide to internal standard peak area ratio of the calibration solution

s = mass of piperonyl butoxide in the sample solution (mg)

w = mass of sample taken (mg)
P = purity of piperonyl butoxide standard (g/kg)

3. METHOD ASSESSMENT

According to the CIPAC method extension guideline, the method extension of the CIPAC 33/EW/M/3 for metofluthrin/*d,d-trans*-cyphenothrin/piperonyl butoxide EW was investigated.

3.1 Check of availability of a CIPAC method for the formulation concerned (Step 1)

Since CIPAC method for piperonyl butoxide EW was available (CIPAC 33/EW/M/3), the applicability of this method for metofluthrin/*d,d-trans*-cyphenothrin/piperonyl butoxide EW was investigated.
The sample subjected to this assessment was SumiPro. The nominal contents of metofluthrin, *d,d-trans*-cyphenothrin and piperonyl butoxide in SumiPro are 1.0, 60 and 100 g/kg, respectively.

3.2 Check whether the concentration of the analyte is inside or outside the acceptability range covered by the samples of the original trial (Step 2)

Scope of the existing CIPAC method: 160 to 167 g/kg (TK).
Acceptability range: 80 to 334 g/kg.
Piperonyl butoxide content in SumiPro: 100 g/kg
The piperonyl butoxide content in SumiPro is within the acceptability content range of the existing CIPAC method.

3.3 Modification of method has to be changed in order to be specific (Step 4)

In the CIPAC 33/EW/M/3, heptadecane is used as the internal standard. However, heptadecane cannot separate from the formulants in SumiPro. Therefore, the internal standard was changed to triphenyl phosphate which was shown good separation with the formulants.
This modification is considered to be a minor modification.

Changed internal standard solution. Weigh into a volumetric flask (100 ml) triphenyl phosphate (1.8 g). Fill to the mark with propan-2-ol and mix well.
Retention time triphenyl phosphate: about 22 min

3.4 Validation study (Step 5)

Specificity, precision and accuracy tests were conducted.

3.4.1 Specificity

The sample solution prepared without addition of the internal standard solution and the solutions of the blank formulation (without piperonyl butoxide) treated in the same way as a sample, piperonyl butoxide standard, metofluthrin standard, *d,d-trans*-cyphenothrin standard and the internal standard were chromatographed. As shown in Figures 1 to 6, there was no significant interference.

3.4.2 Precision

Six separate sub-samples from a sample of metofluthrin/*d,d-trans*-cyphenothrin/piperonyl butoxide EW were analyzed in two laboratories.
The repeatability of this method was satisfactory with the relative standard deviations (RSDs) of 0.1% and 0.2% as shown in Table 1. The typical chromatogram of the sample solution is shown in Figure 7.

Lab 1; Sumitomo Chemical Co., Ltd.
Lab 2; Taoka Chemical Analysis Center Co., Ltd.

Table 1 Precision Test

No.	Content of piperonyl butoxide (g/kg)	
	Lab 1	Lab 2
1	100.8	99.8
2	101.0	99.6
3	101.0	99.1
4	101.0	99.4
5	101.1	99.6
6	101.1	99.5
Mean	101.0	99.5
%RSD	0.1	0.2

3.4.3 Accuracy

The stock solution at an appropriate concentration of piperonyl butoxide was fortified to the blank formulation so that the fortified concentration of piperonyl butoxide was at the level of the specification. The solutions were analyzed, and the recoveries of piperonyl butoxide were calculated by the following equation:

$$R = \frac{C}{C_S} \times 100$$

where, R : recovery (%)
C : observed concentration (g/kg) of piperonyl butoxide
C_S : fortified concentration (g/kg) of piperonyl butoxide

The recoveries were satisfactory as shown in Table 2.

Table 2 Accuracy Test

No.	Recovery (%)
1	98.74
2	98.45
3	98.28
4	98.15
Mean	98.41
%RSD	0.3

4. CONCLUSION

In order to apply the CIPAC 33/EW/M/3 to metofluthrin/*d,d-trans*-cyphenothrin/piperonyl butoxide EW, the internal standard was changed. This modification is considered to be a minor modification.
The shown data demonstrate the validity of the modified method.
The modified method is considered appropriate for the determination of piperonyl butoxide in metofluthrin/*d,d-trans*-cyphenothrin/piperonyl butoxide EW.
Therefore, JAPAC proposes to extend the CIPAC 33/EW/M/3 for metofluthrin/*d,d-trans*-cyphenothrin/piperonyl butoxide EW.

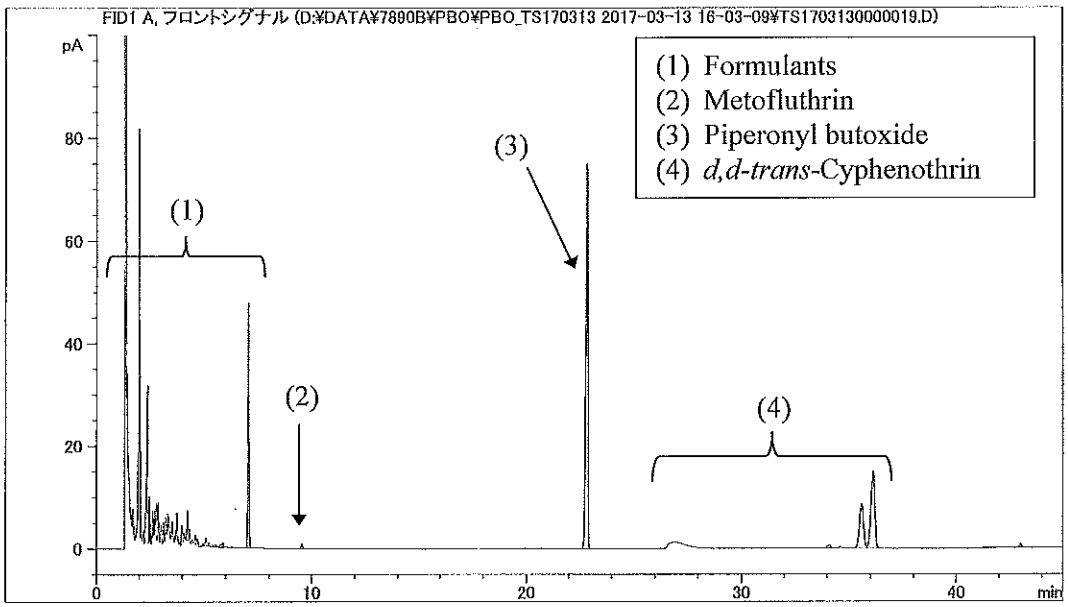

Fig 1 Gas chromatogram of metofluthrin/*d,d-trans*-cyphenothrin/piperonyl butoxide EW, SumiPro (5)

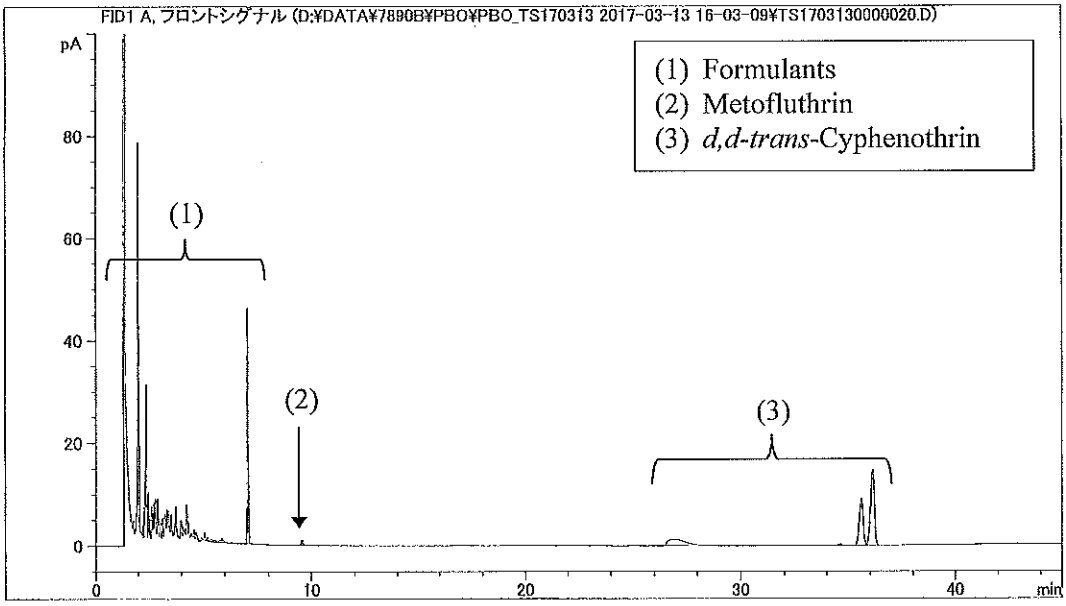

Fig 2 Gas chromatogram of blank formulation (without piperonyl butoxide)

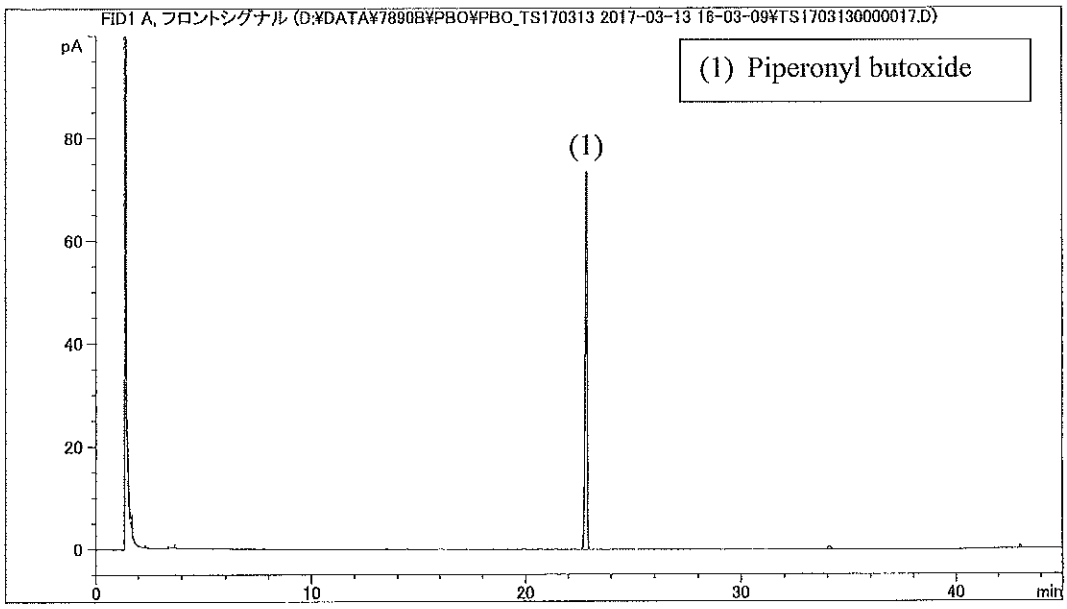

Fig 3 Gas chromatogram of piperonyl butoxide standard

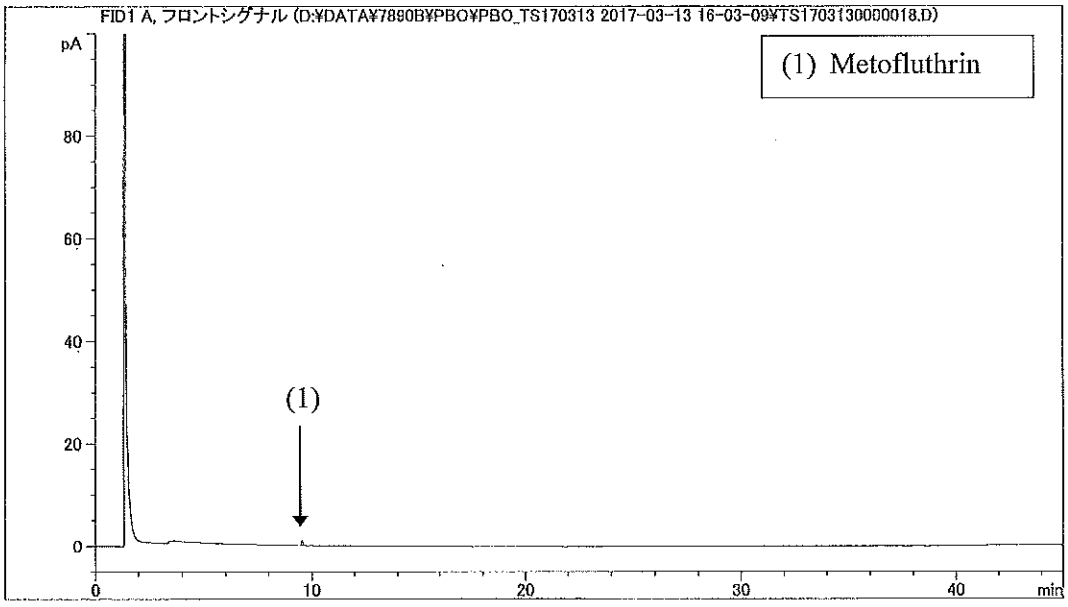

Fig 4 Gas chromatogram of metofluthrin standard

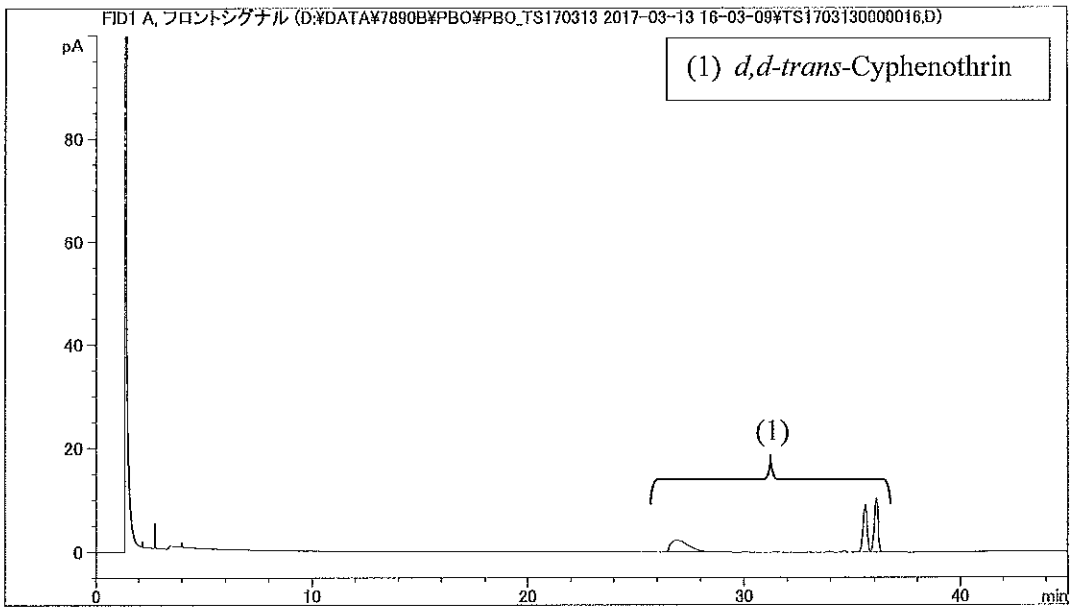

Fig 5 Gas chromatogram of *d,d-trans*-cyphenothrin standard

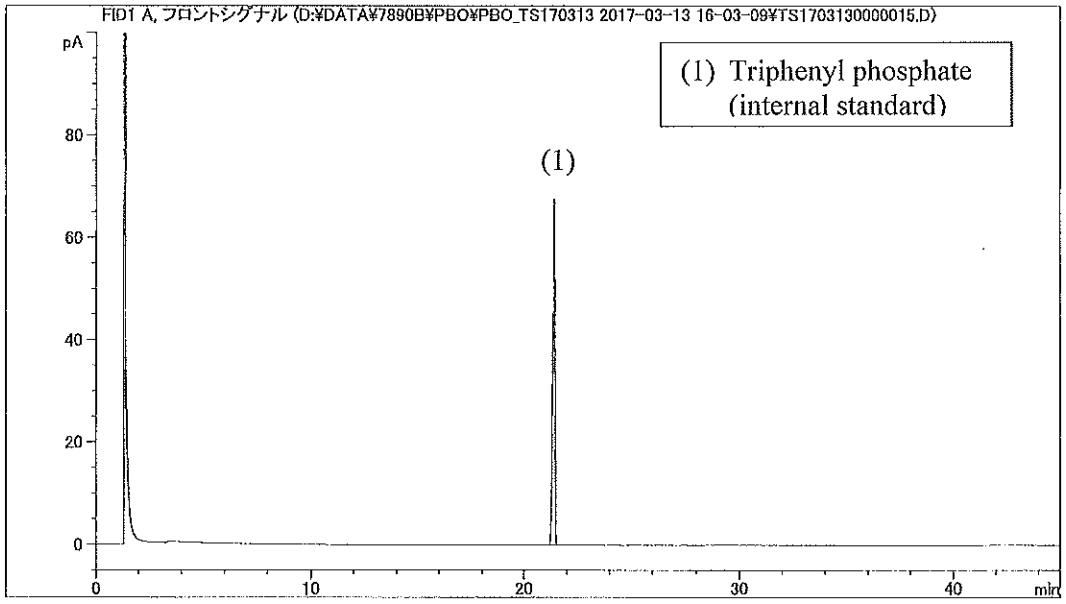

Fig 6 Gas chromatogram of internal standard

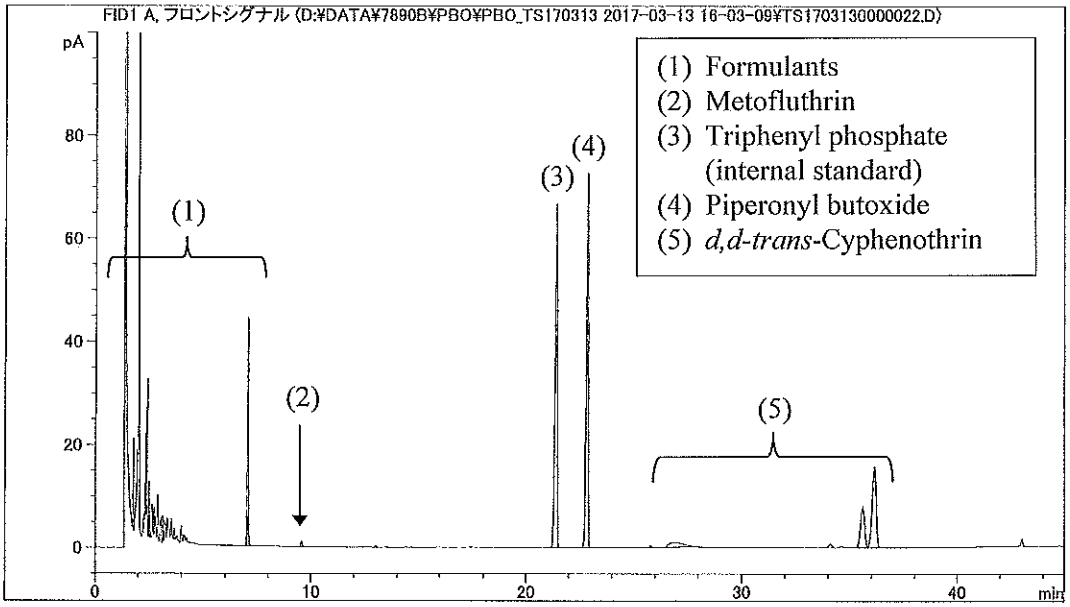

Fig 7 Gas chromatogram of sample solution