PERMETHRIN

331

331/LN/(M2)/-

Applicability to

Permethrin/Pyriproxyfen LN

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

by
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1. INTRODUCTION

As the existing CIPAC methods for permethrin LN, the CIPAC 331/LN/M/3 and the CIPAC 331/LN/(M2)/3 have been established. The former method is the original CIPAC method and the latter method is the provisional extension method of the former method for the determination of the content of permethrin in permethrin/piperonyl butoxide LN.

In order to apply the former method to permethrin/pyriproxyfen LN, it is necessary to add a short column temperature program to assure that all formulants elute from the analytical column. In addition, with this modification, the detector temperature has to be raised. On the other hand, the latter method can be applied to permethrin/pyriproxyfen LN without modifications.
Therefore, the latter method was chosen as the method for permethrin/pyriproxyfen LN, and the applicability was investigated.

This method was found to be applicable for permethrin/pyriproxyfen LN.
This report was prepared to demonstrate the validity of this method for permethrin/pyriproxyfen LN.

2. METHOD DESCRIPTION

PERMETHRIN LONG LASTING INSECTICIDAL NETS 331/LN/(M2)/-

SCOPE The method is suitable for determining permethrin in incorporated insecticidal nets in the presence of piperonyl butoxide.

1 Sampling. Take at least 500 g.

2 Identity tests
2.1 GLC. Use the GLC method below. The retention times of *cis*- and *trans*-permethrin should not deviate by more than 1% from those of the permethrin standard and the intensities of the permethrin isomers should give the same pattern as in the standard (Fig 1).
2.2 GC-MS. 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 spectra of the peaks found at the

retention times assigned to *cis*- and *trans*-permethrin. The mass spectra should match those found from the standard (Figs 2 and 3).

3 Permethrin

OUTLINE OF METHOD The content of permethrin (sum of *cis*- and *trans*-isomers) is determined by capillary GC using flame ionisation detection and dicyclohexyl phthalate as internal standard. The *trans*-isomer fraction is calculated from the chromatogram obtained.

REAGENTS

Heptane

Permethrin working standard technical product of certified purity. Store refrigerated.

Dicyclohexyl phthalate internal standard. Must not show peaks with the same retention times as *cis*-permethrin, *trans*-permethrin and piperonyl butoxide.

Internal standard solution. Dissolve dicyclohexyl phthalate (0.73 g) in heptane (100 ml). Ensure that a sufficient quantity of this solution is prepared for all samples and calibration standards to be analysed.

Calibration solution. Homogenise the permethrin standard. When the permethrin is waxy solid or partly waxy solid homogenise it by warming it to melting and by stirring. Prepare calibration solutions in duplicate. Weigh (to the nearest 0.1 mg) 72 to 88 mg (*s* mg) of permethrin standard into a vial or stoppered flask (200 ml). Add by pipette internal standard solution (10.0 ml) and dissolve. Add by measuring cylinder heptane (90 ml) and mix well (solutions C_A and C_B).

APPARATUS

Gas chromatograph equipped with a split/splitless injection and a flame ionisation detector

Capillary column fused silica, 30 m x 0.25 mm (i.d.), film thickness: 0.25 μm, coated with crosslinked dimethyl polysiloxane (DB-1 or equivalent)

Electric integrator or data system

PROCEDURE

(a) Gas chromatographic conditions (typical):

Column	fused silica, 30 m x 0.25 mm (i.d.), film thickness: 0.25 μm, coated with crosslinked dimethyl polysiloxane (DB-1 or equivalent)

Injection system	
Injector	split injection
Sprit flow	approximately 100 ml/min
Injection volume	1 µl
Detector	flame ionisation
Temperatures	
Column oven	240°C (use a short temperature program to remove formulants, if necessary)
Injection port	265°C
Detector	325°C
Carrier gas	helium, 30 cm/s
Retention times	dicyclohexyl phthalate: about 8.4 min *cis*-permethrin: about 12.4 min *trans*-permethrin: about 12.9 min

(b) Linearity check. Check the linearity of the detector response by injecting 1 µl of solutions with permethrin concentrations 0.5, 1 and 2 times that of the calibration solution before conducting analysis.

(c) System equilibration. Prepare two calibration solutions. Inject 1 µl portions of the first one until the response factors obtained for two consecutive injections differ by less than 1.0%. Then inject a 1 µl portion of the second solution. The response factor for this solution should not deviate by more than 1.0% from that for the first calibration solution, otherwise prepare new calibration solutions.

(d) Preparation of sample solution. Clean a pair of scissors with acetone before use. Cut the sample with the scissors into 5 – 10 mm squares. Prepare sample solutions in duplicate for each sample. Weigh (to the nearest 0.1 mg) sufficient sample to contain 36 to 44 mg (*w* mg) of permethrin into a vial or stoppered flask (100 ml). Add by pipette internal standard solution (5.0 ml) and by measuring cylinder heptane (45 ml). Place the vial or stoppered flask in a water bath (85 – 90°C) for 45 min. Shake the vial or stoppered flask once or twice during the extraction. Filter a portion of each sample solution through a filter paper prior to analysis (solutions S_A and S_B).

(e) Determination. Inject in duplicate 1 µl portions of each sample solution bracketing them by injections of the calibration solutions as follows; calibration solution C_A, sample solution S_A, sample solution S_A, calibration solution C_B, sample solution S_B, sample solution S_B, calibration solution C_A, and so on. Measure the relevant peak areas.

(f) Calculation of permethrin content. Calculate the mean value of each pair of response factors bracketing the two injections of a sample and use this value for calculating the permethrin contents of the bracketed sample injections. Calculate the sum of the *cis*- and *trans*-permethrin peak areas for each injection.

$$f_i = \frac{I_r \times s \times P}{H_s \times 2}$$

$$\text{Content of permethrin} = \frac{f \times H_w}{I_q \times w} \text{ g/kg}$$

where:

f_i = individual response factor
f = mean response factor
H_s = sum of the *cis*- and *trans*-permethrin peak areas in the calibration solution
H_w = sum of the *cis*- and *trans*-permethrin peak areas in the sample solution
I_r = peak area of the internal standard in the calibration solution
I_q = peak area of the internal standard in the sample solution
s = mass of permethrin standard in the calibration solution (mg)
w = mass of sample taken (mg)
P = purity of permethrin working standard (g/kg)

(g) Calculation of trans-isomer fraction percentage.

$$\textit{trans}\text{-isomer fraction percentage} = \frac{H_{wt}}{H_{wt} + H_{wc}} \times 100\,\%$$

where:

H_{wt} = peak area of *trans*-permethrin in the sample solution
H_{wc} = peak area of *cis*-permethrin in the sample solution

3. METHOD ASSESSMENT

According to the CIPAC method extension guideline, the applicability of this method to permethrin/pyriproxyfen LN was investigated. In addition to specificity and repeatability tests, accuracy test was conducted to confirm that permethrin was determined accurately in the presence of pyriproxyfen.

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

3.1 Check of the acceptability range

Scope of the existing CIPAC method: 20 g/kg
Acceptability range: 10 g/kg to 40 g/kg

Permethrin content in permethrin/pyriproxyfen LN; 20 g/kg
The permethrin content in permethrin/pyriproxyfen LN is within the acceptability content range of the existing CIPAC method.

3.2 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 permethrin standard, the pyriproxyfen standard and the internal standard were chromatographed. As shown in Figures 1 to 5, there was no significant interference.

3.3 Precision

Six separate sub-samples from a sample of permethrin/pyriproxyfen LN were analyzed in accordance with the CIPAC 331/LN/(M2)/3.
The repeatability of this method was satisfactory with the relative standard deviations (RSDs) of 0.5% and 0.1% respectively as shown in Tables 1 and 2. The typical chromatogram of the sample solution is shown in Figure 6.

Table 1 Precision Test (Content of permethrin)

No.	Content of permethrin (g/kg)
1	20.2
2	20.1
3	20.0
4	20.1
5	19.9
6	20.0
Mean	20.1
%RSD	0.5

Table 2 Precision Test (*Trans*-isomer fraction percentage)

No.	*Trans*-isomer fraction percentage (%)
1	57.0
2	57.0
3	57.2
4	57.1
5	57.0
6	57.0
Mean	57.1
%RSD	0.1

3.4 Accuracy

The stock solution at appropriate concentrations of permethrin and pyriproxyfen were fortified to the blank formulation so that the fortified concentrations of permethrin and pyriproxyfen were at the levels of each specification. The solutions were analyzed, and the recoveries of permethrin were calculated by the following equation:

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

where, R : recovery (%)

C : observed concentration (g/kg) of permethrin

C_S : fortified concentration (g/kg) of permethrin

The recoveries were satisfactory as shown in Table 3.

Table 3 Accuracy Test

No.	Recovery (%)
1	100.1
2	100.4
3	100.1
4	99.8
Mean	100.1
%RSD	0.2

4. CONCLUSION

The shown data demonstrated the validity of the CIPAC 331/LN/(M2)/3 for permethrin/pyriproxyfen LN.
Therefore, JAPAC proposes that the CIPAC 331/LN/(M2)/3 is applicable to permethrin/pyriproxyfen LN.

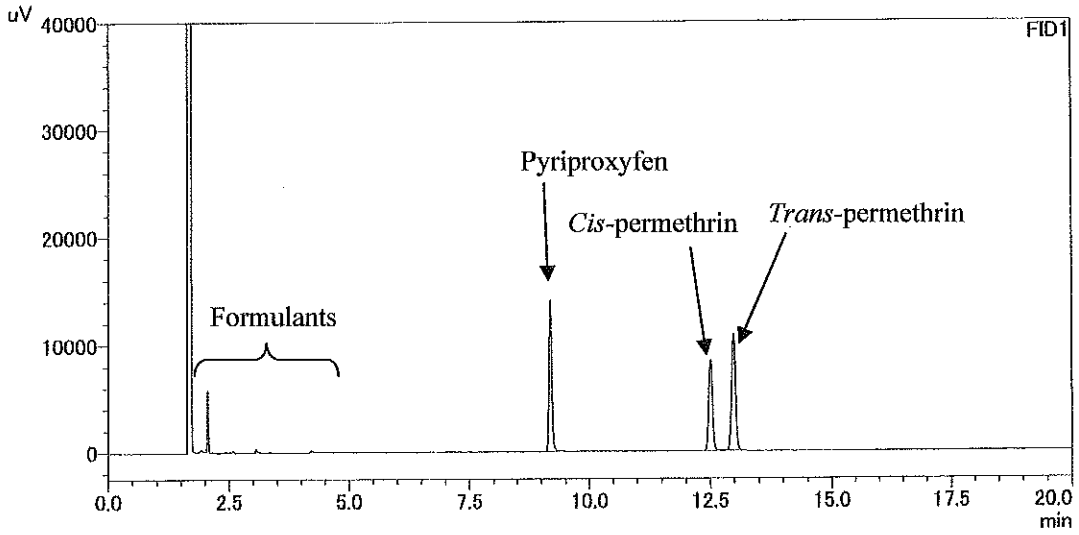

Fig. 1 Gas chromatogram of permethrin/pyriproxyfen LN, Olyset Duo

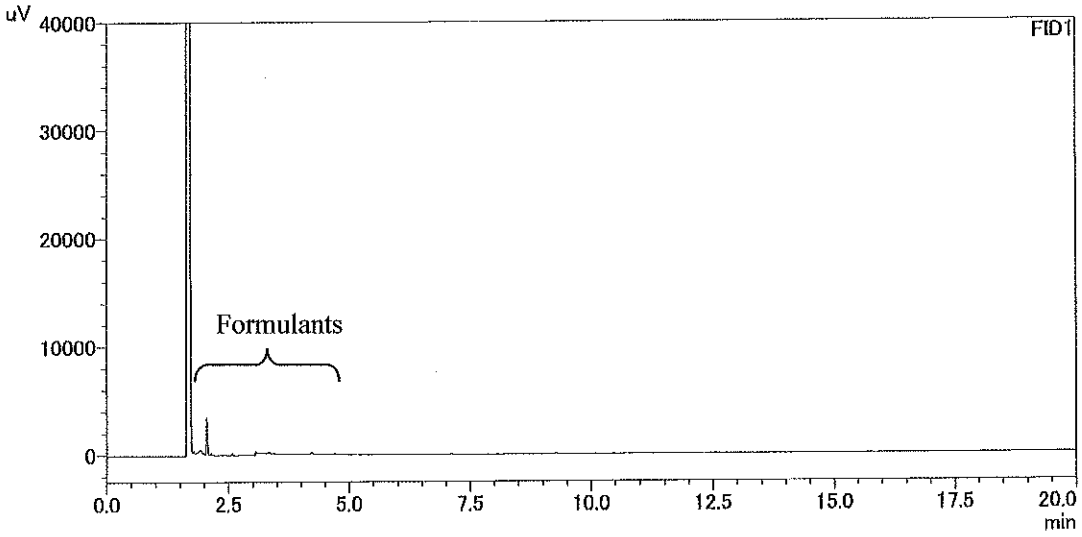

Fig. 2 Gas chromatogram of blank formulation

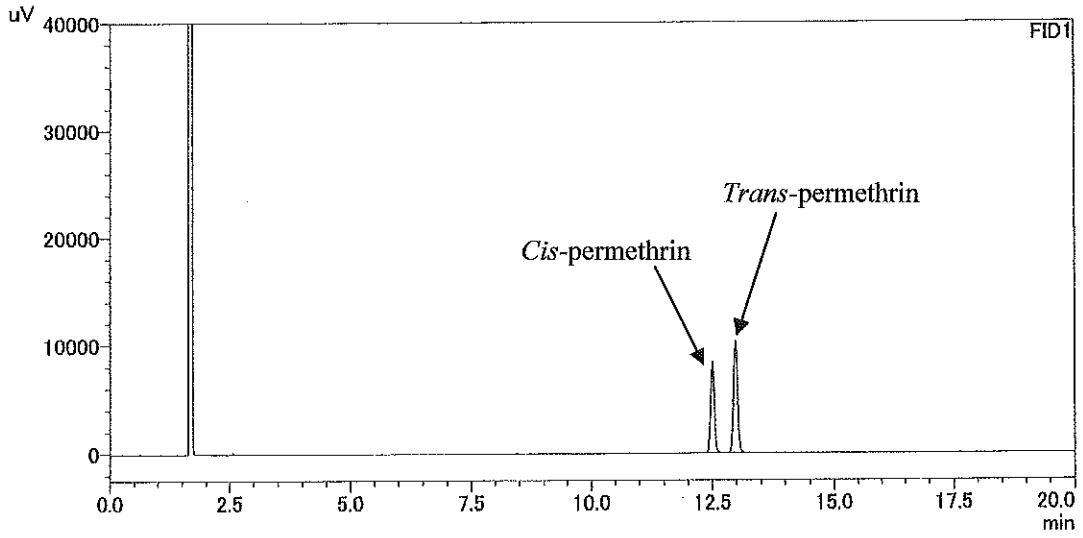

Fig. 3 Gas chromatogram of permethrin standard

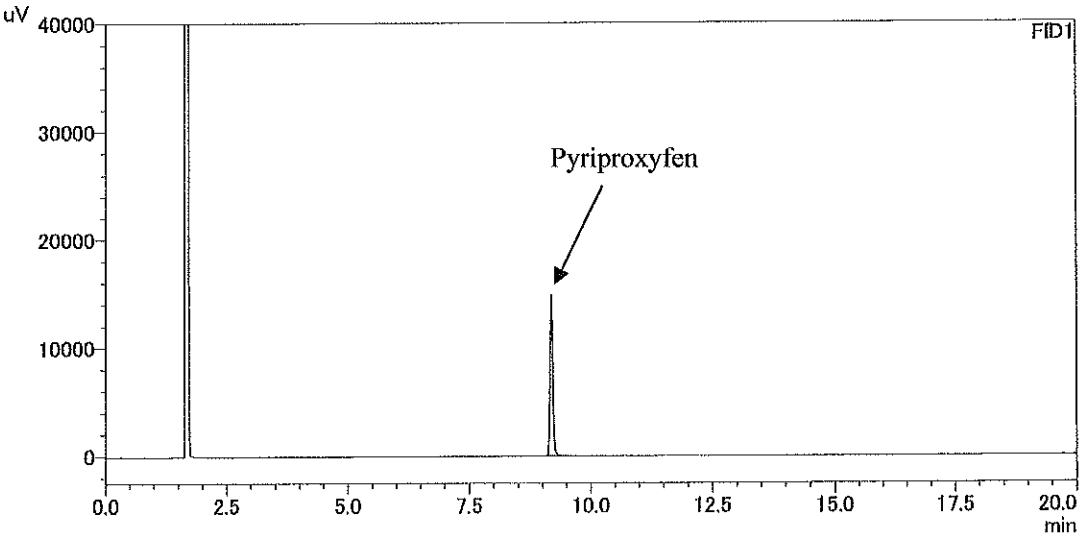

Fig. 4 Gas chromatogram of pyriproxyfen standard

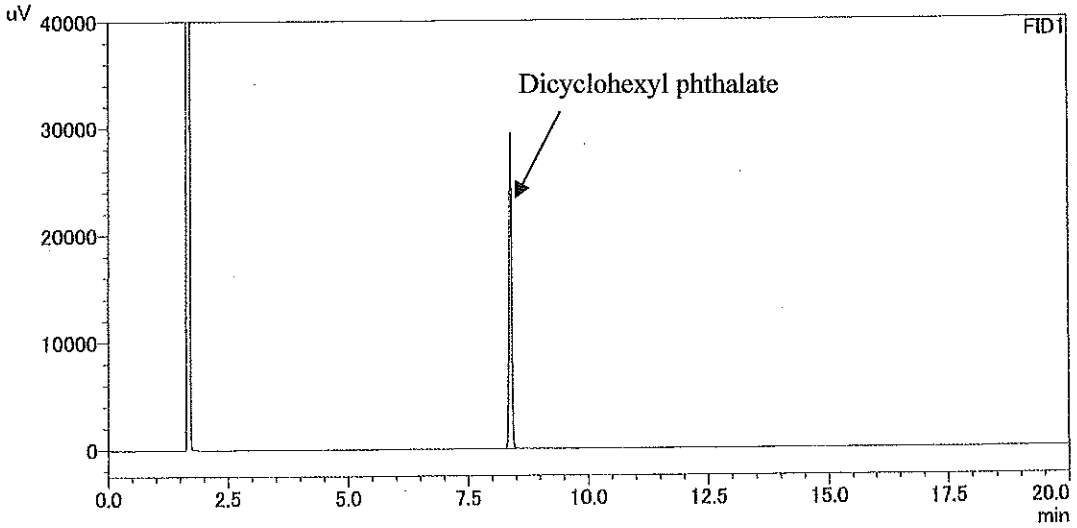

Fig. 5 Gas chromatogram of internal standard

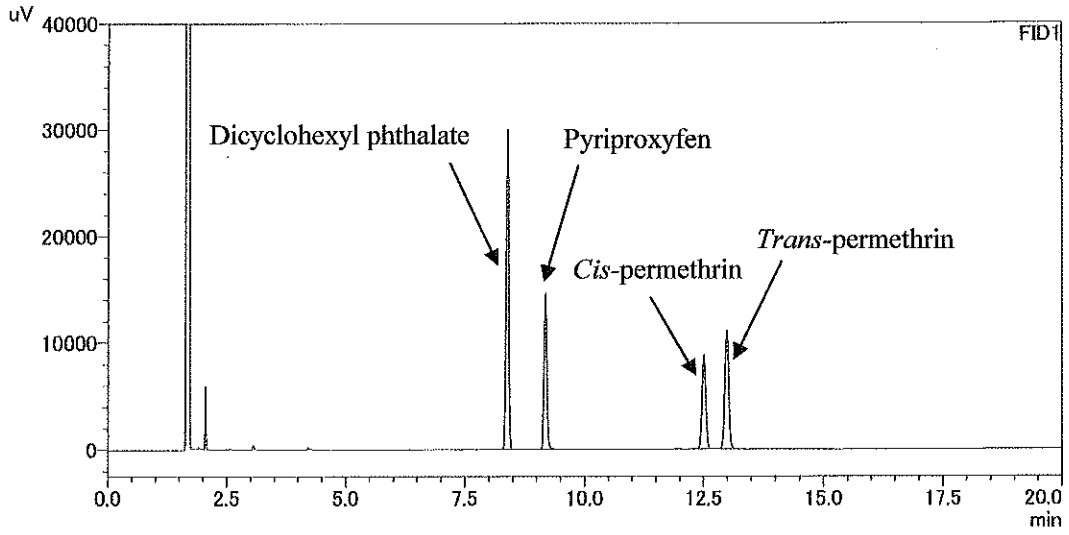

Fig. 6 Gas chromatogram of sample solution, Olyset Duo