PERMETHRIN

331

331/LN/M/-

Method Extension for Permethrin/Piperonyl butoxide LN

Studies for Method Extension of Existing CIPAC Method for Permethrin/Piperonyl butoxide LN

by
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1. INTRODUCTION

The CIPAC 331/LN/M/3 which is intended for the determination of the content of permethrin in permethrin LN was extended to permethrin/piperonyl butoxide LN with a few minor modifications.
This report was prepared to demonstrate the validity of the extension of the existing CIPAC 331/LN/M/3 for permethrin/piperonyl butoxide LN.

2. METHOD DESCRIPTION

PERMETHRIN LONG LASTING INSECTICIDAL NET
Extension method of CIPAC 331/LN/M/3

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 the exciting CIPAC 331/LN/M/3 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 mix solution of the permethrin, the piperonyl butoxide and the internal standard of the existing CIPAC 331/LN/M/3 (triphenyl phosphate) was chromatographed. As shown in Figure 1, the peaks of triphenyl phosphate and piperonyl butoxide were found to elute very closely and it was considered that this poor separation may affect the specificity on the chromatogram by the small variation in the method parameters.

Therefore, dicyclohexyl phthalate was selected as an alternative internal standard.

As shown in Figure 2, the separation of dicyclohexyl phthalate, piperonyl butoxide and permethrin was satisfactory.

In addition, a short temperature program was added to assure that all formulants elute from the analytical column. Also, the temperature of detector was raised slightly according to CIPAC/4105/R.

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 piperonyl butoxide standard and the internal standard were chromatographed under the modified conditions. As shown in Figures 3 to 7, there was no significant interference.

3.2 Check of the acceptability range

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

Permethrin content in permethrin/piperonyl butoxide LN: 20 g/kg
The permethrin 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 the modified method. The repeatability of this method was satisfactory with the relative standard deviations (RSDs) of 0.5% and 0.3% respectively as shown in Tables 1 and 2.

Table 1 Precision Test (Content of permethrin)

No.	Content of permethrin (g/kg)
1	19.2
2	19.4
3	19.2
4	19.3
5	19.1
6	19.3
Mean	19.3
%RSD	0.5

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

No.	*Trans*-isomer fraction percentage (%)
1	56.6
2	56.5
3	56.9
4	56.5
5	56.7
6	56.7
Mean	56.7
%RSD	0.3

4. CONCLUSION

In order to apply the exciting CIPAC method to permethrin/piperonyl butoxide LN, the internal standard and the temperatures of column oven and detector were modified.
These modifications are considered to be minor modifications.

The shown data demonstrate the validity of the modified method. Therefore, the modified method is considered appropriate for the determination of permethrin in permethrin/piperonyl butoxide LN.
JAPAC proposes to extend the exciting CIPAC method for permethrin/piperonyl butoxide LN.

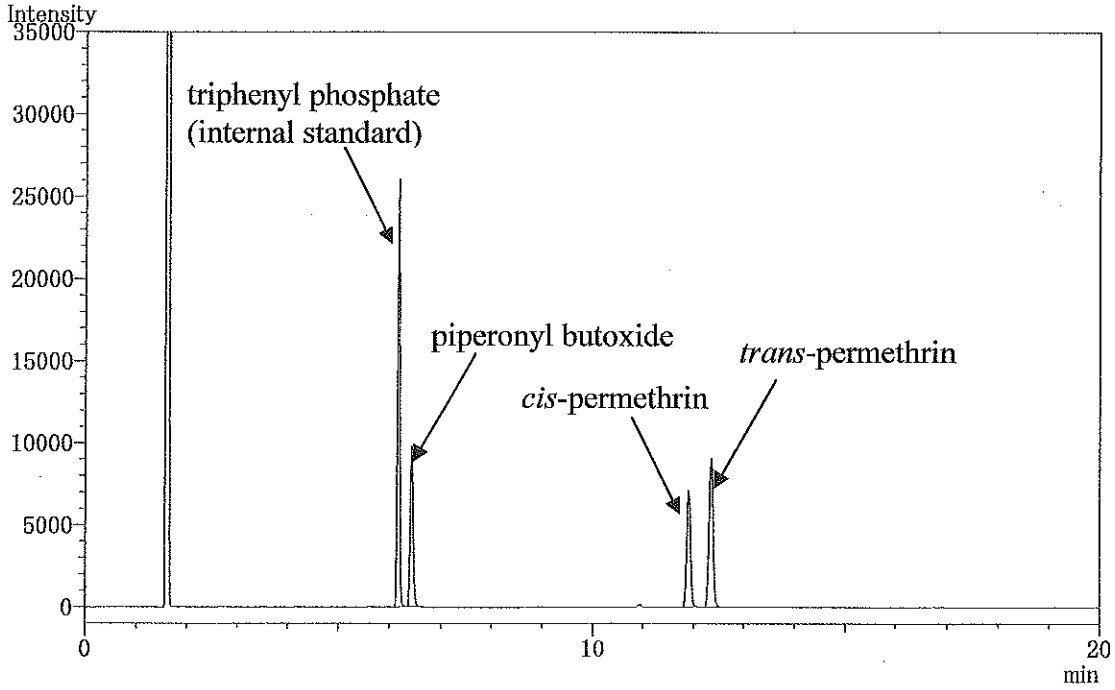

Fig 1 Gas chromatogram of mix solution
(permethrin, piperonyl butoxide and triphenyl phosphate)

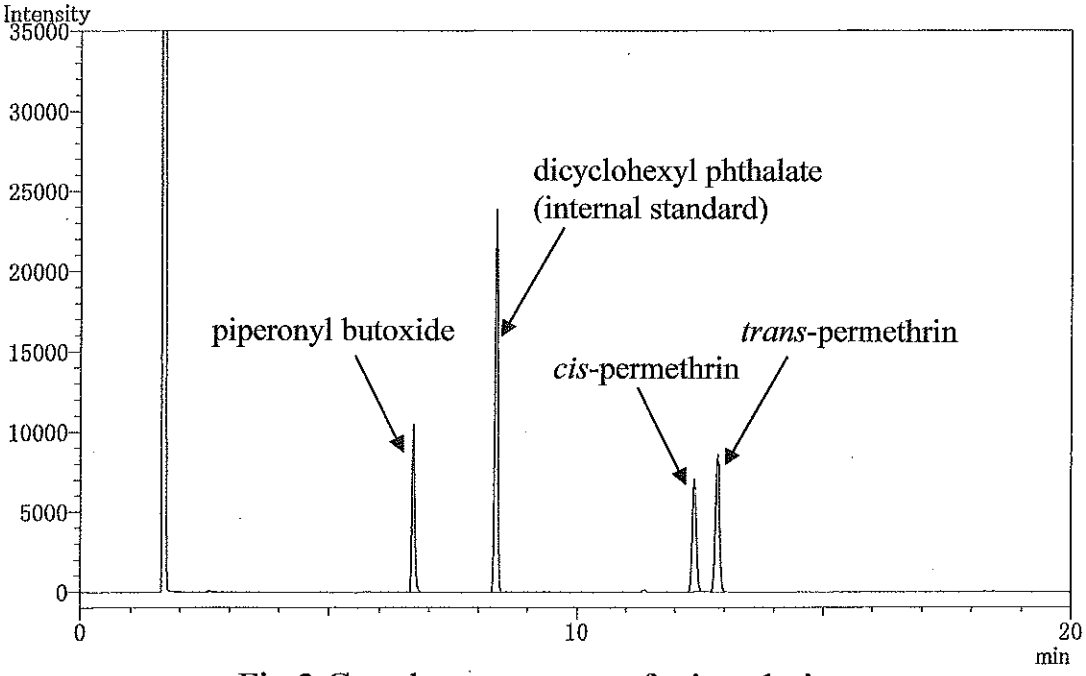

Fig 2 Gas chromatogram of mix solution
(permethrin, piperonyl butoxide and dicyclohexyl phthalate)

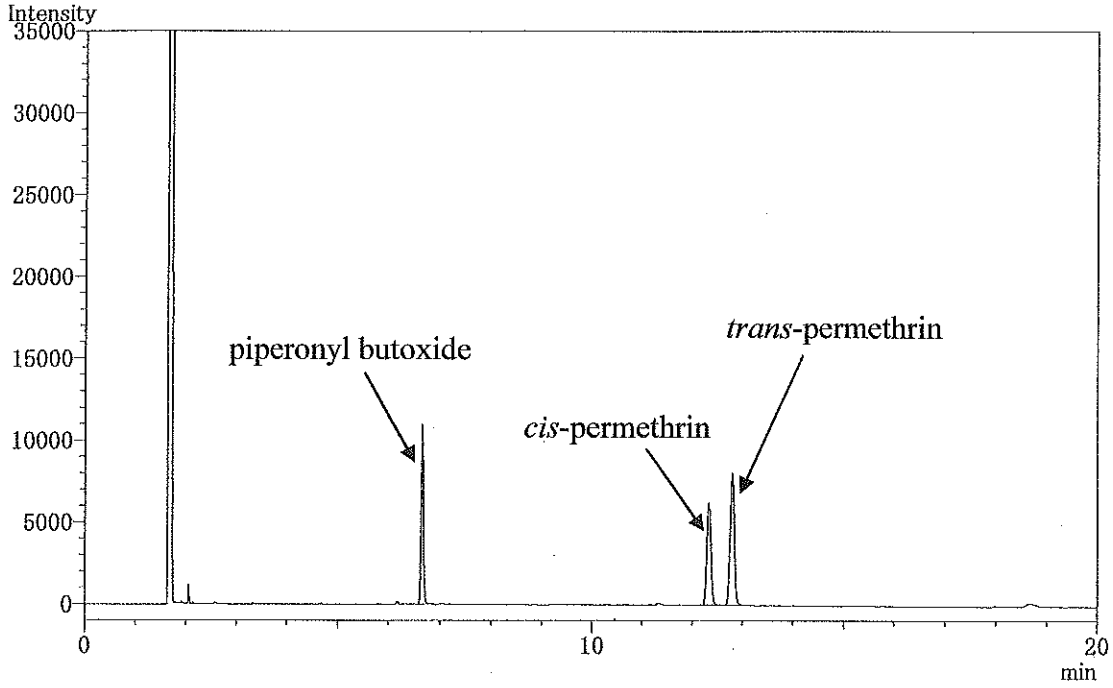

Fig 3 Gas chromatogram of permethrin/piperonyl butoxide LN, Olyset plus

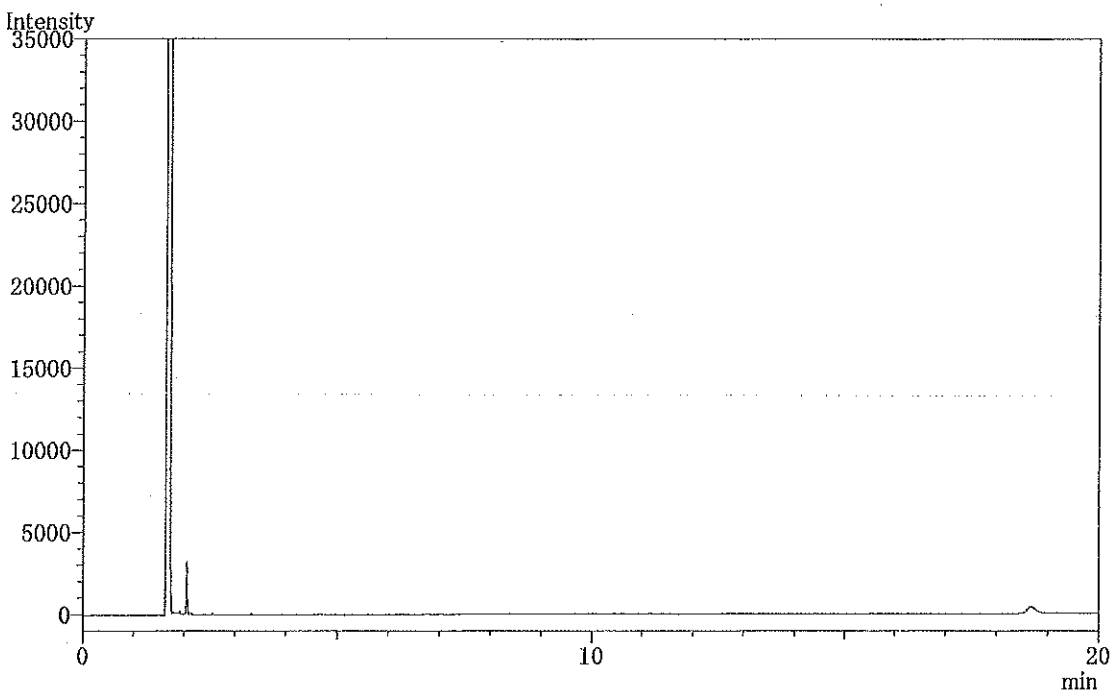

Fig 4 Gas chromatogram of blank formulation

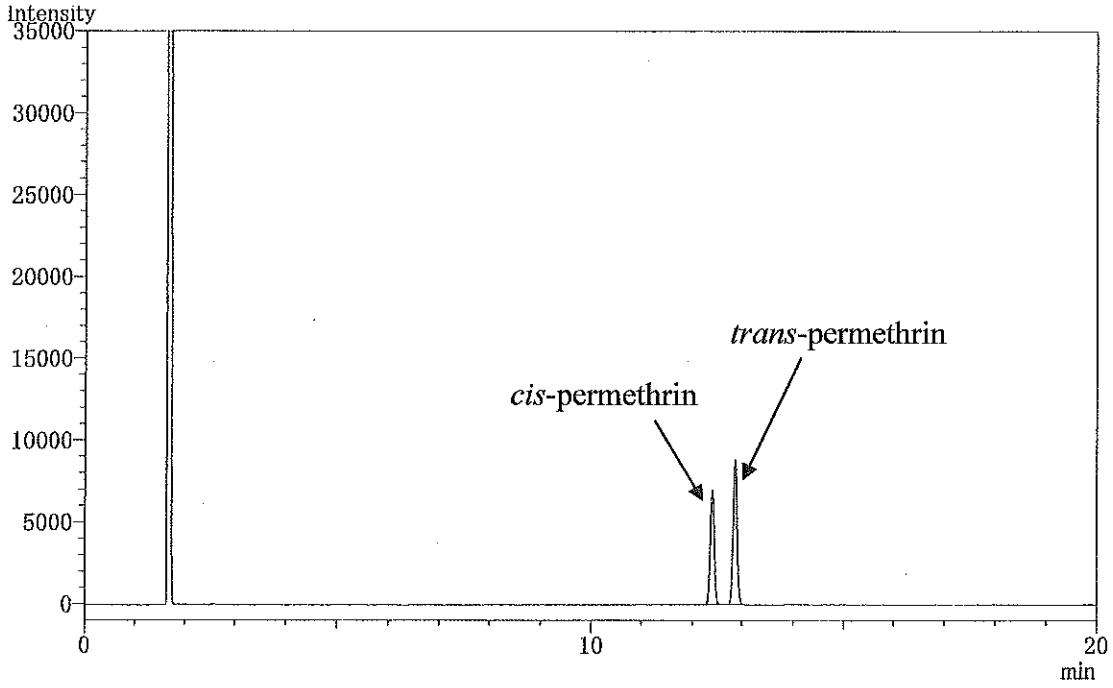

Fig 5 Gas chromatogram of permethrin standard

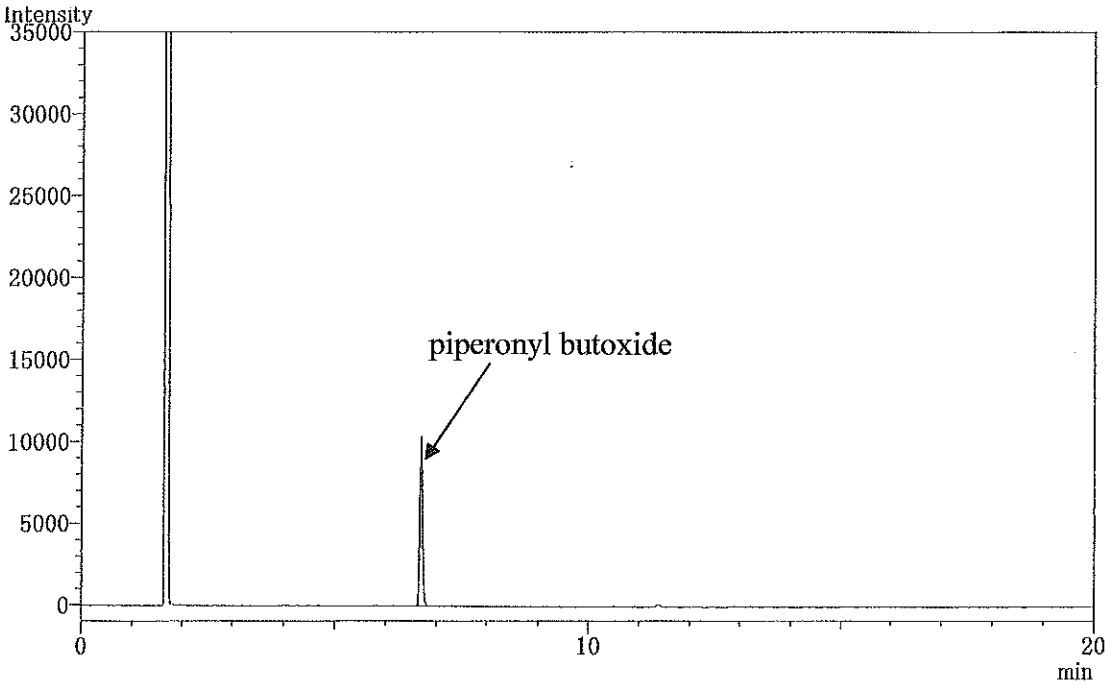

Fig 6 Gas chromatogram of piperonyl butoxide standard

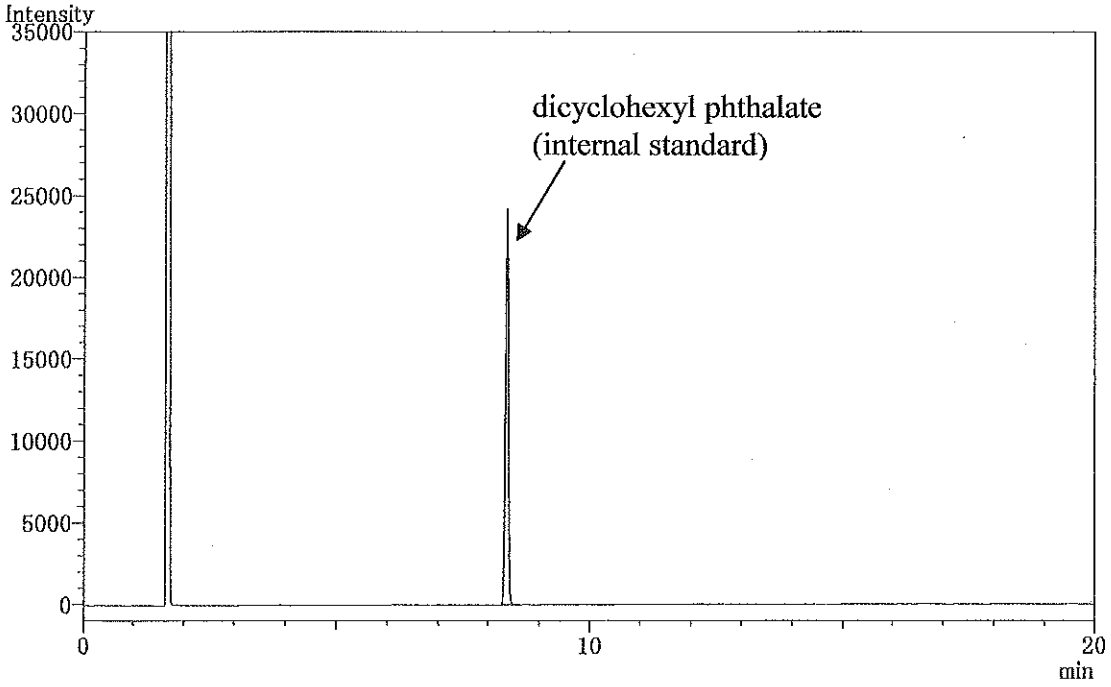

Fig 7 Gas chromatogram of internal standard