CYPHENOTHRIN

804

804/EW/(M)/-

Method Extension for *d,d-trans*-Cyphenothrin EW

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

by
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1. INTRODUCTION

The CIPAC 804/TC/(M)/3 was extended to *d,d-trans*-cyphenothrin oil in water emulsions (EW).

This report was prepared to demonstrate the validity of the extension method of the CIPAC 804/TC/(M)/3 for *d,d-trans*-cyphenothrin EW.

2. METHOD DESCRIPTION

CYPHENOTHRIN OIL IN WATER EMULSIONS
Extension method of CIPAC 804/TC/(M)/3

OUTLINE OF METHOD Cyphenothrin is determined by capillary gas chromatography using flame ionisation detection and triphenyl phosphate as internal standard.

REAGENTS

Acetone

Cyphenothrin enriched working standard product of certified purity and composition. Store refrigerated.

Triphenyl phosphate internal standard. Must not show a peak with the same retention time as peak A, peak B or peak C.

Internal standard solution. Dissolve triphenyl phosphate (2.0 g) in acetone (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 cyphenothrin enriched working standard by stirring or by warming it to melting and by stirring when it is waxy solid or partly waxy solid. Prepare calibration solutions in duplicate. Weigh (to the nearest 0.1 mg) 90 to 110 mg (*s* mg) of cyphenothrin enriched working standard into a volumetric flask (50 ml). Add by pipette internal standard solution (5.0 ml) and dissolve. Make up to volume with acetone 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 50% phenyl 50% dimethyl polysiloxane (DB-17 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 50% phenyl 50% dimethyl polysiloxane (DB-17 or equivalent)
Injection system	
Injector	split injection
Sprit flow	approximately 100 ml/min
Injection volume	1 μl
Detector	flame ionisation
Temperatures	
Column oven	260°C (use a short temperature program to remove formulations components, if necessary)
Injection port	280°C
Detector	280°C
Carrier gas	helium, 30 cm/sec
Retention times	triphenyl phosphate: about 8.9 min enriched cyphenothrin: peak A: about 11.1 min peak B: about 11.3 min peak C: about 11.7.min

Note: peak A consists of the *S*,1*R-trans*, *R*,1*S-trans*, *R*,1*R-trans* and *S*,1*S-trans* isomers
peak B consists of the *R*,1*R-cis* and *S*,1*S-cis* isomers; this peak is usually not detected since the amounts of these isomers are very low.
peak C consists of the *S*,1*R-cis* and R,1*S-cis* isomers;

(b) Linearity check. Check the linearity of the detector response by injecting 1 μl of solutions with cyphenothrin enriched working standard 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. Thoroughly shake the sample container to homogenise the sample before use. Weigh (to the nearest 0.1 mg) sufficient sample to contain 90 to 110 mg (*w* mg) of the cyphenothrin enriched mixture into a volumetric flask (50 ml). Add by

pipette internal standard solution (5 ml) and dissolve completely. Make up to volume with acetone and mix well (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. Calculate the mean value of each pair of response factors bracketing the two injections of a sample and use this value for calculating the enriched cyphenothrin contents of the bracketed sample injections.

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

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

where:

f_i = individual response factor
f = mean response factor
H_s = peak area of enriched cyphenothrin (peak A+B+C) in the calibration solution
H_w = peak area of enriched cyphenothrin (peak A+B+C) 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 enriched cyphenothrin working standard in the calibration solution (mg)
w = mass of sample taken (mg)
P = purity of enriched cyphenothrin working standard (g/kg)

3. METHOD ASSESSMENT

According to the CIPAC method extension guideline, the method extension of the CIPAC 804/TC/(M)/3 for *d,d-trans*-cyphenothrin EW was investigated.

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

Since CIPAC method for cyphenothrin EW was not available, the method extension of the CIPAC 804/TC/(M)/3 for EW was investigated. The sample subjected to this assessment was metofluthrin/*d,d-trans*-cyphenothrin/piperonyl butoxide EW, 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: 944 to 946 g/kg (TC) and 59.2 g/kg (EC).
Acceptability range: above 472 g/kg and 29.6 to 118.4 g/kg.
d,d-trans-Cyphenothrin content in SumiPro: 60 g/kg
The *d,d-trans*-cyphenothrin 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)

A short temperature program was added to assure that all formulants elute from the analytical column.
This modification is considered to be a minor modification.

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 *d,d-trans*-cyphenothrin) treated in the same way as a sample,

d,d-trans-cyphenothrin standard, metofluthrin standard, piperonyl butoxide 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 0.4% and 0.3% 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 *d,d-trans*-cyphenothrin (g/kg)	
	Lab 1	Lab 2
1	59.9	60.6
2	59.8	60.5
3	59.7	60.3
4	59.6	60.1
5	59.5	60.2
6	59.2	60.1
Mean	59.6	60.3
%RSD	0.4	0.3

3.4.3 Accuracy

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

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

where, R : recovery (%)
C : observed concentration (g/kg) of *d,d-trans*-cyphenothrin
C_S : fortified concentration (g/kg) of *d,d-trans*-cyphenothrin

The recoveries were satisfactory as shown in Table 2.

Table 2 Accuracy Test

No.	Recovery (%)
1	99.93
2	99.72
3	99.54
4	99.65
Mean	99.71
%RSD	0.2

4. CONCLUSION

In order to extend the CIPAC 804/TC/(M)/3 to *d,d-trans*-cyphenothrin EW, a short temperature program was added to assure that all formulants elute from the analytical column. This modification is considered to be a minor modification.
The shown data demonstrate the validity of this method. This method is considered appropriate for the determination of *d,d-trans*-cyphenothrin in metofluthrin/*d,d-trans*-cyphenothrin/piperonyl butoxide EW.
Therefore, JAPAC proposes to extend the CIPAC 804/TC/(M)/3 for *d,d-trans*-cyphenothrin EW.

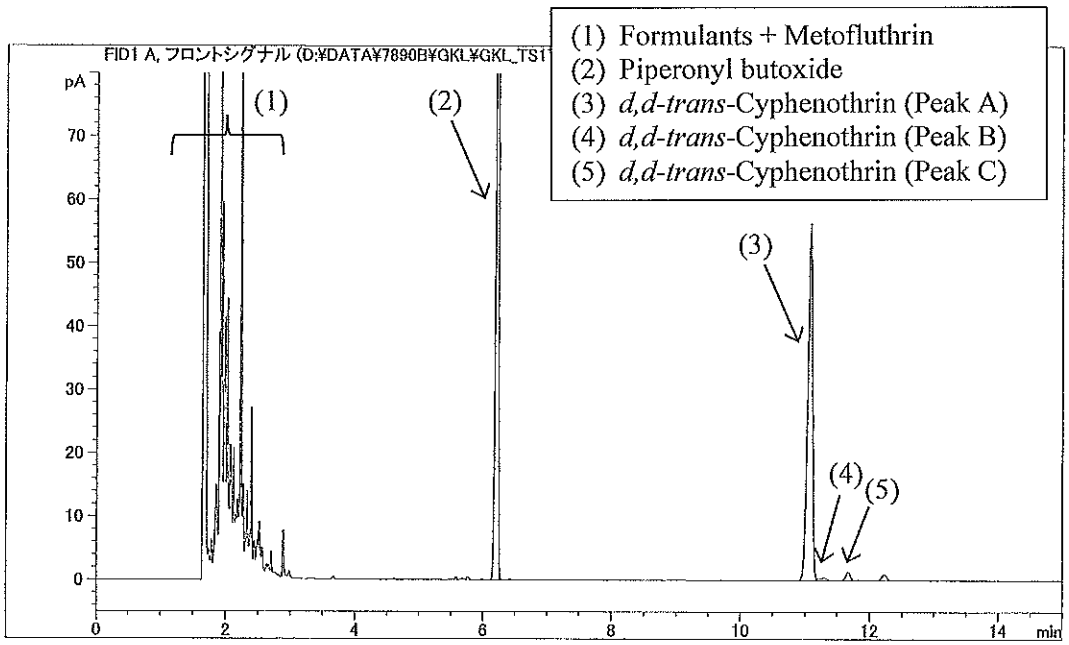


Fig. 1 Gas chromatogram of metofluthrin/*d,d-trans*-cyphenothrin/piperonyl butoxide EW, SumiPro

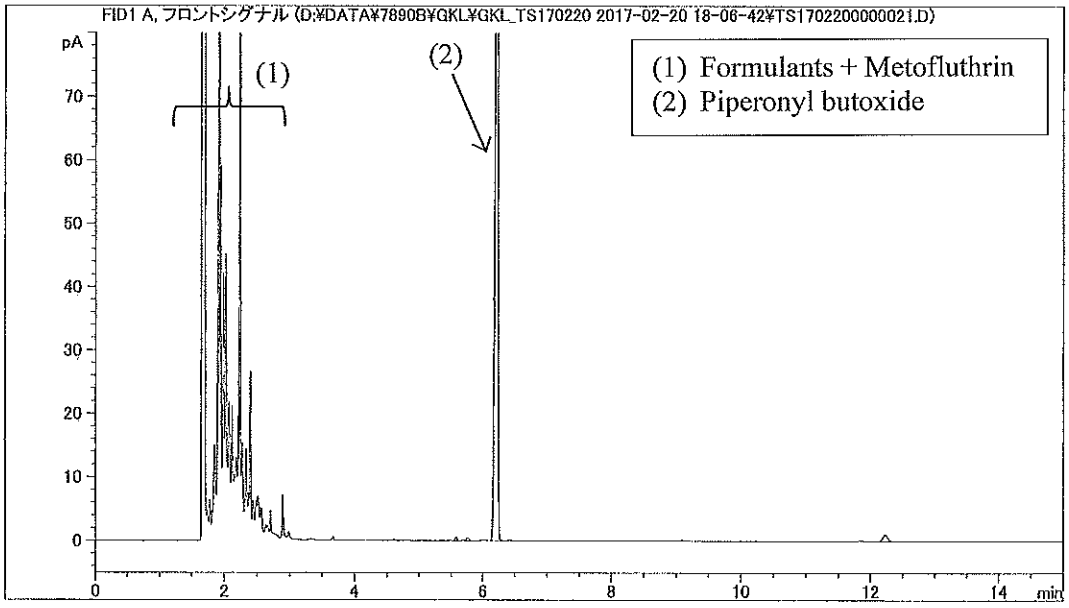


Fig 2 Gas chromatogram of blank formulation (without *d,d-trans*-cyphenothrin)

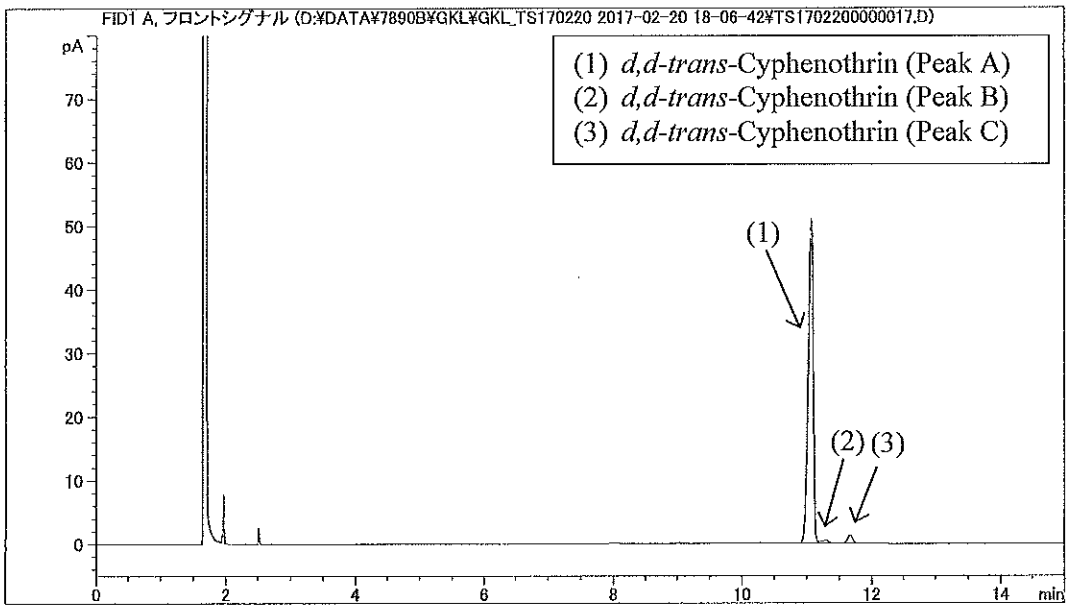


Fig. 3 Gas chromatogram of *d,d-trans*-cyphenothrin standard

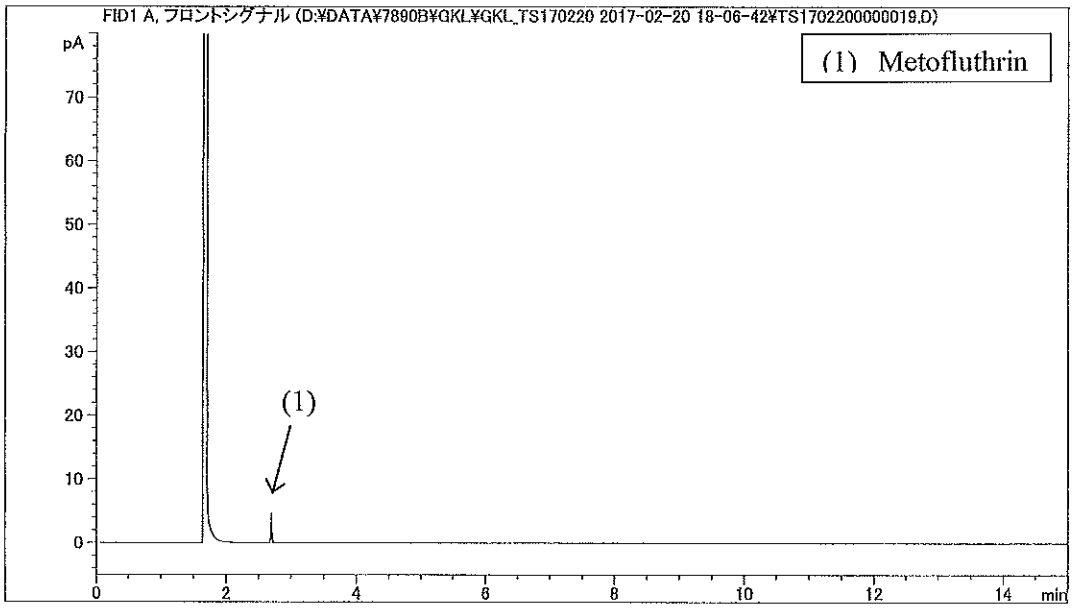


Fig 4 Gas chromatogram of metofluthrin standard

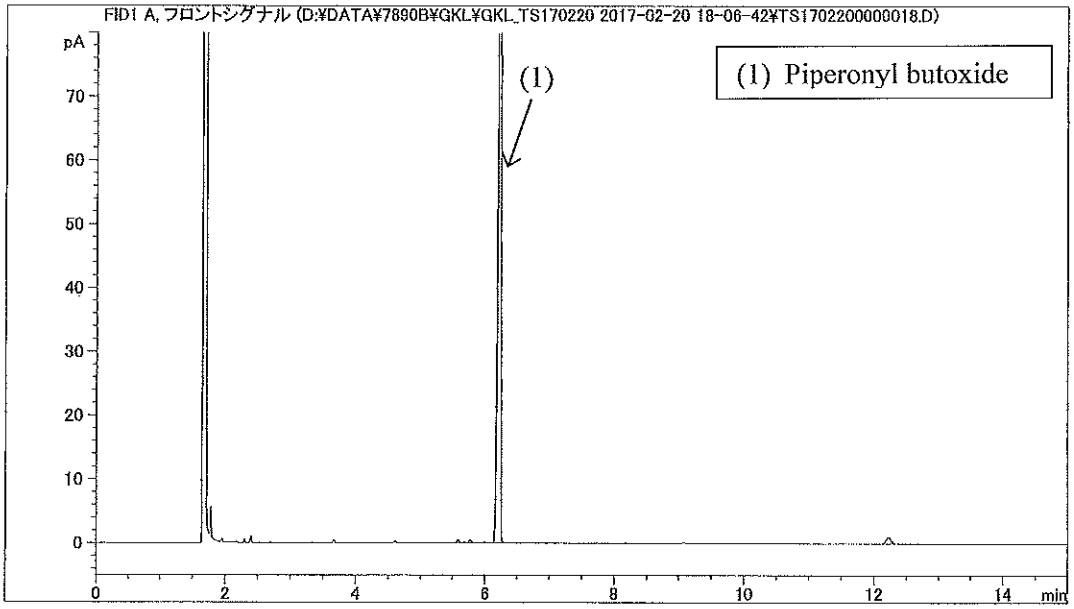


Fig 5 Gas chromatogram of piperonyl butoxide standard

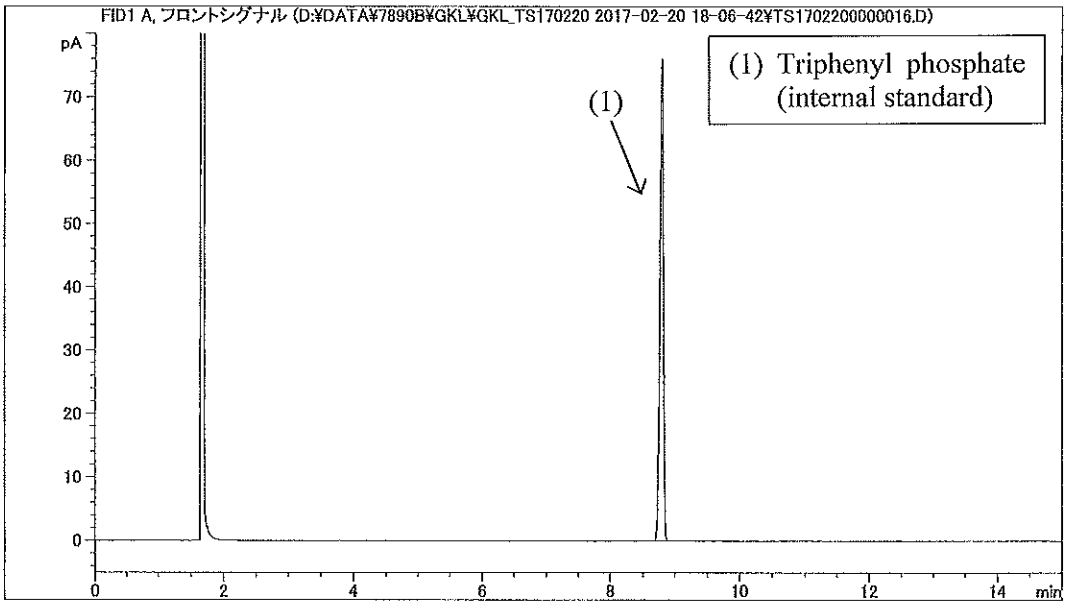
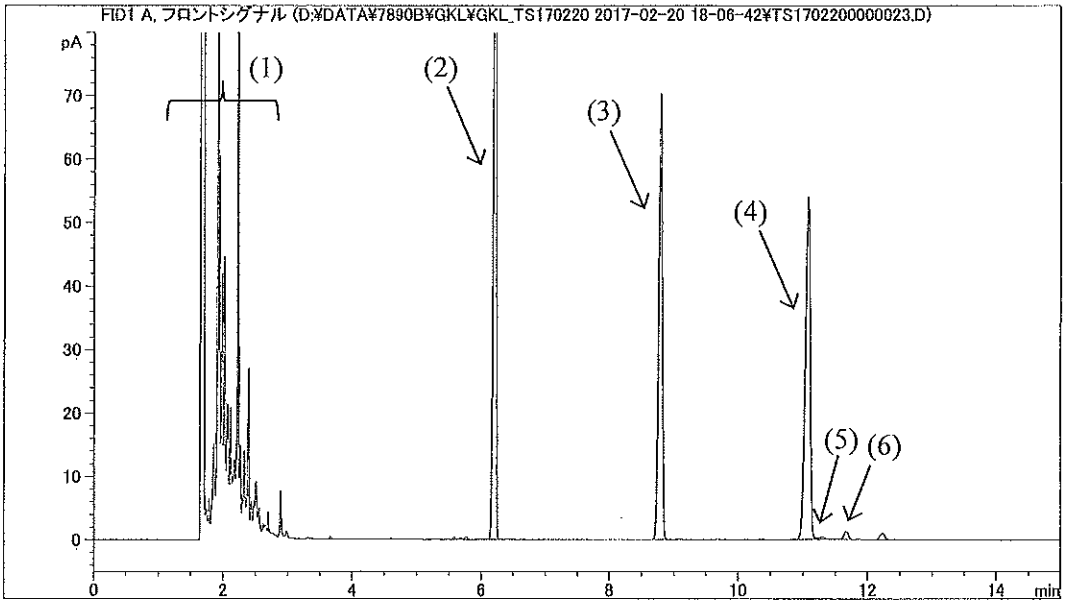


Fig. 6 Gas chromatogram of internal standard



(1) Formulants + Metofluthrin
(2) Piperonyl butoxide
(3) Triphenyl phosphate (internal standard)
(4) *d,d-trans*-Cyphenothrin (Peak A)
(5) *d,d-trans*-Cyphenothrin (Peak B)
(6) *d,d-trans*-Cyphenothrin (Peak C)

Fig. 7 Gas chromatogram of sample solution