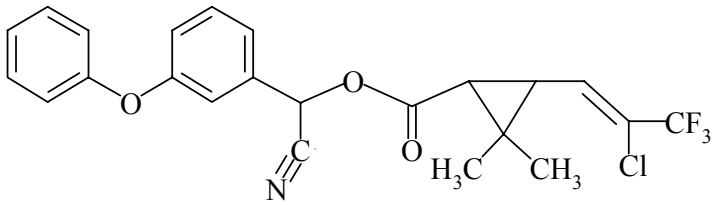
LAMBDA-CYHALOTHRIN
463



ISO common name	Lambda-cyhalothrin
Chemical name	A mixture (1:1) of *(S)*-α-cyano-3-phenoxybenzyl-(*Z*)-(1*R*,3*R*)-3-(2-chloro-3,3,3-trifluoropropenyl)-2,2-dimethyl-cyclopropanecarboxylate and (*R*)-α-cyano-3-phenoxybenzyl-(*Z*)-(1*S*,3*S*)-3-(2-chloro-3,3,3-trifluoropropenyl)-2,2-dimethyl-cyclopropanecarboxylate (IUPAC); cyano(3-phenoxyphenyl)methyl 3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethyl-cyclopropanecarboxylate (CA; *91465-08-6*)
Empirical formula	$C_{23}H_{19}ClF_3NO_3$
RMM	449.9
m.p.	49.2 °C
v.p.	2×10^{-7} Pa at 20 °C
Solubility	In purified water (pH 6.5) 0.005 mg/l; buffered water (pH 5.0) 0.004 mg/l; soluble in a range of organic solvents
Description	The pure material is colourless crystalline solid. The technical material is a viscous brown semi-solid mass which is liquid at 50 °C
Formulations	Wettable powders, emulsifiable concentrates, ULV formulations, and in mixtures with other pesticides

LAMBDA-CYHALOTHRIN TECHNICAL
*463/TC/M/-

1 Sampling. Homogenize the bulk material by heating to about 50 °C and mix thoroughly before taking the sample. Take at least 25 g. Re-homogenise before taking a sub-sample for analysis.

2 Identity tests. The identity of the active ingredient is established by comparison with the equivalent authentic standard using at least two of the following techniques.

2.1 GLC. Use the GLC method below. The relative retention time of lambda-cyhalothrin with respect to the internal standard for the sample solution, should not deviate by more than 1% from that for the calibration solution.

2.2 NMR. Use a solution in deuterochloroform containing tetramethylsilane as internal standard. The NMR spectrum of lambda-cyhalothrin displays the following characteristics:

a complex multiplet	at	δ	7.50-6.90
a double quartet	at	δ	6.78
a singlet	at	δ	6.38
a broadened triplet	at	δ	2.28
a doublet	at	δ	2.03
a singlet	at	δ	1.29
a singlet	at	δ	1.21

2.3 Infrared. Prepare a Nujol mull from the sample and a KBr disk from lambda-cyhalothrin standard and scan from 4000 to 600 cm^{-1}. The spectrum produced from the sample should not differ significantly from that of the standard.

3 Lambda-cyhalothrin

OUTLINE OF METHOD The sample is dissolved in dichloromethane containing hexacosane as internal standard. Separation is carried out in the split injection mode using a dimethyl polysiloxane WCOT fused silica capillary column with automatic injection and flame ionisation detector. The lambda-cyhalothrin is determined by comparison with calibration solutions.

* CIPAC method 1990. Prepared by PAC-GB. Chairman: S Bailey. Based on a method supplied by ICI.

REAGENTS

Dichloromethane
Hexacosane internal standard. Select for use a bath which, when chromatographed under the conditions given below for the determination of lambda-cyhalothrin, gives no peak with a similar retention time to lambda-cyhalothrin.
Internal standard solution. Dissolve hexacosane (2.0 g) in dichloromethane (500 ml: Solution I). Ensure a sufficient quantity of this solution is prepared for all samples and calibration standards being analysed.
Lamda-cyhalothrin working standard, of known lambda-cyhalothrin content (minimum 990 g/kg). A certified standard of known purity will be available from Office of Reference Materials, Laboratory of the Government Chemist, Queens Road, Teddington, Middlesex, England, TW11 0LY.
Calibration solution. Weigh in duplicate (to the nearest 0.1 mg) about 0.1 g of lambda-cyhalothrin s_A and s_B, g) into 150 ml conical flasks. Add to each, 20.0 ml of internal standard solution (solution I) from a pipette and 30 ml of dichloromethane. Shake thoroughly to dissolve the lambda-cyhalothrin. Dilute 5 ml of each solution to 25 ml with dichloromethane (Solutions C_A and C_B). Prepare a solution without internal standard by dissolving about 0.1 g of standard in 50 ml of dichloromethane. Dilute 5 ml of this solution to 25 ml with dichloromethane (Solution S_0).

APPARATUS

Gas chromatograph capable of operating over the range 100 to 300 °C with a flame ionisation detector, split/splitless injector and autosampler
Column 25 m × 0.25 mm (i.d.) and 0.12 μm film thickness or 50 m × 0.32 mm (i.d.) dimethyl polysiloxane (chemically bonded)
Automatic digital integrator or *chromatography data system* compatible with the gas chromatograph
Conical flasks 150 ml

PROCEDURE

(a) Preparation of the sample solutions. Warm the material to 50 °C and mix thoroughly. Weigh in duplicate (to the nearest 0.1 mg) into 150 ml conical flasks, sufficient sample (*w* g) at 50 °C to contain 0.1 g of lambda-cyhalothrin. Allow the flask and sample to cool to room temperature before recording the final weight. Add by pipette to each flask, 20.0 ml of hexacosane Solution I, 30 ml of dichloromethane and shake thoroughly to dissolve the lambda-cyhalothrin. Dilute 5 ml of each solution to 25 ml with dichloromethane (Solution S_A and S_B). Prepare a solution without internal standard by dissolving about 0.1 g in 50 ml of dichloromethane. Dilute 5 ml of this solution to 25 ml with dichloromethane (Solution S_0).

(b) Capillary gas chromatographic conditions

Column 25 m WCOT fused silica 0.25 mm (i.d.) and 0.12 µm film thickness coated with dimethyl polysiloxane (chemically bonded) or 50 m, 0.32 mm (i.d.) and 0.12 µm film thickness.

Injector system

Injector	Split/splitless in the split mode with fused silica liner. It is important that the split liner is acid treated, thoroughly deactivated and conditioned before use, to ensure that lambda-cyhalothrin does not epimerise to the isomer during analysis.
Split ratio	100 : 1
Injection volume	1.0 µl using an autosampler

Detector system

Type	FID
Range	High sensitivity
Temperatures	
Column oven	210 °C
Injector	300 °C
Detector	300 °C

Adjust the column oven temperature if required to obtain retention time windows for lambda-cyhalothrin (10.7-11.4 min) and hexacosane (12.2-13.0 min), but not exceeding 240 °C.

Gas flow rates

Helium or hydrogen (carrier)	1 ml × min^{-1}
Nitrogen (make up) Hydrogen Air	} flow rates as recommended for the gaschromatograph

All gases should be purified through molecular sieves. The carrier gas should be further purified through an oxygen trap.

Calibration	Internal. Calibration solution, peak area measurement
Retention times	cyhalothrin diastereoisomer: about 10.4 min lambda-cyhalothrin : about 11.0 min hexacosane : about 13.1 min

(c) Equilibration of the system. Carry out 1.0 µl injections of Solutions I, C_0 and S_0 and check whether there are any interfering peaks from impurities. If there are, make any necessary corrections by MT 114 but not external calibration.
Inject calibration solutions C_A and C_B to equilibrate the system and use the data from these chromatograms to set the integration parameters. Calculate the response factors for these injections to check stability of the instrument. Response factors should not differ by more than ± 1% of the mean. Where detector sensitivity is shown to be low, the second dilution stage for calibration and sample solutions may be omitted.
(d) Analysis of sample. Carry out 1.0 µl injections of calibration solutions C_A and C_B and sample solutions S_A and S_B in the following sequence and record the integrated areas of the peaks. Injection sequence : C_{A1}, S_{A1}, S_{A2}, C_{B1}, C_{A2}, S_{B1}, S_{B2}, C_{B2}.
(e) Calculation. Calculate the relative response factors (f_1, f_2 etc) for the pair of calibration injections which bracket the sample injections e.g. use C_{A1} and C_{B1} for sample injections S_{A1}, S_{A2}, etc. and obtain the mean response factor *f*. Sample analysis should be repeated if calibration response factors f_1 and f_2 differ by more than ± 2% of the mean *f*.

$$\text{Relative response factor} = \frac{H_s}{I_r \times s \times P}$$

where:
H_s = area of lamda-cyhalothrin peak in the calibration solution
I_r = area of hexaxosane peak in the calibration solution
s = mass of lambda-cyhalothrin analytical standard in calibration solution (g)
P = purity of the lambda-cyhalothrin standard (g/kg)

The mass of internal standard is common to both calibration and sample solution and has therefore been omitted.

For each sample injection, e.g. S_{A1}, calculate the lambda-cyhalothrin content.

$$\text{Lambda-cyhalothrin content} = \frac{H_w}{f \times I_q \times w}$$

where:
f = mean relative response factor
H_w = mean area of lambda-cyhalothrin peak in the sample solution
I_q = area of the hexacosane peak in the sample solution
w = mass of sample (g)

Calculate the lambda-cyhalothrin content of the sample as the mean of the four determinations as follows:

Sample injection	Use relative response factor from	Lambda-cyhalothrin	
S_{A1}	C_{A1} and C_{B1}	Q %	X %
S_{A2}	C_{A1} and C_{B1}	R %	
S_{B1}	C_{A2} and C_{B2}	S %	Y %
S_{B2}	C_{A2} and C_{B2}	T %	

Take the mean of the two values X and Y as the lambda-cyhalothrin content

Repeatability r = 19.0 g/kg at 800-900 g/kg active ingredient content

Reproducibility R = 54.7 g/kg at 800-900 g/kg active ingredient content

LAMBDA-CYHALOTHRIN WETTABLE POWDERS
*463/WP/M/-

1 Sampling. Take at least 500 g.

2 Identity tests. As for 463/TC/M/2.

3 Lambda-cyhalothrin. As for **463**/TC/M/3 except substitute the following for *(a)*:

(a) Preparation of the sample solution. Weigh in duplicate (to the nearest 0.1 mg) into 150 ml conical flasks, sufficient sample (*w* g) to contain about 0.1 g of lambda-cyhalothrin. Add by pipette to each flask, 20.0 ml of hexacosane Solution I, and 30 ml of dichloromethane. Shake the flasks thoroughly for 5-10 minutes (use an ultrasonic water bath if available) to dissolve the lambda-cyhalothrin. Allow the insoluble material to settle and filter the supernatant liquid through an appropriate filter paper. Dilute 5 ml of each filtrate to 25 ml with dichloromethane (Solutions S_A and S_B). Prepare a solution without internal standard by shaking a similar amount of sample with 50 ml of dichloromethane. Filter and dilute 5 ml of filtrate to 25 ml with dichloromethane (Solution S_0).

* CIPAC method 1990. Prepared by PAC-GB. Chairman: S Bailey. Based on a method supplied by ICI.

Repeatability r = 4.4 g/kg at 80-120 g/kg active ingredient content

Reproducibility R = 6.6 g/kg at 80-120 g/kg active ingredient content

4. Suspensibility

APPARATUS AND REAGENTS As for **463**/TC/M/3 together with:

Separating funnel 250 ml
Round bottom flask 250 ml
Phase separating paper 1-PS (available from Whatman)

PROCEDURE

(a) Preparation of suspension MT 15.1 (*i*)
(b) Determination of sedimentation MT 15.1 (*ii*)
(c) Determination of lambda-cyhalothrin in the bottom 25 ml of suspension. Transfer the bottom one-tenth of suspension from the suspensibility test quantitatively to a 250 ml glass-stoppered separating funnel. Use a maximum volume of 25 ml of distilled water to rinse the 250 ml graduated cylinder and combine the suspension and washings.
Add 25 ml of dichloromethane to the separating funnel, stopper, and shake for one minute. Formation of an emulsion at this stage may be overcome by adding 1 g of sodium chloride crystals to the aqueous layer and re-shaking the contents of the funnel. Run the separating dichloromethane layer through phase-separating paper into a clean, dry 250 ml round-bottom flask. Repeat the extraction with a further three 25 ml aliquots of dichloromethane, combining all four extracts. Remove the dichloromethane under reduced pressure at 60 °C using
a rotary evaporator and dissolve the residue in the 250 ml flask in 2.0 ml of internal standard solution and dilute to 25 ml with dichloromethane. Determine the lambda-cyhalothrin content of the solution by gas chromatography as in **463**/TC/M/3, based on duplicate injections of calibration and sample solutions.
(d) Calculation

$$Q = \frac{H_w \times I_r \times s \times P}{H_s \times I_q \, 1000}$$

$$\text{Suspensibility} = \frac{111(c - Q)}{c}$$

where:

c = mass of lambda-cyhalothrin in the sample taken for the preparation of the suspension (g)

Q = mass of lambda-cyhalothrin in the 25 ml remaining in the suspensibility cylinder (g)

LAMBDA-CYHALOTHRIN EMULSIFIABLE CONCENTRATES
*463/EC/M/-

1 Sampling. Take at least 500 ml.

2 Identity tests. As for **463**/TC/M/2.

3 Lambda-cyhalothrin. As for **463**/TC/M/3.

Repeatability r = 6.2 g/kg at 100-150 g/kg active ingredient content
4.4 g/kg at 40-60 g/kg active ingredient content

Reproducibility R = 13.4 g/kg at 100-150 g/kg active ingredient content
9.3 g/kg at 50-60 g/kg active ingredient content

LAMBDA-CYHALOTHRIN ULTRA-LOW VOLUME FORMULATIONS
*463/UL/M/-

1 Sampling. Take at least 500 ml.

2 Identity tests. As for **463**/TC/M/2.

3 Lambda-cyhalothrin. As for **463**/TC/M/3 except substitute the following:
(a) Preparation of the sample solution. Weigh in duplicate (to the nearest 0.1 mg) into 150 ml conical flasks, sufficient sample (*w* g) to contain about 0.1 g of lambda-cyhalothrin. Add by pipette to each flask, 20.0 ml of internal standard solution (Solution I), and 20 ml of dichloromethane. Shake the flasks thoroughly to dissolve the lambda-cyhalothrin.

* CIPAC method 1990. Prepared by PAC-GB. Chairman: S Bailey. Based on a method supplied by ICI.

Dilute 5 ml of each solution to 25 ml with dichloromethane (Solution S_A and S_B). Prepare a solution without internal standard by shaking a similar amount of sample with dichloromethane to give a total volume of 50 ml. Dilute 5 ml of this solution to 25 ml with dichloromethane (Solution S_0).

and add to *(d) Analysis of sample*:
When main components have eluted following an injection of low strength product such as ULV formulation, the column oven temperature should be raised to 300 °C for 5 minutes to prevent interference from late eluting components with subsequent injections.

Repeatability r = 0.2 g/kg at 5-10 g/kg active ingredient content

Reproducibility R = 0.8 g/kg at 5-10 g/kg active ingredient content