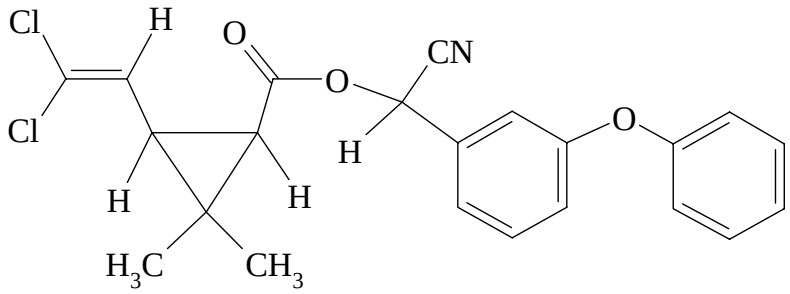
ALPHA-CYPERMETHRIN
454



ISO common name	Alpha-cypermethrin
Chemical name	A racemate of (*S*)-α-cyano-3-phenoxybenzyl (1*R*, 3*R*)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane-carboxylate and (*R*)-α-cyano-3-phenoxybenzyl (1*S*, 3*R*)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane-carboxylate (IUPAC); [1α(*S**), 3α]-(±)-cyano(3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane-carboxylate (CA; *67375-30-8*)
Empirical formula	$C_{22}H_{19}Cl_2NO_3$
RMM	416.3
m.p.	80.5 °C
v.p.	1.7×10^{-7} Pa at 20 °C
Density	1.12 g/cm^3 at 20 °C
Solubility	In water: 5-10 µg/l at 25 °C; acetone: 620 g/l; cyclohexanone: 515 g/l; hexane: 7g/l; xylene: 351 g/l
Description	Colourless crystals
Stability	Very stable in acidic and neutral media, hydrolysed in strongly alkaline media, thermally stable up to 200 °C
Formulations	Wettable powders, emulsifiable concentrates, suspension, concentrates and ultra-low-volume liquids

ALPHA-CYPERMETHRIN TECHNICAL
*454/TC/(M)/-

1 Sampling. Take at least 100 g.

2 Identity tests

2.1 GLC. Use the GLC method below. The relative retention times of alpha-cypermethrin with respect to the internal standard for the sample solution should not deviate by more than 1 % from those of the calibration solution.

2.2.Infrared. Prepare potassium bromide discs from the sample and from alpha-cypermethrin standard, using approximately 15 mg material and 300 mg potassium bromide. Scan the discs from 4000 to 400 cm^{-1}. The spectrum produced from the sample should not differ significantly from that of the standard.

3 Alpha-cypermethrin

OUTLINE OF METHOD Alpha-cypermethrin is dissolved in tetrahydrofuran and determined by capillary gas chromatography in the split injection mode using flame ionisation and internal standardisation.

REAGENTS

Tetrahydrofuran

Alpha-cypermethrin standard of known purity. Store below 4 °C.

Di(2-ethylhexyl) phthalate (dioctyl phthalate, DOP), internal standard, purity at least 980 g/kg and giving no peaks with similar retention times to alpha cypermethrin

Citric acid 5 % solution. Dissolve citric acid (25 g) in water (500 ml).

Internal standard solution. Dissolve dioctyl phthalate (5.0 g) in tetrahydrofuran (500 ml). Ensure sufficient quantity of this solution is prepared for all the samples and calibration solutions to be analysed.

Calibration solution. Weigh in duplicate (to the nearest 0.1 mg) into two volumetric flasks (100 ml) 100 mg alpha-cypermethrin standard (*s* mg). Add tetrahydrofuran (about 70 ml) to each and agitate the flasks gently to dissolve the standard. Add by pipette to each flask internal standard solution (10.0 ml) and from a measuring cylinder citric acid solution (10 ml). Make up to volume with tetrahydrofuran and mix well (solutions C_A and C_B). (NOTE: Citric acid is added to stop epimerisation of alpha-cypermethrin in solution)

* Provisional CIPAC method 1997. Prepared by PAC-UK. Based on a method supplied by American Cyanamid, UK

APPARATUS

Gas chromatograph capable of operating over the range 100 to 300 °C, fitted with a flame ionisation detector, split/splitless injector and autosampler
Capillary column fused silica, 30 m × 0.25 mm with DB-1 of 0.25 μm film thickness (or equivalent dimethyl polysiloxane phase)
Electronic integrator or data system

PROCEDURE
(a)Operating conditions (typical):

Column	Fused silica, 30 m × 0.25 mm (i.d.) and 0.25 μm film thickness coated with dimethyl poly-siloxane packing.
Injection system	
Injector	Split/splitless with fused silica liner containing a 1 cm plug of glass wool. It is important that the split liner is thoroughly deactivated and conditioned before use, to ensure no degradation of alpha-cypermethrin occurs.
Split ratio	approximately 75-100 : 1
Split vent	approximately 75 ml/min
Injection volume	1 μl
Detector	Flame ionisation
Temperatures	
Column oven	225 to 235 °C, isothermal
Injection port	260 °C
Detector	300 °C
Gas flow rates	
Helium (carrier gas)	approximately 0.8 ml/min (140 kPa at 230 °C)
Helium (make up)	60 ml/min or optimum for instrument
Septum purge	2 ml/min
Hydrogen	25 to 30 ml/min) or as recommended for
Air	200 t0 300 ml/min) the particular instrument
Retention times	alpha-cypermethrin cis II: approximately 27 min alpha-cypermethrin cis I: approximately 29 min DOP: approximately: 14 min

Purify all gases through molecular sieves. Purify the carrier gas further

through an oxygen trap.

(b) Preparation of sample. Weigh (to the nearest 0.1 mg) in duplicate into two volumetric flasks (100 ml) sufficient sample to contain 100 mg alpha-cypermethrin (*w* mg). Add tetrahydrofuran (about 70 ml) and agitate the flasks gently to dissolve. Then add by pipette to each flask internal standard solution (10.0 ml) and by measuring cylinder citric acid solution (10 ml). Make up to volume with tetrahydrofuran and mix well (solutions S_A and S_B).

(c) Equilibration of the system. Inject a portion of one of the calibration solutions. Adjust the column oven temperature to obtain retention time windows for dioctyl phthalate 12.2 to 14.9 min, for the cis II isomer 24.0 to 29.7 min and for the cis I isomer 22.7 to 27.7 min. In order to obtain adequate resolution the retention times of the cis I and the cis II peaks relative to the DOP peak should be not less than 1.9 and 2.0 respectively. Carry out alternate 1.0 µl injections of the calibration solutions C_A and C_B until the response factors consistently (at least two injections of each) differ by less than ± 1 % of the mean.

(d) Determination. Inject into the gas chromatograph 1.0 µl portions of the calibration solutions C_A and C_B and the sample solutions S_A and S_B in the following sequence and record the alpha-cypermethrin integrated peak areas.
Injection sequence: C_{A1}, S_{A1}, S_{A2}, C_{B1}, C_{A2}, S_{B1}, S_{B2}, C_{B2}.
Calculate the relative response factors (f_1, f_2, etc) for the pair of calibration solutions which bracket the sample solutions e.g. use C_{A1} and C_{B1} for sample injections S_{A1} and S_{A2} etc and obtain the mean response factor *f*. Repeat sample analysis if calibration response factors f_1 and f_2 differ by more than ± 2 % of the mean *f*. Calculate for each sample injection e.g. S_{A1} the alpha-cypermethrin *cis* II content.

(e) Calculation

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

$$\text{Alpha-cypermethrin content} = \frac{f \times H_w}{I_q \times w} \text{ g/kg}$$

where:
f = average relative response factor
H_s = area of alpha-cypermethrin cis II peak in the calibration solution
H_w = area of alpha-cypermethrin cis II peak in the sample solution
I_r = area of internal standard peak in the calibration solution
I_q = area of internal standard peak in the sample solution
s = mass of alpha-cypermethrin in the calibration solution (mg)
w = mass of sample taken (mg)
P = purity of alpha-cypermethrin reference substance (g/kg)

Calculate the alpha-cypermethrin cis II content of the sample as the mean of the four determinations as follows:

Sample injection	Use response factor from	Content g/kg		
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 values X and Y as the alpha-cypermethrin content.

Repeatability r = 17 g/kg at 954 g/kg active ingredient content
Reproducibility R = 20 g/kg at 954 g/kg active ingredient content

ALPHA-CYPERMETHRIN WETTABLE POWDERS
[*]**454**/WP/(M)/-

[*] **1 Sampling.** Take at least 1 kg.

2 Identity tests.
2.1 GLC. As for alpha-cypermethrin technical **454**/TC/(M)/2.1.
2.2 Infrared. Extract a suitable portion of the sample with acetone. Evaporate the solvent with a gentle stream of clean, dry air and proceed as for alpha-cypermetrin technical **454**/TC/(M)/2.2.

3 Alpha-cypermethrin. As for alpha-cypermethrin technical **454**/TC/(M)/3, except:
(b) Preparation of sample. Weigh (to the nearest 0.1 mg) in duplicate into two volumetric flasks (100 ml) sufficient sample to contain 100 mg alpha-cypermethrin (*w* mg). Add tetrahydrofuran (about 70 ml) and place the flasks in an ultrasonic bath for 15 min with occasional swirling to fully disperse the sample. Then add by pipette to each flask internal standard solution (10.0 ml) and by measuring cylinder citric acid solution (10 ml). Make up to volume with tetrahydrofuran and mix well. Filter through a suitable paper e.g. GF/A or use a filter unit e.g. PTFE 0.45 μm (solutions S_A and S_B).

Repeatability r = 1.2 g/kg at 49.4 g/kg active ingredient content

[*] Provisional CIPAC method 1997. Prepared by PAC-UK. Based on a method supplied by American Cyanamid, UK

Reproducibility R = 1.4 g/kg at 49.4 g/kg active ingredient content

4 Suspensibilty. (Draft method)

(a) Preparation of suspension. MT 15.1 (*i*).

(b) Determination of sedimentation. MT 15.1 (*ii*).

(c) Determination of alpha-cypermethrin in the bottom 25 ml of suspension. After removal of the top 225 ml of suspension, transfer the remaining 25 ml of suspension quantitatively to a volumetric flask (100 ml) with tetrahydrofuran (about 50 ml). Add by pipette internal standard solution (5.0 ml) and by measuring cylinder citric acid solution (5 ml), and dilute to volume with tetrahydrofuran (about 75 ml) and place the flask in an ultrasonic bath for 10 min. Allow to cool to room temperature and make up to volume with tetrahydrofuran. Filter through a suitable paper (e.g. GF/A) or use a filter unit (e.g. PTFE 0.45 μm) before analysis. Determine the mass of alpha-cypermethrin (*Q* g) according to **454**/TC/(M)/3*(c)*.

(d) Calculation

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

where:

c = mass of alpha-cypermethrin in the sample taken for the preparation of the suspension (g)

Q = mass of alpha-cypermethrin in the bottom 25 ml of suspension (g)

ALPHA-CYPERMETHRIN EMULSIFIABLE CONCENTRATES

[*] **454**/EC/(M)/-

1 Sampling. Take at least 1 l.

2 Identity tests.

2.1 GLC. As for alpha-cypermethrin technical **454**/TC/(M)/2.1.

[*] Provisional CIPAC method 1997. Prepared by PAC-UK. Based on a method supplied by American Cyanamid, UK.

3 Alpha-cypermethrin. As for alpha-cypermethrin technical **454**/TC/(M)/3, except:
(b) Preparation of sample. Weigh (to the nearest 0.1 mg) in duplicate into two volumetric flasks (100 ml) sufficient sample to contain 100 mg alpha-cypermethrin (*w* mg). Add tetrahydrofuran (about 70 ml) and swirl to dissolve. Then add by pipette to each flask internal standard solution (10.0 ml) and by measuring cylinder citric acid solution (10 ml). Make up to volume with tetrahydrofuran and mix well (solutions S_A and S_B).

Repeatability r = 2.6 g/kg at 107 g/kg active ingredient content
Reproducibility R = 4.1 g/kg at 107 g/kg active ingredient content

ALPHA-CYPERMETHRIN SUSPENSION CONCENTRATES
[*] **454**/SC/(M)/-

1 Sampling. Take at least 1 l.

2 Identity tests.
2.1 GLC. As for alpha-cypermethrin technical **454**/TC/(M)/2.1.

3 Alpha-cypermethrin As for alpha-cypermethrin technical **454**/TC/(M)/3, except:
(b) Preparation of sample. Mix the sample thoroughly. Weigh (to the nearest 0.1 mg) in duplicate into two volumetric flasks (100 ml) sufficient sample to contain 100 mg alpha-cypermethrin (*w* mg). Add by measuring cylinder citric acid solution (10 ml) and swirl to fully disperse the formulation. Then add tetrahydrofuran (about 70 ml) in approximately 10 to 15 ml portions, swirling the flasks in between each addition to disperse the sample fully. Place the flasks in an ultrasonic bath for 15 min with occasional swirling. Add by pipette to each flask internal standard solution (10.0 ml), make up to volume with tetrahydrofuran and mix well. Filter through a suitable paper e.g. GF/A or use a filter unit e.g. PTFE 0.45 μm (solutions S_A and S_B).

Repeatability r = 2.9 g/kg at 95 g/kg active ingredient content
Reproducibility R = 3.2 g/kg at 95 g/kg active ingredient content

[*] Provisional CIPAC method 1997. Prepared by PAC-UK. Based on a method supplied by American Cyanamid, UK

4 Suspensibility (Draft method)

(a) Preparation of suspension and determination of sedimentation. MT 161.

(b) Determination of alpha-cypermethrin in the bottom 25 ml of suspension. As for **454**/WP/(M)/4*(c).*

ALPHA-CYPERMETHRIN ULTRA LOW VOLUME SOLUTIONS
* **454**/UL/(M)/-

1 Sampling. Take at least 1 l.

2 Identity tests.
2.1 GLC. As for alpha-cypermethrin technical, **454**/TC/(M)/2.1.

3 Alpha-cypermethrin As for alpha-cypermethrin technical, **454**/TC/(M)/3, except:
(b) Preparation of sample. Weigh (to the nearest 0.1 mg) in duplicate into two volumetric flasks (100 ml) sufficient sample to contain 100 mg alpha-cypermethrin (*w* mg). Add tetrahydrofuran (about 70 ml) and swirl to dissolve. Then add by pipette to each flask internal standard solution (10.0 ml) and by measuring cylinder citric acid solution (10 ml). Make up to volume with tetrahydrofuran and mix well (solutions S_A and S_B).

Repeatability r = 1.3 g/kg at 17 g/kg active ingredient content
Reproducibility R = 1.4 g/kg at 17 g/kg active ingredient content

* Provisional CIPAC method 1997. Prepared by PAC-UK. Based on a method supplied by American Cyanamid, UK