FENVALERATE

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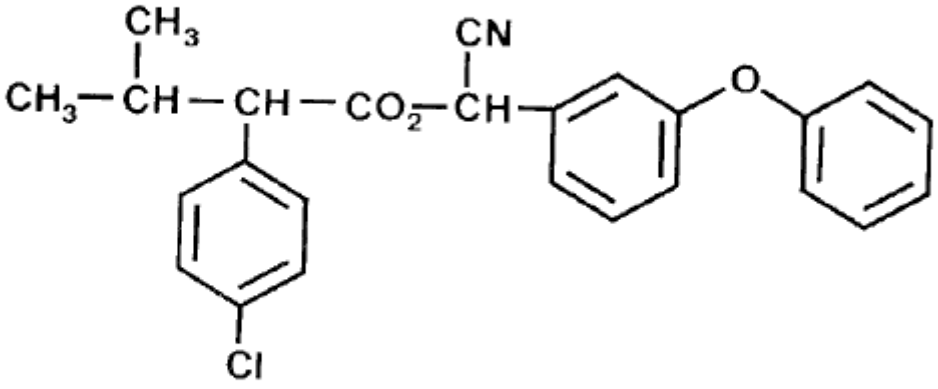

ISO common name	Fenvalerate
Chemical name	(*RS*)-α-cyano-3-phenoxybenzyl(*RS*)-2-(4-chlorophenyl)-3-methylbutyrate (IUPAC); cyano(3-phenoxyphenyl)methyl 4-chloro-α-(1-methylethyl)benzeneacetate (CA; *51630-58-1*)
Empirical formula	$C_{25}H_{22}ClNO_3$
RMM	419·9
Description	Technical material is a viscous yellow or brown liquid, sometimes partly crystallized at room temperature
v.p.	37 μPa at 25°C
Solubility	In: water less than 1 mg/l (technical); hexane less than 77 g/l; acetone, cyclohexanone, ethanol, xylene, chloroform more than 450 g/l; at 20°C
Formulations	Emulsifiable concentrates and ULV concentrates

Note: Fenvalerate is a mixture of the two diastereoisomeric forms of α-cyano-3-phenoxybenzyl 2-(4-chlorophenyl)-3-methylbutyrate, each of which is present as a pair of enantiomers. Following the nomenclature used in the method below, the two diastereoisomers are: (α*R*,2*R*) + (α*S*,2*S*) and (α*R*,2*S*) + (α*S*,2*R*). The ratio of the two enantiomers in each diastereoisomer is 1 : 1.

FENVALERATE TECHNICAL

*334/TC/(M)/–

1 Sampling. Homogenize the bulk material by warming at between 60°C and 65°C until no crystals remain, and mixing thoroughly before taking the sample. Take at least 100 g.

2 Identity tests. MT 163, *p. 180.*

3 Fenvalerate

SCOPE This method is intended for the determination of total fenvalerate in technical material. The method is unsuitable for the determination of the diastereoisomer ratio.

OUTLINE OF METHOD The sample is dissolved in 4-methylpentan-2-one containing diphenyl phthalate as internal standard. Separation is carried out on a column of Chromosorb W-HP coated with Apiezon L and the fenvalerate determined by comparison with calibration solutions.

REAGENTS

4-Methylpentan-2-one (methyl isobutyl ketone) MIBK
Diphenyl phthalate (DPP) internal standard solution (Solution I)
DPP solution. Dissolve DPP (10 g) in MIBK (500 ml). Ensure a sufficient quantity of this solution is prepared for all samples and standards being analysed.
Fenvalerate working standard of known fenvalerate content (minimum 900 g/kg) with a diastereoisomer ratio similar to that of the sample being analysed. Store the standard in a cool, dry place, preferably in a desiccator. The isomers may crystallize out of the mixture at ambient temperature and the analytical standard must be homogeneous before use. A certified standard of fenvalerate will be available from the Office of Reference Materials, National Physical Laboratory, Department of Trade and Industry, TW11 0LW, England. This material should be used to calibrate the working standard.
Calibration solution. Homogenize the standard by warming the sealed bottle of fenvalerate standard (purity P) at between 60°C and 65°C until no crystals remain, and then shake the bottle. Weigh in duplicate (to the nearest 0·1 mg) approximately 0·2 g of standard (s_A and s_B g). Transfer to 50 ml volumetric flasks and dissolve in a few ml of MIBK. Add by pipette, 10·0 ml of internal standard solution to each flask and dilute to 50 ml with MIBK (Solutions C_A and C_B). Prepare a solution *without* internal standard by dissolving 0·1 g of fenvalerate standard in 25 ml of MIBK (Solution C_0).

* Provisional CIPAC method 1986. Prepared by the Pyrethroids Panel of PAC–GB. Chairman: P G Baker (Laboratory of the Government Chemist). Based on methods supplied by Shell Research Limited, Sittingbourne, Kent, England, and Sumitomo Chemical Co. Limited, Kitahama, Higashi-Ku, Osaka, Japan.

APPARATUS

Gas chromatograph capable of operating over the range 100 to 300°C with a flame ionization detector and fitted for on-column injection with a separate injector heating control. At the point of injection the temperature should be at least 10°C above the column temperature.
Column 1 m × 3 mm i.d. glass column packed with 2% Apiezon L on Chromosorb W-HP, 100 to 120 mesh. The glass column should first be silylated using the following method:

Fill the column with 5% DMCS in dry toluene (1 min). Wash out the column thoroughly with dry toluene and then with acetone. Condition the column (empty) in a chromatographic oven at 100°C with nitrogen passing through at 20 ml/min for at least 1 h. The chromatographic support material sometimes causes on-column decomposition. It is sometimes necessary to silylate Chromosorb W-AW as not all pre-silylated commercial batches of support material are sufficiently inert for analysis of fenvalerate. Pack the column, and if it is necessary to plug the end of the column, this should be done with dimethyldichlorosilane treated silica wool. Before use condition a freshly prepared column by purging with nitrogen overnight at 260°C. During this operation the column must not be connected to the detector.
Electronic integrator compatible with the gas chromatograph
Microsyringe 10 µl
Volumetric flasks 50 ml
Pipette 10 ml

PROCEDURE

(*a*) *Preparation of the sample solutions.* Homogenize the sub-sample by the method given for the standard. Prepare a solution *without* internal standard by dissolving about 0·2 g in 50 ml of MIBK (Solution S_0). Weigh in duplicate (to the nearest 0·1 mg) into 50 ml volumetric flasks sufficient sample (w_A and w_B g) to contain approximately 0·2 g of fenvalerate. Add by pipette, 10·0 ml of DPP internal standard solution to each flask and then dilute to volume with MIBK (Solutions S_A and S_B).

(*b*) *Gas chromatographic conditions:*
Column

Material	Glass (silylated)
Length × i.d.	1·0 m × 3 mm
Stationary phase/recommended solvent	Apiezon L/dichloromethane
Solid support	Chromosorb W-HP 100 to 120 mesh (125 to 150 µm)
Mass ratio: stationary phase/support	2/98
Typical packing density	0·29 g/ml
Typical column efficiency (number of theoretical plates determined for DPP peak)	1500 (The fenvalerate peak is split due to partial resolution of the isomers therefore column efficiency is calculated using DPP peak)

Detector system	
Type	FID
Sensitivity	No special requirements
Temperatures	
Column oven	Use a temperature of 245°C and control to ±0·5°C throughout the analyses
Injection port	The temperature should be at least 10°C higher than that of the column
Detector	250°C
Carrier gas	Nitrogen (oxygen-free i.e. contains less than 10 ppm) 0·05 litre/min
Calibration	Internal. Response factor, peak area measurement
Quantity to be injected	2 µl of a solution containing 4 mg of fenvalerate/ml MIBK. 'On column' injection i.e. on to or just into the support material is essential to ensure satisfactory chromatography. Fenvalerate is thermally labile, and on-column decomposition can occur from active sites on silica, or glass wool, column glass or support material. If silylated glass wool or silica plug is used, it is recommended that the syringe needle should penetrate through the plug into the column packing material. Two forms of on-column decomposition of fenvalerate can occur. These appear as either a discrete peak in front of the fenvalerate pair of peaks or as a shoulder in front of the peaks. It is not usual to obtain complete separation of the diastereoisomeric pair.
Retention times (typical)	DPP: 2·8 min (α*R*, 2*S*) + (α*S*, 2*R*): 8 min (α*R*, 2*R*) + (α*S*, 2*S*): 9·5 min (see Fig. 12).

(*c*) *Equilibration of the system.* Check for interfering components by injecting solutions I, C_0 and S_0. If any interfering compounds are present, make any necessary corrections by MT 114 or by using external calibration. Inject standard solutions C_A and C_B to set the integrator parameters. Fenvalerate to DPP peak area ratios in solutions C_A and C_B should not differ by more than 0·5% of their mass adjusted mean value (area/mass ratio).

(*d*) *Analysis of sample.* Carry out injections of 2 µl 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 three peaks:

Injection sequence C_{A1}, S_{A1}, S_{A2}, C_{B1}, C_{A2}, S_{B1}, S_{B2}, C_{B2}

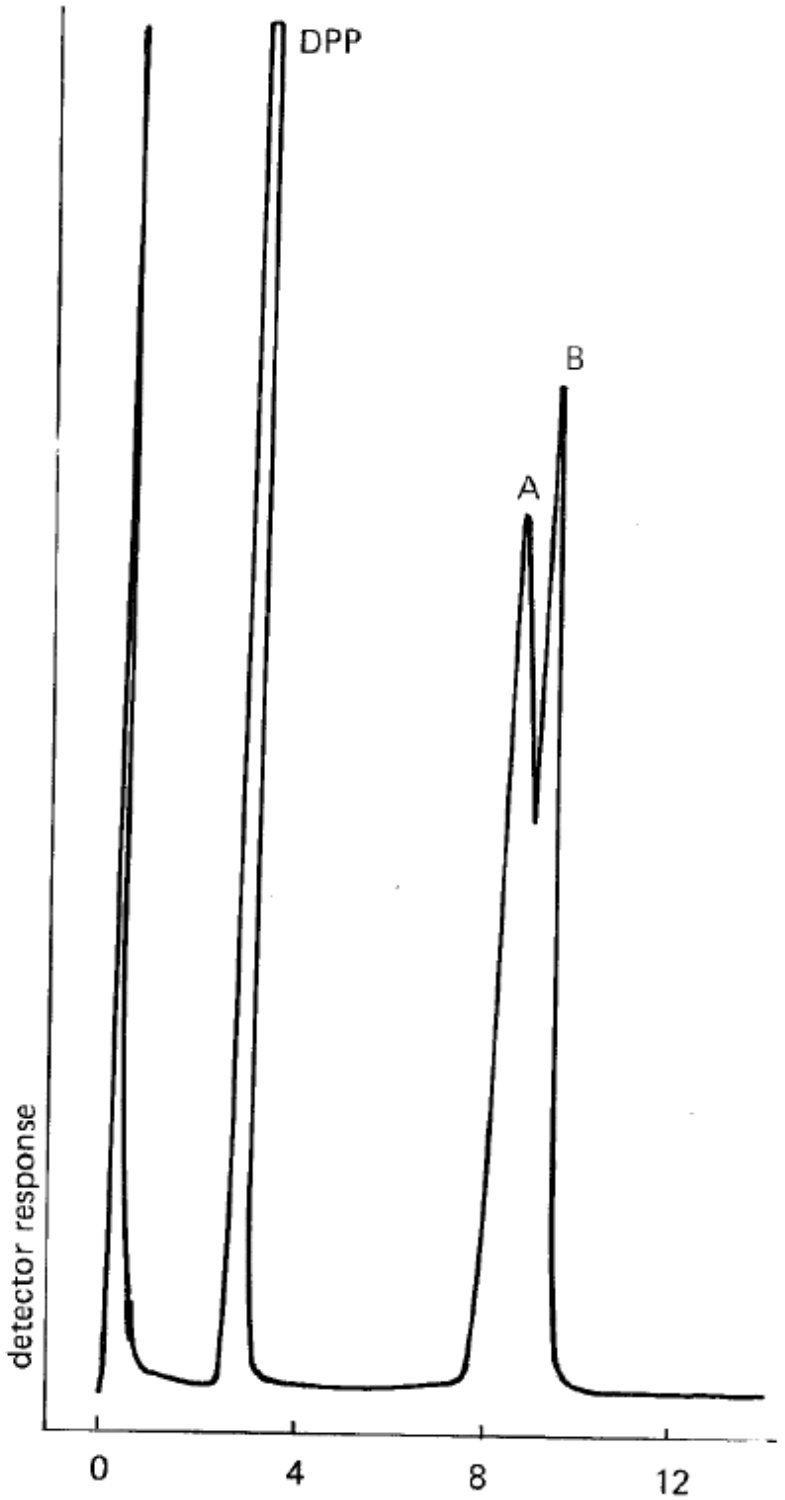

Fig. 12 Typical HPLC chromatogram of fenvalerate; DDP = diphenyl phthalate (int. stand.); A = (αR, 2*S*) + (αS + 2*R*) diastereoisomer pair; B = (αR, 2*R*) + (αS + 2*S*) diastereoisomer pair.

(*e*) *Calculation*. For each sample injection calculate the fenvalerate content.

$$\text{Fenvalerate content} = \frac{R \times s \times P}{R' \times w} \text{ g/kg}$$

where:

R = total fenvalerate to DPP peak area ratio of the sample injections
R' = mean total fenvalerate to DPP peak area ratio of the calibration solution injections C_{A1} and C_{A2}
s = mass of fenvalerate standard in calibration solution (g)
w = mass of sample (g)
P = purity of the fenvalerate standard (g/kg)

The mass of internal standard is common to both calibration and sample solution and so does not enter into the calculation. Report the values obtained for fenvalerate content for each injection of the sample solutions.

Repeatability r_{95} = 13 g/kg at 945 g/kg active ingredient content
Reproducibility R_{95} = 25 g/kg at 945 g/kg active ingredient content