ETOFENPROX TECHNICAL

Interim specification WHO/IS/97.24.1

1. Specification

1.1 Material

The material shall consist of etofenprox together with related manufacturing impurities and shall be in the form of a white to yellow solidified melt at ambient temperature, free from extraneous matter or added modifying agents.

1.2 Chemical and physical requirements

The material, sampled from any part of the consignment (see method WHO/M/1), shall comply with the requirements of section 1.1 and with the following requirements.

1.2.1 *Etofenprox content (g/kg basis)*

The etofenprox content shall be declared (not less than 990 g/kg) and, when determined by the method described in section 2.1, the content obtained shall not differ from that declared by more than 5 g.

1.2.2 *Melting point*

The melting point of the material, determined by the method described in WHO/M/5, shall not be lower than 36 and shall not be depressed when mixed with an equal quantity of pure etofenprox.

1.2.3 *pH of aqueous dispersion*

The pH value of aqueous dispersion, determined by the method described in WHO/M/25, shall lie in the range 5 to 6.

1.2.4 *Material, insoluble in acetone*

The material insoluble in acetone, determined by the method described in WHO/M/21.R1, shall not be higher than 1 g/kg.

1.2.5 *Water content*

The water content, determined by the method described in WHO/M/7R1, shall not be higher than 1 g/kg.

1.3 Packing and marking of packages

The technical etofenprox shall be packed in suitable clean containers, as specified in the order.

All packages shall bear, durably and legibly marked on the container, the following.

Manufacturer's name
Technical etofenprox to specification WHO/IS/97.24.1
Batch or reference number, and date of test
Net weight of contents
Date of manufacture

and the following minimum cautionary notice.

Etofenprox is an insecticide with an action similar to the pyrethroids that act predominantly on the central nervous system. It may be hazardous if swallowed. Do not inhale spray mist. Avoid skin contact; wear protective gloves, clean protective clothing, and a face mask (surgical type) when handling the material. Wash hands and exposed skin thoroughly after using.

Keep containers out of the reach of children and well away from foodstuffs and animal feed and their containers.

Etofenprox is toxic to aquatic wildlife. Avoid accidental contamination of water.

If poisoning occurs, call a physician. Treatment is symptomatic.

WHO has classified etofenprox as unlikely to present acute hazard in normal use.

2. Methods of determining chemical and physical properties

2.1 Etofenprox content

2.1.1 *Outline of method*

The sample is dissolved in cyclohexane containing di-cyclohexyl phthalate as internal standard. Separation is carried out by gas-liquid chromatography with a flame ionization detector on a column of Chromosorb W-HP coated with silicone AN-600. The etofenprox is determined by comparison with calibration solutions.

2.1.2 *Special apparatus*

Gas-liquid chromatograph. Capable of operating over the range 100 to 300 with a flame ionization detector, injection port heater and on-column injection system and equipped with a suitable recorder or electronic integrator.

*Chromatographic column***.** Glass column 2 m long, 3 mm internal diameter packed with 5% silicone AN-600 on Chromosorb W-HP (60-80 mesh) or equivalent.

Injection volume. 1.0 µl.

Automatic digital integrator or chromatography data system compatible with the gas chromatograph.

Before use condition a freshly prepared column by purging with nitrogen overnight at 290 . During this operation the column must not be connected to the detector to avoid contamination by any initial "bleed" of the stationary phase.

2.1.3 *Special reagents*

Cyclohexane, p.a.

Internal standard. Di-cyclohexyl phthalate. Select for use a batch which, when chromatographed under the conditions given below for the determination of etofenprox, gives no peak with a similar retention time to etofenprox.

Etofenprox working standard. Analytical standard of known etofenprox content (minimum 999 g/kg).

2.1.4 *Preparation of standard solutions*

Internal standard solution

Dissolve 1 g di-cyclohexyl phthalate in 200 ml cyclohexane. As the reagent dissolves slowly in the solvent, it may be necessary to use an ultrasonic bath or to warm the solution. Before use, allow the solution to return to room temperature. Keep the solution in thermostated bath if room temperature varies by more than 1.

Etofenprox calibration solution

Weigh in duplicate (to the nearest 0.1 mg) about 0.12 g of etofenprox standard (M_A and M_B, g) into separate 100 ml stoppered volumetric flasks. Add 20.0 ml of di-cyclohexyl phthalate internal standard solution, shake to dissolve the etofenrox and dilute to 100 ml with cyclohexane. (Solutions C_A and C_B). Keep the solution in thermostated bath if room temperature varies by more than 1.

Prepare a solution without internal standard by dissolving about 0.12 g of standard in 100 ml of cyclohexane. (Solution C_O).

2.1.5 *Operating conditions*

The conditions given below are typical values and may have to be adapted to obtain optimal results from a given apparatus.

Temperatures

Column oven	230
Injector	270
Detector	270

Adjust the column oven temperature if required to obtain retention time windows for etofenprox (approximately 19 min) and di-cyclohexyl phthalate (approximately 9.5 min), but not exceeding 300 .

Gas flow rate

Nitrogen	50 ml min^{-1}
Hydrogen	40 ml min^{-1}
Air	500 ml min^{-1}

2.1.6 *Sample preparation*

Sampling

Homogenize the bulk material by heating to about 40 and mix thoroughly until no crystals remain before taking at least 100 g as a sub-sample for analysis.

Preparation of the sample solutions. Homogenize the material by the method given here above for sampling.

Weigh (to the nearest 0.1 mg) in duplicate sufficient sample (w g) to contain about 0.12 g of etofenprox into 100 ml stoppered volumetric flasks. Add to each flask 20 ml of di-cyclohexyl phthalate internal standard solution by pipette, shake the flasks thoroughly to dissolve the etofenprox and dilute to 100 ml with cyclohexane. (Solution S_A and S_B).

Prepare a solution without internal standard by dissolving about 0.12 g of etofenprox in 100 ml of cyclohexane (Solution S_O).

2.1.7 *Equilibration of the system*

Inject at least 3 x 1.0 µl of one of the etofenprox calibration solution C to equilibrate the system and use the data from these chromatograms to set the integrator parameters if one is being used and also to assess the stability of the system.

Inject 1.0 µl portions of the internal standard solution, and C_O and S_O solutions and check whether there are any interfering peaks from impurities. If there are, make any necessary corrections.

2.1.8 *Analysis of sample*

Carry out injections of 1.0 µl of the etofenprox calibration solutions C_A and C_B and sample solutions S_A and S_B in the following sequence and record either the integrated areas of the peaks or measure by triangulation from the product of EL x JK^2 (height x base).

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 etofenprox calibration injections which bracket the sample injections, e.g. use C_{A1} and C_{B1} for sample injection S_{A1}, S_{A2} etc., and obtain the mean response factor f.

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

where:

H_s = Area of etofenprox peak from the etofenprox calibration solution.
I_r = Area of di-cyclohexyl phthalate peak in the etofenprox calibration solution.
M = Mass of etofenprox analytical standard in the etofenprox calibration solution (g)
P = Purity of the etofenprox analytical standard (g/kg).

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

Successive measurements of the response factors should agree to within 0.5% of their mean value. If not repeat the analysis.

2.1.9 *Calculation*

Calculate the etofenprox content for each sample injection, e.g. S_{A1} by the following equation:

$$\text{Etofenprox content (g/kg)} = \frac{H_w}{f \times I_q \times \underline{w}}$$

where

f = mean relative response factor
H_w = area of the etofenprox peak in the sample solution
I_q = area of the di-cyclohexyl phthalate peak in the sample solution
$\underline{w}$ = mass of sample (g).

Take the mean of the four values corresponding to the four injections S_{A1}, S_{A2}, S_{B1}, S_{B2}.

Calculate the etofenprox content of the sample as the mean of the four determinations as follows:

Sample injection	Use relative response factor from	Etofenprox	
S_{A1}	C_{A1} and C_{B1}	Q%	)
			) U%
S_{A2}	C_{A1} and C_{B1}	R%	)
S_{B1}	C_{A2} and C_{B2}	S%)	
			) V%
S_{B2}	C_{A2} and C_{B2}	T%	)

Q and R, S and T should agree to within 0.5 % of their respective mean values (U and V). U and V should agree to within 1% of their mean values. Take the mean of the two values U and V as the total etofenprox content.