

TECHNICAL DELTAMETHRIN

Specification WHO/SIT/24.R1
Approved 25 September 1989

1. Specification

1.1 Material

The material shall consist of deltamethrin together with related manufacturing compounds and shall be in the form of a white to cream-coloured crystalline powder, free from extraneous impurities 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 *Deltamethrin content (g/kg basis)*

The deltamethrin content shall be declared (not less than 980 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 ± 25 g/kg.

1.2.2 *Deltamethrin R-isomer content (g/kg basis)*

The deltamethrin R-isomer content determined by the method described in section 2.2 shall not be higher than 10 g/kg.

1.2.3 *Acid chloride content*

The content of acid chloride corresponding to deltamethrin, determined by the method described in section 2.3, shall not be higher than 2 g/kg.

1.2.4 *Acid and anhydride content*

The content of acid and anhydride corresponding to deltamethrin, determined by the method described in section 2.4, shall not be higher than 10 g/kg.

1.2.5 *Melting point*

The melting point of the material determined by the method WHO/M/5.R1, shall not be lower than 98°C.

1.2.6 *Optical rotation*

The optical rotation $[\alpha]_D^{20}$ of the material determined by the method described in section 2.5 shall be equal to $57 \pm 1.5^\circ$.

1.3 **Packing and marking of packages**

The technical deltamethrin 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 deltamethrin to specification WHO/SIT/24.R1
Batch or reference number, and date of test
Net weight of contents
Date of manufacture

and the following minimum cautionary notice:

Deltamethrin is a pyrethroid that acts predominantly on the central nervous system: high dosages have been found to cause tonic seizures in experimental animals. A high concentration in air may be an irritant and contact with the concentrated product may induce a temporary tingling sensation, particularly on the face. 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. Deltamethrin is toxic to aquatic wildlife. Avoid accidental contamination of water. If poisoning occurs, call a physician. Treatment is symptomatic.

2. **Methods of determining chemical and physical properties**

2.1 **Deltamethrin content**

2.1.1 *Outline of method*

The sample is dissolved in a mixture of dioxane and iso-octane. The deltamethrin content is determined by comparing the response of the sample with that of a deltamethrin standard by high-performance liquid chromatography (HPLC), using a silica column and a mixture of dioxane and iso-octane as mobile phase.

2.1.2 *Special apparatus*

1. *Liquid chromatograph.* The instrument should be one that is designed for use with stainless steel columns and that is equipped with: (a) a pumping system able to maintain a pressure of 15 MPa; (b) a UV spectrophotometer detector able to measure UV absorbance at 254 nm¹, and (c) a loop-type injector.
2. *Liquid chromatographic column.* The column should be a stainless steel tube 15-18 cm long and 4.6 mm in internal diameter packed with silica (LiChrosorb SI 60, 5 µm Merck 9388, or equivalent)².
3. *Recorder.* 1 mV full-scale sensitivity or integrator.

2.1.3 *Special reagents*

Deltamethrin standard. Analytical grade, of known purity (at least 990 g/kg).

1,4-Dioxane. HPLC grade. Check the peroxides content and purify if necessary. Dioxane is mixed with 1.5 ml of water per litre, before use.

Iso-octane. HPLC grade.

Mobile phase. A degassed mixture of 5 ml of dioxane and 95 ml of iso-octane. Diluting solvent: dioxane-iso-octane: 20 + 80 (v/v).

2.1.4 *Preparation of the calibration solution*

Weigh (to the nearest 0.1 mg), in duplicate, about 50 mg of deltamethrin standard into two 50 ml volumetric flasks (C₁ and C₂). Add into both flasks a small amount of diluting solvent (20 ml of dioxane + 80 ml of iso-octane) and shake the flasks to dissolve the standard. Dilute to volume with the same solvent³ and homogenize.

2.1.5 *Operating conditions for high-performance liquid chromatography*

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

Column temperature	ambient
Flow rate	1 to 1.6 ml/min
Wavelength	254 nm
Injection volume	20 µl (loop-type injector)

¹ Check the linearity of the detector in the concentration zone used for the determination.

² Check that the column does separate the deltamethrin from its R-stereoisomer.

³ Since no internal standard is used, the volumes of the solutions have to be adjusted at the same temperature. Avoid temperature fluctuations during the determination.

Detector sensitivity	set to obtain peak heights between 60 and 90% full-scale deflection
Retention time of deltamethrin	about 9 min

2.1.6 *Sample preparation and analysis*

Weigh (to the nearest 0.1 mg) two portions of the sample containing about 50 mg of deltamethrin in each portion into two 50 ml volumetric flasks (S₁ and S₂). Add a small amount of diluting solvent (20 ml of dioxane + 80 ml of iso-octane) and shake to dissolve the samples. Dilute to volume with the same solvent⁴ and homogenize.

Inject 20 µl of calibration solution from one of the two flasks (C₁ or C₂) until the peak areas (or heights) of two successive injections agree to within 1%.

Inject the calibration solutions from flasks C₁ and C₂ and sample solutions from flasks S₁ and S₂ in succession in the following sequence: C₁ S₁, C₂ S₁, C₁ S₂, C₂ S₂.

2.1.7 *Calculation*

For each of the above four groups (i.e., C₁ versus S₁, C₂ versus S₁, C₁ versus S₂, and C₂ versus S₂) calculate the deltamethrin content.

$$\text{Deltamethrin content (g/kg)} = \frac{a_2 \times m_1 \times p}{a_1 \times m_2}$$

Where:

- a₁ = deltamethrin peak area (or height) of the calibration solution
- a₂ = deltamethrin peak area (or height) of the sample solution
- m₁ = mass of deltamethrin standard in the calibration solution (mg)
- m₂ = mass of sample taken (mg)
- p = purity of deltamethrin standard (g/kg)

The four results should agree to within ± 3% of their mean value. If not, repeat the analysis.

⁴ Since no internal standard is used, the volumes of the solutions have to be adjusted at the same temperature. Avoid temperature fluctuations during the determination.

2.2 Deltamethrin R-isomer content

2.2.1 *Outline of method*

The sample is dissolved in a mixture of dioxane and iso-octane. The R-isomer content is determined by comparing the response of the sample with that of an R-isomer standard by high-performance liquid chromatography (HPLC), using a silica column and a mixture of dioxane and iso-octane as mobile phase.

2.2.2 *Special apparatus*

1. *Liquid chromatograph.* The instrument should be one that is designed for use with stainless steel columns and that is equipped with: (a) a pumping system able to maintain a pressure of 15 MPa; (b) a UV spectrophotometer detector able to measure UV absorbance at 254 nm⁵, and (c) a loop-type injector.
2. *Liquid chromatographic column.* The column should be a stainless steel tube 15-18 cm long and 4.6 mm in internal diameter packed with silica (LiChrosorb SI 60, 5 µm, Merck 9388, or equivalent)⁶.
3. *Recorder.* 1 mV full-scale sensitivity or integrator.

2.2.3 *Special reagents*

Deltamethrin R-isomer standard. Analytical grade, of known purity.

1,4-Dioxane. HPLC grade. Check the peroxides content and purify if necessary. Dioxane is mixed with 1.5 ml of water per litre, before use.

Iso-octane. HPLC grade.

Mobile phase. Degassed mixture of 5 ml of dioxane and 95 ml of iso-octane.

2.2.4 *Preparation of the calibration solution*

Weigh (to the nearest 0.01 mg) about 20 mg of deltamethrin R-isomer into a 50 ml volumetric flask. Dissolve and make up to volume with the mobile phase mixture. Pipette 10.0 ml of this solution into a 100 ml volumetric flask, make up to volume with the mobile phase mixture⁷ and homogenize.

⁵ Check the linearity of the detector in the concentration zone used for the determination

⁶ Check that the column does separate the deltamethrin from its R-stereoisomer.

⁷ Since no internal standard is used, the volumes of the solutions have to be adjusted at the same temperature. Avoid temperature fluctuations during the determination.

2.2.5 *Operating conditions for high-performance liquid chromatography*

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

Column temperature	ambient ⁸
Flow rate	1-1.7 ml/min
Wavelength	254 nm
Injection volume	20 µl (loop-type injector)
Retention times:	
R-isomer	about 8 min
deltamethrin	about 9 min

2.2.6 *Sample preparation and analysis*

Weigh (to the nearest 0.1 mg) about 200 mg of the sample into a 50 ml volumetric flask. Add 2.5 ml of dioxane to dissolve, make up to volume with iso-octane and homogenize. Inject 20 µl of the calibration solution until the peak areas of the two successive injections agree to within 5%. Inject the sample solution in duplicate. The results should agree to within 5%. If not, repeat the injections.

2.2.7 *Calculation*

$$\text{R-isomer content (g/kg)} = \frac{a_2 \times m_1 \times p}{a_1 \times m_2 \times 10}$$

Where: a_1 = R-isomer peak area of the calibration solution
 a_2 = R-isomer peak area of the sample solution
 m_1 = mass of R-isomer standard in the calibration solution (mg)
 m_2 = mass of sample taken (mg)
 p = purity of the R-isomer standard (g/kg)

2.3 **Acid chloride content corresponding to deltamethrin**

2.3.1 *Reagents*

1. A 0.02 mol/l standardized solution of potassium hydroxide in methanol
2. Neutralized methanol. Add 3 drops of a 10 ml/l solution of bromophenol blue in methanol to 100 ml of methanol. If necessary, add a 0.1 mol/l solution of hydrochloric acid in methanol (obtained by diluting 8 ml of 12 mol/l hydrochloric acid to 100 ml with methanol) dropwise until a yellow colour develops.

⁸ Since no internal standard is used, the volumes of the solutions have to be adjusted at the same temperature. Avoid temperature fluctuations during the determination.

Add dropwise reagent no. 1 until a purple-blue colour develops.

2.3.2 Procedure

Transfer about 2 g (weighed to the nearest 0.1 mg) of the product (w g) into a 200 ml Erlenmeyer flask. Add 100 ml of neutralized methanol and warm to dissolve. Then cool to room temperature and allow it to stand for 5 min. Titrate with the standard 0.02 mol/l methanolic potassium hydroxide (reagent no. 1) to a purple-blue end-point (t ml).

2.3.3 Calculation

The milliequivalent for 1 g corresponding to the acid chloride is given by the equation.

$$B = \frac{t \times c}{w}$$

Where: t = volume (ml) of standard methanolic potassium hydroxide used
c = molarity of the methanolic potassium hydroxide
w = mass (g) of the sample taken

The acid chloride content (g/kg) is then given by:

$$\frac{B \times 316.45 \times 1000}{1000 \times 1} = B \times 316.45$$

2.4 Content of acid and anhydride corresponding to deltamethrin

2.4.1 Acid

2.4.1.1 Reagents

1. Standardized 0.02 mol/l solution of sodium hydroxide in ethanol.
2. Neutralized ethanol. To 100 ml of ethanol add 10 drops of a 10 ml/l solution of a-naphtholbenzein in ethanol. Add dropwise 0.02 mol/l ethanolic sodium hydroxide (reagent no. 1) until a true green colour develops.

2.4.1.2 Procedure

Transfer a sample of about 2 g (weighed to the nearest 0.1 mg) of product (w₁ g) into a 200 ml Erlenmeyer flask. Add 100 ml of neutralized ethanol. Warm to dissolve, cool in ice, and immediately titrate the ice-cooled solution with the standard 0.02 mol/l ethanolic sodium hydroxide solution to a true green end-point (t₁ ml).

2.4.1.3 *Calculation*

The milliequivalent for 1 g corresponding to acid + acid chloride is given by the equation.

$$C = \frac{t_1 \times c}{w_1}$$

Where: t_1 = volume (ml) of standard ethanolic sodium hydroxide used
 c = molarity of the ethanolic sodium hydroxide
 w_1 = mass (g) of the sample taken

The acid content (g/kg) is then given by:

$$\frac{(C - B) \times 297.95 \times 1000}{1000 \times 1} = (C - B) \times 297.95$$

Where: B is the milliequivalent for 1 g corresponding to the acid chloride, determined by method 2.3.

2.4.2 *Anhydride*2.4.2.1 *Reagents*

1. *0.01 mol/l solution of aniline in cyclohexane.*

2. *Standardized 0.01 mol/l perchloric acid solution in glacial acetic acid.*

- (a) *Preparation.* Mix 1.46 g of 700-720 ml/l perchloric acid carefully with glacial, anhydrous acetic acid (about 200 ml) and pure acetic anhydride (50 ml) and make up to one litre with acetic acid. The flask should be well cooled while the reagents are being mixed.
- (b) *Standardization.* Weigh (to the nearest 0.01 mg) about 0.02 g (w g) of anhydrous sodium carbonate and dissolve it in acetic acid (30 ml). Add a-naphtholbenzein indicator 1% solution in benzene (2 drops) and titrate with the perchloric acid until the colour of the solution changes from yellow orange to dark green (t ml).

$$\begin{aligned} \text{Molarity} &= \frac{1000w}{52.994t} \\ &= \frac{18.87w}{t} \end{aligned}$$

(c) Note: when titrating with perchloric acid in glacial acetic acid the following points should be noted:

- There should be complete absence of water; if water is present a satisfactory end-point cannot be obtained.
- Titrations and standardizations should be carried out at the same temperature because acetic acid has a large coefficient of thermal expansion.

2.4.2.2 Procedure

Weigh a sample of about 1 g (to the nearest 0.1 mg) of product (w_2 g) into a 200 ml Erlenmeyer flask. Add 10 ml (accurately measured) of 0.01 mol/l aniline solution in cyclohexane and 10 ml of glacial acetic acid. Stopper the flask, mix and allow to stand for 1 hour at 20-25°C. Titrate with 0.01 mol/l perchloric acid in the presence of a 10 g/l solution of crystal violet in glacial acetic acid until the initially purple colour turns emerald green (t_2 ml). Run a blank test in the same conditions but omitting the sample (T ml).

2.4.2.3 Calculation

The milliequivalent for 1 g corresponding to anhydride and to two times acid chloride is given by the equation:

$$D = \frac{(T - t_2) \times c}{w_2}$$

Where: T = volume (ml) of 0.01 mol/l standardized perchloric acid used in the blank titration

t_2 = volume (ml) of 0.01 mol/l standardized perchloric acid used

c = molarity of the perchloric acid

w_2 = mass (g) of the sample taken.

$$\begin{aligned} \text{The anhydride content (g/kg)} &= \frac{(D - 2B) \times 577.9 \times 1000}{1000 \times 1} \\ &= (D - 2B) \times 577.9 \end{aligned}$$

Where: B is the milliequivalent for 1 g corresponding to the acid chloride determined by method 2.3.

2.5 Specific rotation

2.5.1 *Special apparatus*

Polarimeter designed to operate to the nearest 0.01°.

2.5.2 *Procedure*

Weigh (to the nearest 0.1 mg) approximately 2 g of deltamethrin into a 50 ml volumetric flask, dissolve in toluene, and make up to volume with toluene at a temperature of $20 \pm 0.5^\circ\text{C}$. Determine the zero-point of the polarimeter and the rotation angle of polarized light at the wavelength of the D line of sodium ($\lambda = 589.3 \text{ nm}$) at $20 \pm 0.5^\circ\text{C}$.

2.5.3 *Calculation*

The specific rotation is given by the equation

$$[\alpha]_{\text{D}}^{20} = \frac{a \times 10\,000}{l \times c}$$

Where: a = rotation angle (in degrees) at $20 \pm 0.5^\circ\text{C}$
 l = length (in cm) of the polarimetric tube
 c = sample concentration in g/l.

DELTAMETHRIN WATER-DISPERSIBLE POWDER

Specification WHO/SIF/42.R1
Approved 25 September 1989

1. Specification

1.1 Description and ingredients

The material shall consist of a homogeneous mixture of technical deltamethrin together with filler and other necessary formulants and shall be in the form of a fine, free-flowing, whitish powder that wets out readily on stirring into water. The technical deltamethrin used in the manufacture of the water-dispersible powder shall comply with the requirements of specification WHO/SIT/24.R1.

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 *Deltamethrin content (g/kg basis)*

The content of deltamethrin, determined by the method described in section 2.1, shall not differ from the nominal content by more than the following amount:

<i>Nominal content</i>	<i>Tolerance permitted</i>
Up to 25 g/kg	±15% of the nominal content
Above 25 g/kg	±10% of the nominal content

The average content of all samples taken shall not be lower than the nominal content.

1.2.2 *Deltamethrin R-isomer content (g/kg basis)*

The deltamethrin R-isomer content, determined by the method described in section 2.2, shall not be higher than 2% of the deltamethrin content found under section 1.2.1

1.2.3 *Acidity or alkalinity*

The acidity or alkalinity of the powder, determined by the method described in WHO/M/3, shall not be higher than 5 g/kg calculated as H₂SO₄, or 5 g/kg calculated as NaOH.

1.2.4 *Sieving after heat stability treatment*

Not less than 98% of the powder after the heat stability treatment (section 2.4) shall pass through a 75 µm sieve when tested by the method described in WHO/M/4.R1.

1.2.5 *Suspensibility*

In standard hard water after heat stability treatment. When tested by the method described in section 2.3, a minimum of 50% of the deltamethrin (0.025 g/l) shall be in suspension 30 minutes after agitating a suspension containing 0.05 g/l of deltamethrin prepared in standard hard water from the powder subjected to the heat stability treatment described in section 2.4.

1.2.6 *Heat stability*

The powder after treatment as described in section 2.4 shall comply with the requirements of sections 1.2.1, 1.2.2 and 1.2.3 of this specification.

1.3 **Packing and marking of packages**

The deltamethrin water-dispersible powder shall be packed in suitable clean drums, as specified in the order. The drums shall contain a lining or bag of polyethylene or equivalent, with a nominal thickness of 0.1 mm. The lining or bag shall be hermetically sealed after filling.

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

Manufacturer's name
Deltamethrin water-dispersible powder to specification WHO/SIF/42.R1
Deltamethrin g/kg
Batch or reference number, and date of test
Net weight of contents
Date of formulation

and the following minimum cautionary notice:

Deltamethrin is a pyrethroid that acts predominantly on the central nervous system; high dosages have been found to cause tonic seizures in experimental animals. A high concentration in air may be an irritant, and contact with the concentrated product may induce a temporary tingling sensation, particularly on the face. 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 product. Wash hands and exposed skin thoroughly after using.

Keep containers out of reach of children and well away from foodstuffs and animal feed and their containers. Deltamethrin is toxic to aquatic wildlife. Avoid accidental contamination of water. If poisoning occurs, call a physician. Treatment is symptomatic.

2. Methods of determining chemical and physical properties

2.1 Deltamethrin content

2.1.1 *Outline of method*

Deltamethrin is extracted from the sample with a mixture of dioxane and iso-octane. The deltamethrin content is determined by comparing the response of the sample with that of a deltamethrin standard by high-performance liquid chromatography (HPLC), using a silica column and a mixture of dioxane and iso-octane as mobile phase.

2.1.2 *Special apparatus*

1. *Liquid chromatograph.* The instrument should be one that is designed for use with stainless steel columns and that is equipped with: (a) a pumping system able to maintain a pressure of 15 MPa; (b) a UV spectrophotometer detector able to measure UV absorbance at 254 nm¹, and (c) a loop-type injector.
2. *Liquid chromatographic column.* The column should be a stainless steel tube 15-18 cm long and 4.6 mm in internal diameter packed with silica (LiChrosorb SI 60, 5 µm, Merck 9388, or equivalent)².
3. *Recorder.* 1 mV full-scale sensitivity or integrator.

2.1.3 *Special reagents*

Deltamethrin standard. Analytical grade, of known purity (at least 990 g/kg).

1,4-Dioxane. HPLC grade. Check the peroxides content and purify if necessary. Dioxane is mixed with 1.5 ml of water per litre, before use.

Iso-octane. HPLC grade.

Mobile phase. A degassed mixture of 5 ml of dioxane and 95 ml of iso-octane. Diluting solvent: dioxane-iso-octane: 20:80 (v/v).

2.1.4 *Preparation of the calibration solution*

Weigh (to the nearest 0.1 mg), in duplicate, about 50 mg of deltamethrin standard into two 50 ml volumetric flasks (C₁ and C₂). Add into both flasks a small amount of diluting solvent (20 ml of dioxane + 80 ml of iso-octane) and shake the flasks to dissolve the standard. Dilute to volume with the same solvent³ and homogenize.

¹ Check the linearity of the detector in the concentration zone used for the determination.

² Check that the column does separate the deltamethrin from its R-stereoisomer.

³ Since no internal standard is used, the volumes of the solutions have to be adjusted at the same temperature. Avoid temperature fluctuations during the determination.

2.1.5 *Operating conditions for high-performance liquid chromatography*

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

Column temperature	ambient
Flow rate	1-1.6 ml/min
Wavelength	254 nm
Injection volume	20 µl (loop-type injector)
Detector sensitivity	set to obtain peak heights between 60 and 90% full-scale deflection
Retention time of deltamethrin	about 9 min

2.1.6 *Sample preparation and analysis*

Weigh (to the nearest 0.1 mg) two portions of the sample containing about 50 mg of deltamethrin in each portion into two glass-stoppered conical flasks (S₁ and S₂). Pipette in 50 ml of diluting solvent (20 ml of dioxane + 80 ml of iso-octane). Extract for 15 minutes in an ultrasonic bath. Filter rapidly to avoid any solvent loss or alternatively centrifuge a part of the suspensions. The extracts, which must be clear, are used for the analysis.

Inject 20 µl of calibration solution from one of the two flasks (C₁ or C₂) until the peak areas (or heights) of two successive injections agree to within 1%.

Inject the calibration solutions from flasks C₁ and C₂ and sample solutions from flasks S₁ and S₂ in succession in the following sequence: C₁ S₁, C₂ S₁, C₁ S₂, C₂ S₂.

2.1.7 *Calculation*

For each of the above four groups (i.e., C₁ versus S₁, C₂ versus S₁, C₁ versus S₂, and C₂ versus S₂) calculate the deltamethrin content.

$$\text{Deltamethrin content (g/kg)} = \frac{a_2 \times m_1 \times P}{a_1 \times m_2}$$

Where

- a₁ = deltamethrin peak area (or height) of the calibration solution
- a₂ = deltamethrin peak area (or height) of the sample solution
- m₁ = mass of deltamethrin standard in the calibration solution (mg)
- m₂ = mass of sample taken (mg)
- P = purity of deltamethrin standard (g/kg)

The four results should agree to within ±3% of their mean value. If not, repeat the analysis.

2.2 Deltamethrin R-isomer content

2.2.1 *Outline of method*

The sample is dissolved in a mixture of dioxane and iso-octane. The R-isomer content is determined by comparing the response of the sample with that of an R-isomer standard by high-performance liquid chromatography (HPLC), using a silica column and a mixture of dioxane and iso-octane as mobile phase.

2.2.2 *Special apparatus*

1. *Liquid chromatograph.* The instrument should be one that is designed for use with stainless steel columns and that is equipped with: (a) a pumping system able to maintain a pressure of 15 MPa; (b) a UV spectrophotometer detector able to measure UV absorbance at 254 nm⁴, and (c) a loop-type injector.
2. *Liquid chromatographic column.* The column should be a stainless steel tube 15-18 cm long and 4.6 mm in internal diameter packed with silica (LiChrosorb SI 60, 5 mm, Merck 9388, or equivalent)⁵.
3. *Recorder.* 1 mV full-scale sensitivity or integrator.

2.2.3 *Special reagents*

Deltamethrin R-isomer standard. Analytical grade, of known purity.

1,4-Dioxane. HPLC grade. Check the peroxides content and purify if necessary. Dioxane is mixed with 1.5 ml of water per litre, before use.

Iso-octane. HPLC grade.

Mobile phase. Degassed mixture of 5 ml of dioxane and 95 ml of iso-octane. Diluting solvent: iso-octane-dioxane: 80:20 (v/v).

2.2.4 *Preparation of the calibration solution*

Weigh (to the nearest 0.01 mg) about 20 mg of deltamethrin R-isomer into a 50 ml volumetric flask. Dissolve and make up to volume with the mobile phase mixture. Pipette 10.0 ml of this solution into a 100 ml volumetric flask, make up to volume with the mobile phase mixture⁶ and homogenize.

⁴ Check the linearity of the detector in the concentration zone used for the determination.

⁵ Check that the column does separate the deltamethrin from its R-stereoisomer.

⁶ Since no internal standard is used, the volumes of the solutions have to be adjusted at the same temperature. Avoid temperature fluctuations during the determination.

2.2.5 *Operating conditions for high-performance liquid chromatography*

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

Column temperature	ambient
Flow rate	1-1.7 ml/min
Wavelength	254 nm
Injection volume	20 µl (loop-type injector)
Retention times:	
R-isomer	about 8 min
deltamethrin	about 9 min

2.2.6 *Sample preparation and analysis*

Weigh (to the nearest 0.1 mg) a sample containing about 200 mg of deltamethrin into a glass-stoppered conical flask. Add 50 ml of diluting solvent. Extract for 15 minutes in an ultrasonic bath. Filter rapidly to avoid any solvent loss or alternatively centrifuge a part of the suspension. The extract, which must be clear, is used for the analysis.

Inject 20 ml of the calibration solution until the peak areas of the two successive injections agree to within 5%. Inject the sample solution in duplicate. The results should agree to within 5%. If not repeat the injections.

2.2.7 *Calculation*

$$\text{R-isomer content (g/kg)} = \frac{a_2 \times m_1 \times P}{a_1 \times m_2 \times 10}$$

Where

- a_1 = R-isomer peak area of the calibration solution
- a_2 = R-isomer peak area of the sample solution
- m_1 = mass of R-isomer standard in the calibration solution (mg)
- m_2 = mass of sample taken (mg)
- P = purity of the R-isomer standard (g/kg)

2.3 **Suspensibility after heat stability treatment**

2.3.1 *Outline of method*

A suspension of known concentration of deltamethrin in standard hard water is prepared, poured into a 250 ml graduated cylinder, maintained at a constant temperature, and allowed to remain undisturbed for 30 minutes. The top nine-tenths are drawn off and the content of deltamethrin in the bottom one-tenth is determined, so allowing to evaluate the active ingredient mass still in suspension after 30 minutes.

2.3.2 *Special apparatus*

1. A 250 ml graduated cylinder with ground-glass stopper and a distance of 20.0-21.5 cm between the bottom and the 250 ml calibration mark.
2. A glass tube, about 40 cm long and about 5 mm in internal diameter, pointed at one end to an opening of 2-3 mm, the other end being connected to a suitable source of suction.

2.3.3 *Special reagent*

Standard hard water. Dissolve 0.304 g of anhydrous calcium chloride and 0.139 g of magnesium chloride hexahydrate in distilled water and make up to one litre. This provides water with a hardness of 342 mg/l, calculated as calcium carbonate. Check the hardness by method WHO/M/26 and correct if appropriate.

2.3.4 *Procedure*

Weigh (to the nearest 1 mg) into a 100 ml beaker an amount of the sample to form 250 ml of a suspension containing 0.05 g/l of deltamethrin. Add a volume of water⁷ at $30 \pm 1^\circ\text{C}$ equal to at least twice the mass of the sample taken. Allow to stand for 30 seconds and then stir by hand for 30 seconds with a glass rod 4-6 mm in diameter, at not more than four revolutions per second, making no deliberate attempt to break up any lumps. Then immediately transfer the mixture quantitatively to the 250 ml graduated cylinder, using water at $30 \pm 1^\circ\text{C}$ for rinsing, and again avoiding mechanical disintegration of lumps. Immediately add sufficient water at $30 \pm 1^\circ\text{C}$ to bring the volume up to the 250 ml mark.

Insert the stopper and invert the cylinder end over end 30 times at the rate of one complete cycle every 2 seconds. During agitation the cylinder must be thermally insulated from the hands to maintain the prescribed temperature of the suspension. This operation should be carried out as smoothly as possible, keeping the axis of rotation fixed. Allow the graduated cylinder to stand for 30 minutes in a water-bath at $30 \pm 1^\circ\text{C}$, taking care that the bath is free from vibrations. Should excessive flocculation occur during the test, the material is unsatisfactory.

At the end of the 30 minutes settling period, insert the glass tube into the cylinder and, with a minimum of disturbance, withdraw nine-tenths of the suspension (i.e., 225 ml) by means of the suction tube in a period of 10-15 seconds. This is achieved by maintaining the tip of the glass tube just below the sinking surface of the suspension. Discard the suspension withdrawn.

⁷ Whenever water is mentioned in this section use standard hard water.

2.3.5 *Determination of deltamethrin in the retained one-tenth of the suspension*2.3.5.1 *Special apparatus*

See 2.1.2 except that:

- the UV spectrophotometer detector must be able to measure UV absorbance at 230 nm,
- the column should be packed with a reverse phase (LiChrosorb RP18, 10 mm or equivalent).

2.3.5.2 *Special reagents*

See 2.1.3 except that the mobile phase has to be changed to "a degassed mixture of 80 ml of acetonitrile and 20 ml of water (HPLC grade)".

2.3.5.3 *Preparation of the calibration solution*

Weigh (to the nearest 0.1 mg) about 50 mg of deltamethrin standard into a 50 ml volumetric flask. Dissolve with acetonitrile (ultrasonic bath can be used to accelerate dissolution). Dilute to volume with acetonitrile and homogenize¹. Pipette 5 ml of the solution obtained into a 50 ml volumetric flask. Dilute to volume with a 50:50 (v/v) mixture of acetonitrile and water, and homogenize⁸.

2.3.5.4 *Operating conditions for high-performance liquid chromatography*

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

Column temperature	ambient
Flow rate	1-1.5 ml/min
Wavelength	230 nm
Injection volume	20 µl (loop-type injector)
Retention time of deltamethrin	6 min

2.3.5.5 *Sample preparation and analysis*

Quantitatively transfer the retained one-tenth of the suspension to a 50 ml volumetric flask, rinsing several times with small quantities of acetonitrile. Dilute to about 1 cm below the mark and place the flask in an ultrasonic bath for 15 minutes to solubilize deltamethrin (a volume contraction occurs), make up to volume with acetonitrile and

⁸ Since no internal standard is used, the volumes of the solutions have to be adjusted at the same temperature. Avoid temperature fluctuations during the determination.

homogenize. Filter rapidly to avoid any solvent loss or centrifuge. The extract, which must be clear, is used from the analysis⁹. Inject 20 µl of the calibration solution until the peak areas (or heights) of two successive injections agree to within 1%.

Inject the sample solution. The peak area (or height) for the sample solution must not differ by more than 20% from the peak area (or height) for the deltamethrin calibration solution. If it differs, adjust the volume of the sample to meet this requirement or prepare another calibration solution with an adapted deltamethrin content. If not, inject the calibration solution and the sample solution in duplicate.

2.3.6 Calculation

For each of the two calibration-solution-versus-sample-solution groups, calculate the deltamethrin content (m_1 mg) in the retained one-tenth of the suspension from the equation¹⁰.

$$m_1 = \frac{a_1 \times m_0}{a_0 \times 10} \text{ (mg)}$$

Where a_0 = deltamethrin area (or height) of calibration solution
 a_1 = deltamethrin area (or height) of sample solution
 m_0 = mass of deltamethrin standard in the calibration solution (mg)

The values m_1 in the duplicate determinations must agree to within $\pm 2\%$ of their mean. From the value obtained in section 2.1.7 for deltamethrin content, calculate the mass of deltamethrin in the initial sample taken for the suspensibility test.

$$\text{Suspensibility \%} = \frac{(m_2 - m_1) \times 111.1}{m_2}$$

Where m_1 = mass of deltamethrin found in the retained one-tenth of the suspension (mg)
 m_2 = mass of deltamethrin in the initial sample taken to prepare the suspension (mg)

⁹ Since no internal standard is used, the volumes of the solutions have to be adjusted at the same temperature. Avoid temperature fluctuations during the determination.

¹⁰ If the volume of the sample is not 50 ml, correct the equation accordingly.

2.4 Heat stability treatment

Fill a 50 ml¹¹ wide-mouthed glass bottle to within 1 cm of the top with the sample. Seal the bottle with a phenolic plastic cap having a soft liner. Turn the cap firmly to ensure a tight seal and place the bottle in a forced-draught oven maintained at $54 \pm 2^\circ\text{C}$ for 3 days. At the end of the heating period, remove the bottle from the oven and allow it to come to room temperature before removing the cap.

¹¹ If a larger quantity of the sample is required for the tests, use a 100 ml bottle.

DELTAMETHRIN EMULSIFIABLE CONCENTRATE

Specification WHO/SIF/43.R1
Approved 25 September 1989

1. Specification

1.1 Description and ingredients

The material shall consist of technical deltamethrin dissolved in suitable solvents with other necessary formulants added. It shall be in the form of a stable liquid free from suspended matter and sediments. The technical deltamethrin used in the manufacture of the concentrate shall comply with the requirements of specification WHO/SIT/24.R1

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 the following requirements.

1.2.1 *Deltamethrin content (g/kg basis)*

The content of deltamethrin, determined by the method described in section 2.1, shall not differ from the nominal content by more than the following amounts:

<i>Nominal content</i>	<i>Tolerance permitted</i>
Up to 25 g/kg	±15% of the nominal content
Above 25 g/kg	±10% of the nominal content

The average content of all samples taken shall not be lower than the nominal content.

1.2.2 *Deltamethrin R-isomer content (g/kg basis)*

The deltamethrin R-isomer content, determined by the method described in section 2.2, shall not be higher than 1% of the deltamethrin content found under section 1.2.1.

1.2.3 *Water content*

The water content, determined by the method described in WHO/M/7.R1, shall not be higher than 5 g/kg.

1.2.4 *Acidity or alkalinity*

The acidity or alkalinity of the concentrate, determined by the method described in WHO/M/3, shall not be higher than 0.5 g/kg calculated as H₂SO₄ or 0.5 g/kg calculated as NaOH.

1.2.5 *Cold test*

No separation of solid or oily material shall occur when the concentrate is tested as described in method WHO/M/23.

1.2.6 *Flash point*

The flash point of the product shall comply with all national and/or international transport regulations (see method WHO/M/10.R1).

1.2.7 *Stability of the emulsion*

In standard soft water. Any separation, including creaming/oiling at the top and oiling/sedimentation at the bottom, of 100 ml of emulsion prepared in standard soft water with 5 ml of concentrate shall not exceed 2 ml when tested as described in WHO/M/13.R3.

In standard hard water. Any separation, including creaming/oiling at the top and oiling/sedimentation at the bottom, of 100 ml of emulsion prepared in standard hard water with 5 ml of concentrate, shall not exceed 2 ml when tested as described in WHO/M/13.R3.

1.2.8 *Heat stability*

The concentrate, after treatment as described in section 2.3, shall comply with the requirements of sections 1.2.1, 1.2.2, 1.2.4 and 1.2.7 of this specification.

1.3 **Packing and marking of packages**

The deltamethrin emulsifiable concentrate shall be packed in suitable, clean containers, as specified in the order. All packages shall bear, durably and legibly marked on the containers, the following:

Manufacturer's name
Deltamethrin emulsifiable concentrate to specification WHO/SIF/43.R1
Deltamethrin g/kg
Batch or reference number, and date of test
Net weight of contents
Instructions for dilution

and the following minimum cautionary notice:

Deltamethrin is a pyrethroid that acts predominantly on the central nervous system; high dosages have been found to cause tonic seizures in experimental animals. A high concentration in air may be an irritant, and contact with the concentrated product may induce a temporary tingling sensation, particularly on the face. 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 this concentrate. Wash hands and exposed skin thoroughly after using.

Keep containers out of reach of children and well away from foodstuffs and animal feed and their containers. Deltamethrin is toxic to aquatic wildlife. Avoid accidental contamination of water. If poisoning occurs, call a physician. Treatment is symptomatic.

2. Methods of determining chemical and physical properties

2.1 Deltamethrin content

2.1.1 Outline of method

The sample is diluted in a mixture of dioxane and iso-octane. The deltamethrin content is determined by comparing the response of the sample with that of a deltamethrin standard by high-performance liquid chromatography (HPLC), using a silica column and a mixture of dioxane and iso-octane as the mobile phase.

2.1.2 Special apparatus

1. *Liquid chromatograph.* The instrument should be one that is designed for use with stainless steel columns and that is equipped with: (a) a pumping system able to maintain a pressure of 15 MPa; (b) a UV spectrophotometer detector able to measure UV absorbance at 254 nm¹; and (c) a loop-type injector.
2. *Liquid chromatographic column.* The column should be a stainless steel tube 15-18 cm long and 4.6 mm in internal diameter packed with silica (LiChrosorb SI 60, 5 mm, Merck 9388, or equivalent)².
3. *Recorder.* 1 mV full-scale sensitivity or integrator.

¹ Check the linearity of the detector in the concentration zone used for the determination.

² Check that the column does separate the deltamethrin from its R-stereoisomer.

2.1.3 *Special reagents*

Deltamethrin standard. Analytical grade, of known purity (at least 990 g/kg).

1,4-Dioxane. HPLC grade. Check the peroxides content and purify if necessary. Dioxane is mixed with 1.5 ml of water per litre, before use.

Iso-octane. HPLC grade.

Mobile phase. A degassed mixture of 5 ml of dioxane and 95 ml of iso-octane. Diluting solvent: dioxane-iso-octane: 20:80 (v/v).

2.1.4 *Preparation of the calibration solution*

Weigh (to the nearest 0.1 mg) two portions of about 50 mg each of deltamethrin standard into two 50 ml volumetric flasks (C_1 and C_2). Add a small amount of diluting solvent (20 ml of dioxane + 80 ml of iso-octane) and shake the flasks to dissolve the standard. Dilute to volume with the same solvent and homogenize.

2.1.5 *Operating conditions for high-performance liquid chromatography*

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

Column temperature	ambient
Flow rate	1-1.6 ml/min
Wavelength	254 nm
Injection volume	20 ml (loop-type injector)
Detector sensitivity	set to obtain peak heights between 60 and 90% full-scale deflection
Retention time of deltamethrin	about 9 min

2.1.6 *Sample preparation and analysis*

Weigh (to the nearest 0.1 mg) two portions of the sample containing about 50 mg of deltamethrin in each portion into two 50 ml volumetric flasks (S_1 and S_2). Add a small amount of diluting solvent (20 ml of dioxane + 80 ml of iso-octane), and shake to dissolve the samples. Dilute to volume with the same solvent³ and homogenize.

Inject 20 ml of the calibration solution from one of the flasks (C_1 or C_2) until the peak areas (or heights) of two successive injections agree to within 1%. Inject the calibration solution from flasks C_1 and C_2 and sample solution from flasks S_1 and S_2 in succession in the following sequence: $C_1 S_1, C_2 S_1, C_1 S_2, C_2 S_2$.

³ Since no internal standard is used, the volumes of the solutions have to be adjusted at the same temperature. Avoid temperature fluctuations during the determination.

2.1.7 Calculation

For each of the above four groups (i.e., C₁ versus S₁, C₂ versus S₁, C₁ versus S₂, and C₂ versus S₂) calculate the deltamethrin content.

$$\text{Deltamethrin content (g/kg)} = \frac{a_2 \times m_1 \times P}{a_1 \times m_2}$$

Where

- a₁ = deltamethrin peak area (or height) of the calibration solution
- a₂ = deltamethrin peak area (or height) of the sample solution
- m₁ = mass of deltamethrin standard in the calibration solution (mg)
- m₂ = mass of sample taken (mg)
- P = purity of deltamethrin standard (g/kg)

The four results should agree to within ±3% of their mean value. If not, repeat the analysis.

2.2 Deltamethrin R-isomer content

2.2.1 Outline of method

The sample is diluted in a mixture of dioxane and iso-octane. The R-isomer content is determined by comparing the response of the sample with that of an R-isomer standard by high-performance liquid chromatography (HPLC), using a silica column and a mixture of dioxane and iso-octane as mobile phase.

2.2.2 Special apparatus

1. *Liquid chromatograph.* The instrument should be one that is designed for use with stainless steel columns and that is equipped with: (a) a pumping system able to maintain a pressure of 15 MPa; (b) a UV spectrophotometer detector able to measure UV absorbance at 254 nm; and (c) a loop-type injector.
2. *Liquid chromatographic column.* The column should be a stainless steel tube 15-18 cm long and 4.6 mm in internal diameter packed with silica (LiChrosorb SI 60, 5 mm, Merck 9388, or equivalent);
3. *Recorder.* 1 mV full-scale sensitivity or integrator.

2.2.3 Special reagents

Deltamethrin R-isomer standard. Analytical grade, of known purity.

1,4-Dioxane. HPLC grade. Check the peroxides content and purify if necessary. Dioxane is mixed with 1.5 ml of water per litre, before use.

Iso-octane. HPLC grade.

Mobile phase. Degassed mixture of 5 ml of dioxane and 95 ml of iso-octane. Diluting solvent: iso-octane-dioxane: 80:20 (v/v).

2.2.4 *Preparation of the calibration solution*

Weigh (to the nearest 0.01 mg) about 20 mg of deltamethrin R-isomer into a 50 ml volumetric flask. Dissolve and make up to volume with the mobile phase mixture. Pipette 10.0 ml of this volume into a 100 ml volumetric flask, make up to volume with the mobile phase mixture and homogenize.

2.2.5 *Operating conditions for high-performance liquid chromatography*

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

Column temperature	ambient
Flow rate	1-1.7 ml/min
Wavelength	254 nm
Injection volume	20 ml (loop-type injector)
Retention times:	
R-isomer	about 8 min
deltamethrin	about 9 min

2.2.6 *Sample preparation and analysis*

Weigh (to the nearest 0.1 mg) a sample containing about 200 mg of deltamethrin into a 50 ml volumetric flask. Add and make up to volume with diluting solvent and homogenize. Inject 20 ml of calibration solution until the peak areas of the two successive injections agree to within 5%. Inject the sample solution in duplicate. The results should agree to within 5%. If not repeat the injections.

2.2.7 *Calculation*

$$\text{R-isomer content (g/kg)} = \frac{a_2 \times m_1 \times P}{a_1 \times m_2 \times 10}$$

Where a_1	= R-isomer peak area of the calibration solution
a_2	= R-isomer peak area of the sample solution
m_1	= mass of R-isomer standard in the calibration solution (mg)
m_2	= mass of sample taken (mg)
P	= purity of the R-isomer standard (g/kg)

2.3 Heat stability

Keep 50 ml of the sample for 3 days at a temperature of $54 \pm 2^\circ\text{C}$ in a glass container sealed to avoid loss of volatile solvent, and then cool to room temperature.

DELTAMETHRIN DUSTABLE POWDER

Specification WHO/SIF/44.R1
Approved 25 September 1989

1. Specification

1.1 Description and ingredients

The material shall consist of a homogeneous mixture of technical deltamethrin together with carriers and any other necessary formulants. It shall be a fine, free-flowing powder, free from hard lumps. The technical deltamethrin used in the manufacture of the powder shall comply with the requirements of specification WHO/SIT/24.R1.

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 *Deltamethrin content (g/kg basis)*

The content of deltamethrin, determined by the method described in section 2.1, shall not differ from the nominal deltamethrin content by more than $\pm 15\%$. The average content of all samples shall not be lower than the nominal content.

1.2.2 *Deltamethrin R-isomer content (g/kg basis)*

The deltamethrin R-isomer content, determined by the method described in section 2.2, shall not be higher than 2% of the deltamethrin content found under section 1.2.1

1.2.3 *Acidity or alkalinity*

The acidity or alkalinity of the powder, determined by the method described in WHO/M/3, shall not be higher than 1 g/kg calculated as H_2SO_4 , or 2 g/kg calculated as NaOH.

1.2.4 *Sieving after heat stability treatment*

Not less than 98% of the powder after heat stability treatment, as described in section 2.3, shall pass through a 150 μm sieve when tested by the method described in WHO/M/4.R1.

1.2.5 *Dustability after heat stability treatment*

After heat stability treatment, as described in section 2.3, the powder shall issue freely without clogging or bridging, when tested in a hand dusting apparatus conforming to specification WHO/EQP/4.R2¹.

1.2.6 *Heat stability*

The powder, after treatment as described in section 2.3, shall comply with the requirements of sections 1.2.1, 1.2.2 and 1.2.3 of this specification.

1.3 **Packing and marking of packages**

The deltamethrin dustable powder shall be packed in suitable clean drums as specified in the order.

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

Manufacturer's name
Deltamethrin dustable powder to specification WHO/SIF/44.R1
Deltamethrin g/kg
Batch or reference number, and date of test
Net weight of contents
Date of formulation

and the following minimum cautionary notice:

Not for application to skin, clothing or bedding. Deltamethrin is a pyrethroid that acts predominantly on the central nervous system; high dosages have been found to cause tonic seizures in experimental animals. A high concentration in air may be an irritant and contact with the concentrated product may induce a temporary tingling sensation in the skin. It may be hazardous if swallowed. Do not inhale a cloud of dust. Avoid skin contact; wear protective gloves and clean protective clothing when handling the material. Wash hands and exposed skin thoroughly after using.

Keep container out of the reach of children and well away from foodstuffs and animal feed and their containers. Deltamethrin is toxic to aquatic wildlife. Avoid accidental contamination of water. If poisoning occurs, call a physician. Treatment is symptomatic.

¹ Equipment for vector control, 3rd ed. Geneva, World Health Organization, 1990, p. 128.

2. Methods of determining chemical and physical properties

2.1 Deltamethrin content

2.1.1 *Outline of method*

Deltamethrin is extracted from the sample with a mixture of dioxane and iso-octane. The deltamethrin content is determined by comparing the response of the sample with that of a deltamethrin standard by high-performance liquid chromatography (HPLC), using a silica column and a mixture of dioxane and iso-octane as mobile phase.

2.1.2 *Special apparatus*

1. *Liquid chromatograph.* The instrument should be one that is designed for use with stainless steel columns and that is equipped with: (a) a pumping system able to maintain a pressure of 15 MPa; (b) a UV spectrophotometer detector able to measure UV absorbance at 230 nm², and (c) a loop-type injector.
2. *Liquid chromatographic column.* The column should be a stainless steel tube 15-18 cm long and 4.6 mm in internal diameter packed with silica (LiChrosorb SI 60, 5 mm, Merck 9388, or equivalent)³.
3. *Recorder.* 1 mV full-scale sensitivity or integrator.

2.1.3 *Special reagents*

Deltamethrin standard. Analytical grade, of known purity (at least 990 g/kg).

1,4-Dioxane. HPLC grade. Check the peroxides content and purify if necessary. Dioxane is mixed with 1.5 ml of water per litre, before use.

Iso-octane. HPLC grade.

Mobile phase. A degassed mixture of 5 ml of dioxane and 95 ml of iso-octane. Diluting solvent: dioxane-iso-octane: 20:80 (v/v).

2.1.4 *Preparation of the calibration solution*

Weigh (to the nearest 0.1 mg) two portions of about 30 mg of deltamethrin standard into two 50 ml volumetric flasks. Add a small amount of diluting solvent (20 ml of dioxane + 80 ml of iso-octane) and shake the flasks to dissolve the standard. Dilute to volume with the same solvent and homogenize. Pipette two 5 ml portions of these solutions into two 50 ml volumetric flasks (C₁ and C₂). Dilute to volume with the diluting solvent and homogenize.

² Check the linearity of the detector in the concentration zone used for the determination.

³ Check that the column does separate the deltamethrin from its R-stereoisomer.

2.1.5 *Operating conditions for high-performance liquid chromatography*

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

Column temperature	ambient
Flow rate	1-1.7 ml/min
Wavelength	230 nm
Injection volume	20 ml (loop-type injector)
Retention time of deltamethrin	about 9 min

2.1.6 *Sample preparation and analysis*

Weigh (to the nearest mg) two portions of the sample containing about 3 mg of deltamethrin in each portion into two 100 ml glass-stoppered conical flasks (S_1 and S_2). Pipette into both flasks 50 ml of diluting solvent (20 ml of dioxane + 80 ml of iso-octane). Extract for 15 minutes in an ultrasonic bath. Filter rapidly to avoid any solvent loss or, alternatively, centrifuge a part of the suspensions. The extracts, which must be clear, are used for the analysis.

Inject 20 ml of the calibration solution from one of the two flasks (C_1 or C_2) until the peak areas (or heights) of two successive injections agree to within 1%. Inject the calibration solution from flasks C_1 and C_2 and sample solution from flasks S_1 and S_2 in succession in the following sequence: $C_1 S_1$, $C_2 S_1$, $C_1 S_2$, $C_2 S_2$.

2.1.7 *Calculation*

For each of the above four groups (i.e., C_1 versus S_1 , C_2 versus S_1 , C_1 versus S_2 , and C_2 versus S_2) calculate the deltamethrin content.

$$\text{Deltamethrin content (g/kg)} = \frac{a_2 \times m_1 \times P}{a_1 \times m_2}$$

Where a_1 = deltamethrin peak area (or height) of the calibration solution
 a_2 = deltamethrin peak area (or height) of the sample solution
 m_1 = mass of deltamethrin standard in the calibration solution (mg)
 m_2 = mass of sample taken (mg)
 P = purity of deltamethrin standard (g/kg)

The four results should agree to within $\pm 3\%$ of their mean value. If not, repeat the analysis.

2.2 Deltamethrin R-isomer content

2.2.1 *Outline of method*

The sample is dissolved in a mixture of dioxane and iso-octane. The R-isomer content is determined by comparing the response of the sample with that of an R-isomer standard by high-performance liquid chromatography (HPLC), using a silica column and a mixture of dioxane and iso-octane as mobile phase.

2.2.2 *Special apparatus*

1. *Liquid chromatograph.* The instrument should be one that is designed for use with stainless steel columns and that is equipped with: (a) a pumping system able to maintain a pressure of 15 MPa; (b) a UV spectrophotometer detector able to measure UV absorbance at 230 nm⁴, and (c) a loop-type injector.
2. *Liquid chromatographic column.* The column should be a stainless steel tube 15-18 cm long and 4.6 mm in internal diameter packed with silica (LiChrosorb SI 60, 5 mm, Merck 9388, or equivalent)⁵.
3. *Recorder.* 1 mV full-scale sensitivity or integrator.

2.2.3 *Special reagents*

Deltamethrin R-isomer standard. Analytical grade, of known purity.

1,4-Dioxane. HPLC grade. Check the peroxides content and purify if necessary. Dioxane is mixed with 1.5 ml of water per litre.

Iso-octane. HPLC grade.

Mobile phase. Degassed mixture of 5 ml of dioxane and 95 ml of iso-octane. Diluting solvent: iso-octane-dioxane: 80:20 (v/v).

2.2.4 *Preparation of the calibration solution*

Weigh (to the nearest 0.01 mg) about 15 mg of deltamethrin R-isomer into a 50-ml volumetric flask. Dissolve and make up to volume with the mobile phase mixture. Pipette 1.0 ml of this solution into a 100-ml volumetric flask and make up to volume with the mobile phase mixture.⁶

⁴ Check the linearity of the detector in the concentration zone used for the determination.

⁵ Check that the column does separate the deltamethrin from its R-stereoisomer.

⁶ Since no internal standard is used, the volumes of the solutions have to be adjusted at the same temperature. Avoid temperature fluctuations during the determination.

2.2.5 *Operating conditions for high-performance liquid chromatography*

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

Column temperature	ambient
Flow rate	1-1.7 ml/min
Wavelength	230 nm
Injection volume	20 ml (loop-type injector)
Retention times:	
R-isomer	about 8 min
deltamethrin	about 9 min

2.2.6 *Sample preparation and analysis*

Weigh (to the nearest 0.1 mg) enough sample to contain about 15 mg of deltamethrin into a 100-ml conical flask. Pipette into the flask, 50 ml of diluting solvent¹. Extract for 15 minutes in an ultrasonic bath. Filter rapidly to avoid any loss of solvent or, alternatively, centrifuge a part of the suspension. The extract, which must be clear, is used for the analysis¹. Inject 20 ml of the calibration solution until the peak areas of the two successive injections agree to within 5%. Inject the sample solution in duplicate. The results should agree to within 5%. If not repeat the injections.

2.2.7 *Calculation*

$$\text{R-isomer content (g/kg)} = \frac{a_2 \times m_1 \times P}{a_1 \times m_2}$$

- Where a_1 = R-isomer peak area of the calibration solution
 a_2 = R-isomer peak area of the sample solution
 m_1 = mass of R-isomer standard in the calibration solution (mg)
 m_2 = mass of sample taken (mg)
 P = purity of the R-isomer standard (g/kg)

2.3 **Heat stability treatment**

Fill a 100 ml wide-mouthed bottle fitted with a vinyl-plastic-lined screw-cap to within 1 cm from the top with the sample. Moreover for the dustability test, section 1.2.5, place 250 g of the sample in a 1 litre wide-mouthed bottle fitted with a vinyl-plastic-lined screw-cap. Place the bottles in an oven maintained at $54 \pm 2^\circ\text{C}$ for 3 days. Take the samples from the oven and allow them to cool to room temperature before removing the caps. After completion of the heat stability treatment, the samples should not be exposed to heat, bright sunshine, or high atmospheric humidity.

DELTAMETHRIN ULTRA-LOW VOLUME LIQUID

Specification WHO/SIF/46
Approved 25 September 1989

1. Specification

1.1 Description and ingredients

The material shall consist of deltamethrin dissolved in suitable solvents with any other necessary formulants. It shall be in the form of a stable liquid, free from suspended matter and sediment. The technical deltamethrin used in the manufacture of the ULV liquid shall comply with the requirements of specification WHO/SIT/24.R1.

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 *Deltamethrin content (g/kg basis)*

The content of deltamethrin, determined by the method described in section 2.1, shall not differ from the nominal content by more than the following amounts:

<i>Nominal content</i>	<i>Tolerance permitted</i>
Up to 25 g/kg	±15% of the nominal content
Above 25 g/kg	±10% of the nominal content

The average content of all samples taken shall not be lower than the nominal content.

1.2.2 *Deltamethrin R-isomer content (g/kg basis)*

The deltamethrin R-isomer content, determined by the method described in section 2.2, shall not be higher than 1% of the deltamethrin content found under section 1.2.1.

1.2.3 *Water content*

The water content, determined by the method described in WHO/M/7.R1, shall not be higher than 5 g/kg.

1.2.4 *Acidity*

The acidity of the material, determined by the method described in WHO/M/3, shall not be higher than 0.5 g/kg calculated as H₂SO₄.

1.2.5 *Cold test*

No separation of solid or oily material shall occur when the product is tested as described in method WHO/M/23.

1.2.6 *Flash point*

The flashpoint, determined by the method WHO/M/10.R1, shall not be lower than 22.8°C and shall comply with all national and international regulations on handling and transport of flammable materials.

1.2.7 *Kinematic viscosity range*

The kinematic viscosity of the product determined at 30°C by the method WHO/M/22 shall be in the following range:

$$5 \text{ to } 10 \text{ mm}^2 \times \text{s}^{-1}$$

1.2.8 *Volatility*

The volatility (evaporation rate) of the product, determined by the method described in WHO/M/24, shall not exceed 500 g/kg.

1.2.9 *Heat stability*

The material after treatment as described in section 2.3 shall comply with the requirements of sections 1.2.1, 1.2.2, 1.2.4 and 1.2.7 of this specification.

1.3 **Packing and marking of packages**

The deltamethrin ULV liquid 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
Deltamethrin ULV liquid to specification WHO/SIF/46
Deltamethrin g/kg
Batch or reference number, and date of test
Net weight of contents
Date of formulation
Type of equipment to be used for application, if required

and the following minimum cautionary notice:

Deltamethrin is a pyrethroid that acts predominantly on the central nervous system, high dosages leading to tonic seizures in experimental animals. A high concentration in air may be an irritant, and contact with concentrated product may induce a temporary tingling sensation, particularly on the face. It may be hazardous if swallowed. Do not inhale spray mist. Avoid skin contact; wear protective gloves, clean protective clothing and face mask when handling the material. Wash hands and exposed skin thoroughly after using. Keep containers out of reach of children and well away from foodstuffs and animal feed and their containers. Deltamethrin is toxic to aquatic wildlife. Avoid accidental contamination of water. If poisoning occurs, call a physician. Treatment is symptomatic.

2. Methods of determining chemical and physical properties

2.1 Deltamethrin content

2.1.1 Outline of method

After dilution of the sample in a mixture of dioxane and iso-octane, the deltamethrin content is determined by comparing the response of the sample with that of a deltamethrin standard, by high performance liquid chromatography on a column packed with alkylcyano bounded silica.

2.1.2 Special apparatus

1. *Liquid chromatograph.* A suitable instrument for use with stainless steel columns, able to maintain a pressure of 15 MPa, and fitted with a 20 ml loop injector.
2. *Detector.* UV spectrophotometer able to measure UV absorbance at 254 nm. Check its linearity in the concentration zone used for the determination.
3. *Liquid chromatographic column.* Stainless steel tube 20 cm long, 4 mm internal diameter packed with alkylcyano bounded silica (Nucleosil 5 CN. MACHEREY-NAGEL 720.007). Check that the column does separate deltamethrin from its R-stereoisomer.
4. *Recorder.* 1 mV full-scale sensitivity or electronic integrator.

2.1.3 Special reagents

Deltamethrin standard. Analytical grade, of known purity (at least 990 g/kg).

1,4-Dioxane. HPLC grade, free of peroxides. Dioxane is mixed with 1.5 ml of water per litre, before use.

Iso-octane. HPLC grade.

Mobile phase. A degassed mixture of 5 ml of dioxane and 95 ml of iso-octane. Diluting solvent: dioxane-iso-octane: 20:80 (v/v).

2.1.4 *Preparation of the calibration solution*

Weigh in duplicate (to the nearest 0.1 mg) approximately 50 mg of deltamethrin standard into 50 ml volumetric flasks. Add a small amount of diluting solvent (20 ml of dioxane + 80 ml of iso-octane) and shake the flasks to ensure dissolution of the standards. Dilute to volume with the same solvent and homogenize¹. (Solution C₁ and C₂).

2.1.5 *Operating conditions for high-performance liquid chromatography*

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

Column temperature	ambient ¹
Flow rate	1-1.6 ml/min
Wavelength	254 nm
Injection volume	20 ml (loop-type injector)
Detector sensitivity	set to obtain peak heights between 60 and 90% full-scale deflection
Retention time of deltamethrin	about 9 min

2.1.6 *Sample preparation*

Weigh in duplicate (to the nearest 0.1 mg) two portions of the sample containing approximately 50 mg of deltamethrin into 50 ml volumetric flasks. Add a small amount of diluting solvent (20 ml of dioxane + 80 ml of iso-octane) and shake the flasks to dissolve the samples. Dilute to volume with same solvent and homogenize¹. (Solution S₁ and S₂).

2.1.7 *Analysis*

With a 20 ml loop-type injector, inject one of the calibration solution (C₁ or C₂) until the peak heights (or areas) of two successive injections agree to within 1%.

Inject the calibration solution from flasks C₁ and C₂ and sample solution from flasks S₁ and S₂ in succession according to the following sequence:

C₁ S₁, C₂ S₁, C₁ S₂, C₂ S₂.

2.1.8 *Calculation*

For each of the above four groups (i.e., C₁ versus S₁, C₂ versus S₁, C₁ versus S₂, and C₂ versus S₂), calculate the deltamethrin content.

¹ Since no internal standard is used, the volumes of the solutions have to be adjusted at the same temperature. Avoid temperature fluctuations during the determination.

$$\text{Deltamethrin content (g/kg)} = \frac{a_2 \times m_1 \times P}{a_1 \times m_2}$$

- Where
- a_1 = deltamethrin peak area (or height) of the calibration solution
 - a_2 = deltamethrin peak area (or height) of the sample solution
 - m_1 = mass of deltamethrin standard in the calibration solution (mg)
 - m_2 = mass of sample taken (mg)
 - P = purity of deltamethrin standard (g/kg)

The four results should agree to within $\pm 3\%$ of their mean value. If not, repeat the analysis.

2.2 Deltamethrin R-isomer content

2.2.1 *Outline of method*

The sample is diluted in a mixture of dioxane and iso-octane. The R-isomer content is determined by comparing the response of the sample with that of an R-isomer standard by high-performance liquid chromatography (HPLC), using a silica column and a mixture of dioxane and iso-octane as mobile phase.

2.2.2 *Special apparatus*

1. *Liquid chromatograph.* The instrument should be one that is designed for use with stainless steel columns and that is equipped with: (a) a pumping system able to maintain a pressure of 15 MPa; (b) a UV spectrophotometer detector able to measure UV absorbance at 230 nm²; and (c) a loop-type injector.
2. *Liquid chromatographic column.* The column should be a stainless steel tube 15-18 cm long and 4.6 mm in internal diameter packed with silica (LiChrosorb SI 60, 5 mm, Merck 9388, or equivalent)³.
3. *Recorder.* 1 mV full-scale sensitivity or integrator.

2.2.3 *Special reagents*

Deltamethrin R-isomer standard. Analytical grade, of known purity.

1,4-Dioxane. HPLC grade. Check the peroxides content and purify if necessary. Dioxane is mixed with 1.5 ml of water per litre, before use.

Iso-octane. HPLC grade.

² Check the linearity of the detector in the concentration zone used for the determination.

³ Check that the column does separate the deltamethrin from its R-stereoisomer.

Mobile phase. Degassed mixture of 5 ml of dioxane and 95 ml of iso-octane.

2.2.4 *Preparation of the calibration solution*

Weigh (to the nearest 0.01 mg) about 15 mg of deltamethrin R-isomer into a 50ml volumetric flask. Dissolve and make up to volume with the mobile phase mixture. Pipette 1.0 ml of this solution into a 100-ml volumetric flask and make up to volume with the mobile phase mixture and homogenize.

2.2.5 *Operating conditions for high-performance liquid chromatography*

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

Column temperature	ambient
Flow rate	1-1.7 ml/min
Wavelength	230 nm
Injection volume	20 ml (loop-type injector)
Retention times:	
R-isomer	about 8 min
deltamethrin	about 9 min

2.2.6 *Sample preparation and analysis*

Weigh (to the nearest 0.1 mg) enough sample to contain about 15 mg of deltamethrin into a 50 ml volumetric flask. Make up to volume with the mobile phase and homogenize.

Inject 20 ml of the calibration solution until the peak areas of the two successive injections agree to within 5%. Inject the sample solution in duplicate. The results should agree to within 5%. If not repeat the injections.

2.2.7 *Calculation*

$$\text{R-isomer content (g/kg)} = \frac{a_2 \times m_1 \times P}{a_1 \times m_2}$$

Where	a_1	= R-isomer peak area of the calibration solution
	a_2	= R-isomer peak area of the sample solution
	m_1	= mass of R-isomer standard in the calibration solution (mg)
	m_2	= mass of sample taken (mg)
	P	= purity of the R-isomer standard (g/kg)

2.3 Heat stability

Keep 100 ml of the sample for 3 days at a temperature of $54 \pm 2^{\circ}\text{C}$ in a glass container sealed to avoid loss of volatile solvent, and then cool to room temperature.