

TECHNICAL ENDOSULFAN

Specification WHO/SIT/27
Approved 25 September 1989

1. Specification

1.1 Material

The material shall consist essentially of a mixture of the a- and b-isomers of endosulfan together with related manufacturing compounds and shall be in the form of cream or brown-coloured granules, flakes or powder with the tendency to agglomeration, free from extraneous impurities and 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 *Endosulfan content*

1.2.1.1 *Total endosulfan content (g/kg)*

The endosulfan content shall be declared (not less than 940 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 ± 20 g.

1.2.1.2 *Endosulfan isomers content*

The content of a-isomer, determined by the method described in section 2.1, shall be in the range 64.0 - 67.0% of the total endosulfan content found in 1.2.1.1.

The content of b-isomer, determined by the method described in section 2.1, shall be in the range 29.0 - 32.0% of the total endosulfan content found in 1.2.1.1.

1.2.2 *Acidity*

The acidity of the material, determined by the method described in WHO/M/3 shall not be higher than 1 g/kg, calculated as H₂SO₄.

1.2.3 *Material insoluble in acetone*

The material insoluble in acetone, determined by the method described in WHO/M/21.R1 shall not be higher than 10 g/kg.

1.2.4 *Water content*

The water content, determined by the method described in section 2.2, shall not be higher than 10 g/kg.

1.2.5 *Melting point*

The melting point, determined by the method WHO/M/5.R1, shall not be less than 80°C and shall not be depressed on admixture with an equal quantity of pure endosulfan.

1.3 **Packing and Marking of Packages**

The technical endosulfan 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 endosulfan to specification WHO/SIT/27
Batch or reference number, and date of test
Net weight of contents
Date of manufacture

and the following minimum cautionary notice:

Endosulfan is a sulfurous acid ester of a chlorinated cyclic diol. It is poisonous if swallowed or inhaled as dusts or mists. Avoid eye and skin contact; wear safety goggles, protective gloves, clean protective clothing, and a respirator when handling the material. Wash thoroughly with soap and water after using.

Keep the material out of reach of children and well away from foodstuffs, animal feed and their containers. If poisoning occurs, call a physician.

Endosulfan is highly toxic to fish. Keep the material and the emptied containers away from ground and surface water.

2. Methods of determining chemical and physical properties

2.1 Endosulfan content

2.1.1 Outline of method

The sample is dissolved in toluene in which di(2-ethylhexyl) phthalate is added as internal standard. The endosulfan content is determined by gas-liquid chromatography using a 10% OV-210 on Chromosorb W-AW-HMDS column.

2.1.2 Special apparatus

1. **Gas-liquid chromatograph.** Designed for use with glass columns and equipped with one on-column injection system, a high-sensitivity hot wire detector and a suitable recorder or electronic integrator.
2. **Chromatographic column.** Borosilicate glass tube 150 cm long, 4 mm in internal diameter, and 6 mm in external diameter, packed with 10% OV-210 on Chromosorb W-AW-HMDS (80-100 mesh).

2.1.3 Special reagents

Endosulfan. Analytical standard grade with known contents of the a- and b-isomer, or pure a-endosulfan and b-endosulfan with known purity.

Di(2-ethylhexyl) phthalate. Internal standard, purity better than 990 g/kg and free from compounds which co-elute with endosulfan isomers under the chromatographic conditions given in section 2.1.6.

2.1.4 Preparation of standard solutions

Internal standard solution. Prepare a toluene solution containing di(2-ethylhexyl) phthalate at a concentration of 8 mg/ml. Sufficient solution should be prepared for all calibration and sample solutions.

Endosulfan calibration solution. Into separate 25 ml conical flasks, weigh in duplicate (to the nearest 0.1 mg) approximately 150 mg (m_1 mg) of analytical standard grade endosulfan. To each flask, add by pipette 10 ml of the internal standard solution and mix thoroughly (solutions A and B). Alternatively, weigh 100 mg of a-endosulfan together with 50 mg of b-endosulfan for preparing the calibration solution.

2.1.5 *Preparation and conditioning of column*

Dissolve 2 g of Silicone OV-210 in acetone. Transfer this solution to a suction flask, add slowly 18 g of Chromosorb W-AW-HMDS (80-100 mesh) and add sufficient acetone to cover the solid support completely. Reduce the pressure in the flask with a water aspirator for 2 minutes. Transfer the contents to a crystallizing dish. Heat the slurry under careful stirring until the liquid has evaporated but the solid support is still moist. Then heat without stirring until the solid support is virtually dry.

Finally dry under vacuum at 60⁰C for 16 hours. Remove fine particles by sieving over a 100 mesh sieve. Fill a glass column (150 cm long, 4 mm i.d.) with the column packing. Condition the column at 250⁰C for at least 16 hours, using carrier gas at about 25 ml min⁻¹. Do not connect the column to the detector during this process.

2.1.6 *Operating conditions for gas-liquid chromatography*

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

Temperatures

Oven	230 ⁰ C.
Injection port	300 ⁰ C.
Detector	250 ⁰ C.

Gas flow rate

Carrier gas (helium) 60 ml min⁻¹.

Retention times

a-endosulfan peak	2.0 min.
b-endosulfan peak	3.5 min.
Internal standard peak	5.5 min.

2.1.7 *Linearity check*

Inject 3 ml of the calibration solution containing about 15 mg endosulfan/ml (section 2.1.4) and adjust the instrument controls so that the maximum of the larger peak (either from a-isomer endosulfan or di-(2-ethylhexyl) phthalate) gives a recorder deflection of 80-90% full scale. Note the volume injected (y ml).

Inject duplicate y ml volumes of each of the calibration solutions (solutions A and B). Measure the internal standard peak area and the area of the endosulfan isomers peaks.

For each injection, calculate the calibration factor F by means of the following equation:

$$F = \frac{m_1 \times B_s \times P}{B_a \times 1000}$$

where: m_1 = mass of standard endosulfan (mg)
 B_s = peak area of internal standard in the calibration solution
 B_a = peak area of standard endosulfan or the a- or the b-isomer peak area in the calibration solution
 P = purity of the standard endosulfan or the a- or the b-isomer (g/kg)

The mass of internal standard is common to both calibration and sample solutions and is therefore omitted. Repeat the injections until the values of F obtained for each calibration solution do not differ from each other by more than $\pm 0.5\%$.

2.1.8 *Sample preparation*

Weigh in duplicate (to the nearest 0.1 mg) about 150 mg (m_2 mg) of technical material into separate 25 ml conical flasks. To each flask, add 10 ml of the internal standard solution using the same pipette as used to prepare the endosulfan calibration solution, and mix thoroughly.

2.1.9 *Analysis of the sample*

Inject duplicate y ml (section 2.1.7) volumes of each sample solution. Bracket each group of four sample injections between injections of one of the two calibration solution, e.g., calibration solution A injection, sample injection 1, 2, 3 and 4 and again calibration solution A injection.

Determine the calibration factors F_a and F_b for each calibration solution injections bracketing four sample injections. Calculate the mean calibration factor F_c from the equation:

$$F_c = \frac{F_a + F_b}{2}$$

If the calibration factors F_a and F_b differ by more than $\pm 0.5\%$ of the mean F_c repeat both calibration solution and sample injections.

If the mean calibration factor F_c differs from F obtained in section 2.1.7 by more than $\pm 2\%$, stabilize the operating conditions and recalibrate before proceeding with the analysis.

2.1.10 Calculation

The content of total endosulfan isomers is calculated using the following equation:

$$\text{content of total endosulfan isomer (g / kg)} = \frac{F_c \times A_s}{m_2 \times A_b} \times 1000$$

where F_c = mean calibration factor (section 2.1.9)
 m_2 = mass (mg) of sample taken
 A_b = area of the internal standard peak in the sample solution
 A_s = area of the endosulfan isomers peaks in the sample solution

The content of a- or b-endosulfan isomer is calculated in a similar manner but using the respective area of a- or b-isomer peak in the equation of the calibration factor F and the following equation:

$$\text{Content of } \alpha \text{ - or } \beta \text{ - endosulfan isomer (g / kg)} = \frac{F_c \times A_s}{m_2 \times A_b} \times 1000$$

where F_c = mean calibration factor for a- or b-endosulfan isomer
 m_2 = mass (mg) of sample taken
 A_b = area of the internal standard peak in the sample solution
 A_s = area of a- or b-endosulfan isomer peak in the sample solution

2.2. Water content

Determine the water content by the Karl Fischer electrometric titration method (see WHO/M/7.R1) or when not practicable, by the Dean and Stark distillation method (WHO/M/8.R1).

ENDOSULFAN EMULSIFIABLE CONCENTRATE

Specification WHO/SIF/49
Approved 25 September 1989

1. Specification

1.1 Description and ingredients

The material shall consist of technical endosulfan dissolved in suitable solvents, with other necessary formulants added. It shall be in the form of a stable liquid, free from suspended matter and sediment. The technical endosulfan used in the manufacture of the concentrate shall comply with the requirements of specification WHO/SIT/27.

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 *Endosulfan content*

1.2.1.1 *Total endosulfan content (g/kg basis)*

The content of endosulfan 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 500 g/kg	$\pm 5\%$ of the nominal content
Above 500 g/kg	± 25 g/kg

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

1.2.1.2 *Endosulfan isomers content*

The content of a-isomer determined by the method described in section 2.1, shall be in the range of 64.0 - 67.0% of the total endosulfan content found in 1.2.1.1.

The content of b-isomer determined by the method described in section 2.1, shall be in the range 29.0 - 32.0% of the total endosulfan content found in 1.2.1.1.

1.2.2 *Water content*

The water content determined by the method described in WHO/M/7.R1, shall not be higher than 0.5 g/kg.

1.2.3 *Acidity or alkalinity*

The acidity or alkalinity determined by the method described in WHO/M/3, shall not be higher than 0.5 g/kg calculated as H₂SO₄ or not higher than 0.5 g/kg, calculated as NaOH. In the event of a dispute, the electrometric determination shall be the referee method.

1.2.4 *Cold test*

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

1.2.5 *Flash point*

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

1.2.6 *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.

1.2.7 *Heat stability*

The emulsifiable concentrate, after treatment as described in section 2.2, shall comply with the requirements of section 1.2.1, 1.2.3 and 1.2.6 of this specification.

1.3 Packing and marking of packages

The endosulfan emulsifiable concentrate 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
Endosulfan emulsifiable concentrate to specification WHO/SIF/49
Endosulfan ... g/kg
Batch or reference number, and date of test
Net weight of contents
Instructions for dilution
Date of formulation

and the following minimum cautionary notice:

Endosulfan is a sulfurous acid ester of a chlorinated cyclic diol. It is poisonous if swallowed or inhaled as dusts or mists. Avoid eye and skin contact; wear safety goggles, protective gloves, clean protective clothing, and a respirator when handling the material. Wash thoroughly with soap and water after using.

Keep the material out of reach of children and well away from foodstuffs, animal feed and their containers. If poisoning occurs, call a physician. Endosulfan is highly toxic to fish. Keep the material and the emptied containers away from ground and surface water.

2. Methods of determining chemical and physical properties

2.1 Endosulfan

2.1.1 *Outline of method*

The sample is dissolved in toluene in which di(2-ethylhexyl) phthalate is added as internal standard. The endosulfan content is determined by gas-liquid chromatography using a 10% OV-210 on Chromosorb W-AW-HMDS column.

2.1.2 *Special apparatus*

- 1 *Gas-liquid chromatograph.* Designed for use with glass columns and equipped with one on-column injection system, a high-sensitivity hot wire detector and a suitable recorder or electronic integrator.
2. *Chromatographic column.* Borosilicate glass tube 150 cm long, 4 mm in internal diameter, and 6 mm in external diameter, packed with 10% OV-210 on Chromosorb W-AW-HMDS (80-100 mesh).

2.1.3 *Special reagents*

Endosulfan. Analytical standard grade with known contents of the a- and b-isomer, or pure a-endosulfan and b-endosulfan with known purity.

Di(2-ethylhexyl) phthalate, internal standard, purity better than 990 g/kg and free from compounds which co-elute with endosulfan isomers under the chromatographic conditions given in section 2.1.6.

2.1.4 *Preparation of standard solutions*

Internal standard solution. Prepare a toluene solution containing di(2-ethylhexyl) phthalate at a concentration of 8 mg/ml. Sufficient solution should be prepared for all calibration and sample solutions.

Endosulfan calibration solution. Into separate 25 ml conical flasks, weigh in duplicate (to the nearest 0.1 mg) approximately 150 mg (m_1 mg) of analytical standard grade endosulfan. To each flask, add by pipette 10 ml of the internal standard solution and mix thoroughly (solutions A and B). Alternatively, weigh 100 mg of a-endosulfan together with 50 mg of b-endosulfan for preparing the calibration solution.

2.1.5 *Preparation and conditioning of column*

Dissolve 2 g of Silicone OV-210 in acetone. Transfer this solution to a suction flask, add slowly 18 g of Chromosorb W-AW-HMDS (80-100 mesh) and add sufficient acetone to cover the solid support completely. Reduce the pressure in the flask with a water aspirator for 2 minutes. Transfer the contents to a crystallizing dish. Heat the slurry under careful stirring until the liquid has evaporated but the solid support is still moist. Then heat without stirring until the solid support is virtually dry.

Finally dry under vacuum at 60°C for 16 hours. Remove fine particles by sieving over a 100 mesh sieve. Fill a glass column (150 cm long, 4 mm i.d.) with the column packing. Condition the column at 250°C for at least 16 hours, using carrier gas at about 25 ml min⁻¹. Do not connect the column to the detector during this process.

2.1.6 *Operating conditions for gas-liquid chromatography*

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

Temperatures

Oven	230°C.
Injection port	300°C.
Detector	250°C.

<i>Gas flow rate</i>	
Carrier gas (helium)	60 ml min ⁻¹ .
<i>Retention times</i>	
a-endosulfan peak	2.0 min.
b-endosulfan peak	3.5 min.
Internal standard peak	5.5 min.

2.1.7 *Linearity check*

Inject 3 ml of the calibration solution containing about 15 mg endosulfan/ml (section 2.1.4) and adjust the instrument controls so that the maximum of the larger peak (either from a-isomer endosulfan or di-(2-ethylhexyl) phthalate) gives a recorder deflection of 80-90% full scale. Note the volume injected (y ml).

Inject duplicate y ml volumes of each of the calibration solutions (solutions A and B). Measure the internal standard peak area and the area of the endosulfan isomers peaks. For each injection, calculate the calibration factor F by means of the following equation:

$$F = \frac{m_1 \times B_s \times P}{B_a \times 1000}$$

- m₁ = mass of standard endosulfan (mg)
- B_s = peak area of internal standard in the calibration solution
- B_a = peak area of standard endosulfan or the a- or the b-isomer peak area in the calibration solution
- P = purity of the standard endosulfan or the a- or the b-isomer (g/kg)

The mass of internal standard is common to both calibration and sample solutions and is therefore omitted. Repeat the injections until the values of F obtained for each calibration solution do not differ from each other by more than ± 0.5%.

2.1.8 *Sample preparation*

Weigh in duplicate (to the nearest 0.1 mg) sufficient sample (m₂ mg) to contain about 150 mg endosulfan into separate 25 ml conical flasks. To each flask, add 10 ml of the internal standard solution using the same pipette as used to prepare the endosulfan calibration solution, and mix thoroughly.

2.1.9 *Analysis of the sample*

Inject duplicate y ml (section 2.1.7) volumes of each sample solution. Bracket each group of four sample injections between injections of one of the two calibration solution, e.g., calibration solution A injection, sample injection 1, 2, 3 and 4 and again calibration solution A injection.

Determine the calibration factors F_a and F_b for each calibration solution injections bracketing four sample injections. Calculate the mean calibration factor F_c from the equation:

$$F_c = \frac{F_a + F_b}{2}$$

If the calibration factors F_a and F_b differ by more than $\pm 0.5\%$ of the mean F_c repeat both calibration solution and sample injections.

If the mean calibration factor F_c differs from F obtained in section 2.1.7 by more than $\pm 2\%$, stabilize the operating conditions and recalibrate before proceeding with the analysis.

2.1.10 Calculation

The content of total endosulfan isomers is calculated using the following equation:

$$\text{content of total endosulfan isomer (g / kg)} = \frac{F_c \times A_s}{m_2 \times A_b} \times 1000$$

where F_c = mean calibration factor for a- or b-endosulfan isomer
 m_2 = mass (mg) of sample taken
 A_b = area of the internal standard peak in the sample solution
 A_s = area of a- or b-endosulfan isomer peak in the sample solution

The content of a- or b-endosulfan isomer is calculated in a similar manner but using the respective area of a- or b-isomer peak in the equation of the calibration factor F and the following equation:

$$\text{Content of } \alpha \text{ - or } \beta \text{ - endosulfan isomer (g / kg)} = \frac{F_c \times A_s}{m_2 \times A_b} \times 1000$$

where F_c = mean calibration factor for a- or b-endosulfan isomer
 m_2 = mass (mg) of sample taken
 A_b = area of the internal standard peak in the sample solution
 A_s = area of a- or b-endosulfan isomer peak in the sample solution

2.2 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.