

TECHNICAL CHLORPYRIFOS

Specification WHO/SIT/21.R2
Approved 25 September 1989

1. Specification

1.1 Material

The material shall consist of chlorpyrifos together with related manufacturing compounds and shall be in the form of a white to pale-coloured crystalline solid, free from extraneous impurities or added modifying agents. Some liquid may be present particularly in hot weather.

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 *Chlorpyrifos content (g/kg basis)*

The chlorpyrifos 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.

1.2.2 *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 H_2SO_4 .

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 5 g/kg.

1.2.4 *Water content*

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

1.2.5 *Melting point*

The melting point of the material, determined by the method described in WHO/M/5.R1, shall not be lower than 41.0°C and shall not be depressed on admixture with an equal quantity of pure chlorpyrifos.

1.3 **Packing and marking of packages**

The technical chlorpyrifos 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 chlorpyrifos to specification WHO/SIT/21.R2
Batch or reference number, and date of test
Net weight of contents
Date of manufacture

and the following minimum cautionary notice:

Chlorpyrifos is an organophosphorus compound that inhibits cholinesterase. It is poisonous if swallowed. It may be absorbed through the skin. Avoid skin contact; wear 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 the reach of children and well away from foodstuffs and animal feed and their containers. If poisoning occurs, call a physician. Atropine and pralidoxime are specific antidotes, and artificial respiration may be needed.

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

2.1 **Chlorpyrifos content**

2.1.1 *Outline of method*

The sample is dissolved in acetonitrile with 1,4-dibromonaphthalene added as internal standard. The chlorpyrifos content is determined by high-performance liquid chromatography (HPLC), using a reverse-phase column and a mixture of acetonitrile, water, and acetic acid 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 pumping system able to maintain a pressure of 11 MPa and with a UV spectrophotometer detector able to measure UV absorbance at 300 nm¹.

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

2. *Liquid chromatographic column.* The column should be a stainless steel tube 25 cm long and 4.6 mm in internal diameter packed with C-18 bonded silica gel (Zorbax ODS or equivalent) and protected with a 2 µm column filter.

2.1.3 *Special reagents*

Chlorpyrifos standard. Analytical grade of known purity better than 997 g/kg.

Internal standard. 1,4-Dibromonaphthalene, m.p. 81-83°C.

Acetonitrile. HPLC grade.

Water. HPLC grade.

Acetic acid glacial. HPLC grade.

Mobile phase. A degassed mixture of 82.0 ml of acetonitrile, 17.5 ml of water, and 0.5 ml of glacial acetic acid.

2.1.4 *Preparation of standard solutions*

Internal standard solution. Weigh (to the nearest 100 mg) 1.5g of 1,4-dibromonaphthalene into a 1000 ml volumetric flask, dissolve and dilute to volume with acetonitrile, and mix.

Chlorpyrifos calibration solution. Weigh (to the nearest 0.1 mg) about 80 mg of chlorpyrifos standard into a 50 ml glass-stoppered conical flask, pipette in 25.0 ml of internal standard solution, and mix well.

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 or 30°C
Flow rate	2 ml/min (at about 7.4 MPa)
Wavelength	300 nm
Detector sensitivity	1.0 AUFS ²
Injection volume	10 µl
Retention times:	
chlorpyrifos	3.55 min
internal standard	7.10 min

² Absorbance unit full scale.

2.1.6 *Sample preparation and analysis*

Weigh (to the nearest 0.1 mg) a quantity of the sample containing about 80 mg of chlorpyrifos into a 50 ml glass-stoppered conical flask, pipette in 25.0 ml of the internal standard solution and mix well.

Inject 10 µl of chlorpyrifos calibration solution and adjust attenuation to give the largest possible on-scale peaks (approximately 1.0 AUFS). Repeat injections until the ratios between chlorpyrifos peak areas (or height) and internal standard peak areas (or height) agree to within ±0.5%.

Without changing conditions, inject 10 µl aliquots of the sample solution until the response ratios agree within ±0.5%. Average the last two response ratios for the sample solution.

2.1.7 *Calculation*

For each injection the response ratio *r* is given by the equation:

$$r = \frac{\text{area (or height) of chlorpyrifos peak}}{\text{area (or height) of internal standard peak}}$$

$$\text{Chlorpyrifos content (g / kg)} = \frac{r_2 \times m_1 \times P}{r_1 \times m_2}$$

- where:
- r_1 = average response ratio for calibration solution.
 - r_2 = average response ratio for sample solution.
 - m_1 = mass of chlorpyrifos standard in the calibration solution (mg).
 - m_2 = mass of sample taken (mg).
 - p = purity of chlorpyrifos standard (g/kg).

CHLORPYRIFOS EMULSIFIABLE CONCENTRATE

Specification WHO/SIF/36.R2
Approved 25 September 1989

1. Specification

1.1 Description and ingredients

The material shall consist of technical chlorpyrifos 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 chlorpyrifos used in the manufacture of the concentrate shall comply with the requirements of specification WHO/SIT/21.R2.

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 Chlorpyrifos content (g/kg basis)

The content of chlorpyrifos, 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 400 g/kg	±5% of the nominal content
Above 400 g/kg	±20 g/kg

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

1.2.2 Water content

The water content, determined by the method described in WHO/M/7.R1, shall not be higher than 2.0 g/kg.

1.2.3 Acidity

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

1.2.4 *Cold test*

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

1.2.5 *Flash point*

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

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

1.3 Packing and marking of packages

The chlorpyrifos 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
Chlorpyrifos emulsifiable concentrate to specification WHO/SIF/36.R2
Chlorpyrifos ... 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:

Chlorpyrifos is an organophosphorus compound that inhibits cholinesterase. It is poisonous if swallowed. It may be absorbed through the skin. Avoid skin contact; wear 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 the reach of children and well away from foodstuffs and animal feed and their containers. If poisoning occurs, call a physician. Atropine and pralidoxime are specific antidotes, and artificial respiration may be needed.

2. Methods of determining chemical and physical properties

2.1 Chlorpyrifos content

2.1.1 Outline of method

The sample is dissolved in acetonitrile with 1,4-dibromonaphthalene added as internal standard. The chlorpyrifos content is determined by high-performance liquid chromatography (HPLC), using a reverse-phase column and a mixture of acetonitrile, water, and acetic acid 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 pumping system able to maintain a pressure of 11 MPa and with a UV spectrophotometer detector able to measure UV absorbance at 300 nm¹.
2. *Liquid chromatographic column.* The column should be a stainless steel tube 25 cm long and 4.6 mm in internal diameter packed with C-18 bonded silica gel (Zorbax ODS or equivalent) and protected with a 2 µm column filter.

2.1.3 Special reagents

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Internal standard. 1,4-Dibromonaphthalene, m.p. 81-83°C.

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Water. HPLC grade.

Acetic acid glacial. HPLC grade.

Mobile phase. A degassed mixture of 82.0 ml of acetonitrile, 17.5 ml of water, and 0.5 ml of glacial acetic acid.

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

2.1.4 Preparation of standard solutions

Internal standard solution. Weigh (to the nearest 100 mg) 1.5g of 1,4-dibromonaphthalene into a 1000 ml volumetric flask, dissolve and dilute to volume with acetonitrile, and mix.

Chlorpyrifos calibration solution. Weigh (to the nearest 0.1 mg) about 80 mg of chlorpyrifos standard into a 50 ml glass-stoppered conical flask, pipette in 25.0 ml of internal standard solution, and mix well.

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 or 30°C.
Flow rate	2 ml/min (at about 7.4 MPa)
Wavelength	300 nm
Detector sensitivity	1.0 AUFS ²
Injection volume	10 µl.
Retention times:	
chlorpyrifos	3.55 min.
internal standard	7.10 min.

2.1.6 Sample preparation and analysis

Weigh (to the nearest 0.1 mg) a quantity of the sample containing about 80 mg of chlorpyrifos into a 50 ml glass-stoppered conical flask, pipette in 25.0 ml of internal standard solution and mix well.

Inject 10 µl of chlorpyrifos calibration solution and adjust attenuation to give the largest possible on-scale peaks (approximately 1.0 AUFS). Repeat injections until the ratios between chlorpyrifos peak areas (or height) and internal standard peak areas (or height) agree to within ±0.5%.

Without changing conditions, inject 10 µl aliquots of sample solution until response ratios agree within ±0.5%. Average the last two response ratios for the sample solution.

² Absorbance unit full scale.

2.1.7 Calculation

For each injection the response ratio r is given by the equation:

$$r = \frac{\text{area (or height) of chlorpyrifos peak}}{\text{area (or height) of internal standard peak}}$$

$$\text{Chlorpyrifos content (g / kg)} = \frac{r_2 \times m_1 \times P}{r_1 \times m_2}$$

- where: r_1 = average response ratio for calibration solution.
 r_2 = average response ratio for sample solution.
 m_1 = mass of chlorpyrifos standard in the calibration solution (mg).
 m_2 = mass of sample taken (mg).
 p = purity of chlorpyrifos standard (g/kg).

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.