

TECHNICAL METHOXYCHLOR

Specification WHO/SIT/4.R5
Approved 25 September 1989

1. Specification

1.1 Material

The material shall consist of methoxychlor together with related manufacturing compounds and shall be in the form of white or cream-coloured granules, flakes, or 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 *Total organic chlorine content (g/kg basis)*

The total organic chlorine content determined by the method described in section 2.1 shall be in the range 295-315 g/kg.

1.2.2 *Hydrolysable chlorine content (g/kg basis)*

The hydrolysable chlorine content determined by the method described in section 2.2 shall be in the range 97-117 g/kg.

1.2.3 *Identity of the active ingredient*

The identity of the active ingredient shall be confirmed by the method described in section 2.3.

1.2.4 *Chloral hydrate content*

The chloral hydrate content determined by the method described in section 2.4 shall not be higher than 0.25 g/kg.

1.2.5 *Acidity*

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

1.2.6 *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.

1.2.7 *Water content*

The water content, determined by the method described in section 2.5, shall not be higher than 10 g/kg.

1.3 **Packing and marking of packages**

The technical methoxychlor 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 methoxychlor to specification WHO/SIT/4.R5
Batch or reference number, and date of test
Net weight of contents
Date of manufacture

and the following minimum cautionary notice:

Keep well away from foodstuffs and animal feed and their containers.

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

2.1 **Total organic chlorine content (revised Stepanow method)¹**

2.1.1 *Outline of method*

The organic chlorine is converted to the chloride ion with sodium in propan-2-ol and then titrated by the silver nitrate/ammonium thiocyanate procedure, or determined electrometrically.

2.1.2 *Determination of total chlorine*

Weigh (to the nearest 0.1 mg) about 1 g of the sample, transfer it to a 250 ml volumetric flask, add 10 ml of chlorine-free and thiophene-free benzene to dissolve the sample, and then make up to the mark with 990 ml/l propan-2-ol. Transfer a 25 ml aliquot to a 250 ml conical flask².

¹ Any other currently used method may be employed for routine purposes, but in the event of a dispute the Stepanow method shall be the referee.

² Direct weighing of the sample may be substituted for the measuring of an aliquot provided the weighing does not introduce an error of more than 0.1% in the sample weighed.

Add 2.5 g of metallic sodium, in the form of ribbon or small pieces. Connect to a reflux condenser and boil gently for at least 1 hour, shaking the flask occasionally. Remove the excess metallic sodium by cautiously adding 10 ml of 500 ml/l aqueous propan-2-ol through the condenser, at the rate of 1-2 drops per second. Boil for an additional 10 minutes, and then add 60 ml of distilled water.

Cool, add 2 or 3 drops of phenolphthalein indicator solution, neutralize by adding 500 g/l nitric acid dropwise, and then add 10 ml in excess. Cool to room temperature and add a slight excess of 0.1 mol/l silver nitrate solution. Then add 3 ml of pure nitrobenzene and 5 ml of 100g/l ferric alum solution and shake vigorously to coagulate the precipitate. Titrate the excess silver nitrate in the filtrate with 0.1 mol/l potassium thiocyanate.

Subtract the quantity of silver nitrate found in the filtrate from that originally added. The difference will be the quantity required to combine with the total chlorine originally present in the sample; 1 ml of 0.1 mol/l silver nitrate is equivalent to 0.003546 g of chlorine. Alternatively, the end-point may be determined electrometrically. Make a blank determination (without sample) following the exact procedure given above but limiting the 0.1 mol/l silver nitrate solution to 5 ml in order to obtain a chloride correction value for all reagents used.

2.1.3 *Determination of inorganic chlorine*

Weigh (to the nearest 0.1 mg) about 1 g of the sample, dissolve it in 10 ml of acetone, and add 100 ml of distilled water. Keep at room temperature for 10 minutes and filter. Acidify the filtrate with 500 g/l nitric acid and proceed as described in section 2.1.2.

2.1.4 *Calculation*

$$\text{Total organic chlorine content (g/kg)} = \left(\frac{v_1 \times 10}{m_1} - \frac{v_2}{m_2} \right) \times 3.546$$

Where v_1 = volume (ml) of 0.1 mol/l silver nitrate equivalent to the total chlorine
 v_2 = volume (ml) of 0.1 mol/l silver nitrate equivalent to the inorganic chlorine
 m_1 = mass (g) of sample used for the total chlorine determination
 m_2 = mass (g) of sample used for the inorganic chlorine determination.

2.2 **Hydrolysable chlorine content**

2.2.1 *Outline of method*

The product is hydrolysed with ethanolic potassium hydroxide and the chloride ion obtained is then titrated by the silver nitrate/ammonium thiocyanate procedure or determined electrometrically.

2.2.2 *Determination of hydrolysable plus inorganic chlorine*

Weigh (to the nearest 0.1 mg) about 0.5 g of the sample into a 250 ml conical flask, add 40 ml of 0.5 mol/l ethanolic potassium hydroxide, and gently reflux for half an hour. Wash down the condenser with distilled water and allow to cool. Add 20 ml of 2 mol/l nitric acid and exactly 25 ml of 0.1 mol/l silver nitrate, and coagulate the precipitated silver chloride by digesting on a steam-bath for half an hour, with frequent stirring. Cool, filter the coagulated silver chloride through a fast paper, and wash thoroughly with distilled water. Add 5 ml of 100 g/l ferric alum solution and titrate the excess silver nitrate in the filtrate with 0.1 mol/l potassium thiocyanate.

Subtract the quantity of silver nitrate found in the filtrate from that originally added. The difference will be the quantity required to combine with the hydrolysable plus inorganic chlorine originally present in the sample; 1 ml of 0.1 mol/l silver nitrate is equivalent to 0.003546 g of chlorine. Alternatively, the end-point may be determined electrometrically.

2.2.3 *Determination of inorganic chlorine*

Weigh (to the nearest 0.1 mg) about 1 g of the sample, dissolve it in 10 ml of acetone, and add 100 ml of distilled water. Keep at room temperature for 10 minutes and filter. Acidify the filtrate with 500 g/l nitric acid, add exactly 25 ml of 0.1 mol/l silver nitrate, and process as described in section 2.2.2.

2.2.4 *Calculation*

$$\text{Hydrolysable chlorine content (g/kg)} = \frac{v_1}{m_1} - \frac{v_2}{m_2} \times 3.546$$

Where v_1 = volume (ml) of 0.1 mol/l silver nitrate equivalent to the hydrolysable plus inorganic chlorine

v_2 = volume (ml) of 0.1 mol/l silver nitrate equivalent to the inorganic chlorine

m_1 = mass (g) of sample used for the hydrolysable plus inorganic chlorine determination

m_2 = mass (g) of sample used for the inorganic chlorine determination.

2.3 Identity test

Prepare potassium bromide discs from the sample and from pure methoxychlor using 0.8 to 1.2 mg of material and about 150 mg of potassium bromide. Scan the discs from 4000 to 400 cm^{-1} . The spectrum produced from the sample disc should not differ significantly from that from the pure material.

2.4 Chloral hydrate content

2.4.1 *Outline of method*

The sample is mixed with water and the chloral hydrate distilled off. The distillate is treated with sodium hydroxide and pyridine and the resulting colour is compared with that from a standard chloral hydrate solution.

2.4.2 *Special reagent*

Standard chloral hydrate solution. Dissolve 5 mg of chloral hydrate in 100 ml of distilled water.

2.4.3 *Special apparatus*

Distillation apparatus consisting of:

- a 500 ml round-bottomed flask, fitted with two necks
- a mechanical stirrer, mercury sealed, to fit flask
- a distillation set to fit flask; the condenser should be a double surface pattern, e.g., Davies type.

2.4.4 *Procedure*

Place 20 g of the sample and 200 ml of carbon-dioxide-free distilled water in a 500 ml round-bottomed flask equipped with a mercury-sealed mechanical stirrer. Heat in an oil-bath at a temperature between 140°C and 160°C, with rapid stirring to prevent superheating, and distil the mixture through a well cooled condenser at such a rate that 100 ml of distillate are obtained in a period of not less than 3 minutes and not more than 1 hour. Collect exactly 100 ml of distillate in a centrifuge tube and centrifuge to effect complete separation of the water-insoluble material.

Place 2 ml of a 400 g/l sodium hydroxide solution in a test-tube and add 1 ml of colourless pyridine and 4 ml of the distillate. In another test-tube place 2 ml of the same 400 g/l sodium hydroxide solution and add 1 ml of colourless pyridine and 4 ml of standard chloral hydrate solution. Shake the two tubes and heat in a bath of boiling water for 1 minute. The red colour that develops in the pyridine layer shall not be darker in the sample solution than in the standard solution.

2.5 Water content

Determine the water content by the Karl Fischer electrometric titration method (see WHO/M/7.R1) or by the Dean and Stark distillation method (see WHO/M/8.R1). The latter may not always be practicable owing to its unreliability at very low water contents. In the event of a dispute the Karl Fischer method shall be the referee.

METHOXYCHLOR EMULSIFIABLE CONCENTRATE

Specification WHO/SIF/11.R5
Approved 25 September 1989

1. Specification

1.1 Description and ingredients

The material shall consist of methoxychlor 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 methoxychlor used in the manufacture of the concentrate shall comply with the requirements of specification WHO/SIT/4.R5.

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 *Methoxychlor content (g/kg basis)*

The content of methoxychlor determined by the method described in section 2.1 (total organic chlorine) and in section 2.2 (hydrolysable chlorine) shall not differ from the nominal content by more than the following amounts:

<i>Nominal methoxychlor content</i>	<i>Tolerance permitted</i>
Up to 500 g/kg	± 4% of the nominal content
Above 500 g/kg	± 20 g/kg

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

1.2.2 *Identity of the active ingredient*

The identity of the active ingredient shall be confirmed by the method described in section 2.3.

1.2.3 *Water content*

The water content, determined by the method WHO/M/7.R1 shall not be higher than 2 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 2.4, shall comply with the requirements of sections 1.2.1 (but applying the method described in section 2.2 hydrolysable chlorine), 1.2.4 and 1.2.7 of this specification.

1.3 **Packing and marking of packages**

The methoxychlor 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
Methoxychlor emulsifiable concentrate to specification WHO/SIF/11.R5
Methoxychlor ... 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:
Keep well away from foodstuffs and animal feed and their containers.

2. Methods of determining chemical and physical properties

2.1 Methoxychlor content - total organic chlorine (revised Stepanow method)

2.1.1 Outline of method

The organic chlorine is converted to the chloride ion with sodium in propan-2-ol and then titrated by the silver nitrate/ammonium thiocyanate procedure, or determined electrometrically.

2.1.2 Procedure

Weigh (to the nearest 0.1 mg) an amount of the sample containing about 0.1 g of methoxychlor and transfer to a 250 ml conical flask. Add 25 ml of 990 ml/l propan-2-ol, shake the flask, and add 2.5 g of metallic sodium, in the form of ribbon or small pieces. Connect to a reflux condenser and boil gently for at least 2 hours shaking the flask occasionally. Remove the excess metallic sodium by cautiously adding 10 ml/l of 500 ml/l aqueous propan-2-ol through the condenser, at the rate of 1-2 drops per second. Boil for an additional 10 minutes, and then add 60 ml of distilled water.

Cool, add 2 or 3 drops of phenolphthalein indicator solution, neutralize by adding 500 g/l nitric acid dropwise, and then add 10 ml in excess. Cool, if necessary, to room temperature, add a slight excess of 0.1 mol/l silver nitrate solution. Then add 3 ml of pure nitrobenzene and 5 ml of 100 g/l ferric alum solution and shake vigorously to coagulate the precipitate. Titrate the excess silver nitrate with 0.1 mol/l potassium thiocyanate.

Subtract the quantity of silver nitrate found in the filtrate from that originally added. The difference will be the quantity required to combine with the total chlorine originally present in the sample; 1 ml of 0.1 mol/l silver nitrate is equivalent to 0.003546 g of chlorine. Alternatively, the end-point may be determined electrometrically.

Make a blank determination (without sample) following the exact procedure given above but limiting the 0.1 mol/l silver nitrate solution to 5 ml in order to obtain a chloride correction value for all reagents used.

2.1.3 Calculation

$$\text{Methoxychlor content (g/kg)} = \frac{v}{m} \times 11.52$$

Where v = volume (ml) of 0.1 mol/l silver nitrate equivalent to the total chlorine
 m = mass (g) of sample used for the total chlorine determination.

2.2 Methoxychlor content - hydrolysable chlorine content

2.2.1 Outline of method

The product is hydrolysed with ethanolic potassium hydroxide and the chloride ion obtained is then titrated by the silver nitrate/ammonium thiocyanate procedure, or determined electrometrically.

2.2.2 Procedure

Weigh (to the nearest 0.1 mg) an amount of sample containing about 0.3 g of methoxychlor and transfer into a 250 ml conical flask. Add 40 ml of 0.5 mol/l ethanolic potassium hydroxide, and gently reflux for half an hour. Wash down the condenser with distilled water and allow to cool. Add 20 ml of 2 mol/l nitric acid and exactly 25 ml of 0.1 mol/l silver nitrate, and coagulate the precipitated silver chloride by digesting on a steam-bath for half an hour, with frequent stirring. Cool, filter the coagulated silver chloride through a fast paper, and wash thoroughly with distilled water. Add 5 ml of 100 g/l ferric alum solution and titrate the excess silver nitrate in the filtrate with 0.1 mol/l potassium thiocyanate.

Subtract the quantity of silver nitrate found in the filtrate from that originally added. The difference will be the quantity required to combine with the hydrolysable plus inorganic chlorine originally present in the sample; 1 ml of 0.1 mol/l silver nitrate is equivalent to 0.003546 g of chlorine.

Alternatively, the end-point may be determined electrometrically.

2.2.3 Determination of inorganic chlorine

Weigh (to the nearest 0.1 mg) about 1 g of the sample, dissolve it in 10 ml of acetone, and add 100 ml of distilled water. Keep at room temperature for 10 minutes and filter. Acidify the filtrate with 500 g/l nitric acid, add exactly 25 ml of 0.1 mol/l silver nitrate and process as described in section 2.1.2.2.

2.2.4 Calculation

$$\text{Hydrolysable chlorine content (g/kg)} = \left(\frac{v_1 \times 10}{m_1} - \frac{v_2}{m_2} \right) \times 3.546$$

Where v_1 = volume (ml) of 0.1 mol/l silver nitrate equivalent to the hydrolysable plus inorganic chlorine

v_2 = volume (ml) of 0.1 mol/l silver nitrate equivalent to the inorganic chlorine

m_1 = mass (g) of sample used for the hydrolysable plus inorganic chlorine determination

m_2 = mass (g) of sample used for the inorganic chlorine determination.

$$\text{Methoxychlor content (g/kg)} = \text{hydrolysable chlorine content} \times 3.369.$$

2.3 Identity test

Evaporate the solvent. Prepare potassium bromide discs from the sample and from pure methoxychlor using 0.8 to 1.2 mg of residue and about 150 mg of potassium bromide. Scan the discs from 4000 to 400 cm^{-1} . The spectrum produced from the sample disc should not differ significantly from that from the pure material.

2.4 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.