TECHNICAL FENTHION

Specification WHO/SIT/15.R3
Approved 25 September 1989

1. Specification

1.1 Material

The material shall consist of fenthion together with related manufacturing compounds and shall be in the form of a yellow-to-dark brown liquid, 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 *Fenthion content (g/kg basis)*

The fenthion 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 or alkalinity*

The acidity or the alkalinity of the material, determined by the method described in WHO/M/3, shall not be higher than 4 g/kg, calculated as H_2SO_4 or 0.5 g/kg calculated as NaOH.

1.2.3 *Material insoluble in acetone*

The material, insoluble in acetone as 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 2 g/kg.

1.3 Packing and marking of packages

The technical fenthion 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 fenthion to specification WHO/SIT/15.R3
Batch or reference number, and date of test
Net weight of contents
Date of manufacture

and the following minimum cautionary notice:

Fenthion is an organophosphorous compound that inhibits cholinesterase. It is poisonous if swallowed or 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 Fenthion content

2.1.1 *Outline of method*

The sample is hydrolysed with a solution of potassium hydroxide in ethylene glycol monoethyl ether, and the resulting 3-methyl-4-(methylthio)phenol is coupled at pH 10.3-10.4 with diazo-3-nitraniline-4-sulfonic acid to form a red-violet azo dye, the absorbance of which is measured at 530 nm. The free 3-methyl-4-(methylthio)phenol, the most likely impurity, is determined by the same method on a sample that has not been hydrolysed. The difference between these values is then taken as the fenthion content.

2.1.2 *Special apparatus*

Spectrophotometer or photoelectric colorimeter capable of measuring absorbance at 530 nm.

2.1.3 *Special reagents*

3-Methyl-4-(methylthio)phenol, pure. This material should have a melting point of 56 ± 0.5^{0}C when tested by method WHO/M/5.R1.

Ethylene glycol monoethyl ether. Reflux 1 litre of pure ethylene glycol monoethyl ether with 50 g of potassium hydroxide pellets for 1 hour, distil, and collect the fraction boiling at 130-140^{0}C.

3-Nitraniline-4-sulfonic acid. Dissolve 10 g of the reagent in 1 litre of hot distilled water. Add activated charcoal, stir, filter, and cool the filtrate in ice. Filter off the crystalline acid, wash with water, and dry at 50^{0}C.

Buffer solution. Dissolve 106 g of anhydrous sodium carbonate in distilled water and make up to 1 litre (solution I). Dissolve 50 g of sodium bicarbonate in distilled water and make up to 1 litre (solution II). Mix 350 ml of solution I with 130 ml of solution II. The pH of the mixture should be in the range 10.3-10.4 at 20^{0}C.

Diazo solution. Dissolve 0.35 g of 3-nitraniline-4-sulfonic acid, purified as described above, in 5 ml of 1 mol/l sodium hydroxide, add about 350 ml of a mixture of ice and water, followed by 5 ml of concentrated hydrochloric acid. Diazotize at 0.5^{0}C with 0.1 mol/l sodium nitrite (about 16.5 ml will be required). Determine the end-point of the diazotization by the spot test on starch-potassium iodide paper. Dilute the solution to 500 ml in a volumetric flask and use immediately.

2.1.4 *Determination of free 3-methyl-4-(methylthio)phenol*

Preparation of a standard curve. Dissolve 400 mg (weighed to the nearest 0.1 mg) of pure 3-methyl-4-(methylthio)phenol in 5 ml of 1 mol/l sodium hydroxide and 10 ml of propan-2-ol and make up to the mark in a 1 litre volumetric flask with distilled water. Transfer 50, 75, 100, 125, 150, and 175 ml of the thoroughly mixed solution into six 500 ml volumetric flasks and dilute to volume with distilled water. The stock solutions thus obtained contain 20, 30, 40, 50, 60, and 70 mg of 3-methyl-4-(methylthio)phenol in 500 ml. Transfer from each of these solutions 5 ml, corresponding to 0.2-0.7 mg of 3-methyl-4-(methylthio)phenol into six 50 ml volumetric flasks, add to each successively 10 ml of propan-2-ol, 20 ml of buffer solution, and 10 ml of diazo solution, and make up to the mark with water. After mixing thoroughly, keep the volumetric flasks for 2 hours in a thermostatically controlled bath at 20^{0}C. Measure the absorbance in a 1 cm cell at 530 nm in a suitable photometer, using the reagents as reference. Plot graphically the measured absorbances, corresponding to 0.2-0.7 mg of 3-methyl-4-(methylthio)phenol. The calibration curve depends on the photometer used and therefore has to be determined for each instrument individually. Because the standard solution of 3-methyl-4-(methylthio)phenol deteriorates on standing, a fresh solution should be made each day.

Procedure. Weigh (to the nearest 0.1 mg) a mass of the sample containing about 5 mg of 3-methyl-4-(methylthio)phenol. Rinse the sample into a 50 ml volumetric flask with propan-2-ol and fill up to the mark. Shake and filter through a fast paper. Transfer 5 ml of the clear solution into a 50 ml volumetric flask and add successively 10 ml of propan-2-ol, 20 ml of buffer solution, and 10 ml of diazo solution. Continue as described above.

Read from the standard curve the amount of 3-methyl-4-(methylthio)phenol corresponding to the absorbance. If the amount is not in the range 0.2-0.7 mg, repeat the determination with a smaller or larger sample.

2.1.5 *Determination of fenthion*

Preparation of a standard curve. Transfer 5 ml of each of the stock solutions (the preparation of which is described in section 2.1.4) into 50 ml volumetric flasks, add successively 3 ml of propan-2-ol from a burette, 30 ml of buffer solution, and 7.5 ml of diazo solution, and fill up to the mark with buffer solution. Continue as described in section 2.1.4. Plot graphically the absorbances determined, corresponding to 0.2-0.7 mg of 3-methyl-4-(methylthio)phenol. The calibration curve depends on the photometer used and therefore has to be determined for each instrument individually.

Procedure. Weigh (to the nearest 0.1 mg) about 0.080 g of the sample and rinse with 25 ml of ethylene glycol monoethyl ether into a 100 ml flask. Add about 1.65 g of potassium hydroxide (approximately 7 pellets), connect to a reflux condenser, and boil for 7 hours. Cool, transfer to a 500 ml volumetric flask, dilute to the mark with water, and mix thoroughly. Transfer 5 ml of this solution into a 50 ml volumetric flask and add successively 3 ml of propan-2-ol from a burette, 30 ml of buffer solution, and 7.5 ml of diazo solution. Dilute to volume with buffer solution. Continue as described in section 2.1.4. Read from the standard curve the amount of 3-methyl-4-(methylthio)phenol corresponding to the absorbance.

2.1.6 *Calculation*

Fenthion content (g/kg)

$$= \left[\frac{m_1 \times 10}{m_3} - \frac{m_2}{m_4} \right] \times 18.05$$

m_1 = total amount (mg) of 3-methyl-4-(methylthio)phenol found after hydrolysis
m_2 = amount (mg) of free 3-methyl-4-(methylthio)phenol (section 2.1.4).
m_3 = mass (g) of sample used for the determination of the total amount of 3-methyl-4 (methylthio)phenol (section 2.1.5).
m_4 = mass (g) of sample used for the determination of free 3-methyl-4 (methylthio)phenol (section 2.1.4).

FENTHION WATER-DISPERSIBLE POWDER

Specification WHO/SIF/38.R1
Approved 25 September 1989

1. Specification

1.1 Description and ingredients

The material shall consist of a homogeneous mixture of technical fenthion together with filler(s) and any other necessary formulants and shall be in the form of a fine, free-flowing powder that wets out readily on stirring into water. The technical fenthion used in the manufacture of the water-dispersible powder shall comply with the requirements of specification WHO/SIT/15.R3.

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 *Fenthion content (g/kg basis)*

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

Nominal content	*Tolerance permitted*
Up to 400 g/kg	- 5 to + 7.5% of the nominal content
Above 400 g/kg	- 20 to + 30 g/kg

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

1.2.2 *Acidity or alkalinity*

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

1.2.3 *Sieving after heat stability treatment*

Not less than 98% of the powder after heat stability treatment (section 2.3) shall pass through a 75 mm sieve when tested by the method described in WHO/M/4.R1.

1.2.4 *Suspensibility*

In standard hard water after heat stability treatment. When tested by the method described in section 2.2, a minimum of 60% of the fenthion (15 g/l) shall be in suspension 30 minutes after agitating a suspension containing 25 g/l of fenthion, prepared in standard hard water from the powder subjected to the heat stability treatment described in section 2.3.

1.2.5 *Heat stability*

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

1.3 Packing and marking of packages

The fenthion 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
Fenthion water-dispersible powder to specification WHO/SIF/38.R1
Fenthion ... g/kg
Batch or reference number, and date of test
Net weight of contents
Date of formulation

and the following minimum cautionary notice:

Fenthion is an organophosphorus compound that inhibits cholinesterase. It is poisonous if swallowed or inhaled. 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, 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 Fenthion content

2.1.1 *Outline of method*

The active ingredient is hydrolysed with a solution of potassium hydroxide in ethylene glycol monoethyl ether, and the resulting 3-methyl-4-(methylthio)phenol is coupled at pH 10.3-10.4 with diazo-3-nitraniline-4-sulfonic acid to form a red-violet azo dye, the absorbance of which is measured at 530 nm. The free 3-methyl-4-(methylthio)phenol, the most likely impurity, is determined by the same method on a sample that has not been hydrolysed. The difference between these values is then taken as the fenthion content.

2.1.2 *Special apparatus*

Spectrophotometer or photoelectric colorimeter capable of measuring absorbance at 530 nm.

2.1.3 *Special reagents*

3-Methyl-4-(methylthio)phenol, pure. This material should have a melting point of 56 ± 0.5^{0}C when tested by method WHO/M/5.R1.

Ethylene glycol monoethyl ether. Reflux 1 litre of pure ethylene glycol monoethyl ether with 50 g of potassium hydroxide pellets for 1 hour, distil, and collect the fraction boiling at 130-140^{0}C.

3-Nitraniline-4-sulfonic acid. Dissolve 10 g of the reagent in 1 litre of hot distilled water. Add activated charcoal, stir, filter, and cool the filtrate in ice. Filter off the crystalline acid, wash with water, and dry at 50^{0}C.

Buffer solution. Dissolve 106 g of anhydrous sodium carbonate in distilled water and make up to 1 litre (solution I). Dissolve 50 g of sodium bicarbonate in distilled water and make up to 1 litre (solution II). Mix 350 ml of solution I with 130 ml of solution II. The pH of the mixture should be in the range 10.3-10.4 at 20^{0}C.

Diazo solution. Dissolve 0.35 g of 3-nitraniline-4-sulfonic acid, purified as described above, in 5 ml of 1 mol/l sodium hydroxide, add about 350 ml of a mixture of ice and water, followed by 5 ml of concentrated hydrochloric acid. Diazotize at 0.5^{0}C with 0.1 mol/l sodium nitrite (about 16.5 ml will be required). Determine the end-point of the diazotization by the spot test on starch-potassium iodide paper. Dilute the solution to 500 ml in a volumetric flask and use immediately.

2.1.4 *Determination of free 3-methyl-4-(methylthio)phenol*

Preparation of a standard curve. Dissolve 400 mg (weighed to the nearest 0.1 mg) of pure 3-methyl-4-(methylthio) phenol in 5 ml of 1 mol/l sodium hydroxide and 10 ml of propan-2-ol and make up to the mark in a 1 litre volumetric flask with distilled water. Transfer 50, 75, 100, 125, 150, and 175 ml of the thoroughly mixed solution into six 500 ml volumetric flasks and dilute to volume with distilled water. The stock solutions thus obtained contain 20, 30, 40, 50, 60, and 70 mg of 3-methyl-4-(methylthio)phenol in 500 ml. Transfer from each of these solutions 5 ml, corresponding to 0.2-0.7 mg of 3-methyl-4(methylthio)phenol into six 50 ml volumetric flasks, add to each successively 10 ml of propan-2-ol, 20 ml of buffer solution, and 10 ml of diazo solution, and make up to the mark with water. After mixing thoroughly, keep the volumetric flasks for 2 hours in a thermostatically controlled bath at 20^0C. Measure the absorbance in a 1 cm cell at 530 nm in a suitable photometer, using the reagents as reference. Plot graphically the measured absorbances, corresponding to 0.2-0.7 mg of 3-methyl-4-(methylthio)phenol. The calibration curve depends on the photometer used and therefore has to be determined for each instrument individually. Because the standard solution of 3-methyl-4-(methylthio)phenol deteriorates on standing, a fresh solution should be made each day.

Procedure. Weigh (to the nearest 0.1 mg) a mass of the sample containing about 5 mg of 3-methyl-4-(methylthio)phenol. Rinse the sample into a 50 ml volumetric flask with propan-2-ol and fill up to the mark. Shake and filter through a fast paper. Transfer 5 ml of the clear solution into a 50 ml volumetric flask and add successively 10 ml of propan-2-ol, 20 ml of buffer solution, and 10 ml of diazo solution. Continue as described above. Read from the standard curve the amount of 3-methyl-4-(methylthio)phenol corresponding to the absorbance. If the amount is not in the range 0.2-0.7 mg, repeat the determination with a smaller or larger sample.

2.1.5 *Determination of fenthion*

Preparation of a standard curve. Transfer 5 ml of each of the stock solutions (the preparation of which is described in section 2.1.4) into 50 ml volumetric flasks, add successively 3 ml of propan-2-ol from a burette, 30 ml of buffer solution, and 7.5 ml of diazo solution, and fill up to the mark with buffer solution. Continue as described in section 2.1.4. Plot graphically the absorbances determined, corresponding to 0.2-0.7 mg of 3-methyl-4-(methylthio)phenol. The calibration curve depends on the photometer used and therefore has to be determined for each instrument individually.

Procedure. Weigh (to the nearest 0.1 mg) a mass of the sample containing about 0.080 g of fenthion into a 100 ml flask. Add 25 ml of ethylene glycol monoethyl ether and about 1.65 g of potassium hydroxide (approximately 7 pellets), connect to a reflux condenser, and boil for 7 hours. Cool, transfer to a 500 ml volumetric flask, dilute to the mark with water, mix thoroughly and filter through a folded filter.

Transfer 5 ml of this solution into a 50 ml volumetric flask and add successively 3 ml of propan-2-ol from a burette, 30 ml of buffer solution, and 7.5 ml of diazo solution. Dilute to volume with buffer solution. Continue as described in section 2.1.4. Read from the standard curve the amount of 3-methyl-4-(methylthio)phenol corresponding to the absorbance.

2.1.6 *Calculation*

Fenthion content (g/kg)

$$= \left[\frac{m_1 \times 10}{m_3} - \frac{m_2}{m_4} \right] \times 18.05$$

where m_1 = total amount (mg) of 3-methyl-4-(methylthio)phenol found after hydrolysis (section 2.1.5)

m_2 = amount (mg) of free 3-methyl-4-(methylthio)phenol (section 2.1.4)

m_3 = mass (g) of sample used for the determination of the total amount of 3-methyl-4-(methylthio)phenol (section 2.1.5)

m_4 = mass (g) of sample used for the determination of free 3-methyl-4-(methylthio)phenol (section 2.1.4).

2.2 Suspensibility after heat stability treatment

2.2.1 *Outline of method*

A suspension of known concentration of fenthion 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 9/10 ths are drawn off and the content of fenthion in the bottom 1/10 th is determined, so allowing to evaluate the active ingredient mass still in suspension after 30 minutes.

2.2.2 *Special apparatus*

1. A 250 ml graduated cylinder with a ground-glass stopper and a distance of 20-21.5 cm between the bottom and the 250 ml graduation.

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 reagents*

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 1 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 10 mg) into a 100 ml beaker a mass of the sample to form 250 ml of a suspension containing 25 g/l of fenthion. Add a volume of water[1] at 30 ± 1°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 diameter, at not more than 4 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 ± 1°C for rinsing, and again avoiding mechanical disintegration of any lumps. Immediately add sufficient water at 30 ± 1°C to bring the volume to the 250 ml mark. Stopper the cylinder and mix by inverting and righting it 30 times at a rate of one complete cycle every 2 seconds. This operation should be carried out as smoothly as possible, keeping the axis of rotation fixed. The cyclinder must be thermally insulated from the hands to maintain the prescribed temperature of the suspension. Allow the graduated cylinder to stand for 30 minutes in a water-bath at 30 ± 1°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 minute settling period, insert the glass tube into the cylinder and, with a minimum of disturbance, withdraw during 10-15 seconds by means of the suction tube nine-tenths of the suspension (i.e. 225 ml). This is achieved by maintaining the tip of the glass tube just below the sinking top level of the suspension. Discard the suspension withdrawn.

Transfer the retained 25 ml of the suspension including the sediment into a 250 ml separating funnel. Rinse the cylinder twice with 50 ml portions of diethyl ether, adding both rinsings to the contents of the separating funnel. Shake, allow the phases to separate, and drain the aqueous layer into a second separating funnel. Add to the second separating funnel 100 ml of ether and 10 ml of saturated sodium chloride solution and shake again. Let the phases separate while occasionally swirling, then discard the aqueous layer.

Wash the two ether extracts separately and successively twice with 50 ml portions of distilled water, each containing 10 ml of saturated sodium chloride solution, using the same solutions for both extracts. Discard the aqueous washings.

Remove all water droplets from the two ether extracts and filter them, in the order in which the extracts were made, through a paper placed on a sintered-glass funnel. Rinse the separating funnels and paper with ether, distil off the solvent, removing the last traces with an air-stream. Dissolve the residue in 100 ml of ethylene glycol monoethyl ether added from a pipette and mix thoroughly. Pipette 10 ml of the solution into a 50 ml volumetric flask, make up to volume with ethylene glycol monoethyl ether and mix thoroughly.

Pipette 10 ml of the solution into a 100 ml flask, add about 1.65 g of potassium hydroxide and 15 ml of ethylene glycol monoethyl ether, connect to a reflux condenser and boil for 7 hours. Cool, transfer to a 500 ml volumetric flask, dilute to the mark with distilled water and mix thoroughly. Transfer 5 ml of this solution into a 50 ml volumetric flask, add successively 3 ml of propan-2-ol from a burette, 30 ml of buffer solution and 7.5 ml of diazo solution. Make up to volume with buffer solution. Continue as described in section 2.1.4. Read from the standard curve the amount of 3-methyl-4-(methylthio)phenol corresponding to the absorbance.

If the amount of 3-methyl-4(methylthio)phenol is outside the range of the standard curve, repeat using a larger or smaller aliquot (as appropriate) from the 500 ml volumetric flask.

2.2.5 *Calculation*[1]

Mass (m_3) (g) of fenthion in the retained one-tenth of the suspension

$$m_3 = 9.025 \times c$$

c = amount (mg) of the 3-methyl-4-(methylthio) phenol found after hydrolysis in 2.2.4.

From the value obtained in section 2.1 for the content of fenthion, calculate the mass of fenthion in the initial sample taken for the suspensibility test.

$$\textit{Suspensibility (\%)} = \frac{(m_4 - m_3) \times 111.1}{m_4}$$

m_3 = mass (g) of fenthion in the retained one-tenth of the suspension (section 2.2.4).
m_4 = mass (g) of fenthion in the initial sample.

[1] In this calculation it is assumed that the ratio of fenthion to free phenolic impurity remains constant throughout the determination.

2.3 Heat stability treatment

Fill a 50 ml[2] 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 70 $\pm$ 1^{0}C for 6 hours. 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.After heat stability treatment, the sample should not be exposed to heat, bright sunshine, or high atmospheric humidity.

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

FENTHION EMULSIFIABLE CONCENTRATE

Specification WHO/SIF/28.R4
Approved 25 September 1989

1. Specification

1.1 Description and ingredients

The material shall consist of technical fenthion 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 fenthion used in the manufacture of the concentrate shall comply with the requirements of specification WHO/SIT/15.R3.

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 *Fenthion content (g/kg basis)*

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

Nominal content	*Tolerance permitted*
Up to 500 g/kg	- 5 to + 7% of the nominal content
Above 500 g/kg	- 20 to + 35 g/kg

The average content of all samples taken shall not be lower 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 g/kg.

1.2.3 *Acidity or alkalinity*

The acidity or alkalinity of the concentrate, determined by the method described in WHO/M/3, shall not be higher than 6 g/kg calculated as H_2SO_4 or 0.5 g/kg calculated as NaOH.

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 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 the method 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 the method 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 section 1.2.1, 1.2.3 and 1.2.6 of this specification.

1.3 Packing and marking of packages

The fenthion 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
Fenthion emulsifiable concentrate to specification WHO/SIF/28.R4
Fenthion ... 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:

Fenthion is an organophosphorus compound that inhibits cholinesterase. It is poisonous if swallowed or inhaled. 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, 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 Fenthion content

2.1.1 *Outline of method*

The active ingredient is hydrolysed with a solution of potassium hydroxide in ethylene glycol monoethyl ether, and the resulting 3-methyl-4-(methylthio)phenol is coupled at pH 10.3-10.4 with diazo-3-nitraniline-4-sulfonic acid to form a red-violet azo dye, the absorbance of which is measured at 530 nm. The free 3-methyl-4-(methylthio)phenol, the most likely impurity, is determined by the same method on a sample that has not been hydrolysed. The difference between these values is then taken as the fenthion content.

2.1.2 *Special apparatus*

Spectrophotometer or photoelectric colorimeter capable of measuring absorbance at 530 nm.

2.1.3 *Special reagents*

3-Methyl-4-(methylthio)phenol, pure. This material should have a melting point of 56 ± 0.5^{0}C when tested by method WHO/M/5.R1.

Ethylene glycol monoethyl ether. Reflux 1 litre of pure ethylene glycol monoethyl ether with 50 g of potassium hydroxide pellets for 1 hour, distil, and collect the fraction boiling at 130-140^{0}C.

3-Nitraniline-4-sulfonic acid. Dissolve 10 g of the reagent in 1 litre of hot distilled water. Add activated charcoal, stir, filter, and cool the filtrate in ice. Filter off the crystalline acid, wash with water, and dry at 50^{0}C.

Buffer solution. Dissolve 106 g of anhydrous sodium carbonate in distilled water and make up to 1 litre (solution I). Dissolve 50 g of sodium bicarbonate in distilled water and make up to 1 litre (solution II). Mix 350 ml of solution I with 130 ml of solution II. The pH of the mixture should be in the range 10.3-10.4 at 20^0C.

Diazo solution. Dissolve 0.35 g of 3-nitraniline-4-sulfonic acid, purified as described above, in 5 ml of 1 mol/l sodium hydroxide, add about 350 ml of a mixture of ice and water, followed by 5 ml of concentrated hydrochloric acid. Diazotize at 0.5^0C with 0.1 mol/l sodium nitrite (about 16.5 ml will be required). Determine the end-point of the diazotization by the spot test on starch-potassium iodide paper. Dilute the solution to 500 ml in a volumetric flask and use immediately.

2.1.4 *Determination of free 3-methyl-4-(methylthio)phenol*

Preparation of a standard curve. Dissolve 400 mg (weighed to the nearest 0.1 mg) of pure 3-methyl-4-(methylthio)phenol in 5 ml of 1 mol/l sodium hydroxide and 10 ml of propan-2-ol and make up to the mark in a 1 litre volumetric flask with distilled water. Transfer 50, 75, 100, 125, 150, and 175 ml of the thoroughly mixed solution into six 500 ml volumetric flasks and dilute to volume with distilled water. The stock solutions thus obtained contain 20, 30, 40, 50, 60, and 70 mg of 3-methyl-4-(methylthio)phenol in 500 ml. Transfer from each of these solujtions 5 ml, corresponding to 0.2-0.7 mg of 3-methyl-4-(methylthio)phenol into six 50 ml volumetric flasks, add to each successively 10 ml of propan-2-ol, 20 ml of buffer solution, and 10 ml of diazo solution, and make up to the mark with water. After mixing thoroughly, keep the volumetric flasks for 2 hours in a thermostatically controlled bath at 20^0C. Measure the absorbance in a 1 cm cell at 530 nm in a suitable photometer, using the reagents as reference. Plot graphically the measured absorbances, corresponding to 0.2-0.7 mg of 3-methyl-4-(methylthio)phenol. The calibration curve depends on the photometer used and therefore has to be determined for each instrument individually. Because the standard solution of 3-methyl-4-(methylthio)phenol deteriorates on standing, a fresh solution should be made each day.

Procedure. Weigh (to the nearest 0.1 mg) a mass of the sample containing about 5 mg of 3-methyl-4-(methylthio)phenol. Rinse the sample into a 50 ml volumetric flask with propan-2-ol and fill up to the mark. Shake and filter through a fast paper. Transfer 5 ml of the clear solution into a 50 ml volumetric flask and add successively 10 ml of propan-2-ol, 20 ml of buffer solution, and 10 ml of diazo solution. Continue as described above. Read from the standard curve the amount of 3-methyl-4-(methylthio)phenol corresponding to the absorbance. If the amount is not in the range 0.2-0.7 mg, repeat the determination with a smaller or larger sample.

2.1.5 *Determination of fenthion*

Preparation of a standard curve. Transfer 5 ml of each of the stock solutions (the preparation of which is described in section 2.1.4) into 50 ml volumetric flasks, add successively 3 ml of propan-2-ol from a burette, 30 ml of buffer solution, and 7.5 ml of diazo solution, and fill up to the mark with buffer solution. Continue as described in section 2.1.4. Plot graphically the absorbances determined, corresponding to 0.2-0.7 mg of 3-methyl-4-(methylthio)phenol. The calibration curve depends on the photometer used and therefore has to be determined for each instrument individually.

Procedure. Weigh (to the nearest 0.1 mg) a mass of the sample containing about 0.080 g of fenthion and rinse with 25 ml of ethylene glycol monoethyl into a 100 ml flask. Add about 1.65 g of potassium hydroxide (approximately 7 pellets), connect to a reflux condenser and boil for 7 hours. Cool, transfer to a 500 ml volumetric flask, dilute to the mark with water, and mix thoroughly. Transfer 5 ml of this solution into a 50 ml volumetric flask and add successively 3 ml of propan-2-ol from a burette, 30 ml of buffer solution, and 7.5 ml of diazo solution. Dilute to volume with buffer solution. Continue as described in section 2.1.4. Read from the standard curve the amount of 3-methyl-4-(methylthio)phenol corresponding to the absorbance.

2.1.6 *Calculation*

Fenthion content (g/kg)

$$= \left[\frac{m_1 \times 10}{m_3} - \frac{m_2}{m_4} \right] \times 18.05$$

m_1 = amount (mg) of 3-methyl-4-(methylthio) phenol found after hydrolysis (2.1.5)
m_2 = amount (mg) of free 3-methyl-4-(methylthio) phenol (2.1.4)
m_3 = mass (g) of sample used for the determination of the total amount of 3-methyl-4 (methylthio) phenol (2.1.5)
m_4 = mass (g) of sample used for the determination of free 3-methyl-4-(methylthio) phenol (2.1.4)

2.2 Heat stability

Keep 100 ml of the sample for 3 days at a temperature of 54 $\pm$ 2^{0}C in a glass container sealed to avoid loss of volatile solvent, and then cool to room temperature.