

PIRIMIPHOS-METHYL TECHNICAL

Specification WHO/SIT/30
Approved 25 September 1989

1. Specification

1.1 Material

The material shall consist of pirimiphos-methyl together with related manufacturing compounds and shall be in the form of a clear or faintly turbid, mobile, red-brown coloured liquid at temperatures above 18⁰C. It shall be free from extraneous impurities or added modifying agents other than stabilizer (to minimize the formation of the S-methyl isomers) and odour suppressants (to minimize the formation of volatile sulfur compounds).

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 *Pirimiphos-methyl content (g/kg basis)*

The pirimiphos-methyl content shall be declared (not less than 880 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 3 g/kg, calculated as H₂SO₄.

1.2.3 *Water content*

The water content, determined by the method described in WHO/M/7.R1, shall not be higher than 2 g/kg.

1.2.4 *Flash point*

The flash point of the product, determined by the method WHO/M/10.R1, shall not be lower than 46⁰C and shall comply with all national and international regulations on handling and transport of flammable materials.

1.3 Packing and marking of packages

The technical pirimiphos-methyl 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 pirimiphos-methyl to specification WHO/SIT/30
Batch or reference number, and date of test
Net weight of contents
Date of manufacture

and the following minimum cautionary notice:

Pirimiphos-methyl is an organophosphorus compound that inhibits cholinesterase. It is poisonous if swallowed.

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 Pirimiphos-methyl content

2.1.1 *Outline of method*

The sample is dissolved in an internal standard solution containing *n*-octadecane. The constituents are separated by gas chromatography on a silicone elastomer SE 30 (E 301) column and detected using flame ionization. The pirimiphos-methyl present is determined by comparison of the peak areas for pirimiphos-methyl and *n*-octadecane with those obtained using a calibration solution.

2.1.2 *Special apparatus*

1. *Gas-liquid chromatograph.* Isothermal oven with a flame ionization detector and injection port heater and equipped with a suitable electronic integrator or with a potentiometric recorder having an effective chart width of not less than 200 mm.
2. *Chromatographic column.* Glass tube 150 cm long, 4 mm internal diameter, packed with 10% SE-30 (E 301) on chromosorb W-HP, 100-120 mesh.

3. *Column conditioning and pre-treatment.* Before use, condition a freshly packed column by purging with nitrogen overnight at 300°C. During conditioning the column must not be connected to the detector. After conditioning, pre-treat the column with 3 x 10 µl injections of 'Silyl 8' at 1 min intervals. The flame ionization detector must not be fitted during pre-treatment.

2.1.3 *Special reagents*

Pirimiphos-methyl standard. Analytical grade, of known purity (minimum 980 g/kg) stored at 0°C.

Internal standard. n-octadecane, free from components which should co-elute with pirimiphos-methyl under the chromatographic conditions given in section 2.1.5.

2.1.4 *Preparation of standard solutions*

Internal standard solution. Weigh 2 g of n-octadecane, dissolve in chloroform and make up to 1000 ml with chloroform (Solution I).

Pirimiphos-methyl calibration solution. Equilibrate the pirimiphos-methyl standard to room temperature and ensure that the standard is homogeneous and free from crystals. Weigh (to the nearest 0.1 mg) about 200 mg of the standard into a 100 ml glass-stoppered conical flask. Add 25.0 ml of internal standard solution by pipette, stopper the flask and shake to dissolve the pirimiphos-methyl. (Solution C).

Prepare a similar solution without internal standard by dissolving a similar amount in 25 ml of chloroform (Solution C₀).

2.1.5 *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

Column oven	Use a fixed temperature between 210 and 220°C and control to ± 0.5°C throughout the analysis.
Injection port	Use a fixed temperature 20 to 30°C above that of the oven.
Detector	As recommended for the model of instrument used. A temperature of up to 80°C above the column oven temperature may be suitable.

Gas flow rates

Hydrogen and air: Optimally set up according to the instruction manual.
 Carrier gas: Nitrogen free from oxygen (less than 10 ppm) 50 ml.
 min⁻¹ but adjust so that a suitable retention time (about
 5.10 min) is obtained for pirimiphos-methyl.

Retention times

n-octadecane 3.49 min.
 pirimiphos-methyl 5.10 min.

2.1.6 *Sample preparation and analysis*

Ensure that samples are homogeneous by equilibrating to room temperature and mixing thoroughly. Weigh (to the nearest 0.1 mg) in duplicate, sufficient sample to contain about 200 mg of pirimiphos-methyl into 100 ml glass-stoppered conical flasks. Add 25.0 ml of internal standard solution with the same pipette used to prepare the calibration solution to each flask, stopper the flasks and shake to dissolve the sample. (Solutions SA and SB).

Prepare a similar solution without internal standard by adding a similar amount of sample to 25 ml of chloroform (Solution S₀).

Equilibration of the system. Before starting the analysis of the sample, inject 3 x 1 ml aliquots of the calibration solution (C) to equilibrate the system and use the data from these chromatograms to set the integration parameters and also to assess the stability of the system. Inject 1 ml portions of Solution I, C₀, and S₀ and check whether there are any interference peaks from impurities. If there are, make any necessary correction.

Analysis of sample. Carry out 1 ml injections of calibration solution (C) and sample solutions (SA and SB) in succession and record the integrated areas of each peak.

Injection sequence = C₁, SA₁, SA₂, C₂, SB₁, SB₂, C₃.

Calculate the relative response factors for the pair of calibration injections which bracket the sample injections, e.g. use C₁ and C₂ for sample injections SA₁ and SA₂, and obtain the mean response factor f.

$$\text{Relative response factor } (f) = \frac{H_s}{I_r \times m_1 \times P}$$

where: H_s = area of pirimiphos-methyl peak in calibration solution
 I_r = area of n-octadecane peak in calibration solution
 m₁ = mass of pirimiphos-methyl standard in calibration solution (mg)
 P = purity of the pirimiphos-methyl standard in calibration solution (g/kg)

The mass of internal standard is common to both calibration and sample solutions and is therefore omitted.

Successive measurements of the response factors should agree to within $\pm 0.5\%$ of their mean value. If not repeat the analysis.

2.1.7 Calculation

For each sample injection, e.g. SA₁, calculate the pirimiphos-methyl content.

$$\text{Pirimiphos - methyl content (g / kg)} = \frac{H_m}{f \times I_q \times m_2}$$

where: H_m = area of pirimiphos-methyl peak in sample solution
 I_q = area of n-octadecane peak in sample solution
 f = mean relative response factor obtained e.g. from C₁ and C₂
 m₂ = mass of sample (mg)

Calculate the pirimiphos-methyl content of the sample as the mean of two determinations as follows:

SAMPLE INJECTION	USE RELATIVE RESPONSE FACTOR FROM	PIRIMIPHOS-METHYL	MEAN
SA ₁	C ₁ and C ₂	Q%]]	X%
SA ₂	C ₁ and C ₂	R%]	
SB ₁	C ₂ and C ₃	S%]]	Y%
SB ₂	C ₂ and C ₃	T%]	

(Q and R) and (S and T) should each agree to within $\pm 0.5\%$ of their respective mean values (X and Y). X and Y should agree to within $\pm 1\%$ of their mean value.

Take the mean of the two determinations X and Y as the pirimiphos-methyl content.

PIRIMIPHOS-METHYL WATER- DISPERSIBLE POWDER

Specification WHO/SIF/52
Approved 25 September 1989

1. Specification

1.1 Description and ingredients

The material shall consist of a homogeneous mixture of technical pirimiphos-methyl together with filler(s) and 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 pirimiphos-methyl used in the manufacture of the water-dispersible powder shall comply with the requirements of specification WHO/SIT/30.

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 *Pirimiphos-methyl content (g/kg basis)*

The content of pirimiphos-methyl 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	± 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.

1.2.2 *Acidity or alkalinity*

The acidity 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.

1.2.3 *Sieving after heat stability treatment*

Not less than 98% of the powder after the heat stability treatment (section 2.3) shall pass through a 75-µm 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 50% of the pirimiphos-methyl (12.5 g/l) shall be in suspension 30 minutes after agitating a suspension containing 25 g/l of pirimiphos-methyl 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 sections 1.2.1 and 1.2.2 of this specification.

1.3 **Packing and marking of packages**

The pirimiphos-methyl water-dispersible powder shall be packed in suitable, clean drums as specified in the order. The containers shall contain an inner liner 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
Pirimiphos-methyl water-dispersible powder to specification WHO/SIF/52
Pirimiphos-methyl ... g/kg
Batch or reference number, and date of test
Net weight of contents
Date of formulation

and the following minimum cautionary notice:

Pirimiphos-methyl 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 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 Pirimiphos-methyl content

2.1.1 Outline of method

The sample is dissolved in an internal standard solution containing *n*-octadecane. The constituents are separated by gas chromatography on a silicone elastomer SE 30 (E 301) column and detected using flame ionization. The pirimiphos-methyl present is determined by comparison of the peak areas for pirimiphos-methyl and *n*-octadecane with those obtained using a calibration solution.

2.1.2 Special apparatus

1. *Gas-liquid chromatograph.* Isothermal oven with a flame ionization detector and injection port heater and equipped with a suitable electronic integrator or with a potentiometric recorder having an effective chart width of not less than 200 mm.
2. *Chromatographic column.* Glass tube 150 cm long, 4 mm internal diameter, packed with 10% SE 30 (E 301) on chromosorb W-HP, 100-120 mesh.
3. *Column conditioning and pre-treatment.* Before use, condition a freshly packed column by purging with nitrogen overnight at 300°C. During conditioning the column must not be connected to the detector. After conditioning, pre-treat the column with 3 x 10 (ml) injections of 'Silyl 8' at 1 min intervals. The flame ionization detector must not be fitted during pre-treatment.

2.1.3 Special reagents

Pirimiphos-methyl standard. Analytical grade of known purity (minimum: 980 g/kg) stored at 0°C.

Internal standard. *n*-octadecane, free from components which should co-elute with pirimiphos-methyl under the chromatographic conditions given in section 2.1.5.

2.1.4 Preparation of standard solutions

Internal standard solution. Weigh 2 g of *n*-octadecane, dissolve in chloroform and make up to 1000 ml with chloroform (solution I).

Pirimiphos-methyl calibration solution. Equilibrate the pirimiphos-methyl standard to room temperature and ensure that the standard is homogeneous and free from crystals. Weigh (to the nearest 0.1 mg) about 200 mg of the standard into a 100 ml glass-stoppered conical flask. Add 25.0 ml of internal standard solution by pipette, stopper the flask and shake to dissolve the pirimiphos-methyl. (Solution C).

Prepare a similar solution without internal standard by dissolving a similar amount in 25 ml of chloroform (Solution C₀).

2.1.5 *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

Column oven	Use a fixed temperature between 210 and 220 ⁰ C and control to $\pm 0.5^{\circ}\text{C}$ throughout the analysis.
Injection port	Use a fixed temperature 20 to 30 ⁰ C above that of the oven.
Detector	As recommended for the model of instrument used. A temperature of up to 80 ⁰ C above the column oven temperature may be suitable.

Gas flow rates

Hydrogen and air	Optimally set up according to the instruction manual.
Carrier gas	Nitrogen free from oxygen (less than 10 ppm) 50 ml. min ⁻¹ but adjust so that a suitable retention time (about 5.10 min) is obtained for pirimiphos-methyl.

Retention times

n-octadecane	3.49 min.
pirimiphos-methyl	5.10 min.

2.1.6 *Sample preparation and analysis*

Weigh (to the nearest 0.1 mg) in duplicate sufficient sample to contain about 200 mg of pirimiphos-methyl into 100 ml glass-stoppered conical flasks. Add 25.0 ml of internal standard solution with the same pipette used to prepare the calibration solution to each flask, stopper the flasks and shake to dissolve the pirimiphos-methyl (Solutions SA and SB). Allow the solid matter to settle and chromatograph the supernatant liquid.

Prepare a similar solution without internal standard by treating a similar amount of sample as described above with 25 ml of chloroform (Solution S₀).

Equilibration of the system. Before starting the analysis of the sample, inject 3 x 1 ml aliquots of the calibration solution (C) to equilibrate the system and use the data from these chromatograms to set the integration parameters and also to assess the stability of the system. Inject 1 ml portions of Solution I, C₀ and S₀ and check whether there are any interference peaks from impurities. If there are, make any necessary correction.

Analysis of sample. Carry out 1 ml injections of calibration solution (C) and sample solutions (SA and SB) in succession and record the integrated areas for each peak.

Injection sequence = C₁, SA₁, SA₂, C₂, SB₁, SB₂, C₃.

Calculate the relative response factors for the pair of calibration injections which bracket the sample injections, e.g. use C₁ and C₂ for sample injections SA₁ and SA₂, and obtain the mean response factor *f*.

$$\text{Relative response factor } (f) = \frac{H_s}{I_r \times m_1 \times P}$$

where: H_s = area of pirimiphos-methyl peak in calibration solution
 I_r = area of n-octadecane peak in calibration solution
 m₁ = mass of pirimiphos-methyl standard in calibration solution (mg)
 P = purity of the pirimiphos-methyl standard in calibration solution (g/kg)

The mass of internal standard is common to both calibration and sample solutions and is therefore omitted. Successive measurements of the response factors should agree to within ± 0.5% of their mean value. If not repeat the analysis.

2.1.7 Calculation

For each sample injection, e.g. SA₁, calculate the pirimiphos-methyl content.

$$\text{Pirimiphos - methyl content (g / kg)} = \frac{H_m}{f \times I_q \times m_2}$$

where: H_m = area of pirimiphos-methyl peak in sample solution
 I_q = area of n-octadecane peak in sample solution
 f = mean relative response factor obtained e.g. from C₁ and C₂

Calculate the pirimiphos-methyl content of the sample as the mean of two determinations as follows:

SAMPLE INJECTION	USE RELATIVE RESPONSE FACTOR FROM	PIRIMIPHOS-METHYL	MEAN
SA ₁	C ₁ and C ₂	Q%]	X%
SA ₂	C ₁ and C ₂	R%]	
SB ₁	C ₂ and C ₃	S%]	Y%
SB ₂	C ₂ and C ₃	T%]	

(Q and R) and (S and T) should each agree to within $\pm 0.5\%$ of their respective mean values (X and Y). X and Y should agree to within $\pm 1\%$ of their mean value.

Take the mean of the two determinations X and Y as the pirimiphos-methyl content.

2.2 Suspending ability

2.2.1 Outline of method

A suspension of known concentration of pirimiphos-methyl 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 9/10ths are drawn off and the content of pirimiphos-methyl in the bottom 1/10th 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 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.

2.2.3 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 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.

2.2.4 Procedure

Weigh (to the nearest 10 mg) into a 100 ml beaker an amount of the sample to form 250 ml of a suspension containing 25 g/l of pirimiphos-methyl. Add a volume of water¹ 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 any 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 a rate of one complete cycle every two 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 $30 \pm 1^{\circ}\text{C}$ care being taken that the bath is free from vibrations.

Should excessive flocculation occur during the test, accompanied by the appearance of transparent liquid, 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 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 and determine the pirimiphos-methyl mass in the bottom one-tenth of suspension by the GLC method described in section 2.1 but with some modifications.

Special apparatus and special reagents: see respectively sections 2.1.2 and 2.1.3.

Preparation of standard solutions: see section 2.1.4, except that the pirimiphos-methyl calibration solution is modified as follows:

"Equilibrate the pirimiphos-methyl standard to room temperature and ensure that the standard is homogeneous and free from crystals. Weigh (to the nearest 0.1 mg) about 200 mg of the standard into a 100 ml glass-stoppered conical flask. Add 25.0 ml of internal standard solution by pipette and 10.0 ml of methanol. Stopper the flask and shake to dissolve the pirimiphos-methyl (solution C)".

Operating conditions: see section 2.1.5.

¹ Whenever water is mentioned in this section, use standard hard water.

Sample preparation. After removal of the top 225 ml of suspension, wash the bottom one-tenth of suspension from the suspensibility cylinder into a 200 ml volumetric flask using methanol for rinsing. Make up to volume with methanol.

Mix well, filter or centrifuge and immediately pipette a 10.0 ml aliquot of the methanol solution into a 100 ml glass-stoppered conical flask. Add 25.0 ml of internal standard solution with the same pipette used to prepare the calibration solution. Stopper the flask and mix well (solution SA). Determine the pirimiphos-methyl mass in the retained one-tenth of the suspension (M_1) as in section 2.1.6 beginning by "Equilibration of the system", but taking into account the dilution factor.

2.2.5 Calculation

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

where: m_1 = mass of pirimiphos-methyl in the retained one-tenth of the suspension (g)
 m_2 = mass of pirimiphos-methyl in the initial sample taken to prepare the suspension (g).

2.3 Heat stability treatment

Fill a 100 ml 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 $70 \pm 2^\circ\text{C}$ for 2 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 completion of the heat stability treatment, the sample should not be exposed to heat, bright sunshine, or high atmospheric humidity.

PIRIMIPHOS-METHYL EMULSIFIABLE CONCENTRATE

Specification WHO/SIF/53
Approved 25 September 1989

1. Specification

1.1 Description and ingredients

The material shall consist of technical pirimiphos-methyl dissolved in suitable solvents, with other necessary formulants added. It shall be in the form of a stable liquid, free from extraneous impurities. The technical pirimiphos-methyl used in the manufacture of the concentrate shall comply with the requirements of specification WHO/SIT/30.

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 *Pirimiphos-methyl content (g/kg basis)*

The content of pirimiphos-methyl 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	± 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.

1.2.2 *Water content*

The water content determined by the method described in section 2.2, shall not be higher than 5 g/kg.

1.2.3 *Acidity*

The acidity determined by method WHO/M/3 shall not be higher than 1 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, determined by the method WHO/M/10.R1, shall not be lower than 38⁰C and 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 concentrate, after treatment as described in section 2.3 shall comply with the requirements of sections 1.2.1, 1.2.3 and 1.2.6 or this specification.

1.3 Packing and marking of packages

The pirimiphos-methyl 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
Pirimiphos-methyl emulsifiable concentrate to specification WHO/SIF/53
Pirimiphos-methyl ... 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:

Pirimiphos-methyl 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 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 Pirimiphos-methyl content

2.1.1 *Outline of method*

The sample is dissolved in an internal standard solution containing *n*-octadecane. The constituents are separated by gas chromatography on a silicone elastomer SE 30 (E 301) column and detected using flame ionization. The pirimiphos-methyl present is determined by comparison of the peak areas for pirimiphos-methyl and *n*-octadecane with those obtained using a calibration solution.

2.1.2 *Special apparatus*

1. *Gas-liquid chromatograph* isothermal oven with a flame ionization detector and injection port heater and equipped with a suitable electronic integrator or with a potentiometric recorder having an effective chart width of not less than 200 mm.
2. *Chromatographic column.* Glass tube 150 cm long, 4 mm internal diameter, packed with 10% SE-30 (E 301) on Chromosorb W-HP, 100-120 mesh.
3. *Column conditioning and pre-treatment.* Before use, condition a freshly packed column by purging with nitrogen overnight at 300°C. During conditioning the column must not be connected to the detector. After conditioning, pre-treat the column with 3 x 10 ml injections of 'Silyl 8' at 1 min intervals. The flame ionization detector must not be fitted during pre-treatment.

2.1.3 *Special reagents*

Pirimiphos-methyl standard. Analytical grade, of known purity (minimum 980 g/kg) stored at 0°C.

Internal standard. n-octadecane, free from components which should co-elute with pirimiphos-methyl under the chromatographic conditions given in section 2.1.5.

2.1.4 Preparation of standard solutions

Internal standard solution. Weigh 2 g of n-octadecane, dissolve in chloroform and make up to 1000 ml with chloroform (Solution I).

Pirimiphos-methyl calibration solution. Equilibrate the pirimiphos-methyl standard to room temperature and ensure that the standard is homogeneous and free from crystals. Weigh (to the nearest 0.1 mg) about 200 mg of the standard into a 100 ml glass-stoppered conical flask. Add 25.0 ml of internal standard solution by pipette, stopper the flask and shake to dissolve the pirimiphos-methyl. (Solution C).

Prepare a similar solution without internal standard by dissolving a similar amount in 25 ml of chloroform (Solution C₀).

2.1.5 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

Column oven	Use a fixed temperature between 210 and 220 ⁰ C and control to $\pm 0.5^{\circ}\text{C}$ throughout the analysis.
Injection port	Use a fixed temperature 20 to 30 ⁰ C above that of the oven.
Detector	As recommended for the model of instrument used. A temperature of up to 80 ⁰ C above the column oven temperature may be suitable.

Gas flow rates

Hydrogen and air:	Optimally set up according to the instruction manual.
Carrier gas:	Nitrogen free from oxygen (less than 10 ppm) 50 ml. min ⁻¹ but adjust so that a suitable retention time (about 5.10 min) is obtained for pirimiphos-methyl.

Retention times

n-octadecane	3.49 min.
pirimiphos-methyl	5.10 min.

2.1.6 *Sample preparation and analysis*

Ensure that samples are homogeneous by equilibrating to room temperature and mixing thoroughly. Weigh (to the nearest 0.1 mg) in duplicate, sufficient sample to contain about 200 mg of pirimiphos-methyl into 100 ml glass-stoppered conical flasks. Add 25.0 ml of internal standard solution with the same pipette used to prepare the calibration solution to each flask, stopper the flasks and shake to dissolve the sample. (Solutions SA and SB).

Prepare a similar solution without internal standard by adding a similar amount of sample to 25 ml of chloroform (Solution S₀).

Equilibration of the system. Before starting the analysis of the sample, inject 3 x 1 ml aliquots of the calibration solution (C) to equilibrate the system and use the data from these chromatograms to set the integration parameters and also to assess the stability of the system. Inject 1 ml portions of Solution I, C₀, and S₀ and check whether there are any interference peaks from impurities. If there are, make any necessary correction.

Analysis of sample. Carry out 1 ml injections of calibration solution (C) and sample solutions (SA and SB) in succession and record the integrated areas of each peak. Injection sequence = C₁, SA₁, SA₂, C₂, SB₁, SB₂, C₃.

Calculate the relative response factors for the pair of calibration injections which bracket the sample injections, e.g. use C₁ and C₂ for sample injections SA₁ and SA₂, and obtain the mean response factor *f*.

$$\text{Relative response factor } (f) = \frac{H_s}{I_r \times m_1 \times P}$$

H_s = area of pirimiphos-methyl peak in calibration solution

I_r = area of n-octadecane peak in calibration solution

m₁ = mass of pirimiphos-methyl standard in calibration solution (mg)

P = purity of the pirimiphos-methyl standard in calibration solution (g/kg)

The mass of internal standard is common to both calibration and sample solutions and is therefore omitted. Successive measurements of the response factors should agree to within ± 0.5% of their mean value. If not repeat the analysis.

2.1.7 Calculation

For each sample injection, e.g. SA₁, calculate the pirimiphos-methyl content.

$$\text{Pirimiphos - methyl content (g / kg)} = \frac{H_m}{f \times I_q \times m_2}$$

where: H_m = area of pirimiphos-methyl peak in sample solution
 I_q = area of n-octadecane peak in sample solution
 f = mean relative response factor obtained e.g. from C₁ and C₂
 m₂ = mass of sample (mg)

Calculate the pirimiphos-methyl content of the sample as the mean of two determinations as follows:

SAMPLE INJECTION	USE RELATIVE RESPONSE FACTOR FROM	PIRIMIPHOS-METHYL	MEAN
SA ₁	C ₁ and C ₂	Q%]	X%
SA ₂	C ₁ and C ₂	R%]	
SB ₁	C ₂ and C ₃	S%]	Y%
SB ₂	C ₂ and C ₃	T%]	

(Q and R) and (S and T) should each agree to within ± 0.5% of their respective mean values (X and Y). X and Y should agree to within ± 1% of their mean value.

Take the mean of the two determinations X and Y as the pirimiphos-methyl content.

2.2 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 method.

2.3 Heat stability

Keep 100 ml of the sample for three days at a temperature of 54 ± 2⁰C in a glass container sealed to avoid loss of volatile solvent and then cool to room temperature.