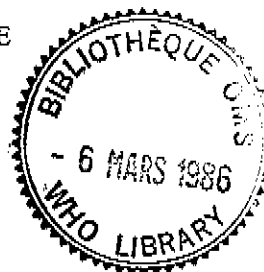


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WORLD HEALTH ORGANIZATION  
ORGANISATION MONDIALE DE LA SANTE



WHO/IS/86.12  
ENGLISH ONLY

INTERIM SPECIFICATIONS FOR DIMETHOATE  
TECHNICAL AND EMULSIFIABLE CONCENTRATE

- 3/10/86

Specifications for pesticides which were recommended by the WHO Expert Committee on Vector Biology and Control, Chemistry and Specifications of Pesticides at its last session in November 1983 have been published in a Manual which is now in the 6th edition<sup>1</sup>. The Expert Committee also recommended that during the period between meetings of the Expert Committee, if the need arises to strengthen an existing specification, WHO should issue interim specifications that would supersede the existing specifications and recommended the use of those interim specifications in connexion with the purchase of pesticides and their formulations.

Interim specifications for new compounds are also issued to assist in the purchasing of good quality products for vector control.

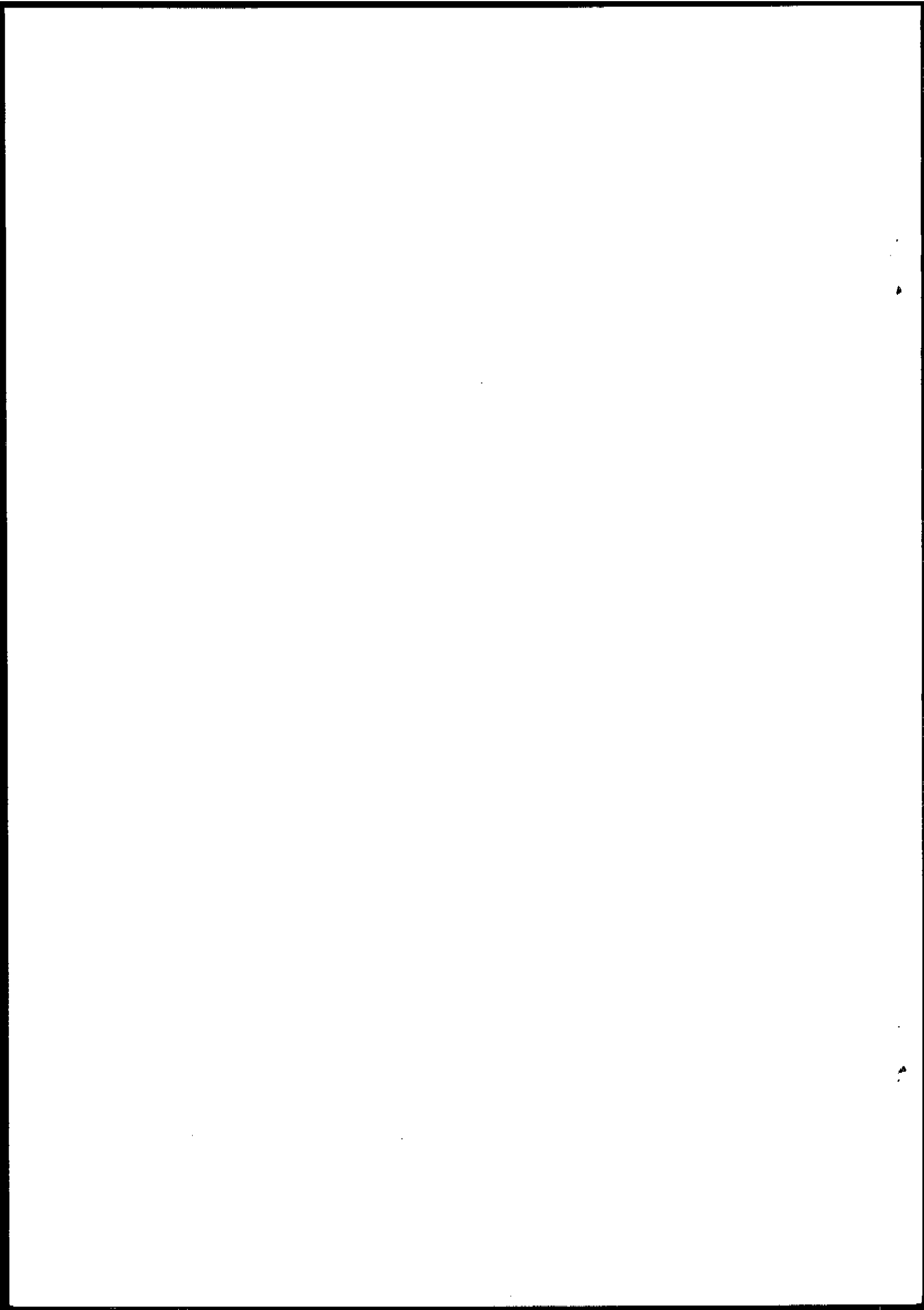
The next meeting of the Expert Committee will discuss the present interim specifications and decide if they should be included in the next edition of the Manual.

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Specification for Pesticides Used in Public Health, Geneva, 1985

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OO-dimethyl S-methylcarbamoylmethyl  
phosphorodithioate.

$C_5H_{12}NO_3PS_2$

RMM : 229.2

## SPECIFICATION

### 1.1 Material

The material shall consist of dimethoate together with related manufacturing compounds and shall be in the form of white grey crystals free from extraneous impurities or added modifying agents.

### 1.2 Chemical and physical requirements

The material, sampled from any part of the consignment,<sup>1</sup> shall comply with the requirements of section 1.1 and with the following requirements:

	Minimum	Maximum
Dimethoate content (section 2.1)	930 g/kg	
Acidity (method WHO/M/3 <sup>2</sup> ) calculated as H <sub>2</sub> SO <sub>4</sub>		10 g/kg
Solid material insoluble in acetone (method WHO/M/21 <sup>2</sup> )		5 g/kg
Water content (section 2.2)		2 g/kg

### 1.3 Packing and marking of packages

The technical dimethoate 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 dimethoate to Interim Specification WHO/IS/1.0094-1  
Batch or reference number, and date of test  
Net weight of contents  
Date of manufacture

and the following minimum cautionary notice:

<sup>1</sup> A sampling procedure is described in method WHO/M/1<sup>2</sup>. However, this does not preclude the purchaser from sampling in any way considered desirable.

<sup>2</sup> Specifications for Pesticides Used in Public Health, Geneva 1985 (6th Edition).

"Dimethoate 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 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 Dimethoate content

2.1.1 Summary of method. The dimethoate is separated from its impurities by gas-liquid chromatography on a non-polar column and determined by flame ionization detection using dibutyl phthalate as internal standard.

#### 2.1.2 Special apparatus

Gas-liquid chromatograph. Capable of operating up to 220°C, fitted with a flame ionization detector, injection port heater and on-column injection system and equipped with a suitable recorder or electronic integrator.

Chromatographic column. Glass column 1 m long, about 2 to 4 mm internal diameter, silanized and packed with 3% m/m silicone OV 17 on Chromosorb G (AW DMCS) 80 to 100 US mesh (180 to 150  $\mu$ m). Before use condition a freshly prepared column by purging with nitrogen overnight at 300°C. During this operation the column must not be connected to the detector, to avoid contamination by any initial 'bleed' of the stationary phase.

#### 2.1.3 Special reagents

Dimethoate standard. Analytical grade of known purity (minimum 990 g/kg). Store at 0°C in the dark. It must yield only one peak on gas chromatography.

Internal standard. Di-n-butylphthalate. Purity about 990 g/kg. When the phthalate is chromatographed it must not give a peak with a similar retention time to that of dimethoate.

#### 2.1.4 Preparation of standard solutions

##### Internal standard solution

Prepare an acetone solution containing di-n-butylphthalate at a concentration of about 10 mg/ml. Sufficient solution should be prepared for all calibration and sample solutions.

Dimethoate calibration solution

Weigh (to the nearest 0.1 mg)  $0.1 \pm 0.005$  g,  $0.2 \pm 0.005$  g and  $0.3 \pm 0.005$  g of standard dimethoate, dissolve each in 20 ml acetone in a 100 ml volumetric flask, add 10 ml internal standard solution and dilute to 100 ml with acetone.

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

Oven. Use any set temperature between  $175^{\circ}\text{C}$  and  $190^{\circ}\text{C}$  but control to  $\pm 0.5^{\circ}\text{C}$  throughout the determination.

Injection port:  $230^{\circ}\text{C}$

Flame detector:  $250^{\circ}\text{C}$

Gas flow rates

Hydrogen and air: optimally set up according to the instruction manual  
Carrier gas : nitrogen (oxygen free).  $50 \text{ ml}\cdot\text{min}^{-1}$ , but adjust so that a suitable retention time (about 8 min) is obtained for dimethoate.

Retention times

Dimethoate	about 8 min
Internal standard	about 12.8 min

2.1.6 Linearity check

Inject 2-6  $\mu\text{l}$  of the calibration solution containing about 2 mg dimethoate/ml (section 2.1.4) and adjust the instrument controls so that the maximum of the larger peak (either from dimethoate or di-n-butylphthalate) gives a recorder deflection of 80-90% full scale. Note the volume injected ( $y \mu\text{l}$ ).

Inject duplicate  $y \mu\text{l}$  volumes of each of the calibration solutions. Measure the dimethoate and di-n-butylphthalate peak areas. For each injection calculate the calibration factor  $F$  by means of the following equation

$$F = \frac{m_1 \times P \times \text{area of di-n-butylphthalate peak}}{1000 \times \text{area of dimethoate peak}}$$

where:  $m_1$  = mass (g) of dimethoate in the calibration solution  
 $P$  = purity (g/kg) of the dimethoate standard.

Repeat the injections until the values of  $F$  obtained for each calibration solution do not differ from each other by more than  $\pm 0.5\%$ .

### 2.1.7 Sample preparation

The material should be melted in a water bath at 60°C before taking samples. Homogenize by mixing until no crystals remain. Weigh (to the nearest 0.1 mg) a sample ( $m_2$  g) to contain about 1.0 g of dimethoate into a 100 ml volumetric flask containing 20 ml acetone. Shake to dissolve, make up to 100 ml with acetone and mix thoroughly. Pipette 20 ml into a 100 ml volumetric flask, add 10 ml internal standard solution, make up to 100 ml with acetone and mix thoroughly.

### 2.1.8 Analysis of the sample

Inject duplicate  $\mu$ l volumes (section 2.1.6) of the sample solution and bracket the injections between injections of the calibration solution containing 2 mg dimethoate/ml, e.g. calibration solution injection, sample injections 1 and 2, and again calibration solution injection.

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

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

If the calibration factors  $F_a$  and  $F_b$  differ by more than  $\pm 0.5\%$  of the mean  $F_c$  repeat both calibration solution and sample solution injections. If the mean calibration factor  $F_c$  differs from  $F$  obtained above (section 2.1.6) by more than  $\pm 2\%$ , stabilize the operating conditions and re-calibrate before proceeding with the analysis.

### 2.1.9 Calculation

$$\text{Dimethoate content (g/kg)} = \frac{5 \times F_c \times A_s}{m_2 \times A_b} \times 1000$$

where  $F_c$  = mean calibration factor for dimethoate (section 2.1.8)  
 $m_2$  = mass (g) of sample taken  
 $A_b$  = area of di-n-butylphthalate peak in the sample solution  
 $A_s$  = area of dimethoate peak in the sample solution.

### 2.2 Water content

Determine the water content by the Karl Fischer electrometric titration method (see WHO/M/7<sup>1</sup>), or by the Dean and Stark distillation method (see WHO/M/8<sup>1</sup>). 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 govern.

<sup>1</sup> Specifications for Pesticides Used in Public Health. Geneva 1985 (6th Edition).

## 1. SPECIFICATION

### 1.1 Description and ingredients

The material shall consist of technical dimethoate 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 dimethoate used in the manufacture of the concentrate shall comply with the requirements of specification WHO/IS/1.0094-1

### 1.2 Chemical and physical requirements

The material sampled from any part of the consignment<sup>1</sup> shall comply with the requirements of section 1.1 and with the following requirements:

#### 1.2.1 Dimethoate content (g/kg basis)

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

<u>Nominal content</u>	<u>Tolerance permitted</u>
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 Cold test

No separation of solid or oily material shall occur when the concentrate is tested as described in section 2.2

#### 1.2.3 Flashpoint

The flashpoint of the product shall comply with all national and/or international transport regulations.

<sup>1</sup> A sampling procedure is described in method WHO/M/1<sup>2</sup>. However, this does not preclude the purchaser from sampling in any way considered desirable.

<sup>2</sup> Specifications for Pesticides Used in Public Health, Geneva. 1985 (6th Edition).

#### 1.2.4 Water content

The water content, determined by the method described in section 2.3, shall not be greater than 2 g/kg.

#### 1.2.5 Acidity

The acidity of the concentrate, determined by method WHO/M/3<sup>1</sup>, shall not be greater than 1 g/kg, calculated as H<sub>2</sub>SO<sub>4</sub>.

#### 1.2.6 Stability of 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.R2<sup>1</sup>.

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.R2<sup>1</sup>.

#### 1.2.7 Heat stability

The concentrate, after treatment as described in section 2.4, shall comply with the requirements of sections 1.2.1 (except that the permitted minimum dimethoate content could be 95% of that found under 1.2.1) and 1.2.6 of this specification.

#### 1.3 Packing and marking of packages

The dimethoate 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  
Dimethoate emulsifiable concentrate to Interim Specification  
WHO/IS/3.0094-1  
Dimethoate ... 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:

<sup>1</sup> Specifications for Pesticides Used in Public Health, Geneva. 1985 (6th Edition).



"Dimethoate 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 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 Dimethoate content

2.1.1 Summary of method. The dimethoate is separated from its impurities by gas-liquid chromatography on a non-polar column and determined by flame ionization detection using dibutyl phthalate as internal standard.

#### 2.1.2 Special apparatus

Gas-liquid chromatograph. Capable of operating up to 220°C, fitted with a flame ionization detector, injection port heater and on-column injection system and equipped with a suitable recorder or electronic integrator.

Chromatographic column. Glass column 1 m long, about 2 to 4 mm internal diameter, silanized and packed with 3% m/m silicone OV 17 on Chromosorb G (AW DMCS) 80 to 100 US mesh (180 to 150  $\mu$ m). Before use condition a freshly prepared column by purging with nitrogen overnight at 300°C. During this operation the column must not be connected to the detector, to avoid contamination by any initial 'bleed' of the stationary phase.

#### 2.1.3 Special reagents

Dimethoate standard. Analytical grade of known purity (minimum 990 g/kg). Store at 0°C in the dark. It must yield only one peak on gas chromatography.

Internal standard. Di-n-butylphthalate. Purity about 990 g/kg. When the phthalate is chromatographed, it must not give a peak with a similar retention time to that of dimethoate.

#### 2.1.4 Preparation of standard solutions

##### Internal standard solution

Prepare an acetone solution containing di-n-butylphthalate at a concentration of about 10 mg/ml. Sufficient solution should be prepared for all calibration and sample solution.

Dimethoate calibration solution

Weigh (to the nearest 0.1 mg), 0.1 0.005 g, 0.2 0.005 g and 0.3 0.005 g of standard dimethoate, dissolve each in 20 ml acetone in a 100 ml volumetric flask, add 10 ml internal standard solution and dilute to 100 ml with acetone.

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

Oven. Use any set temperature between 175°C and 190°C but control to  $\pm 0.5^\circ\text{C}$  throughout the determination

Injection port: 230°C

Flame detector: 250°C

Gas flow rates

Hydrogen and air: optimally set up according to the instruction manual.

Carrier gas : nitrogen (oxygen free), 50 ml.min<sup>-1</sup>, but adjust so that a suitable retention time (about 8 min) is obtained for dimethoate.

Retention times

Dimethoate about 8 min

Internal standard about 12.8 min.

2.1.6 Linearity check

Inject 2-6  $\mu\text{l}$  of the calibration solution containing about 2 mg dimethoate/ml (section 2.1.4) and adjust the instrument controls so that the maximum of the larger peak (either from dimethoate or di-n-butylphthalate) gives a recorder deflection of 80-90% full scale. Note the volume injected ( y  $\mu\text{l}$ ).

Inject duplicate y  $\mu\text{l}$  volumes of each of the calibration solutions. Measure the dimethoate and di-n-butylphthalate peak areas. For each injection calculate the calibration factor F by means of the following equation

$$F = \frac{m_1 \times P \times \text{area of di-n-butylphthalate peak}}{1000 \times \text{area of dimethoate peak}}$$

where  $m_1$  = mass (g) of dimethoate in the calibration solution  
 P = purity (g/kg) of the dimethoate standard.

Repeat the injections until the values of F obtained for each calibration solution do not differ from each other by more than  $\pm 0.5\%$ .

### 2.1.7 Sample preparation

Weigh (to the nearest 0.1 mg) sufficient sample ( $m_2$  g) to contain about 1.0 g of dimethoate into a 100 ml volumetric flask containing 20 ml acetone. Shake to dissolve, make up to 100 ml with acetone and mix thoroughly. Pipette 20 ml into a 100 ml volumetric flask, add 10 ml internal standard solution, make up to 100 ml with acetone and mix thoroughly.

### 2.1.8 Analysis of the sample

Inject duplicate  $y$   $\mu$ l volumes (section 2.1.6) of the sample solution and bracket the injections between injections of the calibration solution containing 2 mg dimethoate/ml, e.g. calibration solution injection, sample injections 1 and 2, and again calibration solution injection.

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

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

If the calibration factors  $F_a$  and  $F_b$  differ by more than  $\pm 0.5\%$  of the mean  $F_c$  repeat both calibration solution and sample solution injections. If the mean calibration factor  $F_c$  differs from  $F$  obtained here above (section 2.1.6) by more than  $\pm 2\%$ , stabilize the operating conditions and re-calibrate before proceeding with the analysis.

### 2.1.9 Calculation

$$\text{Dimethoate content (g/kg)} = \frac{5 \times F_c \times A_s}{m_2 \times A_b} \times 1000$$

where  $F_c$  = mean calibration factor for dimethoate (section 2.1.8)

$m_2$  = mass (g) of sample taken

$A_b$  = area of di-n-butylphthalate peak in the sample solution

$A_s$  = area of dimethoate peak in the sample solution

### 2.2 Cold test

Cool 50 ml of the sample to 0°C. Stir gently with a thermometer at intervals for 1 hour, maintaining the temperature at 0°C.

### 2.3 Water content

Determine the water content by the Karl Fischer electrometric titration method (see WHO/M/7<sup>1</sup>), or by the Dean and Stark distillation method (see WHO/M/8<sup>1</sup>). 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 govern.

1 Specifications for Pesticides Used in Public Health, Geneva, 1985 (6th Edition).

2.4 Heat stability

Keep 50 ml of the sample for 3 days at a temperature of  $50 \pm 1^{\circ}\text{C}$  in a glass container sealed to avoid loss of volatile solvent, and then cool to room temperature.