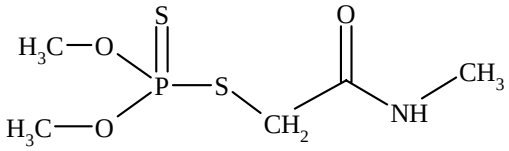
DIMETHOATE
59



ISO common name	Dimethoate
Chemical name	*O,O*-Dimethyl *S*-methylcarbamoyl methyl phosphorodithioate (IUPAC) *O,O*-dimethyl-*S*-[methylamino-2-oxoethyl] phosphorodithioate (CA; *60-51-5*)
Empirical formula	$C_5H_{12}NO_3PS_2$
RMM	229.2
b.p.	Decomposes
v.p.	1.1×10^{-3} Pa at 25 °C
Density, d_4^{20}	1.281
Refractive index n_D^{65}	1.5334
Solubility	In water: 25 g/l. Soluble in most organic solvents except saturated hydrocarbons such as hexane
Stability	Stable as a solid. Half life in aqueous solution: 5 days (pH 7). Readily hydrolysed by aqueous alkali. Slowly hydrolysed by dilute mineral acids
Formulations	Wettable powders, emulsifiable concentrates, soluble liquids and dusts

DIMETHOATE TECHNICAL
[*] **59**/TC/(M/2)/-

GAS CHROMATOGRAPHIC METHOD

1 Sampling. Take at least 100 g. Dimethoate technical may undergo spontaneous zone purification in storage. Store at a maximum temperature of 20 °C. When taking sub-samples heat the sample gently in a water bath at 60 °C until it melts. Homogenise by stirring and remove portions for all the analyses at the same time.

2 Identity tests

2.1 GLC. Use the GLC method below. The relative retention time of dimethoate with respect to the internal standard in the sample solution should not deviate by more than 1% from that of the calibration solution.

2.2 HPLC. As for dimethoate technical **59**/TC/M3/**2.2**, CIPAC E, *p.* 69.

2.2 Infrared. Prepare solutions of the sample and of a standard dimethoate in carbon tetrachloride and carbon disulphide (10 mg/ml for a path length of 0.5 mm or equivalent). Scan the carbon tetrachloride solution from 4000 to 930 cm^{-1} (2.5 to 10.75 µm) and from 590 to 200 cm^{-1} (16.95 to 50 µm) and the carbon disulphide solution from 930 to 590 cm^{-1} (10.75 to 16.95 µm) using solvent compensation. The spectra obtained from the sample should not differ significantly from those from the standard.

2.4 TLC. Carry out a thin-layer chromatography identity test by comparing the sample with the standard using the following conditions:

TLC plate	20 × 20 cm, coated with silica gel 60 F_{254}, 0.25 mm
Eluting solvents	I *n*-hexane-acetone, 2 + 1 (v/v) II chloroform- acetone, 2 + 1 (v/v)
Spraying solution	Dissolve palladium chloride (0.25 g) in concentrated hydrochloric acid (1 ml) and water and make up to 100 ml with ethanol.
Sample solution	Dissolve an amount of sample to contain about 0.2 g of dimethoate in methanol (5 ml).
Reference solution	Dissolve dimethoate standard (0.2 g) in methanol (5 ml).
Loading	10 µl

[*] Provisional CIPAC method 1981.Prepared by the Dimethoate Panel of PAC-UK. Chairman: J F Lovett.

Visualisation	Dry the plate at room temperature for 4 h. Apply a light spray of Palladium chloride solution to the whole surface of the plate and allow to dry for10 min in air.

Chromatographic procedure Apply the sample at the bottom right corner of the plate and the reference solutions at the bottom left and top right corners, all at 30 mm distance from the edges. Place the plate in the until the solvent front has travelled 12 cm. Remove chromatographic tank and develop with solution I the plate from the tank and allow the solvent to evaporate completely. Repeat the development twice more in the same direction. Rotate the plate through 90° about its bottom right hand corner in a clockwise direction. Redevelop with solution II.

3 Dimethoate

OUTLINE OF METHOD The dimethoate is separated from other components by gas chromatography on a non-polar column and determined by flame ionisation detection using dibutyl phthalate as internal standard.

REAGENTS

Acetone

Dimethoate of known purity (minimum 99 %). Store at 0 °C in the dark.

Di-n-butyl phthalate internal standard, with no peaks interfering with the dimethoate peak; purity at least 99%

Internal standard solution. Weigh into a volumetric flask (100 ml) about 1.0 g of di-*n*-butyl phthalate, dissolve in acetone and fill to the mark (Solution X).

Calibration solutions. Weigh (to the nearest 0.1 mg) quantities of 0.1 ± 0.005 g, 0.2 ± 0.005 g and 0.3 ± 0.005 g (*s* mg) of standard dimethoate into volumetric flasks (100 ml). Dissolve in acetone (20 ml), add by pipette to each flask internal standard solution (10.0 ml), and dilute to the mark (Solution C).

Dimethoate solution. Weigh into a volumetric flask (100 ml) about 200 mg standard dimethoate. Dissolve in acetone and fill to the mark (Solution Y).

APPARATUS

Gas chromatograph equipped with a flame ionisation detector

Column glass, 1 m × 2 to 4 mm (i.d.), packed with 3 % OV-17 on Chromosorb G (AW DMCS), 80 -100 mesh or equivalent

Electronic integrator or *data system*

Microsyringe 10 µl

PROCEDURE

(a) Gas chromatographic conditions (typical):

Column		
material	glass	
dimensions	1 m × 2 to 4 mm (i.d.)	
packing	3 % OV-17 on Chromosorb G (AW DMCS), 80 -100 mesh	
Detector	flame ionisation	
Column temperature	175 to 190 °C	
Gas flow rate		
Nitrogen (O_2 free)	50 ml/min	
Hydrogen)	flow rates as recommended for the detector	
Air)		
Theoretical plate number	750/m or more with respect to dimethoate	
Retention times	dimethoate:	about 8 min
	internal standard:	about 11 min

(b) Preparation of sample. Melt the technical material in a water bath at 60 °C before taking samples. Weigh (to the nearest 0.1 mg) sufficient sample to contain about 1.0 g (*w* mg) dimethoate into a volumetric flask (100 ml) containing acetone (20 ml). Shake to dissolve, make up to volume with acetone and mix thoroughly. Pipette 20.0 ml into a volumetric flask (100 ml), add internal standard solution (10.0 ml) using the same pipette as for the preparation of the calibration solutions, make up to volume with acetone and mix thoroughly (Solution S). Prepare in the same way a solution without adding the internal standard solution (Solution Z).

(c) System check. Inject 4 to 5 µl portions of the calibration solutions into the gas chromatograph. Check the peaks for tailing. The ratio

$$\frac{2y}{y+z}1$$

should be between 0.95 and 1.05 for the internal standard peak and between 0.80 and 1.05 for the dimethoate peak.

Where:

y = distance between leading edge of the peak and the peak maximum at 10 % of the peak height

z = distance between the peak maximum and the tailing edge of the peak at 10 % of the peak height

Then inject in duplicate each of the calibration solutions and check that the detector response is linear (correlation coefficient more than 0.999). If so use the 0.2 g calibration solution for the determination.
To ensure that no compounds are present that produce peaks interfering with the dimethoate and internal standard peaks, run chromatograms of the internal standard solution, the dimethoate solution and the sample solution without internal standard (Solutions X,Y,Z respectively).

(d) Determination. Inject in duplicate into the gas chromatograph 4 to 5 µl portions of calibration and sample solutions in the following order:

$$C_1, S_1, C_2, S_2, C_3, \ldots\ldots$$

After elution of the internal standard wait for 3 min before making the next injection. Measure the dimethoate to internal standard peak area ratios (R and R' for the sample and calibration solutions respectively). Calculate the means of C_1 and C_2, C_2 and C_3 and for each sample pair. Individual ratios should not differ by more than ± 1% of their mean.

(e) Calculation

$$\text{Dimethoate content} = \frac{R \times s \times P \times 5}{R' \times w} 2\text{g/kg}$$

where:

R = dimethoate to internal standard peak area ratio of the sample solution
R' = mean dimethoate to internal standard peak area ratio of the calibration solution
s = mass of dimethoate in the calibration solution (mg)
w = mass of sample taken (mg)
P = purity of dimethoate standard (g/kg)

Repeatability r = 12 and 18 g/kg at 890 and 963 g/kg active ingredient content respectively
Reproducibility R = 55 and 51 g/kg at 890 and 963 g/kg active ingredient content respectively

4 Omethoate

OUTLINE OF METHOD The sample is dissolved in acetonitrile and the omethoate, separated on OV 225 on Chromosorb W-HP, is determined with a flame photometric detector in the phosphorus mode using external standardisation.

REAGENTS

Acetonitrile
Omethoate of known purity
Calibration solutions. Prepare solutions of omethoate in acetonitrile at concentrations of 0.1, 0.08, 0.06, 0.02, and 0.01 mg/ml.

APPARATUS

Gas chromatograph with flame photometric detector in the phosphoric mode

PROCEDURE

(*a*) *Operating conditions* (typical):

Column	glass, 1.5 m × 2 mm (i.d.) packed with 3 % OV 225 on Chromosorb W-HP
Oven temperature	185 °C
Injection temperature	200 °C.
Detector temperature	250 °C
Injection volume	1 µl
Carrier gas	nitrogen with less then 10 ppm oxygen
Flow rate carrier gas	40 ml/min
Retention times	omethoate: about 9 min dimethoate: about 12 min
Limit of detection	about 200 mg/kg

(b) Preparation of calibration curve. Allow the system to equilibrate. Then inject 1 µl of portions the calibration solutions, measure the peak heights, and construct the calibration curve.

(c) Preparation of sample. Weigh (to the nearest 0.1 mg) about 100 mg of sample into a volumetric flask (10 ml), make up to the mark with acetonitrile, and shake to dissolve the sample.

(d) Determination. Inject a 1 µl aliquot into the gas chromatograph, measure the peak height, read the corresponding mass of omethoate from the calibration curve and calculate the omethoate content.

DIMETHOATE EMULSIFIABLE CONCENTRATES
*__59__/EC/(M/2)/-

1 Sampling. Take at least 500 ml.

2 Identity tests
2.1 GLC. As for dimethoate technical **59**/TC/(M/2)/**2.1.**
2.2 HPLC. As for dimethoate technical **59**/TC/M3/**2.2**, CIPAC E, *p.* 69.
2.3 TLC. As for dimethoate technical **59**/TC/(M/2)/**2.4.**

3. Dimethoate. As for dimethoate technical **59**/TC/(M/2)/2.1.

(i) Formulations without phenol

Repeatability r	=	8 g/kg at 200 g/kg active ingredient content
	=	14 to 15 g/kg at 368 g/kg active ingredient content
Reproducibility R	=	29 g/kg at 200 g/kg active ingredient content
	=	22 to 33 g/kg at 368 g/kg active ingredient content

(ii) Formulations with phenol as solvent

Repeatability r	=	16 and 15 g/kg at 358 and 386 g/kg active ingredient content respectively
Reproducibility R	=	24 and 32 g/kg at 358 and 386 g/kg active ingredient content respectively

DIMETHOATE SOLUBLE CONCENTRATES
*__59__/SL/(M/2)/-

1 Sampling. Take at least 500 ml.

2 Identity tests
2.1 GLC. As for dimethoate technical **59**/TC/(M/2)/**2.1.**
2.2 HPLC. As for dimethoate technical **59**/TC/M3/**2.2**, CIPAC E, *p.* 69.
2.3 TLC. As for dimethoate technical **59**/TC/(M/2)/**2.4.**

*Provisional CIPAC method 1981. Prepared by the Dimethoate Panel of PAC-UK. Chairman: J F Lovett.

3. Dimethoate. As for dimethoate technical **59**/TC/(M/2)/**2.1.**

(i) Formulations without phenol

Repeatability r	=	8.3 g/kg at 200 g/kg active ingredient content
	=	14 to 15 g/kg at 368 g/kg active ingredient content
Reproducibility R	=	29 g/kg at 200 g/kg active ingredient content
	=	22 to 33 g/kg at 368 g/kg active ingredient content

(ii) Formulations with phenol as solvent

Repeatability r	=	16 and 15 g/kg at 358 and 386 g/kg active ingredient content respectively
Reproducibility R	=	24 and 32 g/kg at 358 and 386 g/kg active ingredient content respectively