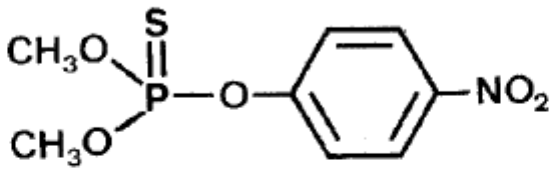
PARATHION-METHYL

10.a



ISO common name	Parathion-methyl
Chemical name	*O,O*-dimethyl *O*-(4-nitrophenyl) phosphorothioate (IUPAC) and CA; *298-00-0*)
Empirical formula	$C_8H_{10}NO_5PS$
RMM	263·2
m.p.	35 to 36°C
v.p.	41·3 mPa at 20°C
Density d_4^{20}	1·358
Refractive index n_D^{35}	1·5515
Solubility	In water 55 60 mg/l at 20°C. Slightly soluble in petroleum and mineral oils.
Description	White crystalline powder. Technical product is a light to dark tan liquid of 80% purity, crystallizing at about 29°C.
Stability	It is hydrolysed by alkali and isomerises on heating
Formulations	Formulated as emulsifiable concentrates, wettable powders and capsule suspension

PARATHION-METHYL TECHNICAL

*10.a/TC/(M1)/–

GAS CHROMATOGRAPHIC METHOD

1 **Sampling.** Take at least 100 g.

2 **Identity tests.** Determine the relative retention time of parathion-methyl with respect to the internal standard, simultaneously with the determination. The identity is confirmed if this relative retention time does not deviate by more than 2% from that of the calibration solution.

3 **Parathion-methyl**

OUTLINE OF METHOD Dissolve the sample in carbon disulphide and determine the parathion-methyl by gaschromatography on SE-30 + OV-210 using *p,p'*-DDE as internal standard.

Reagents

Carbon disulphide, pure.
2,2-bis (4-chlorophenyl)-1,1-dichloroethene, p,p'-DDE, of known purity, better than 99·5%.
Parathion-methyl, of known purity, better than 99·5%.
Internal standard solution. Weigh a mass of 5·0 ± 0·1 g *p,p'*-DDE into a 1 l volumetric flask, dilute to volume with CS_2 and mix thoroughly.
Calibration solution Weigh (to the nearest 0·1 mg) a mass of about 125 mg (*s* mg) parathion-methyl into a 50 ml glass stoppered erlenmeyer. Pipette in 25 ml internal standard solution and mix thoroughly.

Apparatus

Gas chromatograph, equipped with flame ionization detector
Column, glass, 1·2 m × 4 (i.d.) mm, packed with 1·5% SE-30 plus 1·5% OV-210 on gaschrom Q, 80–100 mesh
Recorder

Procedure

(*a*) *Column preparation.* Weigh accurately about 0·12 g SE-30 and about 0·12 g OV-120 into a 250 ml beaker. Add 50 ml chloroform-acetone (3 + 2), cover with watch glass and heat on a steam bath until the stationary phases are dissolved. Speed the dissolution of SE-30 by spreading the material on the walls of the beaker, with a small spatula or a stirring rod. Add enough 80–100 mesh gaschrom Q to yield 1·5% of each phase on the solid support. Heat on the steam bath, stirring frequently until all solvent is removed. Air dry 2 to 3 hours. Pack in column and condition 24 h at 245°C with nitrogen or helium at 30 ml/min. The column should have more than 1200 theoretical plates for *p,p'*-DDE.

(*b*) *Operating conditions*

Column temperature	180 ± 10°C
Injection port temperature	210°C
Detector temperature	250°C
Flow rate carrier gas	N or He 55 to 75 ml/min
Flow rate, air and hydrogen	as specified by the manufacturer
Attenuation and injection volume	Vary injection volume (1–2 µl) and attenuation so that the peak heights of parathion-methyl and *p,p'*-DDE are 60–80% full scale on a 1 mV recorder

(*c*) *Sample preparation.* Weigh to the nearest 0·1 mg into a 50 ml glass stoppered erlenmeyer enough sample to contain about 125 mg (*w* mg) of parathion-methyl. Pipette in 25·00 ml internal solution and mix thoroughly.

(*d*) *Determination.* Inject aliquots (1–2 µl) of the calibration solution until the peak height ratio parathion-methyl: *p,p'*-DDE varies less than 1% for successive injections. Then make duplicate injections of the sample followed by duplicate injections of the calibration solution. Peak height ratios of the calibration solution must be within ±1% of the first accepted values or repeat the series of

injections. Repeat for additional samples. Retention times for parathion-methyl and DDE are 3·5 to 5·5 and 6 to 8 min respectively.

(*e*) *Calculations.* Calculate peak height ratio for both duplicate injections of the calibration solution preceding and following samples. Average the 4 values (R') calculate and average the peak height ratios of the 2 sample injections (R). The content of parathion-methyl:

$$= \frac{R \times s \times p}{R' \times w} \% \text{ m/m}$$

where:

p = purity of standard parathion-methyl % m/m
R = peak height ratio of sample
R' = peak height ratio of calibration solution
s = mass of pure parathion-methyl, mg.
w = mass of sample, mg.

*10.a/TC/(M2)/–

HIGH PRESSURE LIQUID CHROMATOGRAPHIC METHOD

1 Sampling. Take at least 100 g.

2 Identity tests. As for **10.a**/TC/(M1)/2.

3 Parathion-methyl

OUTLINE OF METHOD Dissolve the sample in chloroform and determine the parathion-methyl by high pressure liquid chromatography on silicagel—10 μm, using acetophenone as internal standard.

REAGENTS

Acetophenone, purity better than 99·5%.
Parathion-methyl, of known purity, better than 99·5%.
Chloroform, alcohol free, with less than 0·01% H_2O, distilled in glass.
Silicic acid-water, 75% m/m. Add 25 ml water to 75 g silicic acid (Mallinckrodt Chemical Works, code 2847 or equivalent) and shake until lumps disappear.
Chloroform saturated with water. Shake 700 ml chloroform with 150 ml water for 2 to 3 min and pass through 900 × 25 mm glass tube packed with 100 g silicic acid-water.
Eluant. Blend 200 ml chloroform saturated with water with 300 ml chloroform on a magnetic stirrer for 2 to 3 min under moderated vacuum (about 47 k Pa).
Internal standard solution. Accurately weigh about 115 mg of acetophenone into a 250 ml volumetric flask, dissolve and dilute to volume with chloroform.

Parathion-methyl standard solutions
(*a*) *Stock solution* (700 mg/l). Weigh to the nearest 0·1 mg a mass of about 70 mg (s mg) of pure parathion-methyl into a 100 ml volumetric flask, dissolve and dilute to volume with chloroform.

(*b*) *Working solution* (70 mg/l parathion-methyl + 46 mg/l acetophenone). Pipette 5·00 ml stock solution and 5·00 ml internal standard solution into a 50 ml volumetric flask and dilute to volume with chloroform.

Apparatus

Liquid chromatograph. Waters, Model ALC 202 or equivalent, with 254 nm UV detector and 10 mV recorder.
Liquid chromatographic column. Stainless steel, 300 × 4(id) mm with 10 µm diam. silicagel particles (Waters Associates, Inc., No 27477, or equivalent).
Chromatographic tubes, glass 900 × 25(id) mm with coarse porosity frit in bottom.

Procedure

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

Eluant flow rate	1·2 ml/min (about 4·8 MPa)
Detector sensitivity	0·16 absorbance unit full scale
Temperature	ambient
Valve injection volume	10 µl

(*b*) *Sample preparation.* Weigh (to the nearest 0·1 mg) sufficient sample to contain about 70 mg (*w* mg) of parathion-methyl into a 100 ml volumetric flask and dilute to volume with chloroform. Pipette 5·00 ml sample solution and 5·00 ml internal standard solution into a 50 ml volumetric flask and dilute to volume with chloroform.

(*c*) *Determination.* Pump sufficient eluant through the column to equilibrate the system. Inject 10 µl working standard solution into the column through the sampling valve and adjust the operating conditions to give peak heights of 60–80% full scale and retention times of 3·5 to 5·0 and 5·5 to 8·0 min for parathion-methyl and acetophenone respectively. Repeat the injections until the ratio of the parathion-methyl to the acetophenone peak heights is within ±1% of the previous injection. Without changing conditions, alternatively inject 10 µl aliquots of the working standard solution until the peak height ratios for the sample solution vary less than 1% for successive injections. Average the last two peak height ratios for the sample and for the standard respectively.

(*d*) *Calculation.* The content of parathion-methyl:

$$= \frac{R \times s \times p}{R' \times w} \% \text{ m/m}$$

where:

p = purity of parathion-methyl % m/m
R = average peak height ratios of parathion-methyl and acetophenone for the sample
R' = average peak height ratios of parathion-methyl and acetophenone for the standard
s = mass of the pure parathion-methyl in mg
w = mass of the sample in mg

PARATHION-METHYL CAPSULE SUSPENSIONS

*10.a/CS/(M)/–

1 Sampling. Take at least 500 g.

2 Identity tests. As for **10.a**/TC/(M1)/2.

3 Parathion-methyl

OUTLINE OF METHOD Parathion-methyl is released from the micro capsules by grinding and is extracted into acetonitrile. Dimethoate is added as internal standard and the concentration of parathion-methyl is determined by flame ionization gas liquid chromatography.

REAGENTS

Acetonitrile, pure
Dimethoate, purity better than 99·5%
Parathion-methyl, of known purity, better than 99·5%

APPARATUS

Gas chromatograph, with flame ionization detector, glass lined injection port, 1 mV strip chart recorder and 1·8 m × 2(id) mm glass column packed with 3% OV-17 on 80–100 mesh Supelcoport (Supelco, Inc.).
Sample grinder. Spex Industries Mixer/Mill, No 8000-II (Spex Industries, Inc.) or 40 ml Corning 7726 ml glass tissue grinder (No 441969, Corning Glass Works).
Weighing dishes. With natural Al surface to which sample does not stick. (Fisher Scientific Co., No 8-732, or equivalent.)

PROCEDURE

(*a*) *Operating conditions*

Column temperature	200°C
Injection port temperature	225°C
Detector temperature	250°C
Flow rate carrier gas, helium	35 ml/min
Flow rate, air	400 ml/min
Flow rate, hydrogen	Optimize for maximal sensitivity
Injection volume	1 µl. Injection volume may be varied to give peak heights 50 to 90% full scale.
Retention times	About 3 and 4 min for dimethoate and parathion-methyl respectively

(*b*) *Calibration*. Prepare two duplicate standard solutions by accurately weighing (to the nearest 0·1 mg) about 0·1 g (W_{mp} g) parathion-methyl and about 0·1 g (W_d g) of dimethoate directly into a 50 ml volumetric flask and diluting to volume with acetonitrile. Shake thoroughly to dissolve. Inject about 1 µl of each solution into the gas chromatograph. Repeat the injections until the ratio of the

peak heights is reproducible; then record the peak heights and attenuations for dimethoate and parathion-methyl.

$$f = \frac{P_d \times W_{mp}}{P_{mp} \times W_d}$$

where:

f = correction factor
P_d = peak height × attenuation for dimethoate.
P_{mp} = peak height × attenuation for parathion-methyl.
W_d = mass of dimethoate in g.
W_{pm} = mass of parathion-methyl in g.

Average the results for the two solutions.

(*c*) *Preparation of sample.* Prepare duplicate samples as follows:
Thoroughly shake the sample container to assure that the slurry of the micro-capsules is homogeneous. Withdraw about 1 g sample using a medicine dropper while stirring. Immediately discharge the contents into a tared Al weighing dish and record the exact mass (W g). Transfer to a Mixer/Mill or glass tissue grinder using a small amount of acetonitrile. (If the analytical balance can accommodate the grinder, the sample may be weighed directly in it.) Add about 30 ml acetonitrile and grind ca. 4 min. Quantitively transfer the ground sample to a 100 ml volumetric flask using acetonitrile. Accurately weigh about 0·2 g (W_d' g) dimethoate in tared Al weighing dish, transfer to the volumetric flask and dilute to volume with acetonitrile.

(*d*) *Determination.* Inject about 1 µl of the solution containing the sample and the internal standard into the gas chromatograph. Record the peak heights and the attenuations for dimethoate and parathion-methyl. Analyse duplicate samples.

(*e*) *Calculation.* The content of parathion-methyl

$$= \frac{P'_{mp} \times W'_d \times f \times 100}{P'_d \times W} \% \text{ m/m}$$

where:

f = correction factor
P'_d = peak height × attenuation for dimethoate
P'_{mp} = peak height × attenuation for parathion-methyl
W = mass of sample in g
W'_d = mass of dimethoate in g

Average the result of the duplicate samples.

PARATHION-METHYL EMULSIFIABLE CONCENTRATES

*10.a/EC/(M1)/–

GAS CHROMATOGRAPHIC METHOD

1 **Sampling.** Take at least 500 ml.

2 Identity tests. As for **10.a**/TC/(M1)/2.

3 Parathion-methyl. As for **10.a**/TC/(M1)/3.

PARATHION-METHYL EMULSIFIABLE CONCENTRATES

*__10.a__/EC/(M2)/–

HIGH PRESSURE LIQUID CHROMATOGRAPHIC METHOD

1 Sampling. Take at least 500 ml.

2 Identity tests. As for **10.a**/TC/(M1)/2.

3 Parathion-methyl. As for **10.a**/TC/(M2)/3 except

(*b*) *Sample preparation.* Weigh to the nearest 0·1 mg sufficient sample to contain about 35 mg (*w* mg) of parathion-methyl into a 50 ml volumetric flask and dilute to volume with chloroform. Continue according to **10.a**/TC/(M2)/3 (b) from 'Pipette 5·00 ml of the sample solution . . .'.

(*d*) *Calculation.* The content of parathion-methyl

$$= \frac{R \times s \times p}{R' \times w \times 2} \text{ \% m/m}$$

PARATHION-METHYL WETTABLE POWDERS

*__10.a__/WP/(M1)/–

GAS CHROMATOGRAPHIC METHOD

1 Sampling. Take at least 500 g.

2 Identity tests. As for **10.a**/TC/(M1)/2.

3 Parathion-methyl

OUTLINE OF METHOD Extract parathion-methyl with chloroform-acetone mixture take aliquot, evaporate the solvent. Dissolve residue in carbon disulphide and determine the parathion-methyl by gas chromatography.

REAGENTS AND APPARATUS As for **10.a**/TC/(M1)/3. in addition to
Chloroform-acetone mixture, 9 + 1
DETERMINATION As for **10.a**/TC/(M1)/3 except:

* Provisional AOAC-CIPAC Method 1977.

(*c*) *Sample preparation.* Weigh (to the nearest mg) into a 125 ml round bottle sufficient sample to contain about 625 mg (w mg) of parathion-methyl. Pipette in 50·00 ml of chloroform-acetone mixture (9 + 1), cap and shake mechanically for 30 min. Let settle and pipette 10·00 ml supernate into a 50 ml ground stoppered erlenmeyer. Place the erlenmeyer in a 55°C water bath and evaporate the solvent under a stream of dry air or nitrogen. Pipette in 25·00 ml internal standard solution and mix thoroughly. Continue according to **10.a**/TC/(M1)/3 (d).

(*e*) *Calculation.* As for **10.a**/TC/(M1)/3 (e) except

The content for parathion-methyl

$$= \frac{R \times s \times p \times 5}{R' \times w} \% \text{ m/m}$$