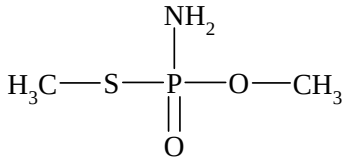
METHAMIDOPHOS
355



ISO common name	Methamidophos
Chemical name	*O,S*-dimethyl phosphoramidothioate (IUPAC, CA; *10265-92-6*)
Empirical formula	$C_2H_8NO_2PS$
RMM	141.1
m.p.	46.1 °C
v.p.	4.2×10^{-3} Pa at 20 °C
d_4^{20}	1.31
n_D^{20}	1.5092
Description	Pure methamidophos is a crystalline solid, the technical material is a colourless to yellowish liquid or crystalline slurry
Solubility	In *n*-hexane: 0.1 - 1 g/l at 20 °C; toluene: 2 - 5 g/l at 20 °C; miscible with water, 2-propanol and dichloromethane
Stability	Half life at pH 4 and 22 °C: 1.8 a at pH 7 and 22 °C: 120 h at pH 9 and 22 °C: 70 h
Formulations	Soluble concentrates

METHAMIDOPHOS TECHNICAL
*355/TC/M/-

1 Sampling. Take at least 100 g.

2 Identity tests

2.1 Infrared. Prepare a KBr disc using 1 mg sample and 300 mg KBr. Scan the disc from 4000 to 400 cm^{-1}. The spectrum produced from the sample disc should not differ significantly from that of an authentic sample.

2.2 HPLC. Use the HPLC method below. The retention time of methamidophos for the sample solution should not deviate by more than 1% from that of the calibration solution.

2.3 TLC. Carry out a thin layer chromatographic identity test by comparing the sample with the standard using the following conditions:

TLC plate	coated with silica gel 60 F_{254} 0.25 mm (e.g. Merck, Darmstadt, FRG, Art.No. 5715)
Solvent	*n*-hexane/acetone (5+3 v/v)
Sample solution	Dissolve an amount of sample containing the equivalent of 60 mg methamidophos in approximately 5 ml methanol in a 10 ml volumetric flask and make up to the mark with methanol. Apply the solution immediately.
Reference solution I	Dissolve 60 mg of methamidophos authentic substance in approximately 5 ml methanol in a 10 ml volumetric flask and make up to the mark with methanol. Apply the solution immediately.
Reference solution II	Mix 5 ml of the sample solution with 5 ml of the reference solution I. Apply the solution immediately.
Sample size	10 µl of reference solution I, II and of the sample solution.
Travelling distance	15 cm
Visualization	Spray the plate with a 0.5% aqueous solution of palladium-II-chloride
R_f *value*	Methamidophos 0.2

3 Methamidophos

OUTLINE OF METHOD A solution of the sample is separated by reversed phase high performance liquid chromatography. The content of active ingredient is determined from peak areas using an external standard.

* CIPAC method 1991. Prepared by the German Committee (DAPA) Chairman: W Dobrat. Based on a method supplied by Bayer AG (FRG)

REAGENTS

Methamidophos reference substance of known purity

Eluent water - acetonitrile (94+6) v/v, premixed

Calibration solution. Weigh (to the nearest 0.1 mg) about .25 g of pure methamidophos (*s* g) into a 100 ml volumetric flask, dissolve in 50 ml water and make up to volume with water.

APPARATUS

Liquid chromatograph equipped with a spectrophotometric detector (wavelength: 210 nm) and loop-injection valve (20 µl)

Liquid chromatographic column stainless steel, 250 ± 4 (i.d.) nm, packed with LiChrospher 100 RP 8, 5 µm

PROCEDURE

(a) Operating conditions (typical):

Eluent flow rate	1.5 ml/min
Detector wavelength	210 nm
Column temperature	35 °C
Valve injection volume	20 µl
Run time	30 min
Retention time	methamidophos: approximately 3.2 min

(b) Preparation of sample. If necessary melt the technical methamidophos and homogenize the sample. Weigh (to the nearest 0.1 mg) sufficient sample (*w* g) to contain 0.25 g of methamidophos into a 100 ml volumetric flask and dilute to volume with water.

(c) Determination. Inject 2 µl of two calibration solutions (different masses of pure methamidophos) alternately until the calibration factor varies by less than 1% for the two last injections. Inject 20 µl of the sample solution in duplicate. Repeat the calibration after the injection of two samples using the two calibration solutions alternately. Measure the relevant peak areas and average the areas of the duplicate injections of the respective samples.

(d) Calculation. Calculate the average calibration factor *f* with the factors of the calibration solution preceding and following the samples.

$$\text{The calibration factor } f = \frac{s \times P}{H_s}$$

$$\text{Methamidophos } = \frac{H_w \times f}{w} \text{ g/kg}$$

where:

H_w = peak area of methamidophos in sample solution
w = mass of sample taken (g)
s = mass of methamidophos reference substance in calibration solution (g)
P = purity of methamidophos reference substance (g/kg)
H_s = peak area of methamidophos in calibration solution

Repeatability r = 9.4 g/kg at 752 g/kg active ingredient content
Reproducibility R = 21.0 g/kg at 752 g/kg active ingredient content

4 Impurities. (draft method)*

SCOPE Determination of by-products in technical material and technical concentrates.

OUTLINE OF METHOD An internal standard is added to the sample, the sample is diluted with a suitable solvent and the impurities are determined by gas liquid chromatography.

REAGENTS
Acetone
Carbon tetrachloride
Methamidophos pure, purity at least 975 g/kg
n-Dodecane, internal standard, purity at least 995 g/kg
O,O,O-Trimethyl phosphorothioate (TMPS), purity at least 990 g/kg
O,O,S-Trimethyl phosphorothioate (*i*-TMPS), purity at least 970 g/kg
O,O-Dimethyl methylphosphoroamidothioate (*N*-methyl amidate), purity at least 990 g/kg
O,S-Dimethyl methylphosphoroamidothioate (*N*-methyl methamidophos), purity at least 910 g/kg
O,O-Dimethyl phosphoroamidothioate (amidate)

APPARATUS
Gas chromatograph equipped with a capillary column, on-column injection, FID detector, recorder and electronic integrator

* Based on a method supplied by Bayer AG (FRG)

PROCEDURE

(a) Gaschromatographic conditions:

Column	glass capillary, silylated, 50 m × 0.3 mm (i.d.)
Packing	SE-54
Detector temperature	300 °C
Temperature program of oven	initial 80 °C for 1 min 80 to 120 °C at 15 °C/min hold at 120 °C for 10 min 120 to 140 °C at 20 °C/min hold at 140 °C for 5 min 140 to 280 °C at 20 °C/min hold at 280 °C for 10 min
Flow rates	hydrogen (carrier gas) about 30 ml/min air about 300 ml/min helium (make-up gas) 20 ml/min
Injection volume	0.4µ l
Retention times	*n*-dodecane: about 16.0 min TMPS: about 7.8 min amidate: about 10.9 min *i*-TMPS: about 11.9 min *N*-methylamidate: about 12.3 min *N*-methylamidophos: about 18.3 min

(b) Determination of response factors. Weigh (to the nearest 0.1 mg) about 0.03 g (*s* g) of the respective impurities, about 0.04 g (*r* g) *n*-dodecane and 0.5 g pure methamidophos into a glass-stoppered flask (500 ml). Add acetone (1 ml), homogenize, and dilute with carbon tetrachloride (300 ml). Inject 0.4 µl portions of this solution into the gas chromatograph under the conditions given under *(a)*. Determine the peak areas of the internal standard and the respective impurities.

(c) Preparation of sample. Weigh (to the nearest 0.1 mg) about 0.3 g (*w* g) of the homogenized sample and about 0.2 g (*q* g) internal standard into a glass-stoppered flask (500 ml). Add acetone (1 ml), homogenize, and dilute with carbon tetrachloride (300 ml).

(d) Determination. Inject portions of this solution into the gas chromatograph under the conditions given under *(a)*. Determine the peak areas of the internal standard and the respective impurities.

(e) Calculation

$$\text{Response factor of i-th impurity} \quad f_i = \frac{s \times I_r \times P}{r \times H_s}$$

where:

s = mass of i-th impurity in the calibration solution (g)
H_s = peak area of the i-th impurity in the calibration solution
I_r = peak area of the internal standard in the calibration solution
P = purity of i-th impurity (g/kg)

$$\text{Content of i-th impurity} = \frac{H_w \times q \times f_i}{w \times I_q} \text{ g/kg}$$

where:

w = mass if internal standard in the calibration solution (g)
q = mass of internal standard in the sample solution (g)
H_w = peak area of the i-th impurity in the sample solution
I_q = peak area of internal standard in the sample solution

METHAMIDOPHOS SOLUBLE CONCENTRATE
*355/TC/M/-

1 Sampling. Take at least 100 g.

2 Identity tests

2.1 HPLC. As for methamidophos technical **355**/TC/M/2.2.

2.2 TLC. As for methamidophos technical **355**/TC/M/2.3.

3 Methamidophos. As for **355**/TC/M/3.

Repeatability r = 8.0 g/kg at 600 g/kg active ingredient content
Reproducibility R = 15.6 g/kg at 600 g/kg active ingredient content

* CIPAC method 1991. Prepared by the German Committee (DAPA)
Chairman: W Dobrat. Based on a method supplied by Bayer AG (FRG)