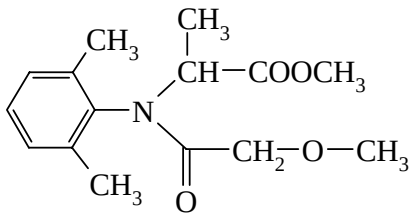
METALAXYL
365



ISO common name	Metalaxyl
Chemical name	Methyl *N*-(2-methoxyacetyl)-*N*-(2,6-xylyl)-*DL*-alaninate (IUPAC); methyl *N*-(2,6-dimethyl-phenyl)-*N*-(methoxyacetyl)-*DL*-alaninate (CA; *57837-19-1*)
Empirical formula	$C_{15}H_{21}NO_4$
RMM	279.3
m.p.	71.8-72.3 °C
v.p.	0.29 mPa at 20 °C
Solubility	In water: 7.1 g/l at 20 °C, benzene: 550 g/l, dichloro-methane: 750 g/l, hexane: 9.1 methanol: 650 g/l, octanol: 270 g/l, propan-2-ol: 270 g/l
Description	Colourless crystals
Stability	Stable in neutral and acidic media at room temperature
Formulations	Wettable powders and suspension concentrates

METALAXYL TECHNICAL
*365/TC/M/-

1 Sampling. Take at least 100 g.

2 Identity tests

2.1 GLC Use the GLC method below. The retention time of metalaxyl from the sample solution should not deviate from that from the calibration solution by more than 0.2 min.

* CIPAC method 1992. Prepared by PAC-CH. Based on a method supplied by Ciba-Geigy, Switzerland.

2.2 Infrared. Prepare potassium bromide discs from the sample and from pure metalaxyl using 1.5 mg material and 300 mg potassium bromide. Scan the discs from 4000 to 600 cm^{-1}. The spectrum produced from the sample disc should not differ significantly from that from the standard.

3 Metalaxyl

OUTLINE OF METHOD Metalaxyl is determined by gaschromatography on a packed column using internal standardization.

REAGENTS

Acetone

Metalaxyl standard of known purity

Methyl stearate internal standard

Calibration solution. Weigh (to the nearest 0.1 mg) into a ground-glass stoppered conical flask (50 ml) 190 to 210 mg (*s* mg) metalaxyl standard and 140 to 160 mg (r mg) internal standard. Add by pipette acetone (25.0 ml) and shake to dissolve. Do not use the solution for periods longer than 48 h.

APPARATUS

Gas chromatograph equipped with a flame ionization detector and an electronic integrator

Column glass, 1.8 m × 2 mm (i.d.) packed with 10% OV-101 on Chromosorb W-HP, 80-100 mesh

PROCEDURE

(a) Operating conditions (typical):

Column	
dimensions	1.8 m × 2 mm (i.d.)
packing	10% OV-101 on Chromosorb 6 W-HP, 80-100 mesh
Temperature	
injection port	225 °C
column	205 °C
detector	260 °C
Gas flow rates	
carrier gas (nitrogen)	35 ml/min

hydrogen	as recommended for the instrument
air	as recommended for the instrument
Injection volume	1 µl
Retention times	metalaxyl: 4.5 min
	methyl stearate: 9.5 min

(b) System equilibration. Prepare two calibration solutions. Inject 1 µl portions of the first one until the response is stable and the ratios of the metalaxyl peak area to the internal standard peak area for successive injections agree within 1%. Inject the second solution. The peak area ratio of that solution (mean of two injections) should not deviate by more than 0.5% from the peak area ratio of the first solution, otherwise repeat the injections or prepare new solutions.
(c) Preparation of sample solution. Weigh (to the nearest 0.1 mg) into a ground-glass stoppered conical flask (100 ml) enough sample to contain 380 to 420 mg pure metalaxyl (*w* mg). Add acetone (50.0 ml) and shake well to dissolve.
(d) Determination. Inject 1 µl portions of the first calibration solution (C) and the sample solutions (S_1, S_2 .....) in the following sequence :
C, C, S_1, S_1, S_2, S_2, C, C, S_3, S_3, S_4, S_4, C, C .....Determine the peak areas.
(e) Calculation. Calculate the mean value of each pair of calibration factors (*f*) bracketing the injections of the two sample solutions. Use the value for calculating the content of these two samples.

$$f = \frac{s \times I_r \times P}{H_s \times r}$$

$$\text{Content of metalaxyl} = \frac{H_w \times q \times f}{w \times I_q} \quad \text{g/kg}$$

where:

H_s	=	area of metalaxyl peak in the calibration solution
H_w	=	area of metalaxyl peak in hte sample solution
I_r	=	area of the internal standard peak in the calibration solution
I_q	=	area of the internal standard peak in the sample solution
s	=	mass of metalaxyl in the calibration solution (mg)
w	=	mass of sample taken (mg)
r	=	mass of the internal standard in the calibration solution (mg)
q	=	mass of the internal standard in the sample solution (mg)
P	=	purity of the metalaxyl standard
f	=	response factor

Repeatability r = 15.5 g/kg at 963 g/kg active ingredient content
Reproducibility R = 20.0 g/kg at 962 g/kg active ingredient content

4 2,6-Dimethylaniline (Draft method)

OUTLINE OF METHOD Determination of 2,6-dimethylaniline in a sample by capillary gas chromatography using internal standardization.

REAGENTS

Carbon tetrachloride
2-Naphthyl benzoate internal standard
2,6-Dimethylaniline of known purity
Stock solution internal standard. Weigh (to the nearest 0.1 mg) into a ground glass stopered flask (250 ml) 45 to 55 mg (*s* mg) internal standard. Add carbon tetrachloride and shake to dissolve. Make up to the mark with carbon tetrachloride.
Stock solution 2,6-dimethylaniline. Weigh (to the nearest 0.1 mg) into a ground glass stoppered flask (500 ml) 15 to 30 mg (*r* mg) 2,6-dimethylaniline standard. Add carbon tetrachloride and shake to dissolve. Make up to the mark with carbon tetrachloride.
Calibration solution Pipette 1.0 ml of the 2,6-dimethylaniline stock solution and 5.0 ml of the internal standard solution into a ground glass stoppered flask (50 ml). Make up to the mark with carbon tetrachloride. do not use the solution for periods longer than 48 h.

APPARATUS

Gas chromatograph equipped with a flame ionization detector and an electronic integrator
Column fused silica capillary, length 8 m, inner diameter 0.32 mm, coated with DB 1701, film thickness 0.25 µm

PROCEDURE

(a) Operating conditions (typical):
Temperature

injection port	75 °C
column	75 °C for 2 minutes, then 75 to 90 °C with 6 °C/min, then 90 to 290 °C with 15 °C/min, then290 °C for 5 minutes
detector	290 °C

Gas flow rates	
carrier gas (hydrogen)	55 cm/s
Make-up gas (nitrogen)	30 ml/min
Injection volume	1 µl
Retention times	2,6-Dimethylaniline : about 3.6 minutes

(b) Preparation of sample solution. Weigh (to the nearest 0.1 mg) enough sample to contain about 90 to 110 mg (*w* mg) pure metalaxyl into a 50 ml volumetric flask. Add by pipette 5.0 ml of the internal standard stock solution. Add carbon tetrachloride and shake to dissolve. Dilute to volume with carbon tetrachloride. In case of a dispersion centrifuge or filter the dispersion through a 0.45 µm filter. The clear solution is then ready for injection.

(c) Determination. Set the integration parameters and stabilize the instrument by injecting 1 µl aliquots of the calibration solution until the response ratios agree within 5 %. Then inject 2 aliquots of the calibration solution followed by 2 aliquots of the sample solution.

(d) Evaluation. Comparison of peak areas. For each injection calculate.

$$\text{Correction factor: } f = \frac{s \times I_r}{r \times 500 \times H_s}$$

where:

H_s = peak area of the of the pure dimethylaniline in the calibration solution
s = mass of the pure dimethylaniline, calculated as 100.0 % content (mg)
r = peak area of the internal standard in the calibration solution
I_r = mass of the internal standard in an aliquot of the internal standard stock solution for the calibrating solution (mg)

$$\text{Content of 2,6-dimethylaniline } = \frac{H_w \times q \times f \times 1000}{w \times I_q} \text{ g/kg}$$

where:

H_w = peak area of 2,6-dimethylaniline in the calibration solution
w = mass of sample taken (mg)
I_q = peak area of internal standard in the calibration solution
q = mass of the internal standard in an aliquot of the internal standard stock solution for the test solution (mg)

METALAXYL WETTABLE POWDERS
*365/WP/M/-

1 Sampling. Take at least 500 g.

2 Identity tests.
2.1 GLC. As for metalaxyl technical **365**/TC/M/2.1.
2.2 Infrared. Prepare a suspension of the formulation containing approximately 2 g of technical metalaxyl in n-hexane (50 ml). Warm to 60 to 65 °C for 3 min (water bath). Filter this suspension and allow the clear filtrate to cool in an ice bath. Separate the crystals from the mother liquor by filtration and wash with cold *n*-hexane (30 ml). Dry the crystals in vacuum at room temperature. Proceed as for metalaxyl technical 365/TC/M/2.2.

3 Metalaxyl. As for metalaxyl technical **365**/TC/M/3, except:
(c) Preparation of sample solution. Weigh (to the nearest 0.1 mg) into a ground-glass stoppered conical flask enough sample to contain 380 to 420 mg (*w* mg) pure metalaxyl. Add acetone (50 ml) and place the flask in an ultrasonic bath for 10 min. Allow to settle inert materials or centrifuge the solution. Use the clear solution for the determination.

Repeatability r	=	5.3 g/kg at 265 g/kg active ingredient content 3.1 g/kg at 157 g/kg active ingredient content
Reproducibility R	=	6.7 g/kg at 265 g/kg active ingredient content 3.1 g/kg at 157 g/kg active ingredient content

4 2,6 Dimethylaniline (Draft method). As for metalaxyl technical **365**/TC/M/4.

5 Suspensibility (proposed method)
(a) Preparation of suspension. MT15.1 (*i*)
(b) Determination of sedimentation. MT 15.1 (*ii*)
(c) Determination of metalaxyl in the bottom 25 ml of suspension. After removal of the top 225 ml of suspension transfer the residual 25 ml quantitatively with water to a round-bottomed flask (100 ml). Evaporate the water under vacuo. Add internal standard (*q* g) and acetone (50 ml) and proceed according to **365**/WP/M/3 (*c*).

* CIPAC method 1992. Prepared by PAC-CH. Based on a method supplied by Ciba-Geigy, Switzerland.

$$\text{Mass of metalaxyl (Q)} = \frac{H_w \times q \times f}{w \times I_q} \quad \text{g/kg}$$

where:

H_w	=	area of metalaxyl in the sample solution
I_q	=	area of internal standard peak in the sample solution
f	=	response factor
q	=	mass of internal standard in the sample solution (mg)

(d) Calculation

$$\text{Suspensibility} = \frac{111(c - Q)}{c}$$

where:

c = mass of metalaxyl in the sample taken for preparing the suspension (mg)
Q = mass of metalaxyl in the bottom 25 ml of suspension (mg)

METALAXYL POWDERS FOR DRY SEED TREATMENT
[*]**365**/DS/M/-

1 Sampling. Take at least 500 g.

2 Identity tests.
2.1 GLC. As for metalaxyl technical **365**/TC/M/2.1.
2.2 Infrared. Prepare a suspension of the formulation containing approximately 2 g of metalaxyl in n-hexane (30 ml) and add charcoal (about 1 g). Warm to 60 to 65 °C for 3 min (waterbath). Filter the suspension, add n-propanol (2 ml) and charcoal (about 1 g) and warm to 60 to 65 °C for 3 min. Filter the mixture and allow the clear filtrate to cool in an ice bath. Separate the crystals by filtration and dry in vacuo at room temperature. Proceed as for metalaxyl technical **365**/TC/M/2.2.

3 Metalaxyl. As for metalaxyl wettable powders **365**/WP/M/3.

Repeatability r = 5.7 g/kg at 347 g/kg active ingredient content

Reproducibility R = 6.5 g/kg at 347 g/kg active ingredient content

4 2,6 Dimethylaniline (Draft method). As for metalaxyl technical **365**/TC/M/4.

[*] CIPAC method 1992. Prepared by PAC-CH. Based on a method supplied by Ciba-Geigy, Switzerland.

METALAXYL FLOWABLE CONCENTRATES FOR SEED TREATMENT

[*] **365**/FS/M/-

1 Sampling. Take at least 1 kg. Before use homogenize the sample by vigorous shaking or stirring for 5 min.

2 Identity tests.

2.1 GLC. As for metalaxyl technical **365**/TC/M/2.1.

2.2 Infrared. Place 5 to 6 g of the formulation on top of a silicagel-60 column (35 g, column dimensions 25 × 2.5 (i.d.) mm). Elute the metalaxyl with acetone (100 ml). Evaporate the solvent in vacuo. Add to the residue *n*-propanol (2 ml) and charcoal (1 g). Warm to 60 to 65 °C (waterbath) and filtrate the warm suspension. Allow the filtrate to cool. Separate the crystals by filtration and dry in vacuo at room temperature. Proceed as for metalaxyl technical **365**/TC/M/2.2.

3 Metalaxyl. As for metalaxyl wettable powders **365**/WP/M/3.

Repeatability r = 8.1 g/kg at 339 g/kg active ingredient content

Reproducibility R = 15.0 g/kg at 339 g/kg active ingredient content

4 2,6 Dimethylaniline (Draft method). As for metalaxyl technical **365**/TC/M/4.

[*] CIPAC method 1992. Prepared by PAC-CH. Based on a method supplied by Ciba-Geigy, Switzerland.