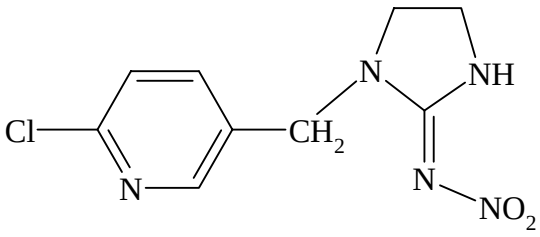
# IMIDACLOPRID
# 582




| | |
|---|---|
| *ISO common name* | Imidacloprid |
| *Chemical name* | 1-(6-Chloro-3-pyridylmethyl)-*N*-nitroimidazolidin-2-ylideneamine (IUPAC); 1-[(6-chloro-3-pyridinyl)methyl]-4,5-dihydro-*N*-nitro-1*H*-imidazol-2-amine (CA; *105827-78-9*) |
| *Empirical formula* | $C_9H_{10}ClN_5O_2$ |
| *RMM* | 255.7 |
| *m.p.* | 143.8°C |
| *v.p.* | $4 \times 10^{-10}$ Pa at 20 °C |
| *Solubility* | In water: 510 mg/l at 25 °C; acetonitrile: 50 g/l; toluene: 0.69 g/l |
| *Description* | Colourless crystalline solid |
| *Stability* | Stable under normal storage conditions and in neutral and weakly acidic media; slow hydrolysis in aqueous alkaline environment |
| *Formulations* | Wettable powders, emulsifiable concentrates, suspension concentrates and granules |

# IMIDACLOPRID TECHNICAL
*__582__/TC/(M)/-

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

**2 Identity tests**

**2.1 HPLC.** Use the HPLC method below. The relative retention time obtained from the sample should not deviate by more than 1 % from that of the standard obtained under the same conditions.

**2.2 Infrared.** Prepare potassium bromide disks from the sample and from a pure standard taking 2 mg of material and 1 g potassium bromide. Scan the disk from 1700 to 1400 $cm^{-1}$ using a Fourier Transform IR spectrometer. The spectrum obtained from the sample should not differ significantly from that of the standard (Fig 16).

**2.3 $^{1}$H-NMR** Weigh into a bottle (15 ml) fitted with a Polyseal cap sufficient sample to contain 2 ± 0.02 g imidacloprid. Add deutero-chloroform (1.5 to 2 ml), cap the bottle and place it in an ultrasonic bath for 15 min. Filter a portion of the solution through a 0.45 µm filter into a FT-NMR flask. Record the NMR spectrum. Reference the spectrum to the solvent peak at 7.26 ppm and compare it from 4.3 – 0.0 ppm with the spectrum of pure imidacloprid (Fig 17).

**3 Imidacloprid**

OUTLINE OF METHOD The sample is extracted with acetonitrile and determined by reversed phase liquid chromatography using propiophenone as internal standard.

REAGENTS

*Acetonitrile* HPLC grade
*Methanol* HPLC grade
*Water* HPLC grade
*Mobile phase* acetonitrile-water, 60 + 40 (v/v), thoroughly degassed
*Imidacloprid* standard of known purity. Store under refrigeration.
*Propiophenone* internal standard
*Internal standard solution.* Dissolve propiophenone (25 g) in methanol (1 l).
*Calibration solution.* Weigh (to the nearest 0.1 mg) into a bottle (150 ml) imidacloprid standard ( about 200 mg, *s* mg). Add by pipette internal standard solution (5.0 ml) and acetonitrile (95 ± 10 ml). Cap the bottle with a Polyseal lid, place it in an ultrasonic bath for 1 min, and then mix thoroughly. Transfer 100 (± 20) µl of this solution to an auto-injection

* Provisional AOAC-CIPAC method 1997

vial (2 ml). Add acetonitrile (1 to 1.5 ml) to the vial, cap and mix thoroughly.

APPARATUS

*High performance liquid chromatograph* able to generate more the 7 MPa pressure and equipped with an auto-injector and a spectrophotometric detector capable of measuring at 252 nm

*Chromatographic column* 250 × 4.6 mm (i.d.) packed with 5 µm octadecyl-silane bonded silica gel

*Electronic integrator* or *data system*

*Mechanical shaker*

*Ultrasonic bath*

*Sampler* riffle type

*Filter* porosity 0.45 µm, solvent compatible

PROCEDURE

*(a) .Operating conditions* (typical)

| | |
|---|---|
| *Mobile phase* | acetonitrile – water, 60 + 40 (v/v) |
| *Column temperature* | ambient |
| *Flow rate* | about 1.2 ml/min |
| *Injection volume* | 1µl, 10 µl for the formulation with fertiliser |
| *Detector wavelength* | 252 nm |
| *Retention times* | imidacloprid: about 2.1 min<br>internal standard: 4.1 min |

*(b)Equilibration of the system.* Pump the mobile phase through the column or at least 15 min and until the system is equilibrated (flat baseline). Adjust the operating parameters so that the elution times of the imidacloprid and propiophenone peaks are within 1.9 to 2.5 and 4.0 to 4.4 min respectively. Make repetitive injections of the calibration solution and calculate the response ratios by dividing the imidacloprid peak areas by that of the internal standard peak areas. The response ratios for the calibration solution injections (*R'*) must agree within ± 1 % for two consecutive injections before continuing.

*(c)Preparation of the sample solution.* Weigh (to the nearest 0.1 mg) into a bottle (150 ml) enough sample to contain about 200 mg (*w* mg) imidacloprid. Add by pipette internal standard solution (5.0 ml) and acetonitrile (95 ± 10 ml). Cap the bottle with a Polyseal lid, place it in an ultrasonic bath for 1 min, and then mix .thoroughly. Filter the sample through a 0.45µm porosity filter. Transfer 100 (± 20) µl of this solution to an auto-injection vial (2 ml). Add acetonitrile (1 to 1.5 ml) to the vial, cap and mix thoroughly.

*(e) Determination.* Inject duplicate amounts of each sample solution (no more than 3 samples, i.e. 6 injections) between bracketing standard solution injections. Calculate the response ratios of the sample injections (*R*) by dividing the imidacloprid peak areas by the internal standard peak areas. The response ratios of the sample injections must agree within ± 1 % (± 0.5 % of their average). If not, repeat the determination starting with the calibration injections. Re-inject the calibration solution. Average the response ratios of the calibration solution injections immediately preceding and following the sample solution injections. These must agree within ± 1 % (± 0.5 % of their average) or repeat any portion of the determination that does not meet this criterion.

*(d)Calculation.*

$$R' = \frac{H_s}{I_r}$$

$$R = \frac{H_w}{I_q}$$

$$\text{Content of imidacloprid} = \frac{R'_a \times s \times P}{R_a \times w} \text{ g/kg}$$

where:

| | | |
|---|---|---|
| $H_s$ | = | area of the imidacloprid peak in the calibration solution |
| $H_w$ | = | area of the imidacloprid peak in the 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 |
| $R_a$ | = | average of the two response ratios of the calibration solution injections |
| $R'_a$ | = | average of the two response ratios of the sample solution injections |
| $s$ | = | mass of imidacloprid in the calibration solution (mg) |
| $w$ | = | mass of sample taken (mg) |
| $P$ | = | purity of the imidacloprid standard (g/kg) |

**Repeatability r** = 14 g/kg at 977 g/kg active ingredient content
**Reproducibility R** = 31 g/kg at 977 g/kg active ingredient content

## IMIDACLOPRID WETTABLE POWDERS
## *582/WP/(M)/-

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

**2 Identity tests**
**2.1 HPLC.** As for imidacloprid technical **582**/TC/(M)/2.1.
**2.2 Infrared.** Weigh into a bottle (15 ml) fitted with a Polyseal cap sufficient sample to contain 0.15 ± 0.03 g imidacloprid. Add dichloromethane (2 ml), cap the bottle and place it in an ultrasonic bath for 15 min. Filter the solution through a 0.45 µm filter into a flask. Remove the solvent by rotary evaporation and continue as for imidacloprid technical **582**/TC/(M)/2.2.
**2.3 $^{1}$H-NMR** As for imidacloprid technical **582**/TC/(M)/2.3.

**3 Imidacloprid.** As for imidacloprid technical **582**/TC/(M)/3.

**Repeatability r** = 10 g/kg at 750 g/kg active ingredient content
**Reproducibility R** = 35 g/kg at 750 g/kg active ingredient content

## IMIDACLOPRID SUSPENSION CONCENTRATES
## *582/SC /(M)/-

**1 Sampling**. Take at least 1 l.

**2 Identity tests**
**2.1 HPLC.** As for imidacloprid technical **582**/TC/(M)/2.1.
2**.2 Infrared.** As for imidacloprid Wettable powders **582**/WP/(M)/2.2.
**2.3 $^{1}$H-NMR** As for imidacloprid technical **582**/TC/(M)/2.3.

**3 Imidacloprid.** As for imidacloprid technical **582**/TC/(M)/3 except:
*(c) Preparation of the sample solution.* Mix the sample thoroughly using a spatula, spoon or similar device. Dislodge any "caked" material from the bottom or sides of the container, re-disperse it and then vigorously shake the material for 1 min before sampling. Continue as for imidacloprid technical **582**/TC/(M)/3*(c)*.

**Repeatability r** = 3 g/kg at 214 g/kg active ingredient content
**Reproducibility R** = 14 g/kg at 214 g/kg active ingredient content

* Provisional AOAC-CIPAC method 1997

# IMIDACLOPRID GRANULES

[*] **582**/GR /(M)/-

**1 Sampling**. Take at least 1kg.

**2 Identity tests**

**2.1 HPLC.** As for imidacloprid technical **582**/TC/(M)/2.1.

2**.2 Infrared.** Weigh into a bottle (15 ml) fitted with a Polyseal cap sufficient sample to contain 0.10 ± 0.03 g imidacloprid. Add distilled water (5 ml) and dichloromethane (5ml), cap the bottle and shake it on a mechanical shaker for 30 min. Allow the layers to separate. Using a syringe, remove a few millilitres from the dichloromethane layer and filter the solution through a 0.45 µm filter into a flask. Remove the solvent by rotary evaporation and continue as for imidacloprid technical **582**/TC/(M)/2.2.

**2.3 $^{1}$H-NMR** Weigh into a bottle (15 ml) fitted with a Polyseal cap sufficient sample to contain 2 ± 0.02 g imidacloprid. Add deutero-chloroform (1.5 to 2 ml), cap the bottle and shake it on a mechanical shaker for 30 min. Filter a portion of the solution through a 0.45 µm filter into a FT-NMR flask. Record the NMR spectrum. Reference the spectrum to the solvent peak at 7.26 ppm and compare it from 4.3 – 0.0 ppm with the spectrum of pure imidacloprid (Fig 17).

**3 Imidacloprid.** As for imidacloprid technical **582**/TC/(M)/3 except:

*Calibration solution*. Weigh (to the nearest 0.1 mg) into a bottle (250 ml) imidacloprid standard ( about 200 mg, *s* mg). Add by pipette internal standard solution (5.0 ml) and acetonitrile (150 ± 10 ml). Cap the bottle with a Polyseal lid, place it in an ultrasonic bath for 1 min, and then mix thoroughly. Transfer 100 (± 20) µl of this solution to an auto-injection vial (2 ml). Add acetonitrile (1 to 1.5 ml) to the vial, cap and mix thoroughly.

and

*(c)Preparation of the sample solution.* Pour the entire sample across the centre of a riffle type sampler, collecting the riffled portions in the metal trays. Select one of the portions to continue riffling until a riffled portion of sample is between 35 to 45 g. Weigh (to the nearest 10 mg) the entire portion (*w* mg) into a bottle (250 ml). Take care to transfer all dust in the

[*] Provisional AOAC-CIPAC method 1997

sample bottle. Pipette internal standard solution (5.0 ml) into the bottle and add acetonitrile (150 ± 10 ml). Cap the bottle with a Polyseal lid. Shake the bottle on a mechanical shaker for 60 min and allow the insoluble material to settle. Filter the supernatant solution through a 0.45µm porosity filter, collecting 100 (± 20) µl into an auto-injection vial (2 ml). Add acetonitrile (1 to 1.5 ml), to the vial, cap and mix thoroughly.

**Repeatability r** = 0.8 g/kg at 10.5 g/kg active ingredient content
**Reproducibility R** = 1.0 g/kg at 10.5 g/kg active ingredient content

## IMIDACLOPRID FERTILISER FORMULATIONS

[*] **582**/XX /(M)/-

**1 Sampling**. Take at least 1kg.

**2 Identity tests**

**2.1 HPLC.** As for imidacloprid technical **582**/TC/(M)/2.1.

**2.2 Infrared** As for imidacloprid granules **582**/GR/(M)/2.2.

**2.3 $^{1}$H-NMR** Weigh into a bottle (15 ml) fitted with a Polyseal cap sufficient sample to contain 2 ± 0.02 g imidacloprid. Add deutero-chloroform (1.5 to 2 ml), cap the bottle and shake it on a mechanical shaker for 30 min. Filter a portion of the solution through a 0.45 µm filter into a FT-NMR flask. Record the NMR spectrum. Reference the spectrum to the solvent peak at 7.26 ppm and compare it from 4.3 – 0.0 ppm with the spectrum of pure imidacloprid (Fig 17).

**3 Imidacloprid.** As for imidacloprid technical **582**/TC/(M)/3 except:

*Calibration solution*. Weigh (to the nearest 0.1 mg) into a bottle (250 ml) imidacloprid standard ( about 200 mg, *s* mg). Add by pipette internal standard solution (5.0 ml) and methanol (150 ± 10 ml). Cap the bottle with a Polyseal lid, place it in an ultrasonic bath for 1 min, and then mix thoroughly. Transfer 100 (± 20) µl of this solution to an auto-injection vial (2 ml). Add methanol (1 to 1.5 ml) to the vial, cap and mix thoroughly.

and

[*] Provisional AOAC-CIPAC method 1997

*(c)Preparation of the sample solution.* Pour the entire sample across the centre of a riffle type sampler, collecting the riffled portions in the metal trays. Select one of the portions to continue riffling until a riffled portion of sample is between 35 to 45 g. Weigh (to the nearest 10 mg) the entire portion (*w* mg) into a bottle (250 ml). Take care to transfer all dust in the sample bottle. Pipette internal standard solution (5.0 ml) into the bottle, add methanol (95 ± 10 ml) and cap the bottle with a Polyseal lid. Shake the bottle on horizontally a mechanical shaker for 60 min and allow the insoluble material to settle. Filter a portion of the supernatant solution through a 0.45 µm porosity filter into an auto-injection vial (2 ml).

**Repeatability r** = 0.8 g/kg at 10.5 g/kg active ingredient content
**Reproducibility R** = 1.0 g/kg at 10.5 g/kg active ingredient content

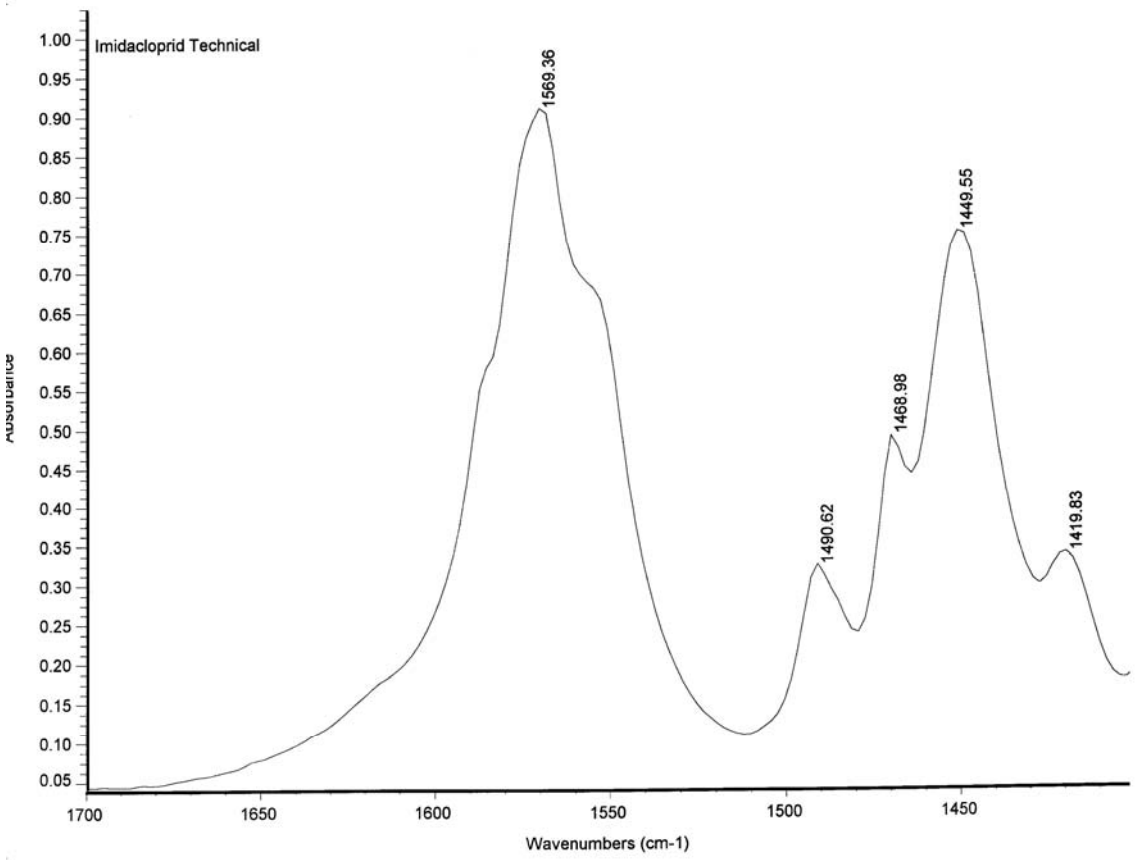



**Fig. 16** Infrared spectrum of imidacloprid technical

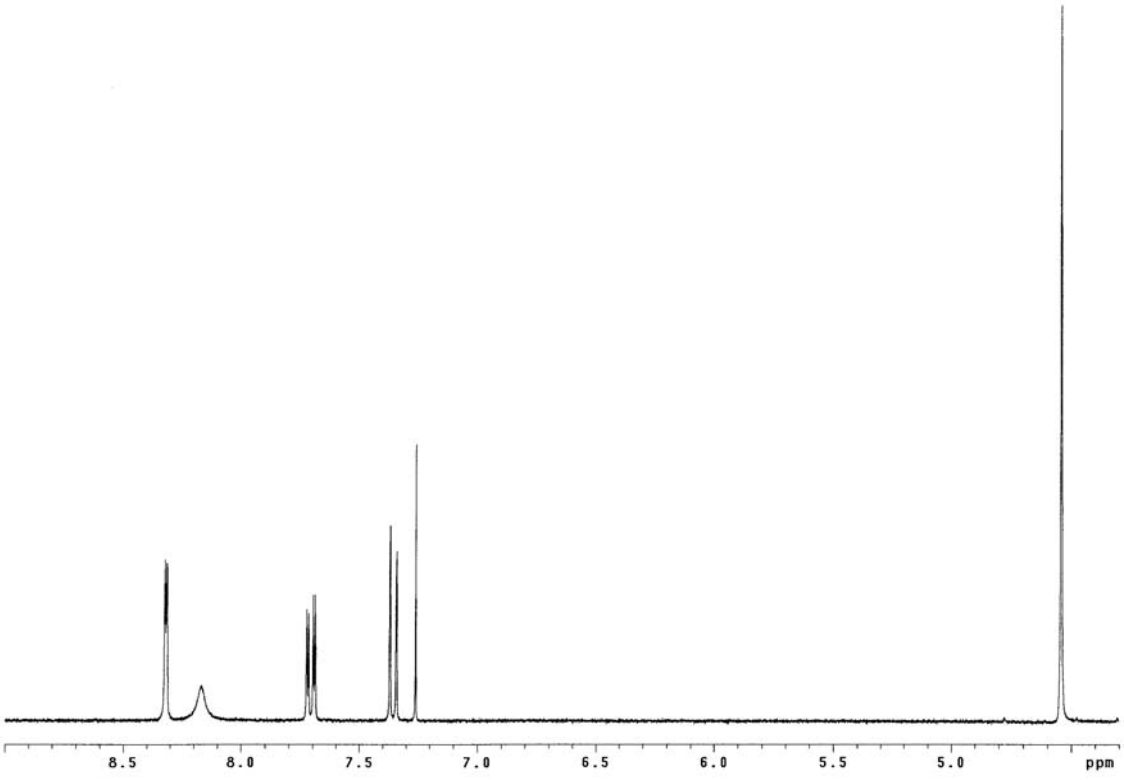



**Fig. 17** $^{1}$H-NMR spectrum of imidacloprid