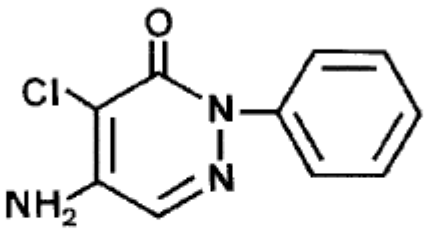
CHLORIDAZON

111



ISO common name	Chloridazon
Other names	Pyrazon
Chemical name	5-Amino-4-chloro-2-phenyl-2*H*-pyridazin-3-one (IUPAC); 5-amino-4-chloro-2-phenyl-3(2*H*)-pyridazinone (CA; *1698-60-8*)
Empirical formula	$C_{10}H_8ClN_3O$
RMM	221·6
m.p.	205–206°C
v.p.	Less than 10^{-5} Pa at 20°C
Solubility	In water: 0·4 g/kg at 20°C; in methanol: 34 g/kg; in acetone: 28 g/kg; in benzene: 0·7 g/kg; in dichloromethane: 3·3 g/kg; in ethyl acetate: 6 g/kg at 20°C
Description	The pure material is a white crystalline solid with faint characteristic odour (the technical material usually contains some of the 4-amino-5-chloro-isomer)
Stability	At least 2 years at normal conditions
Formulations	Wettable powders and suspension concentrates

CHLORIDAZON TECHNICAL

***111**/TC/M/–

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

2 **Identity tests**

2.1 **Infrared.** Prepare potassium bromide discs from the sample and from pure chloridazon using 1·3 to 1·5 mg material and 300 mg potassium bromide. Scan the

* CIPAC method 1986. Prepared by the German Committee (DAPA), Chairman Dr W Dobrat. Based on a method supplied by BASF (FRG).

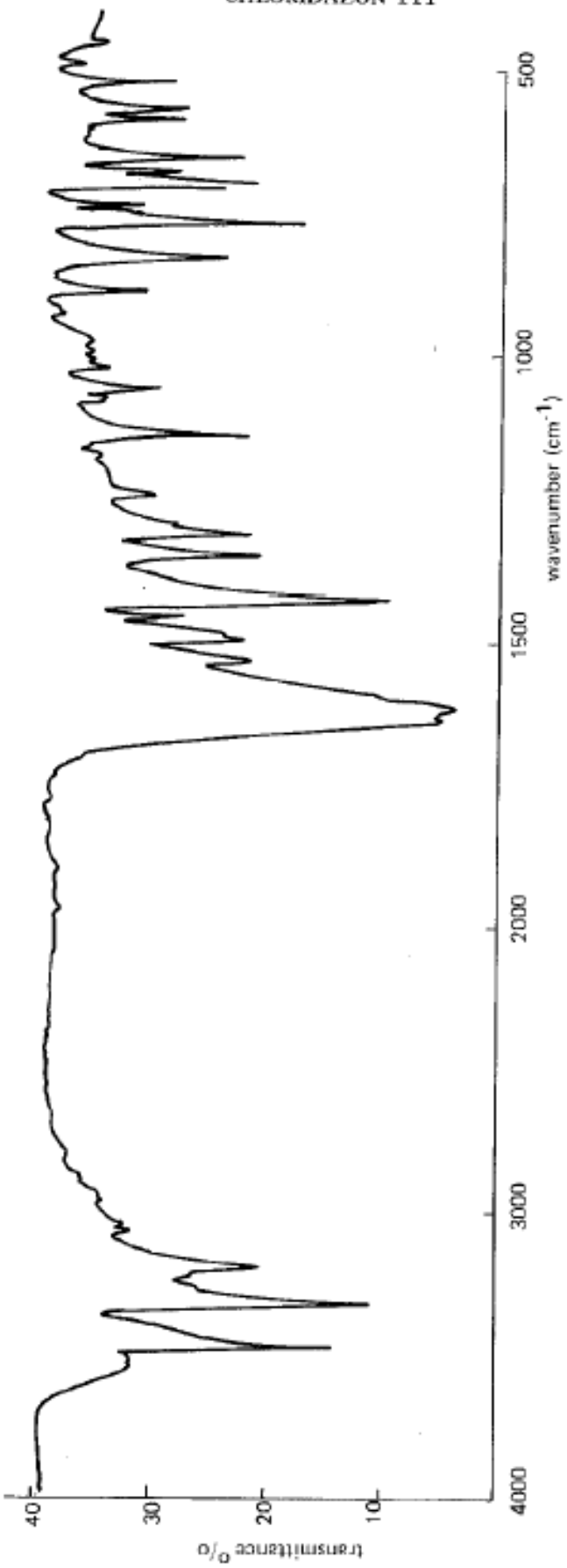


Fig. 2 IR spectrum of chloridazon pure (KBr disc).

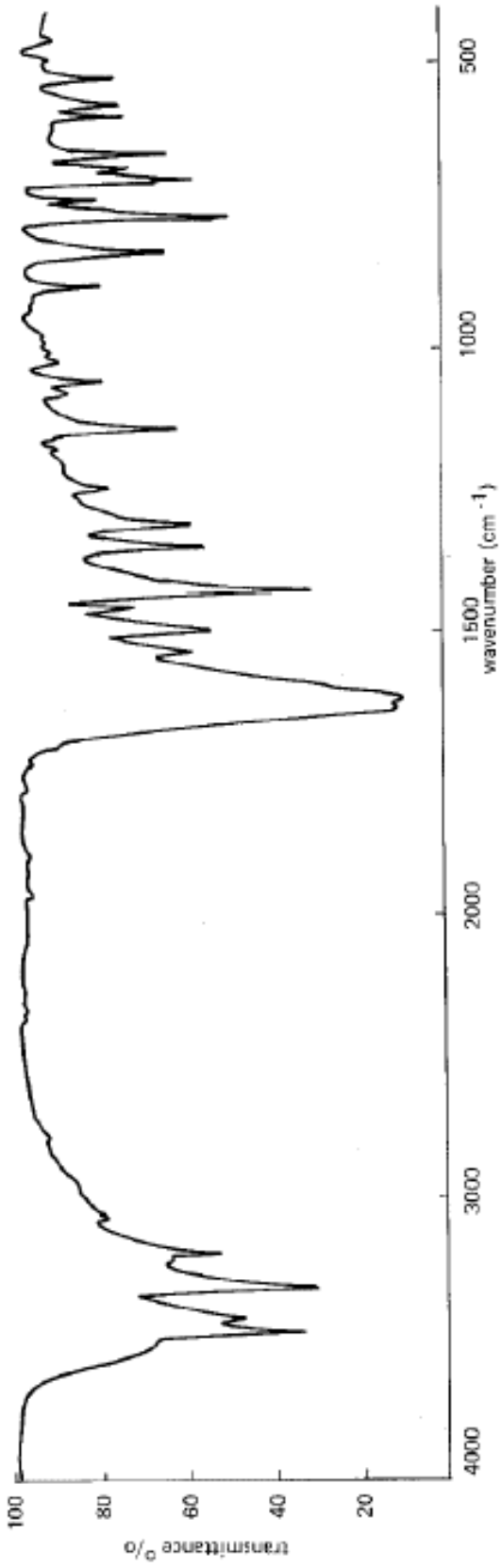


Fig. 3 IR spectrum of chloridazon technical (KBr disc).

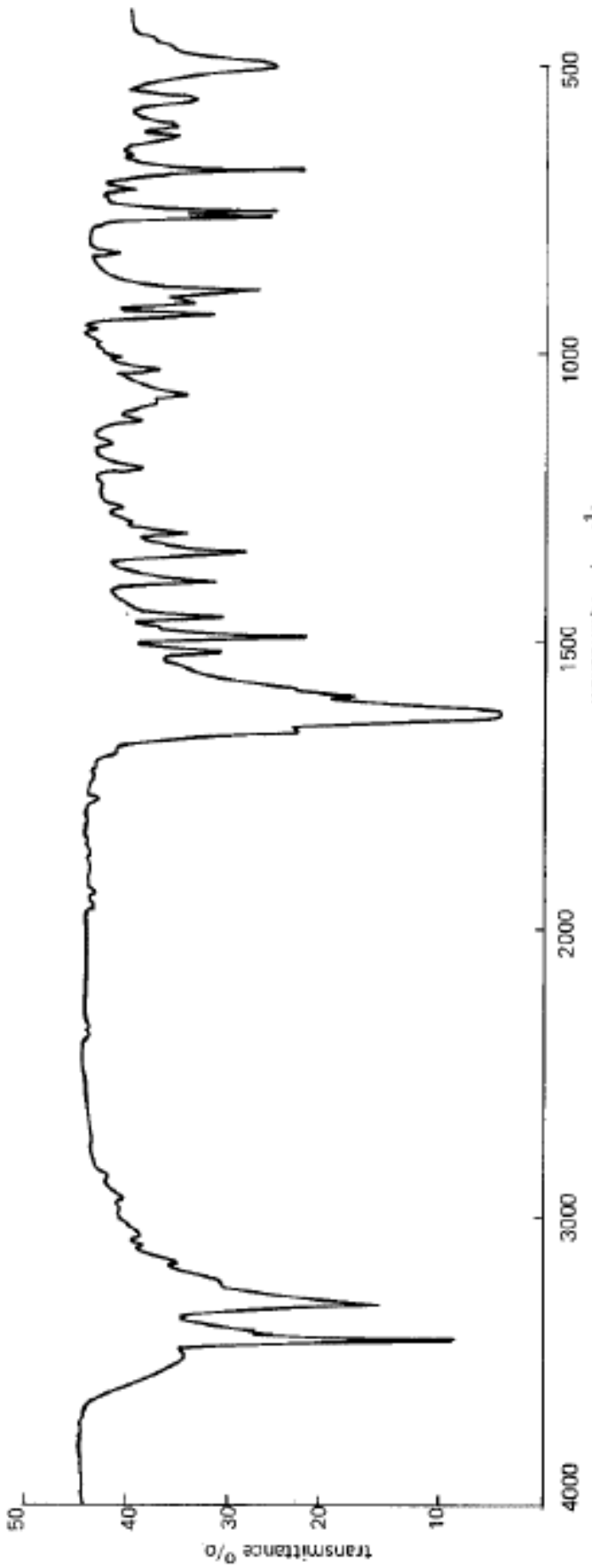


Fig. 4 IR spectrum of the pure 4-amino-5-chloro-isomer (KBr disc)

discs from 4000 to 400 cm^{-1}. The spectrum produced from the sample disc should not differ significantly from that from the standard (Fig. 2). If a sharp additional absorption band at 3428 cm^{-1} is observed, the 4-amino-5-chloro isomer of chloridazon is present, too (Fig. 3; compare Fig. 4).

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

3 Chloridazon

OUTLINE OF METHOD The active ingredient is chromatographed by HPLC on a reverse phase C18 column using methanol/water as mobile phase, and quantitatively determined by UV detection with external calibration.

REAGENTS

Methanol HPLC grade
Water HPLC grade
Mobile phase methanol-water 60 + 40 (v/v)
Chloridazon standard of known purity
Calibration solutions. Weigh (to the nearest (0·1 mg) about 70–80 mg of pure chloridazon (*s* mg) into a 100 ml volumetric flask and dissolve quantitatively in 60 ml methanol by means of an ultrasonic bath. Add 39 ml of water and mix. Then cool down to room temperature, make up to volume with water, and mix well. Pipette 10·0 ml of this solution into a 100 ml volumetric flask and make up to volume with mobile phase. Adjust the amount of chloridazon (*s* mg) such that the peak height is not more than 0·8 AUFS (absorbance unit full scale). In case of doubt, check the linearity of the detector. Prepare two calibration solutions of similar concentrations. Do not use the same calibration solutions for periods longer than one week.

APPARATUS

HPLC system, consisting of:

high precision HPLC pump
injection valve with 10 µl loop, e.g. Rheodyne 7125
stainless steel column 250 × 4 mm, packed with LiChrosorb RP18 7 µm from Merck or equivalent
variable wavelength UV detector with linear response at high absorbance values, e.g. Perkin Elmer LC 75
data system with recorder for peak evaluation

PROCEDURE

(a) *Chromatographic conditions:*

Column	stainless steel column 250 × 4 mm
Stationary phase	LiChrosorb RP18, 7 µm, Merck e.g. Hibar prepacked column from Merck
Mobile phase	methanol/water, 60/40 (v/v)
Injection volume	10 µl

Flow rate	1 ml/min
Detector wavelength	286 nm
Detector sensitivity	1 absorbance unit full scale
Chart speed	1 cm/min
Retention times	chloridazon: about 5 min 4-amino-5-chloro-isomer: about 7 min
Temperature	ambient

(*b*) *Preparation of sample solutions*. Weigh (to the nearest 0·1 mg) into a 100 ml volumetric flask enough sample (*w* mg) to contain about 70–80 mg pure chloridazon. Dissolve in 60 ml methanol by means of an ultrasonic bath. Add 39 ml of water and mix, then cool down to room temperature, make up to volume with water, and mix well. Pipette 10·0 ml of this solution into a 100 ml volumetric flask and make up to volume with mobile phase. The concentration of chloridazon should be similar to its concentration in the calibration solutions. Prepare two solutions for each sample.

(*c*) *Determination of chloridazon*. Inject 10 µl portions of both the calibration solutions. Inject each calibration solution at least two times and calculate the average peak area related to the corresponding mass (*s* mg). The individual values should not deviate from the mean by more than ±0·8%, otherwise repeat the calibration. Then inject in duplicate 10 µl portions of each sample solution bracketing them by injections of the calibration solutions as follows: calibration solution I, sample solution 1, sample solution 1, calibration solution II, sample solution 2, sample solution 2, calibration solution I, sample solution 3, sample solution 3, calibration solution II, and so on for other sample solutions. Measure the relevant peak areas. Calculate the mean value of each pair of calibration factors (*f*) bracketing two sample injections and use this value for evaluating the two bracketed sample runs.

(*d*) *Calculation*

Calibration factor:

$$f = \frac{H_s}{s}$$

where:

H_s = peak area of chloridazon in the calibration solution
s = mass of chloridazon standard in the calibration solution (mg)

$$\text{Chloridazon content} = \frac{H_w \cdot P}{f \cdot w} \text{ g/kg}$$

where:

H_w = peak area of chloridazon in the sample solution
w = mass of the sample taken (mg)
P = purity of chloridazon standard (g/kg)

The content of chloridazon is the mean value of the results of the two sample solutions.

Repeatability r_{95} = 13·1 g/kg at 844 g/kg active ingredient content
Reproducibility R_{95} = 24·2 g/kg at 844 g/kg active ingredient content
Based on a study with 22 participants and 110 values.

CHLORIDAZON WETTABLE POWDERS

*111/WP/M/–

1 Sampling. Take at least 1 kg.

2 Identity tests. As for **111**/TC/M/2.

3 Chloridazon. As for **111**/TC/M/3 except:

(*b*) *Preparation of sample solutions.* Weigh (to the nearest 0·1 mg) into a 100 ml volumetric flask enough sample (*w* mg) to contain about 70–80 mg pure chloridazon. Add 60 ml of methanol and treat in an ultrasonic bath for 10 min. (Note that some formulation additives might be insoluble). Add 39 ml of water and mix. Then cool down to room temperature, make up to volume with water and mix well. Pipette 10·0 ml of the solution into a 100 ml volumetric flask and make up to volume with mobile phase. The concentration of chloridazon should be similar to its concentration in the calibration solutions. Prepare two solutions for each sample.

Repeatability r_{95} = 8·8 g/kg at 646 g/kg active ingredient content
Reproducibility R_{95} = 13·9 g/kg at 646 g/kg active ingredient content

Based on a study with 22 participants and 110 values.

4 Suspensibility

(*a*) *Preparation of suspension.* MT 15·1(i)

(*b*) *Determination of sedimentation.* MT 15·1(ii)

(*c*) *Determination of chloridazon in the bottom 25 ml of suspension.* After removal of the top 225 ml of suspension, transfer the 25 ml remaining in the cylinder to a tared evaporating dish. Rinse the cylinder with water (3 × 10 ml) to remove any residue and add the rinsings to the dish. Evaporate to nearly dryness on a boiling water bath. Dry in an oven at 100°C for 5 min, cool and reweigh. Extract the residue by ultrasonic treatment with methanol using successive portions of about 10 ml. Transfer quantitatively to a 100 ml volumetric flask and depending on the mass of the residue, choose the volume and the dilutions with methanol and subsequently with water in order to obtain a final concentration of about 70–80 mg/l chloridazon in methanol + water (60/40). Determine the chloridazon concentration in the methanol/water solution using the HPLC method.

* CIPAC method 1986. Prepared by the German Committee (DAPA), Chairman Dr W Dobrat. Based on a method supplied by BASF (FRG).

(*d*) *Calculation of suspensibility*

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

where:

c = mass of chloridazon in the sample taken for the preparation of the suspension (g)

Q = mass of chloridazon in the bottom 25 ml of suspension (= mass (g) of chloridazon in the methanol/water solution)

CHLORIDAZON SUSPENSION CONCENTRATES

*111/SC/M–

1 Sampling. Take at least 1 l.

2 Identity tests. As for **111**/TC/M/2.

3 Chloridazon. As for **111**/TC/M/3 except:

(*b*) *Preparation of sample solution.* Thoroughly shake the sample container to assure that the suspension is homogeneous. Immediately weigh (to the nearest 0·1 mg) into a 100 ml volumetric flask enough sample (w mg) to contain about 70–80 mg of pure chloridazon. Continue according to **111**/TC/M/3b.

Repeatability r_{95} = 4·4 g/kg at 361 g/kg active ingredient content
Reproducibility R_{95} = 12·0 g/kg at 361 g/kg active ingredient content
Based on a study with 22 participants and 110 values.

4 Suspensibility

(*a*) *Preparation of suspension and determination of sedimentation* MT 161, CIPAC 1C, *p. 2294*

(*b*) *Determination of chloridazon in the bottom 25 ml of suspension.* As for **111**/WP/M/4.

* CIPAC method 1986. Prepared by the German Committee (DAPA), Chairman Dr W Dobrat. Based on a method supplied by BASF (FRG).