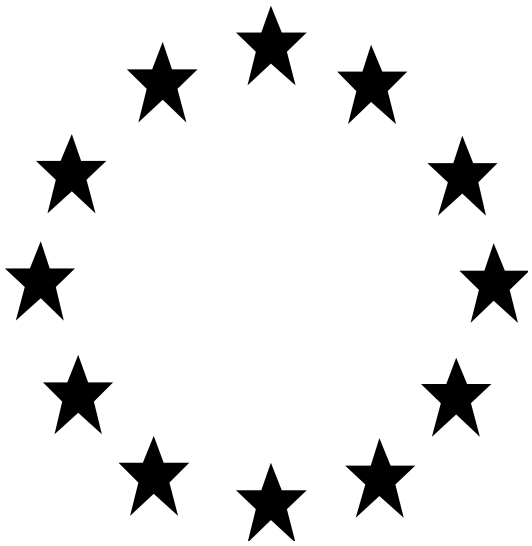


Draft Assessment Report (DAR)

- public version -

Initial risk assessment provided by the rapporteur Member State Germany for the existing active substance

CHLORIDAZON

of the third stage (part A) of the review programme referred to in Article 8(2) of Council Directive 91/414/EEC

Volume 3, Annex B, B.1 – B.5

July 2005

Draft
Assessment Report

12 December 2004

Chloridazon

Volume 3

Annex B

Summary, Scientific Evaluation and Assessment

Rapporteur Member State: Germany

Contents

Annex B

Chloridazon

B-1: Identity

B.1 Identity

B.1.1 Identity of the active substance (Annex IIA 1 and 3.1)

B.1.1.1 Name and address of applicant(s) for inclusion of the active substance in Annex I (Annex IIA 1.1)

Applicant:
BASF Aktiengesellschaft
Agricultural Products
Global Product Safety & Registration
P.O. Box 120
D-67114 Limburgerhof

Contact:
[redacted]

Alternative person:
[redacted]

Affiliates or representatives:
BASF Aktiengesellschaft
Agricultural Products
Business Management
P.O. Box 120
D-67114 Limburgerhof

Contact
[redacted]

B.1.1.2 Common name and synonyms (Annex IIA 1.3)

Chloridazon (ISO)
Pyrazon (USA, Canada, Denmark, Poland)
PAC (Japan)

B.1.1.3 Chemical name (Annex IIA 1.4)

IUPAC: 5-amino-4-chloro-2-phenylpyridazin-3(2H)-one

CAS: 5-amino-4-chloro-2-phenyl-3(2H)-pyridazinone

B.1.1.4 Manufacturer's development code number (Annex IIA 1.5)

BAS 119 H, LAB 13 033, Reg. No.13 033

B.1.1.5 CAS, EEC and CIPAC numbers (Annex IIA 1.6)

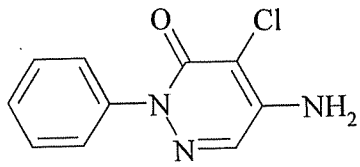
CAS: 1698-60-8
CIPAC: 111
EEC No.: 216-920-2
EG Index No.:606-035-00-3

B.1.1.6 Molecular and structural formulae, molecular mass (Annex IIA 1.7)

Molecular formular: $C_{10}H_8ClN_3O$

Molecular mass: 221.65 g/mol

Structural formula:



B.1.1.7 Manufacturer or manufacturers of the active substance (Annex IIA 1.2)

[redacted]

[redacted]

B.1.1.8 Method or methods of manufacture (Annex IIA 1.8)

Confidential information, see Annex C.

B.1.1.9 Specification of purity of the active substance (Annex IIA 1. 9)

920 g/kg (minimum purity) which is in line with the FAO specification (AGP: CP/346, 1997)

B.1.1.10 Identity of isomers, impurities and additives (Annex IIA 1.10)

Confidential information, see Annex C.

B.1.1.11 Analytical profile of batches (Annex IIA 1.11)

Confidential information, see Annex C.

B.1.2 Identity of the plant protection product (Annex IIIA 1)

B.1.2.1 Current, former and proposed trade names and development code numbers (Annex IIIA 1.3)

Trade Name: Pyramin WG, Pyramin DF

Code Number:	Plant Protection Product:	BAS 119 33 H
	Active Substance:	Chloridazon or BAS 119 H
	BASF internal No.:	Reg. No. 013 033

B.1.2.2 Manufacturer or manufacturers of the plant protection product (Annex IIIA 1.2)

[redacted]

B.1.2.3 Type of the preparation and code (Annex IIIA 1.5)

Water dispersible granule (WG).

B.1.2.4 Function (Annex IIA 3.1; Annex IIIA 1.6)

Herbicide.

B.1.2.5 Composition of the preparation (Annex IIIA 1.4)

Confidential information, see Annex C.

B.1.3 References relied on

Annex point/ reference number	Author(s)	Year	Title source (where different from company) report no. GLP or GEP status (where relevant), published or not BBA registration number	Data protection claimed Y/N	Owner
AIIA-1.8; AIIA-1.9; AIIA-1.10; AIIA-1.11	Keller, E.	2003	Dossier for the Evaluation of the Plant Protection Product BAS 119 33 H containing chloridazon - Doc J. 2002/1000193 not GLP, unpublished CHE2003-1062	Y	BAS
AIIA-1.8	Ohnsorge, U.	2003	Chloridazon TC - Process of Manufacture and Beginning Materials. 2003/1011756 not GLP, unpublished CHE2003-1061	Y	BAS
AIIA-1.9; AIIA-1.10	Ohnsorge, U.	2001	Chloridazon TC - Composition of the Techn. Active Ingredient. 2001/1009903 not GLP, unpublished CHE2001-643	Y	BAS
AIIA-1.10; AIIA-4.1; AIIA-4.1.2	Liesner, M.	1991	Validation of HPLC method CP 012 for determination of technical impurities of chloridazon (pyrazon). 1991/10089; PCP01086 GLP, unpublished CHE2001-570	Y	BAS
AIIA-1.10	Ohnsorge, U.	2004	Chloridazon TC - coverage of impurities by tox. studies. 2004/1019814 not GLP, unpublished CHE2004-1412	Y	BAS
AIIA-1.10	Ohnsorge, U.	2004	Requirements for chloridazon EU Re-Registration. 2004/1020018 not GLP, unpublished CHE2004-1540	Y	BAS
AIIA-1.10	Ohnsorge, U.	2004	Chloridazon TC - composition certified limits, rationale. 2004/1005088 not GLP, unpublished CHE2004-1410	Y	BAS
AIIA-1.10	Schmidt	1986	Charakterisierung von Chloridazon techn. (N121). 1986/1001471 not GLP, unpublished CHE2004-1414	Y	BAS

[1] Only notifier listed

Annex point/ reference number	Author(s)	Year	Title source (where different from company) report no. GLP or GEP status (where relevant), published or not BBA registration number	Data protection claimed Y/N	Owner[1]
AIIA-1.11	Liesner, M.	1991	Composition of five batches of technical chloridazon (pyrazon) by HPLC. 91/10104 GLP, unpublished CHE2001-644	Y	BAS

Codes of owner

BAS: BASF Aktiengesellschaft

Annex B

Chloridazon

B-2: Physical and chemical properties

B.2 Physical and chemical properties

B.2.1 Physical and chemical properties of the active substance (Annex IIA 2)

Table B.2.1-1: Summary of the physical and chemical properties of the active substance chloridazon

Section (Annex point)	Study	Purity (w/w)	Method	GLP	Results	Comment / Conclusion	Reference
B.2.1.1.1 (IIA 2.1)	Melting point, freezing point or solidification point of purified active substance	99.9	OECD 102 (Capillary method) (DSC)	Y	205.9 - 206.8 °C 207 °C		Daum, 1999 (CHE2001-645)
B.2.1.1.2 (IIA 2.1)	Boiling point of purified active substance					see B.2.1.1.3	
B.2.1.1.3 (IIA 2.1)	Temperature of decomposition or sublimation	99.9	OECD 102 (DSC)	Y	Thermal conversion is not observed up to 360 °C.		Daum, 1999 (CHE2001-645)
B.2.1.2 (IIA 2.2)	Relative density of purified active substance	99.9	OECD 109 ≡ EEC A3 (gas pyknometer)	Y	$D_4^{20} = 1.51$		Kästel, 1999 (CHE2001-647)
B.2.1.3.1 (IIA 2.3)	Vapour pressure of purified active substance	99.9	EEC A 4 (effusion method)	Y	$1 \cdot 10^{-9}$ Pa (20 °C) $3 \cdot 10^{-9}$ Pa (25 °C), both calculated		Kästel, 1999 (CHE2001-647)
B.2.1.3.2 (IIA 2.3)	Volatility, Henry's law constant of purified active substance		Calculation	N	$5.3 \cdot 10^{-10}$ Pa m^3 mol^{-1} (20 °C) water solubility: 420 mg/L vapour pressure: $1 \cdot 10^{-9}$ Pa		Mayer-Rentschler, 2000 (CHE2004-1387)

Section (Annex point)	Study	Purity (w/w)	Method	GLP	Results	Comment / Conclusion	Reference
B.2.1.4.1 (IIA 2.4)	Appearance: physical state	99.9 93.0	Visual assessment	Y Y	crystalline soild solid		Daum, 1999 (CHE2001-645) Panek, 1990 (CHE2001-648)
B.2.1.4.2 (IIA 2.4)	Appearance: colour	99.9 93.0	Visual assessment	Y Y	colourless light yellow-brown or straw		Daum, 1999 (CHE2001-645) Panek, 1990 (CHE2001-648)
B.2.1.4.3 (IIA 2.4)	Appearance: odour	99.9 93.0	Organoleptic assessment	Y Y	odourless faint grassy or herbal		Daum, 1999 (CHE2001-645) Panek, 1990 (CHE2001-648)
B.2.1.5.1 (IIA 2.5)	Spectra of purified active substance	99.9	UV/VIS	Y	λ_{max} [nm] ε 210 18577 229 25043 286 10088 300 7949		Daum, 1999 (CHE2001-649)
			IR NMR MS		Spectra are consistent with given structure of chloridazon.		
B.2.1.5.2 (IIA 2.5)	Spectra for impurities of toxicological, ecotoxicological or environmental concern		IR NMR MS		No impurities of toxicological or environmental significance.		

Section (Annex point)	Study	Purity (w/w)	Method	GLP	Results	Comment / Conclusion	Reference
B.2.1.6 (IIA 2.6)	Solubility in water of purified active substance	99.9	OECD 105 ≡ EEC A6 (flask method)	Y	0.422 g/L (deionised water) 0.422 g/L (pH 7) 0.410 g/L (pH 4) all at 20 °C		Daum, 2000 (CHE2001-650)
B.2.1.7 (IIA 2.7)	Solubility in organic solvents of the active substance as manufactured	99.8	EPA No. 63-8	Y	at 20 °C [g/L] Acetone 12.4 Acetonitrile 8.4 Ethyl acetate 3.7 Toluene 0.1 Dichlormethane 0.19 *n*-Heptane insoluble Methanol 15.1 Iso-Propanol 5.4 Octanol 3.1 Olivenöl 0.2 Lutrol® 26.7		Redeker, 1991 (CHE2001-651)
B.2.1.8 (IIA 2.8)	Partition coefficient of purified active substance	98.8 (radiopurity)	OECD 107 (shaking method)	N	log $P_{O/W}$ = 1.2 (25 °C)		Patel, 1987 (CHE2003-1064)
B.2.1.9.1 (IIA 2.9)	Hydrolysis rate of purified active substance	> 97.7 (radiopurity)	EPA No. 161-1	N	stable at pH 5, 7 and 9 at 25 °C for 30 d		Ellenson und Brem, 1988 (WAS2001-267)
B.2.1.9.2 (IIA 2.9)	Direct phototransformation in purified water of purified active substance	99 (radiopurity) >97.7	EPA Subdivision N § 161-2, 161-3 EPA 161-2	Y Y	[4,5-^{14}C]chloridazon: DT_{50}: 150 h (25 °C, pH 7, 342 h irradiation within 3 weeks) No none-volatile degradation products were greater than 10 % of appl. radioactivity. 18 % of TRR were volatile product. 9 % was likely to be CO_2.		Ellenson et al. 1989 (LUF) Tanaka, 1992 (LUF)

Section (Annex point)	Study	Purity (w/w)	Method	GLP	Results	Comment / Conclusion	Reference
B.2.1.9.3 (IIA 2.9)	Quantum yield of direct photodegradation	98.9 (radiopurity)	OECD Draft Test Guideline (1990)	Y	$\Phi = 2 \cdot 10^{-4}$ mol/Einstein Frank/Klöpffer calculation DT_{50}: 75.6 d March 36.8 d April 25.9 d May 21.6 d June		Sarafin, 1992 (LUF9800155) Scharf, 1999 (LUF2001-225)
B.2.1.9.4 (IIA 2.9)	Dissociation constant (pK_a) of purified active substance	99.9	OECD 112 (titration method)	Y	Chloridazon does not dissociate in water, no pK_a value could be determined.		Daum, 1999 (WAS2001-268)
B.2.1.10 (IIA 2.10)	Stability in air, indirect phototransformation		Calculation Atkinson AOPWIN 1.88	N	$K_{OH} = > 34.2 \cdot 10^{-12}$ cm³molecule^{-1} s^{-1}. DT_{50}: < 0.29 d [12 h day, $8 \cdot 10^5$ OH radicals/cm³]		von Götz, 2000 (LUF2001-226)
B.2.1.11.1 (IIA 2.11)	Flammability of active substance as manufactured	93.5	EEC A 10	Y	The test substance is not considered highly flammable.		Löffler, 1999 (CHE2001-652)
B.2.1.11.2 (IIA 2.11)	Autoflammability of active substance as manufactured	93.5	EEC A 16	Y	The test substance does not ignite up to 400 °C.		Löffler, 1999 (CHE2001-652)
B.2.1.12 (IIA 2.12)	Flash point of the active substance as manufactured				Not applicable as the melting point of chloridazon is above 40 °C.		

Section (Annex point)	Study	Purity (w/w)	Method	GLP	Results	Comment / Conclusion	Reference
B.2.1.13 (IIA 2.13)	Explosive properties of active substance as manufactured	93.5	EEC A 14	Y	No thermal or mechanical sensitivity with respect to shock or friction was observed.		Löffler, 1999 (CHE2001-652)
B.2.1.14 (IIA 2.14)	Surface tension	99.9	EEC A 5	Y	71.7 mN/m (0.5 % w/w) 72.1 mN/m (1.0 % w/w) 71.7 mN/m (0.5 % and 2.0 % w/w) all at 20 °C	The substance cannot be regarded as surface active.	Kästel, 1999 (CHE2001-647)
B.2.1.15 (IIA 2.15)	Oxidising properties of active substance as manufactured		EEC A 17	Y	Chloridazon has no oxidising potential. The molecule contains no moiety which is of oxidising potential.		Löffler, 1999 (CHE2001-652)

B.2.1.16: Summary of data presented under points B.2.1.1 to B.2.1.15

Chloridazon is a colourless stable solid (mp. 206 - 207 °C). It is poorly soluble in most of the tested organic solvents and slightly soluble in water. The vapour pressure ($1 \cdot 10^{-9}$ Pa) and volatility ($5.3 \cdot 10^{-10}$ Pa m^3 mol^{-1}, 20 °C) of chloridazon are very low. The active substance is hydrolytically stable and undergoes rapidly a photolytical degradation.
Under the test conditions the technical material is not explosive, has no auto-ignition temperature and does not burn.

B.2.2 Physical, chemical and technical properties of the plant protection products (Annex IIIA 2)

Product name: Pyramin WG (containing 650 g/kg chloridazon, WG)

Table B.2.2-1: Summary of the physical, chemical and technical properties of the plant protection product

Section (Annex point)	Study	Method	Results	Comment/Conclusion	Reference
B.2.2.1.1 (IIIA 2.1)	Appearance: colour	Visual assessment	Dark brown	Acceptable	Kaestel, R. (1999) PHY2001-517
B.2.2.1.2 (IIIA 2.1)	Appearance: odour	Olfactory assess-ment	Moderate smoky	Acceptable	Kaestel, R. (1999) PHY2001-517
B.2.2.1.3 (IIIA 2.1)	Appearance: physical state	Visual assessment	Solid	Acceptable	Kaestel, R. (1999) PHY2001-517
B.2.2.2.1 (IIIA 2.2)	Explosive properties		The active substance and the formulants have no potential for explosivity due to their chemical structure. The substances have no chemical groups indicating explosive properties. Exam-ples are given in table A6.1 of appendix 6 in the 'Manual of Tests and Criteria of the United Na-tions'.	Acceptable	Loeffler, U. (1999) PHY2001-518
B.2.2.2.2 (IIIA 2.2)	Oxidising properties		The test has not been carried out because neither the active ingredient nor the formulants have oxidising properties. The molecules contain no moiety which is of oxidising nature (see appen-dix 6 in the 'Manual of Tests and Criteria of the United Nations').	Acceptable	Loeffler, U. (1999) PHY2001-518
B.2.2.3.1 (IIIA 2.3)	Flash point		Not relevant.		

Section (Annex point)	Study	Method	Results	Comment/Conclusion	Reference
B.2.2.3.2 (IIIA 2.3)	Flammability	EEC A 10	Not highly flammable.	Acceptable	Loeffler, U. (1999) PHY2001-518
B.2.2.3.3 (IIIA 2.3)	Auto-flammability	EEC A 16	Not self-ignitable.	Acceptable	Loeffler, U. (1999) PHY2001-518
B.2.2.4.1 (IIIA 2.4)	Acidity/alkalinity		Not necessary due to pH-value.		
B.2.2.4.2 (IIIA 2.4)	pH	CIPAC MT 75.2	8.9 at 1 % concentration in CIPAC water D; after accelerated storage for 2 weeks at 54 °C: 8.7 at 1 % concentration in CIPAC water D	Acceptable	Kaestel, R. (1999) PHY2001-517
B.2.2.5.1 (IIIA 2.5)	Kinematic viscosity		Not applicable.		
B.2.2.5.2 (IIIA 2.5)	Dynamic viscosity		Not applicable.		
B.2.2.5.3 (IIIA 2.5)	Surface tension	EEC 5 1.6.1 (Plate Method)	55.1 mN/m (at 0.5 % concentration) 51.1 mN/m (at 1.0 % concentration) 45.6 mN/m (at 2.0 % concentration)	Acceptable	Kaestel, R. (1999) PHY2001-517
B.2.2.6.1 (IIIA 2.6)	Relative density		Not applicable.		
B.2.2.6.2 (IIIA 2.6)	Bulk (tap) density	CIPAC MT 169	Pour: 571 g/L Tap: 656 g/L	Acceptable	Kaestel, R. (1999) PHY2001-517
B.2.2.7.1 (IIIA 2.7)	Storage stability	CIPAC MT 46	Physically and chemically stable after storage for 2 weeks at 54 °C. There is less than 1 % decrease in the active substance content. The alteration of the observed physical properties (pH-range, suspensibility, dispersibility, wet sieving, dust content) are negligible.	Acceptable	Kaestel, R. (1999) PHY2001-517
B.2.2.7.2 (IIIA 2.7)	Low temperature stability		No liquid preparation.		

Section (Annex point)	Study	Method	Results	Comment/Conclusion	Reference
B.2.2.7.3 (IIIA 2.7)	Shelf-life	GIFAP Monograph 17	Physically and chemically stable after storage for 2 years at ambient temperature. The product shows no loss of active substance over the storage period. The alteration of the observed physical properties (appearance, pH-value, suspensibility, wet sieving, wettability, dispersibility, persistent foaming, dustiness) are negligible.	Acceptable	Kaestel, R. (2001) PHY2001-519; Kaestel, R. (2001) PHY2001-520; Kaestel, R. (2001) PHY2001-521; Koenig, W. (2001) PHY2003-467
B.2.2.8.1 (IIIA 2.8.1)	Wettability	CIPAC MT 53.3	0 s (without swirling in CIPAC water D)	Acceptable	Kaestel, R. (1999) PHY2001-517
B.2.2.8.2 (IIIA 2.8.2)	Persistent foaming	CIPAC MT 47.1	Foam after 1 min: 0 mL (at 2.0 % concentration in CIPAC water C)	Acceptable	Kaestel, R. (1999) PHY2001-517
B.2.2.8.3.1 (IIIA 2.8.3)	Suspensibility	CIPAC MT 168	96 % (at 2.0 % concentration in CIPAC water D) After accelerated storage for 2 weeks at 54 °C: 86 % (at 2.0 % concentration in CIPAC water D)	Acceptable	Kaestel, R. (1999) PHY2001-517
B.2.2.8.3.2 (IIIA 2.8.3)	Spontaneity of dispersion	CIPAC MT 174	91 % After accelerated storage for 2 weeks at 54 °C: 90 %	Acceptable	Kaestel, R. (1999) PHY2001-517
B.2.2.8.4 (IIIA 2.8.4)	Dilution stability		Not applicable.		
B.2.2.8.5 (IIIA 2.8.5)	Wet sieve test	CIPAC MT 167	Residue on a 75 µm sieve: 0 % After accelerated storage for 2 weeks at 54 °C: Residue on a 75 µm sieve: 0 %	Acceptable	Kaestel, R. (1999) PHY2001-517

Section (Annex point)	Study	Method	Results	Comment/Conclusion	Reference
B.2.2.8.6.1 (IIIA 2.8.6)	Particle size distribution	Laser light diffraction spectrometry, MALVERN Mastersizer S CIPAC MT 170 Air jet sieving	Suspension medium: Water 10 % < 0.5 µm 90 % < 4.9 µm R ≤ 10 %: 500 µm R ≥ 90 %: 75 µm R ≤ 50 µm: 0.7 %	Acceptable	Kaestel, R. (1999) PHY2001-517
B.2.2.8.6.2 (IIIA 2.8.6)	Dust content	CIPAC MT 171	< 0.8 mg	Acceptable	Kaestel, R. (1999) PHY2001-517
B.2.2.8.6.3 (IIIA 2.8.6)	Attrition	DAPF method Fk 81, Fk 36.1, Method is equivalent to CIPAC MT 178.2	Fine portion ≤ 50 µm: 1.8 %	Acceptable	Kaestel, R. (1999) PHY2001-517
B.2.2.8.7.1 (IIIA 2.8.7)	Emulsifiability, emulsion stability and re-emulsifiability		Not applicable.		
B.2.2.8.7.2 (IIIA 2.8.7)	Stability of dilute emulsion		Not applicable.		
B.2.2.8.8.1 (IIIA 2.8.8)	Flowability	CIPAC MT 172	100 % (through a 5 mm sieve spontaneously)	Acceptable	Kaestel, R. (1999) PHY2001-517
B.2.2.8.8.2 (IIIA 2.8.8)	Pourability (rinsability)		Not applicable.		
B.2.2.8.8.3 (IIIA 2.8.8)	Dustability		Not applicable.		

Section (Annex point)	Study	Method	Results	Comment/Conclusion	Reference
B.2.2.9.1 (IIIA 2.9)	Physical compatibility with other products	ASTM method E 1518-93	2 different mixtures of BAS 119 33 F/ WH 15931 with other plant protection products were tested. All of them were determined to be compatible in aqueous tank mixtures. Test substances: BAS 119 33 F and BAS 9150 3 H/ FH 15346 (Betanal Progress OF) or BAS 517 22 H/ WH 14009 (Focus Ultra)	Acceptable	Kaestel, R. (1999) PHY2001-522
B.2.2.9.2 (IIIA 2.9)	Chemical compability with other products	ASTM method E 1518-93	There were no indications of chemical reactions between the mixed products.	Acceptable	Kaestel, R. (1999) PHY2001-522
B.2.2.10 (IIIA 2.10)	Adherence and distribution to seeds		No seed dressing formulation.		

B.2.2.11: Summary and evaluation of data presented under points B.2.2.1 to B.2.2.10 (IIIA 2.11)

Pyramin WG is a dark brown, free flowing water dispersible granule with a moderate smoky odour. It has neither explosive nor oxidising properties and it is not highly flammable. Its pH-value of 8.9 lies within the naturally occurring range. The results of the accelerated storage test and the shelf life test confirm its stability at least for two years under practical and commercial conditions. Its technical properties indicates no particular problems when used as recommended.

B.2.3 References relied on

Annex point/ reference number	Author(s)	Year	Title source (where different from company) report no. GLP or GEP status (where relevant) published or not BBA registration number	Data protection claimed Y/N	Owner[1]
AIIA-2.1.1; AIIA-2.1.3; AIIA-2.4; AIIA-2.4.1; AIIA-2.4.2	Daum, A.	1999	Determination of the melting point and the appearance of chloridazon (Reg No. 13033; BAS 119H). 99/10866 GLP, unpublished CHE2001-645	Y	BAS
AIIA-2.1.2	Iijima, K.	2000	Screening test for thermal stability of chloridazon. 2000/1013459 GLP, unpublished CHE2001-646	Y	BAS
AIIA-2.2	Anonymos	1999	Excerpt regarding dangerous goods. 1999/1009036 not GLP, published CHE2004-1396	N	-
AIIA-2.2; AIIA-2.3.1; AIIA-2.14	Kästel, R.	1999	Physical Properties of chloridazon (PAI). 99/10293 GLP, unpublished CHE2001-647	Y	BAS
AIIA-2.3.2	Mayer-Rentschler, U.	2000	Henry's law constant of chloridazon. 2000/1023132 not GLP, unpublished CHE2004-1387	Y	BAS
AIIA-2.3.2	Ohnsorge, U.	2000	Henry's law constant for chloridazon. BASF 2000/1003870 not GLP, unpublished LUF2001-223	Y	BAS

[1] Only notifier listed

Annex point/ reference number	Author(s)	Year	Title source (where different from company) report no. GLP or GEP status (where relevant), published or not BBA registration number	Data protection claimed Y/N	Owner[1]
AIIA-2.4; AIIA-2.4.1; AIIA-2.4.2	Panek, E.J.	1990	Product chemistry: Determination of the colour, physical state, odor, melting point, bulk density and pH of chloridazon (pyrazon) TGAI. 90/5047 GLP, unpublished CHE2001-648	N	BAS
AIIA-2.5; AIIIA-2.5.1	Daum, A.	1999	UV-, NMR-, IR, MS-Spectra of chloridazon (BAS 119H, Reg. No. 13033). 99/11439 GLP, unpublished CHE2001-649	Y	BAS
AIIA-2.6	Daum, A.	2000	Determination of the solubility in water of chloridazon (Reg. No. 13033, BAS 119H). 2000/1013487 GLP, unpublished CHE2001-650	Y	BAS
AIIA-2.7	Redeker, J.	1991	Determination of the Solubility of Chloridazon in Organic Solvents at 20 °C. 91/10098 GLP, unpublished CHE2001-651	N	BAS
AIIA-2.8	Patel, J. R.	1987	Partition Coefficient (1-octanol/water)of ^{14}C-Pyrazon at 25+/-1 °C. Report No. M8719. 87/5075 not GLP, unpublished CHE2003-1064	N	BAS
AIIA-2.9.1; AIIA-7.2.1.1	Ellenson, J.L. and Brem, G.	1988	Hydrolysis of ^{14}C-pyrazon in pH 5, 7 and 9 solutions at 25 degrees Celsius. BASF 88/5518 not GLP, unpublished WAS2001-267	N	BAS
AIIA-2.9.2; AIIA-7.2.1.2	Ellenson, J.L. et al.	1989	Photolysis of BAS 119 H in pH 7 aqueous solution at 25 degrees Celsius. BASF 89/5090 not GLP, unpublished LUF2001-228	N	BAS
AIIA-2.9.2; AIIA-7.2.1.2	Scharf, J.	1999	Photolytical halflife of chloridazon in the top layer of aqueous systems. BASF 99/10693 not GLP, unpublished LUF2001-225	Y	BAS

Annex point/ reference number	Author(s)	Year	Title source (where different from company) report no. GLP or GEP status (where relevant), published or not BBA registration number	Data protection claimed Y/N	Owner[1]
AIIA-2.9.2; AIIA-7.2.1.2	Tanaka, F.S.	1992	Aqueous photolysis of 14C-chloridazon at pH 7. BASF 92/5090 GLP, unpublished LUF2001-229	N	BAS
AIIA-2.9.3; AIIA-7.2.1.2	Sarafin, R.	1992	Chloridazon - Determination of quantum yield. BASF 1992/10441 GLP, unpublished LUF98-00155	N	BAS
AIIA-2.9.4	Daum, A.	1999	Determination of the dissociation constant of chloridazon (Reg. No. 13033, BAS 119H). BASF 99/10990 GLP, unpublished WAS2001-268	Y	BAS
AIIA-2.10; AIIA-7.2.2	Sarafin, R.	1992	Laboratory study on the volatilisation of chloridazon after application of BAS 119 33 H on soil and plant surface. BASF 92/11838 GLP, unpublished LUF98-00151	N	BAS
AIIA-2.10	von Götz N.	2000	Photochemical oxidative degradation of chloridazon (BAS 119 H) (QSAR Estimates). 1999/11873 not GLP, unpublished CHE2003-1256	Y	BAS
AIIA-2.10	von Götz, N.	2000	Photochemical oxidative degradation of chloridazon (BAS 119 H) (QSAR Estimates). BASF 99/11873 not GLP, unpublished LUF2001-226	Y	BAS
AIIA-2.11; AIIA-2.11.2; AIIA-2.13; AIIA-2.14; AIIA-2.15	Löffler, U.	1999	Evaluation of safety characteristics according to 92/68/EC (A9-A17). 99/11008 GLP, unpublished CHE2001-652	Y	BAS

Annex point/ reference number	Author(s)	Year	Title source (where different from company) report no. GLP or GEP status (where relevant), published or not BBA registration number	Data protection claimed Y/N	Owner[1]
AIIIA-2.1; AIIIA-2.4; AIIIA-2.5.3; AIIIA-2.6.1; AIIIA-2.6.2; AIIIA-2.7.1; AIIIA-2.8.1; AIIIA-2.8.2; AIIIA-2.8.3; AIIIA-2.8.5; AIIIA-2.8.6; AIIIA-2.8.8	Kästel, R.	1999	Physical and chemical properties of BAS 11933 H. 99/10294 GLP, unpublished PHY2001-517	Y	BAS
AIIIA-2.2; AIIIA-2.3	Löffler, U.	1999	Safety characteristics of the crop protection product BAS 11933 H. 99/10494 GLP, unpublished PHY2001-518	Y	BAS
AIIIA-2.7; AIIIA-4.1.3	Kästel, R.	2001	Shelf life in original container of BAS 119 33 H, 24-month-storage - Physical properties. 2001/1009093 GLP, unpublished PHY2001-519	Y	BAS
AIIIA-2.7	König, W.	2001	Amendment No. 1 to study code PCF 01958: Shelf life in original container of BAS 119 33 H, 24 month storage - analytical results. 2001/1010606 GLP, unpublished PHY2003-467	Y	BAS
AIIIA-2.7	König, W.	2001	Shelf Life Study of BAS 11933 H - Analytical Results. 2001/1009105 GLP, unpublished PHY2001-521	Y	BAS
AIIIA-2.9.2	Kästel, R.	1999	Physical and chemical compatibility in aqueous tank mixtures of BAS 11933 H with other products. 1999/10246 not GLP, unpublished PHY2001-522	Y	BAS

Codes of owner

BAS: BASF Aktiengesellschaft

Annex B

Chloridazon

B-3: Data on application
and further information

B.3 Data on application and further information

B.3.1 Data on application relevant to the active substance (Annex IIA 3.1 to 3.6)

B.3.1.1 Function

BAS 119 33 H is used as herbicide.

B.3.1.2 Effects on harmful organisms

BAS 119 33 H acts as a systemic soil and leaf herbicide.

B.3.1.3 Field of use

The use of chloridazon and its formulations is solely in the agricultural field.

B.3.1.4 Harmful organisms

The range of weeds which are susceptible (> 85 %) to chloridazon is represented by:

Apera spica-venti, Capsella bursa pastoris, Galeopsis tetrahit, Lamium purpureum, Matricaria chamomilla, Papaver rhoeas, Poa annua, Polygonum persicaria, Senecio vulgaris, Sinapis arvensis, Solanum nigrum, Stellaria media, Thlaspi arvensis, Veronica hederifolia and *persica*

Weeds which are less susceptible (60 - 85 %) to chloridazon:

Amaranthus retroflexus, Anagallis arvensis, Atriplex patula, Centaurea cyanus, Chenopodium album, Lamium amplexicaule, Mercurialis annua, Myosotis arvensis, Polygonum aviculare, Polygonum convolvulus, Raphanus raphanistrum, Viola arvensis

Not sufficiently controlled (< 60 % weed control) by chloridazon:

Agropyron repens, Cirsium arvense, Convolvulus arvensis and *Calystegia arvensis, Euphorbia spec., Fumaria officinalis, Galium aparine*

B.3.1.5 Mode of action

The pyridazinone compound chloridazon belongs to the group of photosynthesis inhibitor herbicides.

The herbicidal effects of chloridazon are primarily due to its inhibition of the photosynthetic electron transport within the chloroplasts through binding to the D1-protein of photosystem II. When applied pre-plant incorporated, pre- or post-emergence, the compound selectively

controls important annual broad-leaved weeds in sugar and fodder beets as well as redbeet and mangels.

Plant uptake and translocation. The selective systemic herbicide is rapidly absorbed by the roots and shoot parts with translocation acropetally and, to a lower extent, basipetally to all plant parts. When applied pre-emergence, chloridazon is taken up via the roots and shoot parts of the plant influenced by the soil moisture, temperature and slightly by the relative humidity.

Mechanism of selectivity. Studies on the mechanism of selectivity of chloridazon showed no notable differences in the uptake of the compound between weeds and the crop species sugar beet.

Since the metabolic degradation of chloridazon was found to be more rapid in the crop species than in weeds, it is suggested that the mechanism of herbicide selectivity lies in a different rate of metabolism.

B.3.1.6 Information on the occurrence or possible occurrence of the development of resistance and appropriate management strategies

Chloridazon belongs to the chemical class of the pyridazinones. Chloridazon acts as a photosynthesis inhibitor in the chlorophyll biosynthesis pathway.

In spite of their long term use and broad spectrum of weeds targeted no resistance in weeds has evolved to the chlorophyll biosynthesis inhibitors as a result of selection pressure due to these herbicides. Chloridazon was registered in 1966 in Europe and used primarily as the single preemergence herbicide. Since 1972 with the registration of phenmedipham also combinations at postemergence application were established to minimise the risk of resistant plants.

Today the application of chloridazon is mostly preemergence with two postemergence applications of soil and leaf herbicides to follow in order to provide a season long weed and grass control.

In summary, the risk of developing resistance in target weeds when applying chloridazon is low.

B.3.2 Data on application relevant to the plant protection product (Annex IIIA 3)

B.3.2.1 Field of use envisaged

The use of chloridazon and its formulations is solely in the agricultural field.

B.3.2.2 Effects on harmful organisms

BAS 119 33 H acts as a systemic soil and leaf herbicide.

B.3.2.3 Details of intended use

BAS 119 33 H has been used predominantly in beet crops.

B.3.2.4 Application rate

The application rate is 4.0 kg/ha of the preparation BAS 119 33 H. In terms of active ingredient, this is 2600 g as/ha.

B.3.2.5 Concentration of active substance in material used

Under the assumption that in practical farming the spray volume varies between 200 and 400 L/ha, the concentration of the active substance in the spray varies between 13 g/L and 6.5 g/L.

B.3.2.6 Method of application

The intended method of application is spraying by means of each type of spraying equipment which is normally used in practical agricultural production.

B.3.2.7 Number and timing of applications and duration of protection

The number of applications is 1 (one) - 3 (three). The timing of the application is between pre seeding resp. pre-emergence up to crop growth stage 19 (BBCH Code). The growth of weeds should not exceed the growth stage 14 -16 (BBCH Code).

B.3.2.8 Necessary waiting periods or other precautions to avoid phytotoxic effects on succeeding crops

It is not necessary to establish waiting periods or other precautions to avoid phytotoxic effects on succeeding crops.

There are no limitations on the choice of succeeding crops in the full growing period. After a crop failure only sugar and fodder beet, beet root, maize and chard can be grown.

B.3.2.9 Proposed instructions for use

For effective weed control, chloridazon can be used pre- and post-emergence of the crop. In pre-emergence, the compound can be used prior to seeding with shallow incorporation into the soil, or after seeding of the crop. When soil moisture is a low, preplant incorporation (ppi) of chloridazon provides higher levels of herbicidal efficacy compared to applications after seeding of the crop.

At post-emergence, chloridazon is also taken up by the shoot of the weeds. For best effects in post-emergence, weeds should be small and soil should be moist.

In farming practice, chloridazon is usually integrated in spray sequences and tank mixes with other soil or foliar herbicides. Examples for common uses of chloridazon in sugar beets are

1. chloridazon in pre-emergence followed by two post-emergence applications of chloridazon in tankmix with phenmedipham and ethofumesate herbicides

2. three post-emergence applications of chloridazon in tankmix with phenmedipham and ethofumesate herbicides.

The summary of all information concerning pre-emergence application is given in Table B.3.2-1.

Table B.3.2-1 Effect of pre-emergence application on the effectiveness of: Pyramin WG (BAS 119 33 H, 65 % as/kg) at 3 and 4 kg/ha against weeds in sugar beets (applied using spray application equipment) – Average values over trials in sugar beets, carried out in the UK, in France and Germany. The years of testing range from 1985 to 1995.

	3.0 kg/ha Pyramin WG (50 - 100 days after treatment)		4.0 kg/ha Pyramin WG (50 - 100 days after treatment)	
	average	n	average	n
PFLANS	*1	67	1	68
AETCY	**25	5	40	17
ALOMY	35	1	65	5
AMARE	0	2	46	4
ANGAR	50	1	58	10
ANTAR	99	1		
APESV	98	2	100	1
ATXPA	76	5	81	4
BRSNW	35	5	48	5
CAPBP	86	5	96	7
CHEAL	52	40	74	42
FUMOF	23	5	19	5
GAETE	37	9		
GALAP	32	49	43	35
LAMAM	80	3	73	3
LAMPU	72	18	91	10
MATCH	93	20	96	16
MATIN	98	1	99	1
MERAN	33	14	57	26
MYOAR	78	2	81	2
POAAN	100	1	100	1
POLAV	58	8	76	11
POLCO	56	20	67	18
POLPE	56	6	83	3
RAPRA	40	1	77	11
SOLNI	50	4	85	4
SONAR	76	2	84	2
STEME	70	25	84	22

	3.0 kg/ha Pyramin WG (50 - 100 days after treatment)		4.0 kg/ha Pyramin WG (50 - 100 days after treatment)	
	average	n	average	n
THLAR	67	7	99	7
VERPE	86	10	89	7
VIOAR	92	9	63	7

* PFLANS = first evaluation at 1 - 2 leaf stage of weeds and grasses
** Herbicidal efficacy on weeds and grasses = third evaluation > 40 days after application

pre-emergence = just after seeding time up to one week after seeding

The summary information concerning post-emergence application is given in Table B.3.2-2.

Table B.3.2-2 Effect of rate of application at postemergence application on the effectiveness of Pyramin WG (BAS 119 33 H, (65 % as/kg)) against weeds in sugar beets (applied using spray application equipment) - Average values from 45 trials carried out in Europe in the year 1986 – 1999

	Pyramin post-emergence		Pyramin post-emergence	
	3.0 kg/ha	**n**	**4.0 kg/ha**	**n**
PFLANS	*0	24	0	17
AMARE			38	2
ANGAR	**55	1	70	1
ATXPA	40	2	47	1
CAPBP	98	3		
CHEAL	44	14	49	4
FUMOF	63	1		
GALAP	22	13	61	4
LAMPU	78	6	84	2
MATIN	97	1	97	1
POAAN	92	2		
POLAV	74	3	27	4
POLCO	60	11	84	5
POLPE	92	1		
STEME	60	10	67	4
THLAR	91	4	100	2
VERPE	72	5	94	3
VIOAR	38	5		

*PFLANS = first evaluation at 1 - 2 leaf stage of weeds and grasses
**Herbicidal efficacy on weeds and grasses = third evaluation > 40 days after application

The number of weeds sufficiently controlled by chloridazon is lower than at pre-emergence. But several important weeds are still strongly affected. Thus, chloridazon is a valuable partner for other post-emergence herbicides.

Table B.3.2-3 gives an example of a spray program containing chloridazon + Betanal Progress in post-emergence.

Table B.3.2-3 Effect of Pyramin WG + Betanal Progress repeated 3 times at post-emergence application against weeds in sugar beets (applied using spray application equipment) - Average values from 60 trials carried out in Europe in the year 1991 – 1999

	Pyramin WG + Betanal Progress post-emergence	
	3 x (1 + 1.5) L, kg/ha	n
PFLANS	*0	60
ALOMY	**8	1
AMARE	85	13
ATXPA	97	1
BRSNW	87	6
CAPBP	99	5
CHEAL	98	44
FUMOF	72	3
GALAP	94	31
LAMAM	100	3
LAMPU	99	10
MATCH	95	17
MATIN	100	1
MERAN	89	8
POAAN	100	4
POLAV	91	11
POLCO	99	26
POLPE	23	4
SOLNI	99	2
SONAR	100	6
STEME	100	9
THLAR	100	9
VERPE	100	3
VIOAR	99	7

* PFLANS = first evaluation at 1 - 2 leaf stage of weeds and grasses
** Herbicidal efficacy on weeds and grasses = third evaluation > 40 days after application

The direct comparison of the efficacy of soil + leaf herbicide to the solo leaf herbicide shows the advantage of the combination of soil and leaf herbicide (Table B.3.2-4).

Different weeds, like AMARE, ATXPA, FUMOF, MATCH and STEME were better controlled than with the contact herbicide only.

Table B.3.2-4 **Effect of Pyramin WG + Betanal Progress (3 x (1.0 + 1.5) L, kg/ha compared to 3 times 2 L/ha Betanal Progress solo) at post-emergence application on weeds in sugar beets (applied using spray application equipment) -Average values from 26 trials carried out in Europe in the year 1986 – 1999**

[redacted]

B.3.3 Summary of data on application

Summary of representative uses evaluated (Chloridazon, 12.12.2004)

Crop and/ or situation	Member State or Country	Pro-duct name	F G or I	Pests or Group of pests Controlled	Formulation		Application				Application rate per treatment			PHI (days)	Remarks:
(a)			(b)	(c)	Type (d-f)	Conc. of g as/kg (i)	Method, Kind (f-h)	Growth stage & Season (j)	Num-ber min max (k)	Interval between applica-tions (min)	kg as/hL min max	Water L/ha min max	kg as/ha min max	(l)	(m)
Northern Europe															
Beta beet, onion, shallot, garlic, flowers and nursery			F	Weeds (general) up to BBCH 14-16	WG	650	Hydraulic sprayer overall	Pre-seeding Pre-emergence up to BBCH 19	1 3	-	0.65 - 1.3	200 - 400	max. 2.6	[1)]	supported under the provision: max. of 2.6 kg/ha only every third year on the same field
Southern Europe															
Beta beet			F	Weeds (general) up to BBCH 14-16	WG	650	Hydraulic sprayer overall	Pre-seeding Pre-emergence up to BBCH 19	1	-	0.43 - 1.3	200 - 600	max. 2.6	[1)]	supported under the provision: max. of 2.6 kg/ha only every third year on the same field

(a) For crops, the EU and Codex classifications (both) should be used; where relevant, the use situation should be described (*e.g.* fumigation of a structure)
(b) Outdoor or field use (F), glasshouse application (G) or indoor application (I)
(c) *e.g.* biting and suckling insects, soil born insects, foliar fungi, weeds
(d) *e.g.* wettable powder (WP), emulsifiable concentrate (EC), granule (GR)
(e) GCPF Codes - GIFAP Technical Monograph No 2, 1989
(f) All abbreviations used must be explained
(g) Method, *e.g.* high volume spraying, low volume spraying, spreading, dusting, drench
(h) Kind, *e.g.* overall, broadcast, aerial spraying, row, individual plant, between the plant - type of equipment used must be indicated
(i) g/kg or g/L
(j) Growth stage at last treatment (BBCH Monograph, Growth Stages of Plants, 1997, Blackwell, ISBN 3-8263-3152-4), including where relevant, information on season at time of application
(k) Indicate the minimum and maximum number of application possible under practical conditions of use
(l) PHI - minimum pre-harvest interval/[1)] PHI covered by conditions of use
(m) Remarks may include: Extent of use/economic importance/restrictions/RMS: not/supported by available data

B.3.4 Further information on the active substance (Annex IIA 3.7 to 3.9)

B.3.4.1 Recommended methods and precautions concerning handling, storage, transport or fire (Annex IIA 3.7)

Ref.: Gerlach, 2002 (CHE2003-455, Safety data sheet)
Doc. MII

Wear personal protection according to the risk classification and the safety recommendations as given in annex point 10 when handling chloridazon TC.

Store in original container, tightly closed in a dry and well-ventilated place. Avoid temperatures above 40 °C. Do not store with food or feeding-stuff. Keep out of reach of unauthorised persons.

On contact with eye: wash affected eyes immediately for at least 15 minutes under running water with eyelids held open.

On ingestion: rinse mouth immediately and then drink plenty of water, get medical attention.
On skin contact: wash thoroughly with soap and water.

If inhaled: keep patient calm, remove to fresh air, summon medical help.
After inhalation of thermal degradation products administer dexamethasone aerosol without delay.

In the case of combustion CO_2/CO, H_2O, N_2/NO_x and HCl will be generated.

Sprayed water, foam, CO_2, extinguishing powder or sand are suitable extinguishing media.
Fire-fighters shall wear full protection including self-contained breathing apparatus. Fire fighting water is to be contained.

B.3.4.2 Emergency measures in the case of an accident (Annex IIA 3.9)

Ref.: Schenk, 1994 (CHE2001-654)
Doc MII

Chloridazon is classified as efficiently adsorbable onto activated carbon under neutral pH conditions.

Conclusion:
Contaminated solid should be incinerated. In the case of contamination of water the undissolved amount of the product is to be separated by appropriate measures (e.g. filtration). The aqueous phase is to be treated with approximately 1000 mg/L of activated powdered carbon for at least 12 hrs. The separated activated carbon should be incinerated, too. The treated (pH 6.5 - 9) water is to be introduced into a public sewer leading to public owned water treatment works (POTW).

B.3.5 Further information on the plant protection product (Annex IIIA 4)

B.3.5.1 Packaging (type, materials, size, etc.), compatibility of the preparation with proposed packaging materials (Annex IIIA 4.1)

B.3.5.1.1 Description of packaging (Annex IIIA 4.1.1)

BAS 119 33 H is to be marketed in square folding cartons and in square-bottom paper bags, both with an inner barrier of laminated paper/polyethylene, or laminated paper/aluminium/ polyethylene. The bags are heat sealed.

1 kg folding carton:	material:	Cardboard solid fibreboard with inner paper/polyethylene bag
	size:	140 – 180 mm(L) x 80 - 90 mm(W) x 170 - 250 mm(H)
	seal:	heat-sealing
5 kg folding carton:	material:	Cardboard solid fibreboard with inner paper/polyethylene bag
	size:	235 – 239 mm(L) x 148 – 154 mm(W) x 283 – 384 mm(H)
	seal:	heat-sealing
1 kg folding carton:	material:	Cardboard solid fibreboard with inner paper/aluminium/polyethylene bag
	size:	140 – 180 mm(L) x 80 - 90 mm(W) x 170 - 250 mm(H)
	seal:	heat-sealing
5 kg folding carton:	material:	Cardboard solid fibreboard with inner paper/aluminium/polyethylene bag
	size:	235 – 239 mm(L) x 148 – 154 mm(W) x 283 – 384 mm(H)
	seal:	heat-sealing
1 kg bag:	material:	Laminated paper with polyethylene
	size:	153 mm(L) x 72 mm(W) x 381 mm(H)
	seal:	heat -sealing
5 kg bag:	material:	Laminated paper with polyethylene
	size:	240 mm(L) x 120 mm(W) x 640 mm(H)
	seal:	heat -sealing

B.3.5.1.2 Suitability of packaging (Annex IIIA 4.1.2)

Reference number: PHY2001-523
Report: Schreiner (2000)
EU Performance Tests
BASF AG,
Ludwigshafen, Germany
unpublished
Guidelines: None
GLP: No

Reference number: PHY2001-524
Report: Schreiner (2000)
EU Performance Tests
BASF AG,
Ludwigshafen, Germany
unpublished
Guidelines: None
GLP: No

Reference number: PHY2001-525
Report: Schreiner (2000)
EU Performance Tests
BASF AG,
Ludwigshafen, Germany
unpublished
Guidelines: None
GLP: No

EU performance tests were done with the formulation Pyramin WG in 1 kg solid fibre board boxes and 1 kg self-opening square bottom paper bags. The bags, square folding cartons and the outer packagings for Pyramin WG meet the ADR requirements. They are labelled individually with all the use instructions. Several folding cartons are packed in cardboard boxes.
These combination packs meet the requirements of UN 4G/Y (packaging group II) as specified by the ADR/RID regulations for the transport of hazardous goods.

B.3.5.1.3 Resistance of packaging material to its contents (Annex IIIA 4.1.3)

Reference number: PHY2001-519
Report : Kaestel, R., (2001):
Shelf life in original container of BAS 119 33 H, 24 month storage – physical properties
BASF AG, Agrarzentrum Limburgerhof, Limburgerhof, Germany Fed.Rep.,
unpublished
April 26, 2001

Guidelines:	EU directive 91/414 Annex III, paragraph 2.7.3 and GIFAP Monograph No. 17 paragraph 6.2 at 20 °C with 50 % rel. humidity and at 30 °C for 24 months in original container.
GLP:	No
Test material:	Pyramin WG, batch No. 97-1, content of as: 650 g/kg chloridazon

B.3.5.2 Procedures for cleaning application equipment and protective clothing (Annex IIIA 4.2)

Reference number:	PHY2001-519
Report :	Kaestel, R., (2001): Shelf life in original container of BAS 119 33 H, 24 month storage – physical properties BASF AG, Agrarzentrum Limburgerhof, Limburgerhof, Germany Fed. Rep., unpublished April 26, 2001
Guidelines:	EU directive 91/414 Annex III, paragraph 2.7.3 and GIFAP Monograph No. 17 paragraph 6.2 at 20 °C with 50 % rel. Humidity and at 30 °C for 24 months in original container.
GLP:	No
Test material:	Pyramin WG, batch No. 97-1, content of as: 650 g/kg chloridazon

Reference number:	PHY2001-526
Report :	Stadler, R., (2001): Pyramin DF (BAS 119 33 H): Effectiveness of procedures for cleaning application equipment and protective clothing BASF AG, Agrarzentrum Limburgerhof, Limburgerhof, Germany Fed. Rep., unpublished, August 22, 2000
Guidelines:	none
GLP:	No
Test material:	Pyramin WG, content of as: 650 g/kg chloridazon

When the field sprayer is cleaned appropriately with water after the use of Pyramin WG, the contamination of the next spray batch is negligible even in the worst possible case.
Laundering protective clothing with detergents will either suspend or dissolve any contamination efficiently.

B.3.5.3 Re-entry periods, necessary waiting periods or other precautions to protect man, livestock and the environment (Annex IIIA 4.3)

The following safety intervals as defined in Annex IIIA point 4.3 are adequately covered by information described in chapters mentioned below.

- pre-harvest interval for each relevant crop
  see chapters B.7.4 and B.7.10
- re-entry period for livestock to areas to be grazed
  see chapters B.7.4 and B.7.10
- re-entry period for man to crops, building or spaces treated
  see chapter B.6.14
- withholding period from animal feeding stuffs
  see chapters B.7.4 and B.7.10
- waiting period between application and handling to treated products
  see chapters B.7.4 and B.7.10
- waiting period between last application and sowing or planting succeeding crops
  see chapter B.3.2.8.

B.3.5.4 Recommended methods and precautions concerning handling, storage, transport or fire (Annex IIIA 4.4)

Handling and storage
(Warehouse-/User Level)

General information

The product is classified according to council directive 1999/45 EEC.

If applicable:

Hazard Symbol(s)	Xn, N
Hazard designation(s)	harmful, dangerous to the environment

Information on safe handling

Open containers should only be handled in well-ventilated areas. Make provisions for product and fire-fighting water to be retained.

Information on storage

Store out of reach of unauthorised persons. Keep away from food, feed and consumable items. Store in original container under usual warehouse conditions, i. e. dry and frost-free avoiding temperatures above 40 °C.

Keep the product away from sources of ignition – no smoking. Good ventilation is required.

For more detailed information see

- Guidelines for the safe handling of pesticides during their formulation, packing, storage and transport (GIFAP).
- Guidelines for the safe warehousing of crop protection products (GCPF).
- Sichere Lagerung von Pflanzenschutz- und Schädlingsbekämpfungsmitteln (IVA).

Transport information

Follow the general rules and good practice for transport and – if applicable – the Dangerous Goods Regulations. Do not stow the product together with food, feed and consumable items.

General information:

Flammability: not highly flammable
Irritation: not irritant
Temperature limits: keep at temperatures below 40 °C

RID/ADR

ID No.: 3077 Class: 9 Packaging group: III
Orange Warning Plate: 90 (Hazard No.)
3077 (Substance No.)

Declaration for land shipment:
Environmentally hazardous substance, solid, N.O.S (contains chloridazon)

ADNR

ID No.: 3077 Class: 9 Item No.: 12C Packaging group: III

Declaration for inland waterways shipment:
Environmentally hazardous substance, solid, N.O.S (contains chloridazon)

IMDG Code

UN No.: 3077 Class: 9 Packaging group: III MPO: yes
Declaration for sea shipment:
Environmentally hazardous substance, solid, N.O.S (contains chloridazon)

ICAO / IATA-DGR

UN or ID No.: 3077 Class: 9 Packaging group: III

Declaration for shipment by air:
Environmentally hazardous substance, solid, N.O.S (contains chloridazon)

Protective clothing and equipment proposed

If product is handled while not enclosed and if skin contact may occur:

Use tightly fitting safety goggles to protect eyes.
Use respiratory equipment if breathable dust is formed;
Filter P1 (for solid particles, DIN 3181).
Use impermeable gloves for chemicals to protect hands.
Use lightweight protective clothing for body protection.
Keep work area clean.

Avoid contact with product.
Keep working clothes separate from other clothing.
Change badly soiled or soaked clothing.
Wash hands before breaks and at end of work.

Procedures to minimise the generation of waste

Only purchase and store quantities of product required in the short term. Do not mix a volume of spray solution greater than is required for immediate use.

Fire-fighting measures

Fight fire if safe to do so.

Extinguishing media:
Water spray, foam, extinguishing powder, carbon dioxide or sand.

Retain and collect fire-fighting water.

Wear respiratory equipment,
in well-ventilated areas: full-face mask with combination filter, e. g. ABEK-P2 (offers no protection from carbon monoxide!)

in enclosed premises: respirator with independent air supply.

Information on combustion products likely to be generated in the event of fire

In the event of fire the formation of CO/CO_2, H_2O, other gases (e.g. hydrogen cyanide), N_2/NO_x and HCl must be anticipated.

B.3.5.5 Emergency measures in the case of an accident (Annex IIIA 4.5)

Prevent entry into drains, water or soil. If necessary use personal protective equipment.

Spillages of BAS 119 33 H have to be collected with broom and shovel or preferably vacuum cleaner.
Use damp cloth to clean floors and other objects after removal of the product and/or contaminated adsorbent. Adding a detergent will enhance the cleaning process. Place recovered material, contaminated adsorbent and used cleaning materials into closeable receptacles.

Protection of emergency workers and bystanders:
Bystanders are requested to leave the emergency site.
For emergency workers it is a standard safety precaution to wear goggles, rubber gloves, mouth-and-nose-mask and protective clothing during clean-up operations.

First aid measures

General Advice
Remove person from danger zone.
Remove contaminated clothing.

Upon Inhalation
Bring person to the fresh air.
Keep patient calm.
Call medical help.

Following Skin Contact:
Wash skin thoroughly with soap and water.
Call medical help.

Following Eye Contact:
Wash affected eyes for at least 15 minutes under running water with eyelids held open.
Consult an eye specialist.

Upon Ingestion:
Rinse mouth and then drink plenty of water.
Call medical help.

B.3.5.6 Procedures for destruction or decontamination of the plant protection product and its packaging (Annex IIIA 4.6)

Neutralisation procedures (e.g. reaction with alkali to form less toxic compounds) for use in the event of accidental spillage

A neutralisation procedure for BAS 119 33 H cannot be proposed.

Pyrolytic behaviour of the active substance under controlled conditions at 800 °C and the content of polyhalogenated dibenzo-p-dioxins in the products of pyrolysis

Due to a halogen content in the active ingredient and the formulants of less than 60 %, combustion of BAS 119 33 H in a waste incinerator plant does not raise concern about the formation of halogenated dibenzodioxins/-furans.

Detailed instructions for safe disposal of the plant protection product and its packaging

For purposes of disposal, combustion of BAS 119 33 H in a licensed incinerator is recommended. This method of disposal applies also to contaminated packages, which cannot be cleaned or reused.

Although it is possible to incinerate the product at lower temperatures, a combustion at approx. 1100 °C with a residence time of about 2 sec is advised.
By doing so, i.e., operating the incinerator according to the conditions laid down in council directive 94 / 67/ EC resp. directive 2000 / 7 6 / EC of the European Parliament, one will achieve complete combustion and minimise the formation of undesired by-products in the off-gases.

Users are requested to triple rinse empty primary packages as described in the ECPA "Guidelines for the rinsing of agrochemical containers", 1993.

Pressure rinsing or integrated pressure rinsing of the packaging material achieves a similar or even better result. The rinsate must be added to the spray liquid.

To minimise waste of packages it is recommended that empty and rinsed containers are delivered to local container collection stations. If these are not existing, empty and rinsed containers must be rendered unusable and disposed of according to local regulations.

Methods other than controlled incineration for disposal of the plant protection product, contaminated packaging and contaminated material

No other methods for disposal of BAS 119 33 H than those described are available.

B.3.6 References relied on

Annex point/ reference number	Author(s)	Year	Title source (where different from company) report no. GLP or GEP status (where relevant), published or not BBA registration number	Data protection claimed Y/N	Owner[1]
AIIA-3.4	Keller, E.	2002	Testing on herbicidal activity of chloridazon/metabolite B/metabolite B-1 upon preemergence treatment in the glasshouse. 2002/1011927 not GLP, unpublished BIO2003-2628	Y	BAS
AIIA-3.4	Keller, E.	2002	Testing on herbicidal activity of chloridazon and metabolite B upon preemergence treatment in the field. 2002/1011926 not GLP, unpublished BIO2003-2627	Y	BAS
AIIA-3.6	Schmidt, O.	2001	Resistance risk analysis for BAS 119 33 H (chloridazon) in Europe. 2001/1017698 not GLP, unpublished BIO2003-2624	Y	BAS
AIIA-3.7	Gerlach, H.	2002	Safety data sheet - Chloridazon techn. H. 2002/1014978 not GLP, unpublished CHE2003-455	N	BAS
AIIA-3.9	Schenk, W.	1994	Possible Procedures for the Decontamination of Water from Chloridazon Study Code 13 033. 1994/12405 not GLP, unpublished CHE2001-654	Y	BAS

[1] Only notifier listed

Annex point/ reference number	Author(s)	Year	Title source (where different from company) report no. GLP or GEP status (where relevant), published or not BBA registration number	Data protection claimed Y/N	Owner[1]
AIIIA-4.1	Schreiner, B.	2000	EU PERFORMANCE TEST. 2000/1012383 not GLP, unpublished PHY2001-525	Y	BAS
AIIIA-4.1	Schreiner, B.	2000	EU PERFORMANCE TEST. 2000/1012380 not GLP, unpublished PHY2001-524	Y	BAS
AIIIA-4.1	Schreiner, B.	2000	EU PERFORMANCE TEST. 2000/1012378 not GLP, unpublished PHY2001-523	Y	BAS
AIIIA-2.7; AIIIA-4.1.3	Kästel, R.	2001	Shelf life in original container of BAS 119 33 H, 24-month-storage - Physical properties. 2001/1009095 GLP, unpublished PHY2001-519	Y	BAS
AIIIA-4.2	Stadler, R.	2000	Pyramin DF (BAS 119 33 H): Effectiveness of procedure for cleaning application equipment and protective clothing. 2000/1013443 not GLP, unpublished PHY2001-526	Y	BAS

Codes of owner

BAS: BASF Aktiengesellschaft

Annex B

Chloridazon

B-4: Proposals for the classification and labelling

B.4 Proposals for the classification and labelling

B.4.1 Proposals for the classification and labelling of the active substance (Annex IIA 10)

On the basis of the toxicological data submitted, no classification of chloridazon is proposed.

Classification according to Annex I to directive 67/548/EEC:

Hazard symbol:	Xi	
Indication of danger:	Irritant	
Risk phrase:	R 43	May cause sensitisation by skin contact.

The following is proposed in accordance with the latest classification and labelling guidance under Directive 67/548/EEC (i.e. in the 18th ATP published as Directive 93/21/EEC):

Chloridazon

Hazard symbol:		N
Indication of danger:		Dangerous to the environment
Risk phrases:		
	R 51/53	Toxic to aquatic organisms/May cause longterm adverse effects in the aquatic environment

Reasons for classification

For justification of	
For justification of R 51/53	see B 8.4 fate and behaviour in water and B.9.2 Effects on aquatic species

B.4.2 Proposals for the classification and labelling of preparations (Annex IIIA 12.3 and 12.4)

The following is proposed in accordance with the Directive 1999/45/EC:

Preparation: BAS 119 33 H (Pyramin WG; Pyramin DF)

Hazard symbol:	Xn	
Indication of danger:	Harmful	
Risk phrases:	R 20	Harmful by inhalation.
	R 22	Harmful if swallowed.

Reasons for classification

For justification of R 20 see	B.6.11.3:	Inhalation toxicity.
For justification of R 22 see	B.6.11.1:	Oral toxicity.

The following is proposed in accordance with Directive 78/631/EEC in combination with the latest classification and labelling guidance under Directive 67/548/EEC (i.e. in the 18th ATP published as Directive 93/21/EEC):

Pyramin WG (BAS 119 33 H)

Hazard symbol:		N
Indication of danger:		Dangerous to the environment
Risk phrases:		
	R 51/53	Toxic to aquatic organisms/May cause long-term adverse effecst in the Environment

Reasons for classification

For justification of	
For justification of R 51/53	see B 8.4 fate and behaviour in water and B.9.2 Effects on aquatic species
For justification of	

B.4.3 References relied on

No references submitted.

Annex B

Chloridazon

B-5: Methods of analysis

B.5 Methods of analysis

B.5.1 Analytical methods for formulation analysis (Annex IIA 4.1; Annex IIIA 5.1)

B.5.1.1 Analytical method for the determination of pure active substance in the active substance as manufactured (Annex IIA 4.1)

Ref.: Anonymous 1986 (CHE2001-571)
Analytical method CIPAC 111: Determination of chloridazon in chloridazon technical and chloridazon formulations
BASF RegDoc# 1986/11174

CIPAC Method 111/TC/M/3

Principle:

The product is dissolved in mobile phase (methanol/water, 6/4 v/v), chromatographed by HPLC on a reversed phase column (C_{18}) and quantitatively determined by UV-detection at 286 nm with external calibration.

Validation data of the analytical method

The CIPAC-method was collaboratively tested for chloridazon technical and, therefore, is regarded as validated.
Data on repeatability and reproducibility (based on a study with 22 participants and 110 values) proved that this method is suitable for the determination of chloridazon in technical material.

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

B.5.1.1.1 Methods for the determination of significant and/or relevant, impurities and additives (e.g. stabilisers) in the active substance as manufactured

An HPLC method (reversed phase column and UV detection) is used to determine the levels of the minor components [redacted]

The validation study demonstrates that the method is valid with regard to specificity, linearity (only for Reg. No. 13 344), accuracy and precision.

This confidential information is provided in Volume 4 (Annex C).

B.5.1.1.2 Methods for relevant breakdown products, isomers, impurities and additives

There are no components of toxicological, ecotoxicological or environmental concern contained in chloridazon technical. Therefore, a respective analytical method is not required.

B.5.1.2 Analytical methods for formulation analysis (plant protection product) (Annex IIIA 5.1)

Ref.: Anonymous, 1997 (CHE2001-573)
CIPAC Analytical Method 111/WG/M/-: Determination of chloridazon in water dispersible granules
BASF DocID 1997/1001160

Anonymous, 1986 (CHE2001-571)
Analytical method CIPAC 111: Determination of chloridazon in chloridazon technical and chloridazon formulations
BASF DocID 1986/11174

CIPAC Methods 111/WG/M/3 and 111/WP/M/3

Principle:

The product is dissolved in mobile phase (methanol/water, 6/4 v/v), chromatographed by HPLC on a reversed phase column (C_{18}) and quantitatively determined by UV-detection at 286 nm with external calibration.

Validation data of the analytical method

The guideline „Guidance for generating and reporting methods of analysis in support of pre- and post-registration data requirements for Annex II (part A, Section 4) and Annex III (part A, Section 5) of Directive 91/414“ states: “Where collaboratively tested CIPAC or AOC methods are available, additional validation data are not required providing the method was collaboratively tested on the formulation type under consideration“.

Since the method for the active substance was collaboratively tested on an equivalent WP formulation, no further work has to be reported.

Data on repeatability and reproducibility (based on a study with 22 participants and 110 values) proved that this method is suitable for the determination of chloridazon in wettable powders.

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

B.5.1.2.1 Method(s) for relevant breakdown products, isomers, impurities and additives

BAS 119 33 H does not contain any component of toxicological, ecotoxicological or environmental significance. As the product is stable, this holds true for the product as manufactured and after storage at 20 °C for two years as well. Therefore, no respective method is required.

B.5.2 Analytical methods (residue) for plants, plant products, foodstuffs of plant and animal origin, feedingstuffs (Annex IIA 4.2.1; Annex IIIA 5.2)

B.5.2.1 Analytical methods (residue) for plant and plant products

The proposed definition of residues of chloridazon in plant materials includes the parent compound and the metabolite B (5-amino-4-chlor-2,3-dihydro-3-oxo-pyridazin). The enforcement methods developed until 1996 describe procedures, which allow determination of both components of this residue definition (anonymus, 1976; anonymus, 1977; Keller, 1983; Movassaghi, 1997 and Schulz, 1996). Most often these methods are based on determination of parent compound by GC, whereas metabolite B after separate cleanup is quantified by HPLC/UV. Even if most of these methods are discussed below, due to the use of diazomethane or chloroform and the lack of individual validation data, actual requirements of the Guidance Document SANCO 825/00 rev. 6 are not fulfilled. Furthermore, these methods include the determination of the glycoside of chloridazon (metabolite A = 1-phenyl-4-(N-glycosyl)-amino-5-chlor-pyridazone-(6)), which is not included in the definition of the residue. However, omitting the hydrolysis step with hydrochloric acid a determination of residues without the metabolite A seems possible.
All newer methods are specialised for the determination of parent chloridazon or the metabolite B. They are fully validated and based on final determination by HPLC-MS/MS.

Anonymous, 1976
In the BASF Method No. 105 "Gas-chromatographic determination of pyrazon, metabolite A and metabolite B in sugar beet" residues of chloridazon including two metabolites are analysed.
Principle of the method
Residues are extracted from plant material with methanol. One half of the methanol extract is treated with acid for hydrolysis of metabolite A to chloridazon. After partition into chloroform, precipitation (using a solution of ammonium chloride and phosphoric acid) and column clean-up on Al_2O_3, chloridazon is determined by GC using an electron capture detector. After derivatisation with diazomethane, the second half of the methanol extract is analysed for metabolite B also by use of GC/ECD.
Findings
The stated limit of quantitation is 0.1 mg/kg each for parent and metabolite B in sugar beet matrices. Metabolite A was not spiked in validation tests. Individual recovery data and information on the calibration or precision of the method are not presented.

Valid: no (use of chloroform, no individual recovery data, no information on the calibration or precision of the method)

Table B.5.2-1: Validation data for analytical methods for the determination of chloridazon and metabolite B in plant and plant products

Reference	Matrix	Test substance	Fortification level [mg/kg]	Average recovery	RSD [%]	No. of analyses
Anonymous (1976)	Sugar beet tops and roots	Chloridazon	0.1 – 0.5	80	17	n/a
		metabolite B	0.1 – 0.5	72	15	n/a

n/a: not applicable

Anonymous, 1977

In the similar BASF Method No. 116 "Determination of pyrazon, metabolite A and metabolite B in sugar beet" instead of GC/ECD determination HPLC/UV chromatography was used for both analytes.

Principle of the method

Residues are extracted from plant material with methanol. One half of the methanol extract is treated with acid for hydrolysis of metabolite A to chloridazon. After partition into chloroform, precipitation (using a solution of ammonium chloride and hydrochloric acid) and column clean-up on Al_2O_3, chloridazon is determined by HPLC using an UV detector at 230 nm. From the second half of the extract methanol is evaporated. The water containing residue is washed with chloroform and purified by two chromatographic steps (1^{st} charcoal and 2^{nd} silica). The final extract is analysed for metabolite B by use of HPLC/UV at 286 nm.

Findings

The limit of quantitation is 0.1 mg/kg each for parent and metabolite B in sugar beet matrices. Metabolite A was not spiked. Individual recovery data and information on the calibration or precision of the method are not presented.

Valid: no (use of chloroform, no individual recovery data, no information on the calibration or precision of the method)

Table B.5.2-2: Validation data for analytical methods for the determination of chloridazon and metabolite B in plant and plant products

Reference	Matrix	Test substance	Fortification level [mg/kg]	Average recovery	RSD [%]	No. of analyses
Anonymous (1977)	Sugar beet tops and roots	Chloridazon	0.1 – 0.5	74	10	n/a
		metabolite B	0.1 – 0.5	75	10	n/a

n/a: not applicable

Keller, 1983

In the BASF Method No. 213 "GC and HPLC determination of chloridazon, metabolite A, metabolite B in stock beets, red beets (roots and leaves), sugar beets (roots and leaves), soil, water" a nowadays very seldom applied size exclusion chromatography on Sephadex LH 20 is used.

Principle of the method

Residues are extracted with methanol. One half of the methanol extract is treated with acid for hydrolysis of metabolite A. Then, plant pigments and polysaccharides are precipitated using a solution of ammonium chloride and hydrochloric acid. Dichloromethane-water partitioning on a column containing two layers of Extrelut (one neutral on the top and an alkaline on the bottom) is followed by column chromatographic clean-up on alumina with 98 % chloroform in the eluent. Finally, chloridazon is determined by GC using an electron capture detector.

The second half of the methanol extract is analysed for metabolite B by partitioning on Extrelut columns, clean-up by gel chromatography on Sephadex-LH20 and by column chromatography on silica gel. Final determination is done by HPLC using UV detection at 286 nm.

Findings

The limit of quantitation is 0.05 mg/kg each for parent and metabolite B in several beet matrices (roots and leaves). Metabolite A was not spiked. Chromatograms from samples and blank material, individual recovery data and information on the precision of the method, but no calibration graphs/data are presented.

Valid: no (use of chloroform, no calibration graphs/data presented)

Table B.5.2-3: Validation data for analytical methods for the determination of chloridazon and metabolite B in plant and plant products

Reference	Matrix	Test substance	Fortification level [mg/kg]	Average recovery	RSD [%]	No. of analyses
Keller W. (1983)	sugar beet, roots	Chloridazon	0.05	100	6.2	4
			0.5	95	4.5	4
		Metabolite B	0.05	75	9.3	4
			0.5	96	6.4	4
	sugar beet, tops	Chloridazon	0.05	90	4.4	4
			0.5	95	3.7	4
		Metabolite B	0.05	76	6.1	4
			0.5	79	5.0	4
	red beet, roots	Chloridazon	0.05	96	12.6	4
		Metabolite B	0.05	73	5.0	4
	red beet, tops	Chloridazon	0.05	74	3.8	4
		Metabolite B	0.05	74	12.7	4
	stock beets	Chloridazon	0.05	85	25	4
		Metabolite B	0.05	86	4.9	4

Movassaghi, 1994

The BASF Method No. A9202 "Method for determination of chloridazon and its metabolite residues in sugar beet roots, tops and process fractions (refined sugar and molasses)" was developed by BASF.

Principle of the method

This method also uses methanol for sample extraction. After concentration and coagulation, acidic hydrolysis converts the conjugated metabolite A to chloridazon. Elution from two combined Extrelut columns (one neutral on the top and an alkaline on the bottom) with dichloromethane followed by ethyl acetate will separate chloridazon from metabolite B. After silica gel and SPE purification, total chloridazon (including metabolite A) is determined by GC with thermionic specific detection and metabolite B by HPLC/UV at 286 nm.

Findings

The limit of quantitation for sugar beet matrices and refined sugar was 0.05 mg/kg each for parent and metabolite B. In molasses, the limit of quantification was 0.05 mg/kg for chloridazon and 0.20 mg/kg for metabolite B. Acceptable chromatograms from samples and blank material, calibration graphs, individual recovery data and information on the precision of the method are presented.

Valid: yes, according to residue definition for chloridazon and metabolite B
Valid: yes, for risk assessment of chloridazon and metabolite A

Table B.5.2-4: Validation data for analytical methods for the determination of chloridazon including metabolite A and metabolite B in plant and plant products

Reference	Matrix	Test substance	Fortification level [mg/kg]	Average recovery	RSD [%]	No. of analyses
Movassaghi S. (1994)	Sugar beet, tops	Chloridazon	0.05	92	12.5	4
			1.0	91	8.2	4
		Metabolite A	0.05	88	7.8	4
			1.0	75	6.8	4
		Metabolite B	0.05	87	9.0	4
			1.0	86	6.5	4
	Sugar beet, roots	Chloridazon	0.05	94	10.4	6
			1.0	81	13.7	5
		Metabolite A	0.05	91	18.9	4
			1.0	100	11.9	4
		Metabolite B	0.05	91	4.2	4
			1.0	82	14.7	3
	Refined sugar	Chloridazon	0.05	102	14.2	5
			1.0	92	6.2	6
		Metabolite A	0.05	104	12.4	4
			1.0	87	6.1	4
		Metabolite B	0.05	93	23.4	4
			1.0	78	11.4	4
	Molasses	Chloridazon	0.05	103	12.3	4
			1.0	72	8.6	8
		Metabolite A	0.05	88	25.7	4
			1.0	67	3.1	4
		Metabolite B	0.20	82	12.1	2
			1.0	72	4.0	4

Schulz, 1996

A successful independent laboratory validation of BASF Method No. A9202 was presented with the study of Institute Fresenius "Determination of chloridazon, metabolite A and metabolite B in sugar beets - Validation of the method A 9202".

Principle of the method

There are no deviations from the procedure described before.

Findings

The method was validated with sugar beet roots and tops The limit of quantitation was 0.05 mg/kg each for parent and metabolite B. Except from some high results in blank samples (interference), acceptable chromatograms from samples, appropriate calibration graphs, individual recovery data in good quality and information on the precision of the method are presented.

Valid: yes, according to residue definition only for metabolite B

Valid: yes, for risk assessment of chloridazon and metabolite A because they can only be determined as sum

Table B.5.2-5: Validation data for analytical methods for the determination of chloridazon including metabolite A and metabolite B in plant and plant products

Reference	Matrix	Test substance	Fortification level [mg/kg]	Average recovery	RSD [%]	No. of analyses
Schulz, H. (1996)	Sugar beet, tops	Chloridazon	0.05	103	9.0	4
			5	97	17.2	4
		Metabolite A	0.05	86	7.4	4
			5	87	3.0	4
		Metabolite B	0.05	89	4.7	4
			5	88	1.4	4
	Sugar beet, roots	Chloridazon	0.05	96	13	4
			5	93	11.0	4
		Metabolite A	0.05	104	11.5	4
			5	105	7.1	4
		Metabolite B	0.05	80	3.7	4
			5	71	1.1	4

Weber, 2002

The purpose of the study "Determination of chloridazon in onion, oil seed rape, sugar beets (roots), orange, cucumber and wheat (corn) - Validation of the DFG method S 19 (extended revision)" was to test the applicability of a standard multi-residue method for the determination of chloridazon residues in plant matrices.

In a preliminary experiment, two representative plant matrices (onions, rape seed) were selected, fortified with chloridazon and extracted as described in the method. The extracts obtained were further purified by GPC. The specimens were analysed by capillary GC with mass spectrometric detection (MSD). For onions the recoveries ranged from 110 to 132 % at fortification levels of 0.5 and 0.05 mg/kg. In case of oil seed rape, recoveries of 31 and 34 % were observed.

Due to lacking accuracy, the method is not considered as suitable for the determination of chloridazon residues in plant. Furthermore, the metabolite B cannot be determined by GC methods without derivatisation.

Valid: no (lacking accuracy)

Kerl, 2002a

The BASF Method No. 494/0 described in the study of BASF "Validation of the analytical method 494/0: Method for the determination of BAS 119 H in plant matrices" is proposed for enforcement purposes by the notifier.

Principle of the method

Chloridazon is extracted with methanol. After purification by $Ca(OH)_2$ precipitation and a dichloromethane liquid/liquid partition the final determination is performed by HPLC-MS/MS. The LC-MS/MS instrument is calibrated using standards in solvent. A second confirmatory transition is not presented.

Findings

The limit of quantitation for commodities with high water content (cucumber, sugar beet roots and tops), cereals and other dry crops (wheat grain), commodities with high fat content (rape seed), fruits with high acid content (oranges) and commodities, which are difficult to analyse (onions) was 0.05 mg/kg. Acceptable chromatograms from samples and blank materials, an

appropriate calibration graph, individual recovery data and information on the precision of the method are presented.

Valid: yes, according to residue definition for chloridazon

Table B.5.2-6: Validation data for analytical methods for the determination of chloridazon including metabolite A and metabolite B in plant and plant products

Reference	Matrix	Test substance	Fortification level [mg/kg]	Average recovery	RSD [%]	No. of analyses
Kerl, W. (2002a)	Cucumber	Chloridazon	0.05	92	5.5	5
			0.5	105	3.4	5
	Orange		0.05	89	1.9	5
			0.5	107	1.7	5
	Wheat, grain		0.05	97	3.2	5
			0.5	102	5.6	5
	Rape, seed		0.05	74	4.7	5
			0.5	104	4.8	5
	Onion, bulb		0.05	86	2.1	5
			0.5	103	3.5	5
	Sugar beet, root		0.05	96	5.0	5
			0.5	99	5.3	5
	Sugar beet, plant with root		0.05	100	3.1	5
			0.5	97	2.0	5
	Sugar beet, plant without root		0.05	96	3.3	5
			0.5	97	2.8	5

Kang, 2001

An independent laboratory validation of BASF Method No. 494/0 is presented with the study of CEM Analytical Services "Independent laboratory validation of an analytical method for the determination of BAS 119 H residues".

Principle of the method

There are no deviations from the procedure described before, except the use of matrix matched standards for rape seed samples. Again, no second transition was tested for confirmatory purposes.

Findings

The limit of quantitation for all commodities was 0.05 mg/kg. Acceptable chromatograms from samples and blank materials, an appropriate calibration graph, individual recovery data and information on the precision of the method are presented.

Valid: yes, according to residue definition for chloridazon

Table B.5.2-7: Validation data for analytical methods for the determination of chloridazon including metabolite A and metabolite B in plant and plant products

Reference	Matrix	Test substance	Fortification level [mg/kg]	Average recovery	RSD [%]	No. of analyses
Kang, J. (2001)	Sugar beet, whole plant	Chloridazon	0.05	99	1.8	5
			0.5	97	3.3	5
	Sugar beet, roots		0.05	102	1.7	5
			0.5	101	1.4	5
	Sugar beet, leaves w. tops		0.05	100	7.3	5
			0.5	97	8.6	5
	Oilrape, seed		0.05	71	10.8	5
			0.5	69	9.8	5
	Wheat, grain		0.05	107	16.2	5
			0.5	93	5.0	5
	Orange, flesh		0.05	108	6.9	4
			0.5	101	3.5	5
	Onion		0.05	71	5.1	5
			0.5	94	3.6	5
	Cucumber		0.05	105	1.1	5
			0.5	100	1.5	5

Kerl, 2002 b

The BASF Method No. 497/0 "Validation of the analytical method 497/0: Method for the determination of BH 119-Metabolite B in plant matrices" is developed by BASF for the enforcement of metabolite B residues.

Principle of the method

The metabolite B is extracted with methanol. After purification by precipitation (using a solution of ammonium chloride and phosphoric acid), liquid/liquid partition and silica column, the final determination is performed by HPLC-MS/MS. The LC-MS/MS instrument is calibrated using standards in solvent. A second, confirmatory transition is proposed.

Findings

The limit of quantitation for commodities with high water content (cucumber, sugar beet roots and tops), cereals and other dry crops (wheat grain), commodities with high fat content (rape seed), fruits with high acid content (oranges) and commodities, which are difficult to analyse (onions) was 0.05 mg/kg. Acceptable chromatograms from samples and blank materials, an appropriate calibration graph, individual recovery data and information on the precision of the method are presented. Data for the confirmatory transition are not presented.

Valid: yes, according to residue definition for metabolite B

Table B.5.2-8: Validation data for analytical methods for the determination of chloridazon including metabolite A and metabolite B in plant and plant products

Reference	Matrix	Test substance	Fortification level [mg/kg]	Average recovery	RSD [%]	No. of analyses
Kerl, W. (2002b)	Cucumber	Metabolite B	0.05	74	3.1	5
			0.5	78	4.4	5
	Orange		0.05	83	2.3	5
			0.5	87	2.2	5
	Wheat, grain		0.05	82	5.0	5
			0.5	83	3.6	5
	Rape, seed		0.05	90	6.2	5
			0.5	87	2.1	5
	Onion		0.05	82	2.1	5
			0.5	88	2.1	5
	Sugar beet, root		0.05	81	3.2	5
			0.5	79	7.5	5
	Sugar beet, plant with root		0.05	72	9.9	5
			0.5	68	6.2	5
	Sugar beet, plant without root		0.05	86	6.2	5
			0.5	82	3.0	5

Schulz, 2002 a

An independent laboratory validation of BASF Method No. 497/0 is presented with the study of Institute Fresenius "Determination of BH 119-metabolite B in plant matrices - Validation of the method No. 497/0". The "Addendum No. 1 to the report ..." (Schulz, 2002b) clarifies only, that this is an independent laboratory validation of the method No. 497/0.

Principle of the method

There are no deviations from the procedure described before. This includes the lack of a second confirmatory transition.

Findings

The limit of quantitation for commodities with high water content (cucumber, sugar beet roots and tops), cereals and other dry crops (wheat grain), commodities with high fat content (rape seed), fruits with high acid content (lemons) and commodities, which are difficult to analyse (onions) was 0.05 mg/kg. Acceptable chromatograms from samples and blank materials, an appropriate calibration graph, individual recovery data and information on the precision of the method are presented.

Valid: yes, according to residue definition for metabolite B

Table B.5.2-9: Validation data for analytical methods for the determination of chloridazon including metabolite A and metabolite B in plant and plant products

Reference	Matrix	Test substance	Fortification level [mg/kg]	Average recovery	RSD [%]	No. of analyses
Schulz, H. (2002a)	Lemon	Metabolite B	0.05	96.8	17.7	5
			0.5	98.6	20.0	5
	Rape seed		0.05	103.4	7.3	5
			0.5	105.4	7.2	5
	Wheat grain		0.05	76.2	6.2	5
			0.5	80.2	4.7	5
	Cucumber		0.05	77.6	18.0	5
			0.5	102.8	19.6	5
	Onion		0.05	75.2	20.3	5
			0.5	111.8	16.6	5
	Sugar beet, whole plant		0.05	96.2	16.3	5
			0.5	96.6	15.5	5
	Sugar beet, root		0.05	72.4	16.7	5
			0.5	77.2	13.4	5
	Sugar beet, tops w. leaves		0.05	74.2	18.9	5
			0.5	71.6	17.0	5

Kerl, 2003 and Kerl/Mackenroth, 2003

The BASF Method No. 518/0 for the determination of residues of chloridazon and its metabolite A (Kerl, 2003) is validated in a study "Validation of the analytical method 518/0: Method for the determination of chloridazon (Reg. No. 130 33) and BH 119-Glucosid (Reg. No. 262 529) in onions" (Kerl/Mackenroth, 2003).

Principle of the method

Chloridazon and metabolite A (BH 119-Glucosid) are extracted with methanol. After purification by $Ca(OH)_2$ precipitation, an acidic cleavage step and a dichloromethane liquid/liquid partition, the final determination is performed by HPLC-MS/MS. A second confirmatory transition is not presented. Using this procedure the results obtained represent the sum of parent chloridazon originally present and chloridazon formed from BH 119-Glucoside (metabolite A) by acidic cleavage.

Findings

Individual fortification experiments are conducted with parent compound and metabolite A. The limit of quantitation for onion plant without root and onion bulbs was 0.05 mg/kg. Acceptable chromatograms from samples and blank materials, an appropriate calibration graph, individual recovery data and information on the precision of the method are presented.

Valid: yes, for risk assessment of chloridazon and metabolite A because they can only be determined as sum

Table B.5.2-10: Validation data for analytical methods for the determination of chloridazon including metabolite A and metabolite B in plant and plant products

Reference	Matrix	Test substance	Fortification level [mg/kg]	Average recovery	RSD [%]	No. of analyses
Kerl, W. and Mackenroth, C. (2003)	Onion, plant w/o root	Chloridazon	0.05	83	6.1	5
			0.5	83	8.1	5
		Metabolite A	0.05	85	7.0	5
			0.5	106	2.1	5
	Onion, bulb	Chloridazon	0.05	72	10.8	5
			0.5	85	8.1	5
		Metabolite A	0.05	67	13.0	5
			0.5	82	7.9	5

Mayer, 1991

The extractability of chloridazon residues from sugar beet tops and roots with the extraction solvent methanol was tested in the study "The Metabolism of ^{14}C-Chloridazon in Sugar Beets". 94.2 % of the total radioactive residue in tops was extracted with cold methanol. In three out of four trails parent chloridazon or metabolite B were identified as the most important component of the residue. In the 4th trail the metabolite A was found with highest concentration in the extract.

Sugar beet roots contained a smaller part of the total residue of the whole plant. Here, 64 % of the total radioactive residue were extracted into methanol. HPLC results show that the extractable radioactivity mainly consists of chloridazon and metabolite B.

B.5.2.2 Analytical methods (residue) for foodstuffs of animal origin

The proposed definition of residues of chloridazon in foodstuffs of animal origin includes the the metabolite B only. Nevertheless, several methods for the determination of parent chloridazon had been developed. To get an complete overview on the methods available, these studies are also discussed.

B.5.2.2.1 Methods for residues of chloridazon (and para-hydroxy metabolite)

Zehr, 1996

The method No. D9407 "Method for determination of BAS 119 H (chloridazon) and its para-hydroxy metabolite in cow milk and cow tissues including muscle, liver, kidney, and fat" does not allow the determination of metabolite B. It is developed for data generation purposes and covers chloridazon and its para-hydroxy metabolite BH 119-4-OH in cow matrices.

Principle of the method

Tissue samples are extracted with methanol. The extract is filtered, water added and concentrated until only the aqueous portion remains. The aqueous remainder is washed with hexane and the residues are partitioned into ethyl acetate. The organic layer is then passed over a silica gel column and separated into fractions containing chloridazon and BH 119-4-OH. The metabolite BH 119-4-OH is determined by HPLC-UV. The chloridazon containing fraction is further purified on a C18 SPE cartridge and then analysed by GC-ECD.

Milk samples are treated with acetone/acetonitrile, the resulting precipitate is discarded, and upon addition of water the mixture is concentrated to the aqueous portion. After partition with hexane (discarded), the aqueous layer is refluxed with concentrated HCl. After pH adjustment to pH 5, the aqueous mixture is extracted with ethyl acetate. This organic extract is then purified as described for the tissue samples.

Findings

Individual fortification experiments are conducted with parent compound and para-hydroxy metabolite BH 119-4-OH. The limit of quantitation (each of both analytes) for milk and tissue samples was 0.01 mg/kg and 0.05 mg/kg, respectively. Acceptable chromatograms from samples and blank materials, an appropriate calibration graph, individual recovery data and information on the precision of the method are presented.

Valid: yes, only for risk assessment of chloridazon

Table B. 5.2-11 Validation data for analytical methods for the determination of chloridazon and metabolite BH-119-4-OH in animal products

Reference	Matrix:	Test substance	Fortification level [mg/kg]	Average recovery	RSD [%]	No. of analyses
Zehr R. D. (1996)	Bovine milk	Chloridazon	0.01	97.3	18.4	4
			0.10	78.3	24.4	4
			1.00	84.8	10.1	4
		BH 119-4-OH	0.01	94.3	19.5	4
			0.10	84.9	2.9	4
			1.00	84.6	7.8	4
	Bovine muscle	Chloridazon	0.05	109.8	7.1	4
			0.50	102.4	5.8	4
			5.00	103.7	6.7	4
		BH 119-4-OH	0.05	94.4	7.1	4
			0.50	90.5	4.2	4
			5.00	88.5	3.2	4
	Bovine liver	Chloridazon	0.05	94.6	14.9	4
			0.50	112.6	6.0	4
			5.00	90.4	9.4	4
		BH 119-4-OH	0.05	77.8	11.2	4
			0.50	86.9	1.7	4
			5.00	86.3	4.6	4
	Bovine kidney	Chloridazon	0.05	115.9	11.3	4
			0.50	85.5	11.9	4
			5.00	79.5	3.5	4
		BH 119-4-OH	0.05	94.2	10.5	4
			0.50	82.1	6.5	4
			5.00	83.6	10.5	4
	Bovine fat	Chloridazon	0.05	100.9	4.7	4
			0.50	84.3	6.9	4
			5.00	87.1	3.4	4
		BH 119-4-OH	0.05	90.0	5.6	4
			0.50	87.9	8.1	4
			5.00	83.1	4.9	4

Kampke-Thiel, 1998

The applicabilty of the BASF method 983/0 is confirmed in the study "Validation of BASF method 983/0 for the determination of chloridazon (BAS 119 H) and its hydroxy metabolite (BH 119-4-OH) in hen eggs".

Principle of the method

It is stated, that the method is identical to method No. D9407 except for the following modifications:

- the egg samples were extracted with a mixture of acetonitrile/iso-hexane
- the acetonitrile layer is refluxed with concentrated HCl
- pH is adjusted (to an unknown hydrogen ion concentration)

after the silica gel clean-up, the fraction containing chloridazon was not further purified on a C18 SPE cartridge because of its high purity.

Unfortunately, the chapter "Analytical Procedure" is not complete. From that reason it remains unclear, which amount and concentration of HCl is used to reflux the raw extract, which pH has to be adjusted and why evaporated final extracts have to be solved in methanol and not in the solvent used for GC standards (isooctane/2-propanol 90:10).

Individual fortification experiments are conducted with parent compound and para-hydroxy metabolite BH 119-4-OH.

Findings

The limit of quantitation (each of both analytes) for milk and tissue samples was 0.01 mg/kg and 0.05 mg/kg, respectively. Acceptable chromatograms from samples and blank materials, an appropriate calibration graph, individual recovery data and information on the precision of the method are presented.

Valid: yes, only for risk assessment of chloridazon

Table B. 5.2-12 Validation data for analytical methods for the determination of chloridazon and metabolite BH-119-4-OH in animal products

Reference	Matrix:	Test substance	Fortification level [mg/kg]	Average recovery	RSD [%]	No. of analyses
Kampke-Thiel K. (1998)	Hen: Egg	Chloridazon	0.05	83.6	10.9	5
			0.50	100.9	4.6	5
		BH 119-4-OH	0.05	86.2	16.5	5
			0.50	92.6	12.3	5

Steinhauer, 2002

The purpose of the study "Assessment of the multi-residue method DFG S19 (extended revision) for the determination of BAS 119 H (chloridazon) in animal matrices" was to test the applicability of a standard multi-residue method for the determination of parent chloridazon residues in samples of animal origin. The metabolite B was not included in the test, because it cannot be determined by GC methods without derivatisation.

Findings demonstrate that it is possible to detect residues of chloridazon in milk and fat with the DFG S19 multi-residue method. Although the compound can be detected by GC-MS in sufficient sensitivity, accurate quantification is hampered by significant peak enhancement presumably caused by matrix components. In liver, the method is lacking specificity since strong matrix interferences impede the evaluation of chromatograms. The DFG S19 multi-residue method was therefore not considered suitable for the determination of parent chloridazon in animal matrices with the required accuracy and specificity and cannot be recommended for the enforcement of chloridazon residues in food of animal origin.

Therefore, separate methods were developed for the enforcement of residues of the active substance chloridazon.

Valid: no (matrix effects)

Hartl, 2002

In the study "Validation of BASF Method No. 494/0 for the determination of BAS 119 H (chloridazon; Reg. No. 13033) in animal matrices" the determination of the parent compound was studied by BASF.

Principle of the method

In this method the residues of chloridazon are extracted with methanol. Extracts are then purified by a $Ca(OH)_2$ precipitation and washed with hexane to remove interfering matrix components (not necessary for extracts of eggs). The active substance is then extracted into dichloromethane and final determination of the residue is performed by HPLC-MS/MS. For quantification, one transition (m/z 222 → 104) was used.

Findings

The limit of quantitation is 0.01 mg/kg in milk and eggs and 0.05 mg/kg in muscle, liver, kidney and fat. Acceptable chromatograms from samples and blank materials, an appropriate calibration graph, sufficient individual recovery data and information on the precision of the method are presented. A second MS/MS transition (m/z 222 → 92) was proposed as confirmatory technique, but data using this transition are not presented. The determination of metabolite B was not studied.

Valid: yes, only for risk assessment of chloridazon

Table B. 5.2-13 Validation data for analytical methods for the determination of chloridazon in animal products

Reference	Matrix:	Test substance	Fortification level [mg/kg]	Average recovery	RSD [%]	No. of analyses
Hartl M. (2002)	Bovine milk	Chloridazon	0.01	87.3	4.0	4
			0.1	78.6	4.0	5
	Bovine muscle		0.05	75.8	4.0	5
			0.5	81.3	7.3	5
	Bovine liver		0.05	96.0	7.1	5
			0.5	98.7	6.8	5
	Bovine kidney		0.05	70.8	14.0	5
			0.5	84.8	4.6	5
	Bovine fat		0.05	81.5	6.1	5
			0.5	84.9	6.5	5
	Hen egg		0.01	98.4	2.8	5
			0.1	99.7	4.3	4

Class, 2002

An "Independent laboratory validation (ILV) of BASF method No. 494/0 for the determination of chloridazon in animal matrices" was presented by PTRL Europe. A full and successful validation was performed for milk and muscle.

Principle of the method

There are no significant deviations from the procedure described before. However, a cheaper ion trap instrument with atmospheric pressure chemical ionisation (APCI) ion source was used instead of a triple quad instrument with electrospray (ESI) interface.

Findings

The limit of quantitation is 0.01 mg/kg in milk and 0.05 mg/kg in muscle. Acceptable chromatograms from samples and blank materials, an appropriate calibration graph, sufficient individual recovery data and information on the precision of the method are presented. A second MS/MS transition (m/z 222 → 92) was proposed as confirmatory technique, but data using this transition are not presented.

Valid: yes, only for risk assessment of chloridazon

Table B.5.2-14 Validation data for analytical methods for the determination of chloridazon in animal products

Reference	Matrix:	Test substance	Fortification level [mg/kg]	Average recovery	RSD [%]	No. of analyses
Class T. (2002)	Bovine milk	Chloridazon	0.01	89	12	5
			0.1	87	8	5
	Bovine muscle		0.05	80	11	6
			0.5	86	15	7

Zehr, 1996

The extractability of chloridazon residues from goat milk with the solvent mixture acetone/acetonitrile was tested in the study "Accountability of BASF method no. D9407 in goat milk". 95.1 % of the total radioactive residue was extracted with acetone/acetonitrile. The main components were chloridazon and its p-hydroxy metabolite.

B.5.2.2.2 Methods for residues of metabolite B

Hartl, 2001

The BASF method 499/0 was validated in the study of BASF Germany "Validation of BASF method 499/0 for the determination of chloridazon metabolite B (Reg. No. 014 456) in sample materials of animal origin".

Principle of the method

Residues of chloridazon metabolite B are extracted from animal matrices with methanol. Upon addition of water and removal of the organic solvent, the extract is purified by liquid/liquid partition with dichloromethane. An aliquot of the aqueous phase is put on an extrelut column and metabolite B is eluted with ethyl acetate/dichloromethane. The eluate is transferred onto a silica gel cartridge for additional clean up. The final determination is performed by HPLC-MS/MS. For quantification, the transition ions m/z 146 → 117 was used. A second MS/MS transition (m/z 146 → 101) was proposed as confirmatory technique, but data using this transition are not presented.

Findings

The limit of quantitation is 0.01 mg/kg in milk and 0.05 mg/kg in all other tissues. Acceptable chromatograms from samples and blank materials, an appropriate calibration graph, sufficient individual recovery data and information on the precision of the method are presented.

Valid: yes, according to residue definition for metabolite B

Table B. 5.2-15 Validation data for analytical methods for the determination of metabolite B in animal products

Reference	Matrix:	Test substance	Fortification level [mg/kg]	Average recovery	RSD [%]	No. of analyses
Hartl M. (2001)	Bovine milk	Metabolite B	0.01	95.1	5.3	5
			0.10	89.4	6.3	5
	Bovine muscle		0.05	81.7	8.1	5
			0.50	86.6	9.4	5
	Bovine liver		0.05	84.4	12.7	5
			0.50	88.8	2.1	5
	Bovine kidney		0.05	85.0	8.4	5
			0.50	83.2	3.0	5
	Bovine fat		0.05	88.9	4.3	5
			0.50	85.4	2.6	5
	Hen egg		0.05	90.4	5.4	5
			0.50	86.6	11.6	5

Stout, 2001

The "Independent laboratory validation of BASF method number 499/0 (dated July, 2001) for the determination of residues of BAS 119 H metabolite B (Reg. No. 014 456) in animal tissues (liver) and animal products (bovine whole milk) by HPLC/MS/MS" was conducted in the BASF laboratories in the USA.

Principle of the method

There are no significant deviations from the procedure described before.

Findings

A full and successful validation was performed for milk and liver.

Valid: yes, according to residue definition for metabolite B

Table B. 5.2-16 Validation data for analytical methods for the determination of metabolite B in animal products

Reference	Matrix:	Test substance	Fortification level [mg/kg]	Average recovery	RSD [%]	No. of analyses
Stout C. (2001)	Bovine milk	Metabolite B	0.01	87.0	7.0	5
			0.10	90.0	4.2	5
	Bovine liver		0.05	86.0	4.3	4
			0.50	82.0	4.8	5

B.5.3 Analytical methods (residue) soil, water, air (Annex IIA 4.2.2 to 4.2.4; Annex IIIA 5.2)

The proposed definition of residues of chloridazon in soil includes the metabolite B (5-amino-4-chlor-2,3-dihydro-3-oxo-pyridazine) only. The proposed definition of residues of chloridazon in water includes the metabolite B (5-amino-4-chlor-2,3-dihydro-3-oxo-

pyridazine) and the metabolite B-1 (5-amino-4-chlor-2-methyl, 3-hydro-3-oxo-pyridazine). In air the parent compound (chloridazon) has to be determined.

B.5.3.1 Analytical methods (residue) for soil

Keller, 1983

The BASF Method No. 213 "GC and HPLC determination of chloridazon, metabolite A, metabolite B in stock beets, red beets (roots and leaves), sugar beets (roots and leaves), soil, water" is the first study, which meets minimum validation requirements.

Principle of the method

Residues of chloridazon including metabolite A and metabolite B are extracted with methanol. One half of the methanol extract is analysed for chloridazon and metabolite A as described in chapter B.5.2.1.

The second half of the methanol extract is analysed for metabolite B by partitioning on Extrelut columns, clean-up by gel chromatography on Sephadex-LH20 and by column chromatography on silica gel. Final determination is done by HPLC using UV detection at 286 nm.

Findings

The limit of quantitation is 0.05 mg/kg each for parent and metabolite B. Metabolite A was not spiked. Chromatograms from samples and blank material, individual recovery data and information on the precision of the method, but no calibration graphs/data are presented.

Valid: no (use of chloroform, no calibration graphs/data presented)

Grote, 2000

The BASF Method No. 464/0 described in the study "HPLC/DAD Determination of chloridazon (BAS 119 H) and its metabolites B and B-1 in Soil and Sediment" allows the parallel determination of two metabolites and parent chloridazon by HPLC-UV.

Principle of the method

Soil samples are extracted with methanol/water (80+20). After centrifugation acetic acid and sodium chloride are added to the supernatant. The extract is concentrated to the aqueous phase and soaked into the first of two combined Extrelut columns (one dry on the top and a second wetted with NaOH solution on the bottom). Chloridazon and metabolite B-1 are extracted from both Extrelut columns with dichlormethane (eluate 1). After removal of the lower Extrelut column metabolite B is extracted with a dichlormethane/propanol-2 mixture (eluate 2). The eluate 1 is washed with sodium hydroxide and further cleaned up on an alumina SPE column. The eluate 2 is cleaned up on a silica gel SPE column. The final chromatographic analysis of chloridazon and its metabolites B and B-1 is performed by HPLC/DAD detection. For confirmation of results the use of UV spectra and LC/MS measurements are proposed.

Findings

Test were performed with two certified soils and one sediment. The first soil was classified as sand and the second as loam. The limit of quantitation is 0.01 mg/kg each for parent as well as for metabolites B and B-1. Chromatograms from samples and blank material, individual validation data, calibration graphs and information on the precision of the method are presented. For confirmatory purposes UV spectra obtained from a standard solution which is equivalent to a residue level of 0.01 mg/kg are presented. The confirmatory LC/MS determination was performed at a concentration which corresponds to a residue level of 0.4 mg/kg.

Valid: yes

Anonymous, 1977

Additionally, some information on the determination of metabolite B in soil is presented in BASF method No. 116. The principle of this method is described in chapter B.5.2.1. Because of the limited validation conducted in this study, the results are not discussed here.

Valid: no (use of chloroform, no individual recovery data, no information on the calibration or precision of the method)

Table B.5.3-1: Validation data for analytical methods for the determination of chloridazon and its metabolite B in soil and sediment

Reference	Matrix	Test substance	Fortification level [mg/kg]	Average recovery	RSD [%]	No. of analyses
Keller W. (1983)	Soil	Chloridazon	0.05	101	8.3	4
		Metabolite B	0.05	86	8.3	3
			0.5	77	4.6	3
Grote C. (2000)	Standard soil 2.2	Chloridazon	0.01	99.2	8.2	5
			0.1	91.2	4.2	5
			1.0	95.3	2.4	5
		Metabolite B	0.01	83.4	8.3	5
			0.1	85.8	1.5	5
			1.0	80.9	8.4	5
		Metabolite B-1	0.01	92.4	4.0	5
			0.1	93.2	1.1	5
			1.0	95.8	3.2	5
	US soil	Chloridazon	0.01	96.3	6.6	5
			0.1	92.4	2.7	5
			1.0	87.7	8.4	5
		Metabolite B	0.01	76.1	5.2	5
			0.1	81.8	3.9	5
			1.0	84.4	4.3	5
		Metabolite B-1	0.01	88.0	5.4	5
			0.1	90.4	1.0	5
			1.0	87.9	8.3	5
	Sediment	Chloridazon	0.01	90.2	3.3	5
			0.1	94.1	4.4	5
			1.0	96.7	1.6	5
		Metabolite B	0.01	83.4	3.4	5
			0.1	85.8	3.0	5
			1.0	91.3	6.4	5
		Metabolite B-1	0.01	89.8	2.8	5
			0.1	92.8	2.1	5
			1.0	97.3	2.3	5

B.5.3.2 Analytical methods (residue) for water

Keller, 1999

The BASF Method No. 443/0 "HPLC/DAD-determination of chloridazon (BAS 119 H) and its metabolites B and B-1 residues in tap water and surface water" is the only available study, which meets validation requirements.

Principle of the method

In this study the water sample is reduced to 1 % after addition of acetic acid and sodium chloride. Then the concentrate is soaked into the first of two combined Extrelut columns (one dry on the top and a second wetted with NaOH solution on the bottom). Chloridazon and metabolite B-1 are extracted from the Extrelut column with dichlormethane (eluate 1). After removal of the lower Extrelut column metabolite B is extracted with a dichlormethane/propanol-2 mixture (eluate 2). The eluate 1 is washed with sodium hydroxide and further cleaned up on an alumina SPE column. The eluate 2 is filtered through a SPE filter column. The final chromatographic analysis of chloridazon and its metabolites B and B-1 is performed by HPLC/DAD detection. The DAD detector of the HPLC system allows to generate a whole UV spectrum from any peak in the chromatogram for confirmatory purposes. Additionally, an HPLC/MS method is proposed for confirmation.

Findings

Test were performed with tap water and water from a lake. In both water types the limit of quantitation was 0.05 µg/L each for parent as well as for metabolites B and B-1. Chromatograms from samples and blank material, individual validation data, calibration graphs and information on the precision of the method are presented. For confirmatory purposes UV spectra obtained from samples spiked at a residue level of 0.05 µg/L are presented. The confirmatory LC/MS determination was performed at a concentration which corresponds to a residue level of 5µg/L.

Valid: yes

Keller, 1983

Additionally, some information on the determination of chloridazon and its metabolite B in water is presented in the BASF method No. 213. The principle of this method is described in B.5.3.1. The validation data are included in Table B.5.3-2.

Valid: no (use of chloroform, no calibration graphs/data presented)

Table B.5.3-2: Validation data for analytical methods for the determination of chloridazon and its metabolites B and B-1 in drinking and surface water

Reference	Matrix	Test substance	Fortification level [µg/L]	Average recovery	RSD [%]	No. of analyses
Keller W. (1983)	Water	Chloridazon	0.5	85	2.2	4
		Metabolite B	0.5	88	5.5	3
			5	80	1.9	3
Keller, W. (1999)	Tap water	Chloridazon	0.05	89.0	12.6	5
			0.5	95.3	1.7	5
			5.0	95.8	11.1	5
		Metabolite B	0.05	75.9	5.2	5
			0.5	86.4	4.5	5
			5.0	86.8	1.6	5
		Metabolite B-1	0.05	92.1	13.3	5
			0.5	92.5	1.6	5
			5.0	93.2	9.9	5
	Surface water	Chloridazon	0.05	92.0	5.1	5
			0.5	95.1	4.6	5
			5.0	91.1	11.6	5
		Metabolite B	0.05	80.9	12.2	5
			0.5	85.6	3.5	5
			5.0	91.5	5.5	5
		Metabolite B-1	0.05	91.6	3.1	5
			0.5	100.5	4.0	5
			5.0	93.6	5.3	5

B.5.3.3 Analytical methods for air

Class, 1994

The determination of residues in air is described in the study "Validation of an analytical method for the determination of chloridazon in air".

Principle of the method

The method is based on enrichment of chloridazon on tubes filled with activated silica held in place by a glass fibre filter and a polyurethan foam (ORBO 53 tubes). Trapping was simulated for about 6 hours with a sampling rate of approx. 0.5 L/min. The analyte is eluted with methanol aided by sonication. The extracts are analysed without additional cleanup by RP-HPLC-UV.

Findings

No significant losses of spiked chloridazon occurred, when the appropriate amount of air (38 °C; relative humidity of 93 %) was sampled. If stored in the dark at room temperature spiked samples are stable for 5 days. Chromatograms from extracts of sampling tubes and blank material, individual validation data, calibration graphs and information on the precision of the method are presented. Confirmatory procedures are not included.

Valid: yes

Table B.5.3-3: Validation data for analytical methods for the determination of chloridazon in air

Reference	Matrix	Test substance	Fortification level [µg/L]	Average recovery	RSD [%]	No. of analyses
Class, Th. 1994	Air (38 °C / 93 % rel. humidity)	Chloridazon	0.5 µg/tube (equiv. to 3 µg/m^3)	91.1	11.0	4
			15 µg/tube (equiv. to 85 µg/m^3)	92.5	1.9	4

B.5.4 Analytical methods (residue) for body fluids and tissues (Annex IIA 4.2.5; Annex IIIA 5.2)

Analytical methods for the determination of residues of chloridazon in body fluids and/or tissues are not needed, as chloridazon is not classified as acute toxic or very toxic.

B.5.5 Evaluation and assessment

B.5.5.1 Formulation analysis

Analytical methodology is available for the determination of the active substance and the impurities in the technical material as manufactured and for the active substance in the formulation.

Chloridazon in the active substance as manufactured is determined by a HPLC external standard method on a reversed phase column with UV detection (CIPAC method).

Organic impurities in the technical active substance are determined by HPLC on a reversed phase column with UV detection using external standard calculation. The water content was determined using CIPAC MT 30.1 (Karl Fischer titration).

Chloridazon in the formulated product is determined by HPLC external standard method on a reversed phase column with UV detection (CIPAC method).

The methods are validated. Concerning the impurities the linearity is only proven for the main impurity Reg No. 13 344.

B.5.5.2 Residue analysis

For the assessment of the analytical methods for the determination of chloridazon residues the following criteria were used:

- The submitted methods enable the enforcement of the following relevant residue limits (at the time of evaluation):

Matrix	Limit	Comment

plants and plant products	0.3	mg/kg	proposed MRL for sugar beet
	0.5	mg/kg	proposed MRL for red beet
	0.2	mg/kg	proposed MRL for onion
	3	mg/kg	proposed MRL for chard residue definition: chloridazon and metabolite B expressed as choridazon equivalents
animal products	0.1	mg/kg	general residue definition: metabolite B
soil	0.05	mg/kg	limit of quantification, if active substance or metabolite is not highly phytotoxic or toxic to non-target organisms residue definition for enforcement: parent
drinking water	0.1	µg/L	EU drinking water limit residue definition for enforcement: parent, metabolite B and metabolite B-1
surface water	0.6	mg/L	based on the EC_{50} of *Pseudokirchneriella subcapitata* for chloridazon residue definition for enforcement: parent
air	60	µg/m³	based on a proposed $AOEL_{systemic}$ of 0.2 mg/kg bw/d

- Mean recovery rates at each fortification level in the range of 70 to 110 % with a relative standard deviation of ≤ 20 %
- No interfering blanks (< 30 % of the LOQ)
- Methods must employ the simplest approach, involve the minimum cost, and require commonly available equipment.
- The enforcement method for food must be suitable for the determination of all compounds included in the residue definition for enforcement (see B 7.3) and must be checked in an independent laboratory.
- The enforcement methods for environmental matrices must be able to analyse for all compounds of toxicological and/or ecotoxicological significance in soil, water and air (see B 8.9).
- An additional confirmatory method for all matrices is supplied.

According to these criteria adequate analytical methods are listed in Table B.5.5-1. This overview shows, that validated confirmatory methods are not presented for all kinds of food (with one exception). For air no confirmatory method was submitted. Because of the high systemic AOEL only an LOQ of 60 µg/m^3 has to be reached. The submitted method was validated at the much lower LOQ = 3 µg/m^3. Therefore, a confirmation is very simple and a validated confirmatory method is considered not necessary.

Table B.5.5-1: Studies, which describe appropriate analytical procedures (completeness check of analytical methods for monitoring purposes and post-registration control in accordance to guidance document SANCO/825/00 rev . 6)

Matrix type/ crop group	Residue component	Primary Method	Confirmatory method	Independent Lab Validation
Cereals and other dry crops	Chloridazon Metabolite B	Kerl, 2002 a Kerl, 2002 b	No validated method supplied	Kang, 2001 Schulz, 2002 a
Commodities with high water content	Chloridazon Metabolite B	Kerl, 2002 a Kerl, 2002 b	Movassaghi, 1994 Movassaghi, 1994	Kang, 2001 Schulz, 2002 a
Commodities with high fat content	Chloridazon Metabolite B	Kerl, 2002 a Kerl, 2002 b	No validated method supplied	Kang, 2001 Schulz, 2002 a
Fruits with high acid content	Chloridazon Metabolite B	Kerl, 2002 a Kerl, 2002 b	No validated method supplied	Kang, 2001 Schulz, 2002 a
Commodities which are difficult to analyse	Chloridazon Metabolite B	Kerl, 2002 a Kerl, 2002 b	No validated method supplied	Kang, 2001 Schulz, 2002 a
Milk	Metabolite B	Hartl, 2001	No validated method supplied	Stout, 2001
Eggs	Metabolite B	Hartl, 2001	No validated method supplied	Not required
Meat	Metabolite B	Hartl, 2001	No validated method supplied	Not required
Fat (if log $P_{o/w}$>3)	Metabolite B	Hartl, 2001	No validated method supplied	Not required
Kidney/liver	Metabolite B	Hartl, 2001	No validated method supplied	Stout, 2001
Soil	Chloridazon	Grote, 2000	Grote, 2000 (UV spectra)	Generally not required
Drinking water	Chloridazon Metabolite B Metabolite B-1	Keller, 1999 Keller, 1999 Keller, 1999	Keller, 1999 (UV spectra) Keller, 1999 Keller, 1999	Generally not required
Surface water	Chloridazon	Keller, 1999	Keller, 1999 (UV spectra)	Generally not required
Air	Chloridazon	Class, 1994	considered not necessary	Generally not required
Blood	Chloridazon	Analytical methods for the determination of residues of chloridazon in body fluids and/or tissues are not needed, as chloridazon is not classified as acute toxic or very toxic		
Body tissues	Chloridazon			

B.5.6 References relied on

Annex point/ reference number	Author(s)	Year	Title source (where different from company) report no. GLP or GEP status (where relevant), published or not BBA registration number	Data protection claimed Y/N	Owner
AIIA-1.10; AIIA-4.1; AIIA-4.1.2	Liesner, M.	1991	Validation of HPLC method CP 012 for determination of technical impurities of chloridazon (pyrazon). 1991/10089! PCP01086 GLP, unpublished CHE2001-570	Y	BAS
AIIA-4.1; AIIA-4.1.2	Liesner, M. and Mayer, K.	1990	Determination of the impurities in technical chloridazon (pyrazon) by HPLC. 1990/10465 not GLP, unpublished CHE2001-569	Y	BAS
AIIA-4.1.1; AIIIA-5.1.1	Anonymous	1986	Analytical method CIPAC 112: Determination of chloridazon in chloridazon technical and chloridazon formulations. 1986/11174 not GLP, published CHE2001-571	N	-
AIIA-4.2.1	Class, T.	2002	Independent laboratory validation (ILV) of method No. 494/0 for the determination of chloridazon in animal matrices. 2002/1009045 GLP, unpublished MET2003-324	Y	BAS
AIIA-4.2.1	Hartl, M.	2002	Validation of BASF Method No. 494/0 for the determination of BAS 119 H (chloridazon; Reg. No. 13 033) in animal matrices. 2002/1007897 GLP, unpublished MET2003-325	Y	BAS
AIIA-4.2.1	Hartl, M.	2001	Validation of BASF method 499/0 for the determination of chloridazon metabolite B (Reg. No. 014 456) in sample materials of animal origin. 2001/1014785 GLP, unpublished MET2003-323	Y	BAS
AIIA-4.2.1	Kampke-Thiel, K.	1998	Validation of BASF method 983/0 for the determination of chloridazon (BAS 119 H) and its hydroxy metabolite (BH 119-4-OH) in hen eggs. 1998/11343 GLP, unpublished MET2003-326	Y	BAS

[1] Only notifier listed

Annex point/ reference number	Author(s)	Year	Title source (where different from company) report no. GLP or GEP status (where relevant), published or not BBA registration number	Data protection claimed Y/N	Owner[1]
AIIA-4.2.1	Kang, J.	2001	Independent laboratory validation of an analytical method for the determination of BAS 119 H residues. 2001/1009074 GLP, unpublished MET2001-454	Y	BAS
AIIA-4.2.1	Kerl, W.	2003	Technical procedure: Method for the determination of chloridazon (Reg. No. 130 33) and BH 119-Glucosid (Reg. No. 262 529) in plant matrices. 2003/1000942 not GLP, unpublished MET2003-310	Y	BAS
AIIA-4.2.1	Kerl, W.	2002	Validation of the analytical method 494/0: Method for the determination of BAS 119 H in plant matrices. 2002/1008794 GLP, unpublished MET2003-343	Y	BAS
AIIA-4.2.1; AIIIA-5.2	Kerl, W.	2002	Validation of the analytical method 497/0: method for the determination of BH 119-metabolite B in plant matrices. 2002/1008795 ! 121485 GLP, unpublished MET2003-248	Y	BAS
AIIA-4.2.1	Kerl, W. and Mackenroth, C.	2003	Summary of validation data: Validation of the analytical method 518/0: Method for the determination of chloridazon (Reg. No. 130 33) and BH 119-Glucosid (Reg. No. 262 529) in onions. 2003/1001365 not GLP, unpublished MET2003-311	Y	BAS
AIIA-4.2.1	Movassaghi, S.	1994	Method for determination of chloridazon and its metabolite residues in sugar beet roots, tops and process fractions (refined sugar and molasses). Method No. A9202, Study No. 92066. 1994/5041 GLP, unpublished MET2001-451	Y	BAS
AIIA-4.2.1; AIIA-5.2	Schulz, H.	2002	Determination of BH 119-Metabolite B in Plant Materices - Validation of the Method No. 497/0. 2002/1007085! IF-101/30298-00 GLP, unpublished MET2002-440	Y	BAS

Annex point/ reference number	Author(s)	Year	Title source (where different from company) report no. GLP or GEP status (where relevant), published or not BBA registration number	Data protection claimed Y/N	Owner[1]
AIIA-4.2.1	Schulz, H.	2002	Addendum No. 1 to report: Determination of BH 119-metabolite B in plant matrices - independent laboratory validation of the method No. 497/0. 2002/1006294 GLP, unpublished MET2003-327	Y	BAS
AIIA-4.2.1	Schulz, H.	1996	Determination of chloridazon, metabolite A and metabolite B in sugar beets - Validation of the method A 9202. 96/10599 GLP, unpublished MET2001-452	Y	BAS
AIIA-4.2.1	Stout, S.	2001	BAS 119H: Independent laboratory validation of BASF method number 499/0 for the determination of residues of BAS 119 H metabolite B in liver and bovine whole milk by HPLC/MS/MS. 2001/7000443 GLP, unpublished MET2003-322	Y	BAS
AIIA-4.2.1	Zehr, R.D.	1996	Method for determination of BAS 119 H (chloridazon) and its para-hydroxy metabolite in cow milk and cow tissues including muscle, liver, kidney and fat. 96/5087 GLP, unpublished MET2001-453	Y	BAS
AIIA-4.2.2	Grote, C.	2000	Validation of analytical method No. 464/0: HPLC/DAD determination of chloridazon (BAS 119H) and its metabolites B and B-1 in soil and sediment. 2000/1004093 GLP, unpublished MET2001-455	Y	BAS
AIIA-4.2.3	Keller, W.	1999	HPLC-DAD-determination of chloridazon (BAS 119H) and its metabolites B and BI residues in tap water and surface water. 99/10088 GLP, unpublished MET2001-456	Y	BAS
AIIA-4.2.4	Class, T.	1994	Validation of an analytical method for the determination of chloridazon in air. 1994/10214 GLP, unpublished MET1999-526	Y	BAS

Annex point/ reference number	Author(s)	Year	Title source (where different from company) report no. GLP or GEP status (where relevant), published or not BBA registration number	Data protection claimed Y/N	Owner[1]
AIIIA-5.1; AIIIA-5.1.1	Anonymous	1997	Determination of chloridazon in chloridazon water dispersible granules 111/WG/M/-, 1 1997/1001160 not GLP, published CHE2001-573	N	-

Codes of owner

BAS: BASF Aktiengesellschaft