

**Final Report****Determination of Residues of Quinoxifen Applied as EF-1295 in  
Hops  
Four Sites in Germany, 1998****Author**

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**Date**

31 May 1999

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**Study Identification Code**

Test compound: EF-1295

Study code of the Dow AgroSciences: RF 98-200

Study code of GAB: 98251/G1-FPHO

Trial codes of the Dow AgroSciences: RF 98-200-A, RF 98-200-B, RF 98-200-C, RF 98-200-D



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This report contains confidential and proprietary information of Dow AgroSciences which must not be disclosed to anyone except the employees of this company or to persons authorised by law or judicial judgement without the expressed and written approval of Dow AgroSciences.



### Good Laboratory Practices Compliance Statement

This study was conducted according to the published Good Laboratory Practices (GLP) for tests of substances regulated under the Federal Insecticide, Fungicide and Rodenticide Act (40 CFR part 160) and meets the following requirements:

Federal Republic of Germany; Principles of Good Laboratory Practice (GLP); Bundesgesetzblatt Teil I Nr. 47, Neufassung des Chemikaliengesetzes der BRD vom 25. Juli 1994, § 19a Absatz 1, Anhang 1; Bonn 29. Juli 1994

These German requirements are based on the OECD Principles of Good Laboratory Practice which are accepted by regulatory authorities throughout the European Community, the United States of America (FDA and EPA) and Japan (MHW, MAFF and MITI).


  
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Dr. Christian Oberwalder

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31 May 1999  
Date



### Statement of no data confidentiality claims

No claim of confidentiality is made for any information contained in this study on the basis of its falling within the scope of FIFRA 6§10 (d) (1) (A), (B), or (C).

Company: Dow AgroSciences

\_\_\_\_\_  
(Company Agent)

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(Date)

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(Title of Company Agent)

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(Signature of Company Agent)



## Study Identification

Determination of Residues of Quinoxifen Applied as EF-1295 in Hops -  
Four Sites in Germany, 1998

Test material: EF-1295

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Trial RF 98-200-B: 84048 Unterempfenbach, Germany

Trial RF 98-200-C: 84072 Au, Germany

Trial RF 98-200-D: 88069 Tettngang, Germany



## Study timetable:

Study initiation date:	22 June 1998 (GAB), 17 June 1998 (LBP)
Experimental (field part) start date:	29 June 1998 (GAB), 23 June 1998 (LBP)
Field part end date:	11 Sep. 1998 (GAB), 30 Oct. 1998 (LBP)
Analytical start date:	03 November 1998
Analytical end date:	06 November 1998
Study completion date:	31 May 1999



### Statement of Quality Assurance Unit


**Study codes:** 98251/G1-FPHO

**Study title:** Determination of Residues of Quinoxifen Applied as EF-1295 in Hops  
Four Sites in Germany, 1998

The conduct of this study or studies of the same type was inspected periodically. Protocol, draft report and Draft report were audited by the Quality Assurance Unit. The dates are given below:

	Date of audit	Date of report
<b>Protocol:</b>	18/06/98	18/06/98
<b>Experimental phase:</b>	10/07/98	10/07/98
<b>Draft report:</b>	26/02/99	26/02/99
<b>Final report:</b>	31/05/99	31/05/99

Quality assurance manager  
(Dr. Bernardo Pollmann)

31 May 99   
Date / Signature



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## 1 Summary

Objective of this study was to determine the residue decline of EF-1295, containing 250 g/L quinoxyfen, in hops. For this, the test substance was applied according to the recommended used conditions with the maximum recommended number of applications and with the recommended application concentration. After the last application samples were taken at several dates and shipped to the analytical laboratory. The field phase comprised four trials in the main hops growing regions of Germany.

Each field trial comprised two plots of at least 288 m<sup>2</sup> size. One plot was treated with EF-1295 and one remained untreated. EF-1295 was applied three times with a calibrated airblast sprayer simulating a commercial application. The concentration in the spray solution was 0.03 %. The application dates and rates were as follows:

No.	Date	BBCH-Code	Water [L/ha]	Product [L/ha]	Quinoxyfen <sup>1)</sup> [g/ha]
<b>Trial RF98-200-A</b>					
1	23/06/98	38	2166	0.650	163
2	07/07/98	55	2800	0.840	210
3	21/07/98	67	3231	0.969	242
<b>Trial RF 98-200-B</b>					
1	23/06/98	38	2181	0.654	164
2	07/07/98	55	2731	0.819	230
3	21/07/98	67	3203	0.961	240
<b>Trial RF 98-200-C</b>					
1	23/06/98	38	2172	0.638	160
2	07/07/98	55	2783	0.835	209
3	21/07/98	67	3260	0.978	245
<b>Trial RF 98-200-D</b>					
1	29/06/98	60	2720	0.816	204
2	10/07/98	65	3075	0.923	231
3	24/07/98	72	3346	1.004	251

<sup>1)</sup> based on the nominal content of a.i.

Samples were taken 7, 14, 21, 27 to 28 and 35 DALA (days after last application). Until analysis, the samples were stored at temperatures  $\leq -18$  °C for a maximum period of 101 days. Samples were shipped on 11/09/98 (trial RF 98-200-D) and on 28/10/98 (trials RF 98-200-A, RF 98-200-B and RF 98-200-C). All samples arrived at the analytical laboratory in good condition.

The analysis of quinoxifen was performed by the following method in analogy to a published multiresidue method (FILLION et al., 1995):

Extraction:	Cold extraction with acetonitrile
Clean-up:	Solid-phase-extraction on Envi-Carb™ activated carbon and primary amine ion exchanger
Method of determination:	Capillary gas chromatography with electron-capture detection (GC-ECD)
Specificity:	Parent compound
Interferences:	In untreated control samples of hop cones quinoxifen was not detectable.
Recovery ± RSD:	85 % ± 11 % RSD (fresh hop cones) 99 % ± 6 % RSD (dried hop cones)
Fortification levels:	0.01 mg/kg to 1.0 mg/kg
Detection limit:	0.006 mg/kg
Limit of quantitation:	0.02 mg/kg

By this method of analysis the following results were obtained:

Samplin g [DALA]	Commodity	Treatment	Residues in mg/kg			
			RF 98-200-A	RF 98-200-B	RF 98-200-C	RF 98-200-D
7	fresh cones	control	n.d.	n.d.	n.d.	n.d.
		EF-1295	0.47 <sup>1)</sup>	0.53 <sup>2)</sup>	0.44 <sup>2)</sup>	1.00 <sup>2)</sup>
14	fresh cones	EF-1295	0.12	0.10	0.12	0.31
21	fresh cones	EF-1295	< LOQ	0.05	0.03	0.09
28 <sup>3)</sup>	fresh cones	EF-1295	0.03	< LOQ	0.03	0.19
35	fresh cones	control	n.d.	n.d.	n.d.	n.d.
		EF-1295	0.03	< LOQ	0.04	0.05
	dried cones	control	n.d.	n.d.	n.d.	n.d.
		EF-1295	0.04	< LOQ	0.07 <sup>2)</sup>	0.05

DALA: Days after last application

n.d.: not detectable

LOQ: limit of quantitation

1) mean of three determinations

2) mean of two determinations

3) 27 DAA in trials RF 98-200-A, RF 98-200-B and RF 98-200-C

Based on the results of the four trials maximum residue levels (MRLs) were calculated according BBA guideline part IV, 3-6 method 2 (MRL=2\*R(0.75)). The calculated MRLs were 0.300 mg/kg for 28 DALA, 0.095 mg/kg for 35 DALA and, for dried hops, 0.130 mg/kg.



## 2 Time Schedule

Date of protocol	18/06/98
Start of the experimental phase:	23/06/98
End of the experimental field phase:	30/10/98
Shipment of samples:	28/08/98, 11/09/98 and 28/10/98
Start of the analytical phase	03/11/98
End of the analytical phase	06/11/98
Draft report:	05/02/99
Final report:	31/05/99

## 3 Study Objective and Guidelines

The objective of this study was to investigate the decline of quinoxifen in hops and processed products under practical field conditions in Southern Germany. The formulation was applied in the field on hops according to practical use conditions. Samples of treated hops were taken at several dates after application and analysed for residues of quinoxifen.

The study was performed in accordance with the IVA guideline for residue trials, the BBA guidelines part IV, 3-3, part IV 3-6, IV, 3-8, the overall study protocol of the sponsor RF 98-200, the protocol supplements 98251/G1-FPHO and 98368/G1-RHO of GAB/IFU, the protocol supplements RF 0498, RF 0598 and RF0698 of the LBP, and the amendments to these protocol and supplements as well the SOPs of GAB/IFU and LBP.

## 4 Material and Methods

### 4.1 Test Substances and Reference Substance

The test substance is characterised in Table 1. Except appearance and storage conditions all data were provided by Dow AgroSciences.

Table 1: Characterisation of the test substance and reference substance

	Test substance
Name / Code	EF-1295
Batch	PM 1403
GAB-code	98251
Active ingredient	Quinoxifen
Content of a.i.	250 g/L
Expiry date	06/03/2000
Appearance	light brown powder
Density [g/cm <sup>3</sup> ]	1.106 g/mL
Storage	ambient
Safety symbol(s)	Xi
Target(s)	powdery mildew in hops

#### Stability and homogeneity in the spraying solution

Homogeneity of spray solution was obtained by thorough stirring or mixing immediately before application. Stability in spray solution is assumed for the test purpose where the interval between mixing and application was less than 1 h.

## 4.2 Location

The study comprised four residue trials in hops. The trials were located in main hop growing regions of Germany (Hallertau and Tettang, see Figure 1). Region, variety and cultivation were typical for the cultivation of hops. A description of the test site is given in Table 2.

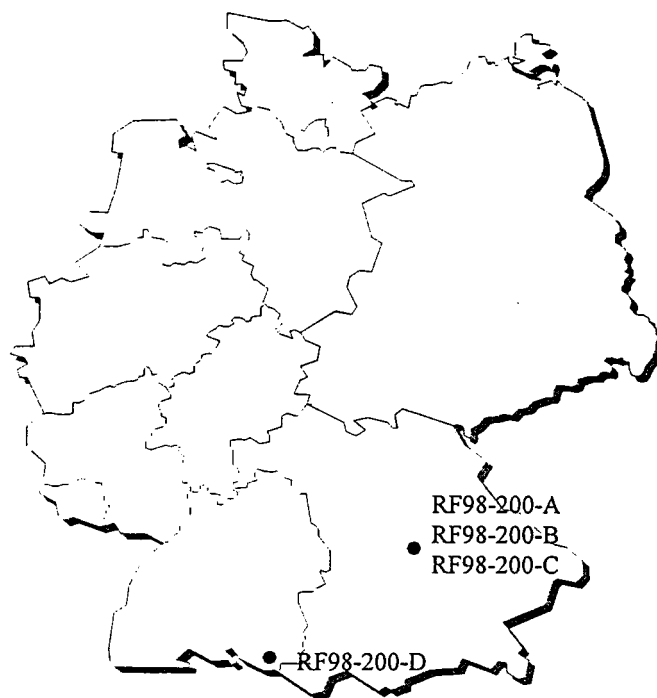


Figure 1: Location of the test sites

Table 2: Description of the test sites

<b>Trial number</b>		<b>RF 98-200-A</b>	<b>RF 98-200-B</b>
Location		Niederlauterbach	Unterempfenbach
Zip code		85283	84048
State		Bayern	Bayern
Meters above sea-level	[m]	450	460
Slope	[%]	3	3
Soil type		sandy loam	sandy loam
pH		6.8	6.7
Organic carbon	[%]	not determined	not determined
<b>Trial number</b>		<b>RF 98-200-C</b>	<b>RF 98-200-D</b>
Location		Au	Tettang
Zip code		84072	88069
State		Bayern	Baden-Württemberg
Meters above sea-level	[m]	495	490
Slope	[%]	~2	~1
Soil type		silty loam	sandy loam
pH		5.4	6.0
Organic carbon	[%]	not determined	> 2%

Weather data for trials RF 98-200-A, RF 98-200-B and RF 98-200-C were taken from LBP, weatherstation Hüll, the weather data for trial RF 98-200-D were taken from the weather station Eriskirch of the German weather service. Summarised data are given in the appendix in Table 27. During treatment and sampling the climatic conditions were measured with equipment directly on the trial site.

### 4.3 Cropping

The crop was cultivated according to normal agricultural practice for the region. A description of the crop is given in Table 3. Maintenance and application of fertilisers (Table 4) was according to good agricultural practice at all sites. No irrigation was applied. The pesticides applied during the trial period are listed in Table 5.

Table 3: Description of the crop

<b>Trial number</b>	<b>RF 98-200-A</b>	<b>RF 98-200-B</b>
Crop	Hops	Hops
Variety	Hallertauer Tradition	Hallertauer Tradition
Date of planting	1996	1996
Plants per ha	2155	2130
Row width	1.45 m	1.45 m
Date of flowering	approx. 21/07/98	approx. 21/07/98
Date of harvest	not recorded	not recorded
<b>Trial number</b>	<b>RF 98-200-C</b>	<b>RF 98-200-D</b>
Crop	Hops	Hops
Variety	Hallertauer Tradition	Spalter
Date of planting	1995	1937
Plants per ha	2299	4167
Row width	1.45 m	1.6 m
Date of flowering	approx. 21/07/98	approx. 10/07/98
Date of harvest	not recorded	24/08 – 28 /08/98

Table 4: Application of fertilisers by the farmer

Date	Product	Rate per ha
<b>Trial RF 98-200-A</b>		
11/03/98	CAN	54 kg N
20/05/98	urea-ammonia-nitrate-solution	70 kg N
05/06/98	SSA + urea-ammonia-nitrate-solution	72 kg N
10/06/98	potash-magnesia fertilizer	165 kg K <sub>2</sub> O, 55 kg MgO
<b>Trial RF 98-200-B</b>		
not available		
<b>Trial RF 98-200-C</b>		
20/06/98	slurry	60 kg N, 30 kg P <sub>2</sub> O <sub>5</sub> , 30 kg K <sub>2</sub> O, 10 kg MgO
<b>Trial RF 98-200-D</b>		
31/03/98	potash-magnesia fertiliser, 30 % K + 10 % MgO	not available
01/04/98	lime nitrogen, 20 % N	not available
20/05/98	complete fertiliser, 12 % N + 12 % P <sub>2</sub> O + 17 % K <sub>2</sub> O, 2 % MgO	not available
08/06/98	Fetrilon	not available
17/06/98	CAN, 27 % N	not available

Table 5: Pesticides applied by the farmer

Date	Product	Active ingredient(s)	Product [kg or L/ha]
<b>Trial RF 98-200-A</b>			
05/06/98	Mitac + Aliette	amitraz 20% fosetyl 74.6%	2.15 L 2.15 kg
24/06/98	Copper + Saprol neu	copperoxychlorite 75.6% triforin 19%	5.40 kg 2.70 L
14/07/98	Copper + Saprol neu	copperoxychlorite 75.6% triforin 19%	10.60 kg 4.10 L
30/07/98	Copper + Saprol neu	copperoxychlorite 75.6% triforin 19%	16.25 kg 5.45 kg
<b>Trial RF 98-200-B</b>			
23/06/98	Copper E + Confidor + Mitac	copperoxychlorite 75.6% imidacloprid 665 g/kg amitraz 20%	6.0 kg 0.17 kg 7.50 L
01/07/98	Copper + Saprol neu	copperoxychlorite 75.6% triforin 19%	7.50 L 3.75 kg
13/07/98	Copper + Saprol neu	copperoxychlorite 75.6% triforin 19%	7.50 kg 3.75 kg
28/07/98	Copper	copperoxychlorite 75.6%	8.10 kg
<b>Trial RF 98-200-C</b>			
25/06/98	Copper	copperchlorite 75.6%	6.0 kg
02/07/98	Mitac	amitraz 20%	7.50 L
27/07/98	Copper + Saprol neu	copperchlorite 75.6% triforin 19%	6.0 L 5.0 L
01/08/98	Copper	copperchlorite 75.6%	6.0 kg
<b>Trial RF 98-200-D</b>			
12/05/98	Aliette WG	fosetyl, 746 g/kg	0.75
23/05/98	Aliette WG + zinc sulphate	fosetyl, 746 g/kg zinc sulphate	1.23 2.00
05/06/98	zinc sulphate	zinc sulphate	2.00
08/06/98	Copper	copperoxychloride 500 g/kg	1.50
20/06/98	Vertimec + Li 700	Abamectin 18 g/L wetting agent	0.02 3.75
22/06/98	Copper	copperoxychlorite 500 g/kg	3.50
10/07/98	Copper + Confidor WG	Kupferoxychlorid 500 g/kg Imidacloprid 665 g/kg	3.50 0.16
25/07/98	Copper	copperoxychlorite 500 g/kg	5.00
08/08/98	Copper	copperoxychlorite 500 g/kg	5.00

#### 4.4 Plot Design

Each trial comprised two variants (1 treated and 1 untreated). A description of the test design and the plots is given in Table 6.

Table 6: Plot design

Treatments	C = untreated (control) T = treated
Replicates per variant	1 of each treatment
Plot size	25.0 m x 12.8 m = 320 m <sup>2</sup> (RF 98-200-A) 25.0 m x 12.8 m = 320 m <sup>2</sup> (RF 98-200-B) 25.0 m x 12.0 m = 300 m <sup>2</sup> (RF 98-200-C) 30.0 m x 9.6 m = 288 m <sup>2</sup> (RF 98-200-D)
Distance between plots	at least 62.1 m (RF 98-200-A) at least 60.6 m (RF 98-200-B) at least 20.2 m (RF 98-200-C) at least 30.0 m (RF 98-200-D)
Shortest distance between plots and end of the field	RF 98-200-A: not available RF 98-200-B: not available RF 98-200-C: not available RF 98-200-D: ≥ 5 m

#### 4.5 Applications

The test substance (EF-1295) was applied three times. The proposed treatment schedule is given in Table 7, details about the actual applications in Table 8 to Table 11. The spray solution was prepared and well homogenised by stirring immediately before application. The actual applied amounts were calculated by measuring the remaining spray solution after treatment.

Table 7: Proposed treatment schedule

Number	Date	Treatment	Product	Product rate(s)	Water rate(s)
<b>Trials RF 98-200-A, RF 98-200-B, RF 98-200-C</b>					
1	13-15 DBA2	C	---	---	---
		T	EF-1295	0.03 % (= 630 mL/ha*)	2100 L/ha
2	13-15 DBA3	C	---	---	---
		T	EF-1295	0.03 % (= 810 mL/ha*)	2700 L/ha
3	34-36 DBH	C	---	---	---
		T	EF-1295	0.03 % (= 960 mL/ha*)	3200 L/ha
<b>Trial RF 98-200-D</b>					
1	63 ± 2 DBH	C	---	---	---
		T	EF-1295	0.03 % (= 780 mL/ha*)	2600 L/ha
2	12 ± 2 DAA1 and 49 ± 2 DBH	C	---	---	---
		T	EF-1295	0.03 % (= 900 mL/ha*)	3000 L/ha
3	12 ± 2 DAA2 and 37 ± 2 DBH	C	---	---	---
		T	EF-1295	0.03 % (= 990 mL/ha*)	3300 L/ha

DBH: days before harvest

DAA1: days after application 1

DAA2: days after application 2

Table 8: Details about treatments in trial RF 98-200-A

Application		1	2	3
Date		23/06/98	07/07/98	21/07/98
Time		10:45/10:50	9:00/9:05	9:20/9:25
Interval	[days]	---	14	14
<b>Device</b>				
Sprayer		Airblast sprayer type Nobili Euro 105-2000		
No. of nozzles <sup>1)</sup>		8	8	8
Pressure	[bar]	18	20	21
Application speed	[km/h]	2.1	2.0	1.7
Technical faults		No	No	No
<b>Dosage</b>				
Spray solution/plot	[L]	69.3	89.6	103.4
Spray solution/ha	[L]	2166	2800	3231
Product/plot	[mL]	20.8	26.9	31.0
Product/ha	[mL]	650	840	969
Concentration	[%]	0.03	0.03	0.03
Rate a.i. <sup>2)</sup>	[g/ha]	163	210	242
Deviation of recommended rate	[%]	+3.1	+3.7	+1.0
<b>Crop/Environment</b>				
Temperature	[° C]	22	21	26
Humidity	[%]	58	78	72
Wind speed	[m/s]	0-1	0-1	0-1
Rainfall treatment day/next day <sup>3)</sup>	[mm]	0.0 / 0.0	4.5 <sup>4)</sup> / 6.7	1.4 <sup>5)</sup> / 1.8
Clouding	[%]	50	5	0
Growth stage <sup>6)</sup>		38	55	67

<sup>1)</sup> hollow cone nozzles of the following size (from top to bottom): 1.5 - 1.8 - 2.0 - 1.8 - 1.5 - 1.2 - 1.2 - 1.2

<sup>2)</sup> based on the nominal content of a.i.

<sup>3)</sup> Data from weather station Hüll,

<sup>4)</sup> Rainfall started approx. 6 to 7 h after application

<sup>5)</sup> No rainfall reported for immediately before and after application

<sup>6)</sup> BBCH code

Table 9: Details about treatments in trial RF 98-200-B

Application		1	2	3
Date		23/06/98	07/07/98	21/07/98
Time		9:55/10:00	8:20/8:25	8:35/8:40
Interval	[days]	-- -	14	14
<b>Device</b>				
Sprayer		Airblast sprayer type Nobile Euro 105-2000		
No. of nozzles <sup>1)</sup>		8	8	8
Pressure	[bar]	18	20	21
Application speed	[km/h]	2.1	2.0	1.7
Technical faults		No	No	No
<b>Dosage</b>				
Spray solution/plot	[L]	69.80	87.40	102.50
Spray solution/ha	[L]	2181	2731	3203
Product/plot	[mL]	20.9	26.2	30.7
Product/ha	[mL]	724	906	1063
Concentration	[%]	0.03	0.03	0.03
Rate a.i. <sup>2)</sup>	[g/ha]	164	230	240
Deviation of recommended rate	[%]	+3.9	+1.2	+0.1
<b>Crop/Environment</b>				
Temperature	[° C]	19	18	24
Humidity	[%]	65	81	78
Wind speed	[m/s]	0-2	0-1	0-1
Rainfall treatment day/next day <sup>3)</sup>	[mm]	0.0 / 0.0	4.5 <sup>4)</sup> / 6.7	1.4 <sup>5)</sup> / 1.8
Clouding	[%]	20	0	5
Growth stage <sup>6)</sup>		38	55	67

<sup>1)</sup> hollow cone nozzles of the following size (from top to bottom): 1.5 - 1.8 - 2.0 - 1.8 - 1.5 - 1.2 - 1.2 - 1.2

<sup>2)</sup> based on the nominal content of a.i.

<sup>3)</sup> Data from weather station Hüll,

<sup>4)</sup> Rainfall started approx. 6 to 7 h after application

<sup>5)</sup> No rainfall reported for immediately before and after application

<sup>6)</sup> BBCH code

Table 10: Details about treatments in trial RF 98-200-C

Application		1	2	3
Date		23/06/98	07/07/98	21/07/98
Time		8:45/8:50	10:10/10:15	10:30/10:35
Interval	[days]	--	14	14
<b>Device</b>				
Sprayer		Airblast sprayer type Nobili Euro 105-2000		
No. of nozzles <sup>1)</sup>		8	8	8
Pressure	[bar]	16	18	20
Application speed	[km/h]	2.2	2.0	1.8
Technical faults		No	No	No
<b>Dosage</b>				
Spray solution/plot	[L]	63.8	83.5	97.8
Spray solution/ha	[L]	2127	2783	3260
Product/plot	[mL]	19.1	25.0	29.3
Product/ha	[mL]	638	835	978
Concentration	[%]	0.03	0.03	0.03
Rate a.i. <sup>2)</sup>	[g/ha]	160	209	245
Deviation of recommended rate	[%]	+1.3	+3.1	+1.9
<b>Crop/Environment</b>				
Temperature	[° C]	18	25	28
Humidity	[%]	66	70	64
Wind speed	[m/s]	0-1	0-1	0-1
Rainfall treatment day/next day <sup>3)</sup>	[mm]	0.0 / 0.0	4.5 <sup>4)</sup> / 6.7	1.4 <sup>5)</sup> / 1.8
Clouding	[%]	15	70	0
Growth stage <sup>4)</sup>		38	55	67

<sup>1)</sup> hollow cone nozzles of the following size (from top to bottom): 1.5 - 1.8 - 2.0 - 1.8 - 1.5 - 1.2 - 1.2 - 1.2

<sup>2)</sup> based on the nominal content of a.i.

<sup>3)</sup> Data from weather station Hüll,

<sup>4)</sup> Rainfall started approx. 6 to 7 h after application

<sup>5)</sup> No rainfall reported for immediately before and after application

<sup>6)</sup> BBCH code

Table 11: Details about treatments in trial RF 98-200-D

Application		1	2	3
Date		29/06/98	10/07/98	24/07/98
Time		12:20	16:25/16:32	11:20/11:24
Interval	[days]	--	11	14
<b>Device</b>				
Sprayer		commercial airblast sprayer (Meyers)		
No. of nozzles <sup>1)</sup>		8	8	8
Pressure	[bar]	12	13	13
Application speed	[km/h]	1.4	1.2	1.1
Technical faults		No	No	No
<b>Dosage</b>				
Spray solution/plot	[L]	78.3	88.6	96.4
Spray solution/ha	[L]	2720	3075	3346
Product/plot	[mL]	23.5	26.6	28.9
Product/ha	[mL]	816	923	1004
Concentration	[%]	0.03	0.03	0.03
Rate a.i. <sup>2)</sup>	[g/ha]	204	231	251
Deviation of recommended rate	[%]	+4.6	+2.5	+1.4
<b>Crop/Environment</b>				
Temperature	[° C]	24.8	18.0 / 29.1	23.9
Humidity	[%]	50	47 / 75	65
Wind speed	[m/s]	0	< 1	0
Rainfall treatment day/next day <sup>3)</sup>	[mm]	0.0 / 1.5	0.2 <sup>4)</sup> / 0.5	0.0 / 0.0
Clouding	[%]	50	30	40
Growth stage <sup>5)</sup>		60	65	72
Leaf surface		dry	dry	dry

<sup>1)</sup> hollow cone nozzles of the following size (from top to bottom): 1.5 - 1.5 - 1.5 - 1.5 - 1.0 - 1.5 - 1.5 - 1.4

<sup>2)</sup> based on the content of a.i.

<sup>3)</sup> Data from weather station Eriskirch

<sup>4)</sup> no rainfall immediately before and after application reported

<sup>5)</sup> BBCH code

## 4.6 Sampling

Hops samples were taken in accordance with the test facility SOPs which are based on the recommendations of BECKER et al. (1990). Each field sample consisted of cones from at least 12 different plants distributed over the plot. No samples were taken from the bordering rows of each plot. For sampling, from each sampled plant at least two to three branches were taken considering lower parts as well as middle and upper parts of the vine. The non treated samples were taken before the treated samples. Non treated and treated samples were placed in PE-bags immediately after picking, labelled and then transported in separate refrigerated containers to the freezers. Details about the sampling schedule and the sampling are given in Table 12 to Table 15.

In trial RF 98-200-D at the last sampling date 12 vines per plot were harvested. The vines were cut shortly above ground and then transported to a picking machine. All cones of the 12 harvested vines were picked mechanically. The picking machine used was a "Wolf WH 140". Picking was done first from the vines from the untreated plot and afterwards from the vines from the treated plot. An aliquot of the picked cones was taken as green hop sample. A further aliquot was dried. This aliquot was packed in nylon net bags which were placed directly on the outlet of warm air in a commercial drying kiln. Duration of drying was 3 h, air temperature was 45 °C. Treated and untreated cones were dried at separate places of the kiln, so that no contamination of the untreated samples could occur. After drying, the amount of dry cones was reduced by taking again an aliquot. This aliquot of dried cones was frozen immediately.

In trial RF 98-200-A, RF 98-200-B and RF 98-200-C hops samples for drying were sampled separately. The sampled cones were transported in nylon net bags to the laboratory kilns (type HLT 0.3, Heindl) supplied with a drying reservoir 30 cm x 30 cm x 42 cm. Separate kilns were used for treated and non treated samples. The process of drying took 6 h, the temperature of the air used for drying was 60 °C. After drying the samples were packed and frozen.

Table 12: Sampling schedule and details about sampling for trial RF 98-200-A

Date	DALA	BBCH	Variant	Sample code	Sample type	Weight field sample	Weight lab. sample	Freezing
28/07/98	7	71	C	RF 98-200-A-01 RF 98-200-A-02	hop cones	0.39 kg 0.43 kg	0.26 kg 0.26 kg	same day <sup>1)</sup>
			T	RF 98-200-A-03 RF 98-200-A-04	hop cones	0.32 kg 0.37 kg	0.26 kg	same day <sup>1)</sup>
04/08/98	14	73	T	RF 98-200-A-05 RF 98-200-A-06	hop cones	0.60 kg 0.93 kg	0.52 kg 0.52 kg	same day <sup>1)</sup> same day <sup>1)</sup>
			T	RF 98-200-A-07 RF 98-200-A-08	hop cones	0.54 kg 0.71 kg	0.54 kg 0.53 kg	same day <sup>1)</sup> same day <sup>1)</sup>
17/08/98	27	83-85	T	RF 98-200-A-09 RF 98-200-A-10	hop cones	0.71 kg 0.75 kg	0.53 kg 0.53 kg	same day <sup>1)</sup> same day <sup>1)</sup>
			C	RF 98-200-A-11 RF 98-200-A-12	hop cones	1.03 kg 1.02 kg	1.03 kg 1.02 kg	same day <sup>1)</sup> same day <sup>1)</sup>
25/08/98	35	89	C	RF 98-200-A-13 RF 98-200-A-14	hop cones	1.29 kg <sup>2)</sup> 1.07 kg <sup>2)</sup>	0.32 kg <sup>3)</sup> 0.27 kg <sup>3)</sup>	same day <sup>4)</sup> same day <sup>4)</sup>
			T	RF 98-200-A-15 RF 98-200-A-16	hop cones	1.25 kg 1.50 kg	1.06 kg 1.24 kg	same day <sup>1)</sup> same day <sup>1)</sup>
			T	RF 98-200-A-17 RF 98-200-A-18	hop cones	1.06 kg <sup>2)</sup> 1.09 kg <sup>2)</sup>	0.28 kg <sup>3)</sup> 0.27 kg <sup>3)</sup>	same day <sup>4)</sup> same day <sup>4)</sup>

Explanation of letters in sample code: C: untreated, T: treated DALA: Days after last treatment

<sup>1)</sup>Samples were frozen on the day of sampling. The exact time was not recorded. The samples were frozen first at the field station at Hüll and then transported to the Bayerische Landesanstalt für Bodenkultur und Pflanzenschutz at Freising

<sup>2)</sup>fresh hops      <sup>3)</sup>dried hops      <sup>4)</sup>after the end of the drying process

Table 13: Sampling schedule and details about sampling for trial RF 98-200-B

Date	DALA	BBCH	Variant	Sample code	Sample type	Weight field sample	Weight lab. sample	Freezing
28/07/98	7	69-71	C	RF 98-200-B-01	hop cones	0.35 kg	0.25 kg	same day <sup>1)</sup>
				RF 98-200-B-02		0.26 kg	0.26 kg	
			T	RF 98-200-B-03	hop cones	0.30 kg	0.25 kg	same day <sup>1)</sup>
				RF 98-200-B-04		0.32 kg	0.26 kg	
04/08/98	14	71-73	T	RF 98-200-B-05	hop cones	0.52 kg	0.52 kg	same day <sup>1)</sup>
				RF 98-200-B-06	hop cones	0.84 kg	0.53 kg	same day <sup>1)</sup>
11/08/98	21	75-78	T	RF 98-200-B-07	hop cones	0.51 kg	0.51 kg	same day <sup>1)</sup>
				RF 98-200-B-08	hop cones	0.51 kg	0.51 kg	same day <sup>1)</sup>
17/08/98	27	81-83	T	RF 98-200-B-09	hop cones	0.58 kg	0.58 kg	same day <sup>1)</sup>
				RF 98-200-B-10	hop cones	0.64 kg	0.52 kg	same day <sup>1)</sup>
25/08/98	35	87-89	C	RF 98-200-B-11	hop cones	1.14 kg	1.04 kg	same day <sup>1)</sup>
				RF 98-200-B-12	hop cones	1.40 kg	1.05 kg	same day <sup>1)</sup>
			C	RF 98-200-B-13	hop cones	1.14 kg <sup>2)</sup>	0.25 kg <sup>3)</sup>	same day <sup>4)</sup>
				RF 98-200-B-14	hop cones	1.05 kg <sup>2)</sup>	0.23 kg <sup>3)</sup>	same day <sup>4)</sup>
			T	RF 98-200-B-15	hop cones	1.14 kg	1.04 kg	same day <sup>1)</sup>
				RF 98-200-B-16	hop cones	1.10 kg	1.10 kg	same day <sup>1)</sup>
			T	RF 98-200-B-17	hop cones	1.08 kg <sup>2)</sup>	0.26 kg <sup>3)</sup>	same day <sup>4)</sup>
				RF 98-200-B-18	hop cones	1.05 kg <sup>2)</sup>	0.25 kg <sup>3)</sup>	same day <sup>4)</sup>

Explanation of letters in sample code: C: untreated, T: treated DALA: Days after last treatment

<sup>1)</sup>Samples were frozen on the day of sampling. The exact time was not recorded. The samples were frozen first at the field station at Hüll and then transported to the Bayerische Landesanstalt für Bodenkultur und Pflanzenschutz at Freising

<sup>2)</sup>fresh hops

<sup>3)</sup>dried hops

<sup>4)</sup>after the end of the drying process

Table 14: Sampling schedule and details about sampling for trial RF 98-200-C

Date	DALA	BBCH	Variant	Sample code	Sample type	Weight field sample	Weight lab. sample	Freezing
28/07/98	7	71	C	RF 98-200-C-01 RF 98-200-C-02	hop cones	0.34 kg 0.32 kg	0.26 kg 0.26 kg	same day <sup>1)</sup>
			T	RF 98-200-C-03 RF 98-200-C-04	hop cones	0.41 kg 0.33 kg	0.25 kg 0.26 kg	same day <sup>1)</sup>
04/08/98	14	73-75	T	RF 98-200-C-05 RF 98-200-C-06	hop cones hop cones	0.66 kg 0.61 kg	0.53 kg 0.52 kg	same day <sup>1)</sup> same day <sup>1)</sup>
			T	RF 98-200-C-07 RF 98-200-C-08	hop cones hop cones	0.63 kg 0.64 kg	0.52 kg 0.53 kg	same day <sup>1)</sup> same day <sup>1)</sup>
17/08/98	27	83-85	T	RF 98-200-C-09 RF 98-200-C-10	hop cones hop cones	0.53 kg 0.58 kg	0.53 kg 0.53 kg	same day <sup>1)</sup> same day <sup>1)</sup>
			C	RF 98-200-C-11 RF 98-200-C-12	hop cones hop cones	1.30 kg 1.21 kg	1.02 kg 1.04 kg	same day <sup>1)</sup> same day <sup>1)</sup>
25/08/98	35	89		C	RF 98-200-C-13 RF 98-200-C-14	hop cones hop cones	1.07 kg <sup>2)</sup> 1.18 kg <sup>2)</sup>	0.24 kg <sup>3)</sup> 0.28 kg <sup>3)</sup>
			T		RF 98-200-C-15 RF 98-200-C-16	hop cones hop cones	1.03 kg 1.19 kg	1.03 kg 1.19 kg
				T	RF 98-200-C-17 RF 98-200-C-18	hop cones hop cones	1.05 kg <sup>2)</sup> 1.16 kg <sup>2)</sup>	0.26 kg <sup>3)</sup> 0.28 kg <sup>3)</sup>

Explanation of letters in sample code: C: untreated, T: treated DALA: Days after last treatment

<sup>1)</sup>Samples were frozen on the day of sampling. The exact time was not recorded. The samples were frozen first at the field station at Hüll and then transported to the Bayerische Landesanstalt für Bodenkultur und Pflanzenschutz at Freising

<sup>2)</sup>fresh hops

<sup>3)</sup>dried hops

<sup>4)</sup>after the end of the drying process

Table 15: Sampling schedule and details about sampling for trial RF 98-200-D

Date	DALA	BBCH	Variant	Sample code	Sample type	Weight field sample	Weight lab. sample	Duration until freezing*
31/07/98	7	76	C	RF 98-200-D-01	hop cones	0.32 kg	0.32 kg	5 min
				RF 98-200-D-02	-	0.32 kg	0.32 kg	
			T	RF 98-200-D-03	hop cones	0.32 kg	0.32 kg	5 min
				RF 98-200-D-04		0.32 kg	0.32 kg	
07/08/98	14	78	T	RF 98-200-D-05	hop cones	0.60 kg	0.60 kg	10 min
				RF 98-200-D-06	hop cones	0.60 kg	0.60 kg	10 min
14/08/98	21	80	T	RF 98-200-D-07	hop cones	0.60 kg	0.60 kg	5 min
				RF 98-200-D-08	hop cones	0.60 kg	0.60 kg	5 min
21/08/98	28	87	T	RF 98-200-D-09	hop cones	0.60 kg	0.60 kg	10 min
				RF 98-200-D-10	hop cones	0.60 kg	0.60 kg	10 min
28/08/98	35	87	C	RF 98-200-D-11	hop cones	1.30 kg <sup>3)</sup>	1.30 kg	0 min
				RF 98-200-D-12	hop cones	1.25 kg <sup>3)</sup>	1.25 kg	0 min
			C	RF 98-200-D-13	hop cones	≅ 6 kg <sup>1)</sup>	0.32 kg <sup>2)</sup>	0 min
				RF 98-200-D-14	hop cones		0.30 kg <sup>2)</sup>	0 min
			T	RF 98-200-D-15	hop cones	1.25 kg <sup>3)</sup>	1.25 kg	0 min
				RF 98-200-D-16	hop cones	1.25 kg <sup>3)</sup>	1.25 kg	0 min
			T	RF 98-200-D-17	hop cones	≅ 6 kg <sup>1)</sup>	0.31 kg <sup>2)</sup>	0 min
				RF 98-200-D-18	hop cones		0.31 kg <sup>2)</sup>	0 min

Explanation of letters in sample code: C: untreated, T: treated DALA: Days after last treatment

\*Samples were frozen immediately after finishing of sampling process, interval gives time between end of sampling and freezing.

<sup>1)</sup>fresh hops

<sup>2)</sup>dried hops

<sup>3)</sup> weight of aliquot taken from the harvested vines. Total weight of all cones of the harvested cones not determined

#### 4.7 Storage and Shipment

Treated and untreated samples were stored in the freezers of the Hopfeninstitut Hüll and the Bayerische Landesanstalt für Bodenkultur und Pflanzenbau (trials RF 98-200-A, RF 98-200-B and RF 98-200-C) and in the freezer at the GAB field station at Tettngang (trial RF 98-200-D), respectively. Storage temperatures were below -18 °C.

All samples determined for analysis were shipped to the following analytical laboratory: IFU Umweltanalytik, Dr. Peter Mende, Bleichstraße 19, 75173 Pforzheim Germany.

The samples from trials RF 98-200-A, RF 98-200-B and RF 98-200-C were shipped on 29/10/98 by freezer truck. They arrived in good conditions on 30/10/98. Details about storage and shipment are given in Table 16..

All samples from trial RF 98-200-D were transported first on 28/08/98 to GAB headquarters. Transport was done by car with the samples in a freezer with dry ice added. The samples arrived at GAB frozen and in good conditions. After intermediate storage at GAB only the samples bound for residue analysis were transported by car in insulated boxes with dry ice to the analytical laboratory. All these samples arrived frozen and in good conditions. Details about the storage and shipment conditions are given in Table 18.

Table 16 Storage and shipment for trials RF 98-200-A, RF 98-200-B and RF 98-200-C

Storage and shipment no.		1
Samples		x-1, x-3, x-5, x-7, x-9, x-11, x-13, x-15, x-17
Storage $T_{max}$	[°C]	-21.0
Longest period with $T > -12$ °C	[d]	0
Maximum storage period	[d]	92
Storage at		Bayerische Landesanstalt für Bodenkultur und Pflanzenschutz, Freising
Shipment to		IFU Umweltanalytik, Pforzheim
Start of shipment		29/10/98
End of shipment		30/10/98
Duration of shipment		1 day
Conditions at arrival		frozen
Kind of shipment		freezer truck

$T_{max}$ =Maximumtemperature

x: trial code

Table 18: Storage and shipment for trial RF 98-200-D

Storage and shipment no.		1	2
Samples		RF 98-200-D-01 to RF 98-200-D-18	x-01 x-03, x-05, x-07, x-09, x-11, x-13, x-15, x-17
Storage $T_{\max}$	[°C]	-20.7	-34.0
Longest period with $T > -12$ °C	[d]	0	0
Maximum storage period	[d]	28	14
Storage at		GAB Biotechnologie field station at Tettngang	GAB Biotechnologie, Niefern- Öschelbronn
Shipment to		GAB Biotechnologie, Niefern- Öschelbronn	IFU Umweltanalytik, Pforzheim
Start of shipment		28/08/98	11/09/98
End of shipment		28/08/98	11/09/98
Duration of shipment		3:30 h	0:20 h
Conditions at arrival		frozen	frozen
Kind of shipment		transport by car in freezer with dry ice	transport by car in freezer with dry ice

Tmax = Maximum temperature

x: trial code



## 4.8 Analysis of Samples

### 4.8.1 Reference Substance for Analysis

The reference substance used for analysis is described in Table 19. The reference substances and solutions prepared in organic solvents were stored refrigerated.

Table 19: Description of the reference substance used for analysis

Type:	Reference Substance
Common name:	Quinoxifen
Supplier:	Dow AgroSciences Ltd. King's Lynn, UK
GAB code:	98368
CAS-No.:	124495-18-7
Lot No.:	AGR296691
Purity:	99.8 %
Expiry date:	30/04/2002
Certificate of analysis:	02/04/1998

### 4.8.2 Sample Material

All samples were stored deep-frozen ( $\leq -18$  °C). Frozen hop cones were homogenised in a large-scale laboratory mixer with addition of dry ice. Always the entire sample was processed. An aliquot (about 200 – 300 g) was taken as laboratory sample and stored deep-frozen until analysis.

### 4.8.3 Procedure for Determination of Quinoxifen

#### 4.8.3.1 Principle of the Method

A modified version of an already published method (FILLION et al., 1995) was used. Residues were extracted with acetonitrile, an aliquot of the acetonitrile phase was dried with anhydrous sodium sulfate and the solvent evaporated. The extract was cleaned by solid-phase-extraction on activated carbon (Envi-Carb™) and primary amino ion exchange. Quinoxifen was eluted with hexane/ethylacetate/toluene and analyzed by capillary gas chromatography with electron-capture detection (GC-ECD).

#### 4.8.3.2 Apparatus

Gas chromatograph with electron-capture detector  
Graduated cylinders (50 mL) with glass stoppers  
Laboratory mixer (Waring Blendor)  
Rotary vacuum evaporator with water bath ( $\approx 45\text{ }^{\circ}\text{C}$ )  
Round-bottomed flasks, 50 mL and 100 mL  
Ultrasound sonification bath  
Volumetric pipettes

#### 4.8.3.3 Reagents

Acetonitrile, HPLC quality  
Ethylacetate, residue analysis quality  
Hexane, residue analysis quality  
Toluene, residue analysis quality  
Elution mixture 1: hexane:ethylacetate 60:40 (v:v)  
Elution mixture 2: hexane:ethylacetate:toluene 40:30:30 (v:v:v)  
Internal GC standard: chlorobicyclen, solution of  $10\text{ }\mu\text{g/mL}$  in iso-octane (Labor Dr. Ehrenstorfer, Augsburg/Germany)  
Amino ion exchange SPE tubes (250 mg, 3 mL, prepared from Bakerbond No. 7028-00)  
Envi-Carb™ SPE tubes (500 mg, 6 mL, Supelco No. 5-7094)  
Sodium chloride p.a.  
Sodium sulfate p.a., anhydrous

#### 4.8.3.4 Preparation of Quinoxifen Standard Solutions

A stock solution ( $1\text{ mg/mL}$  effective concentration) was prepared by weighing 21.2 mg quinoxifen analytical standard and adjusting the volume to 21.2 mL with acetonitrile. From this stock solution, dilutions to  $10\text{ }\mu\text{g/mL}$  and  $1\text{ }\mu\text{g/mL}$  were prepared in toluene.

#### 4.8.3.5 Extraction

Accurately 25 g sample or 12.5 g (dried hop cones only) were weighed (weight) and homogenized for at least two minutes with 100 mL acetonitrile in a laboratory mixer. Sodium chloride ( $\approx 20\text{ g}$ ) was added and mixed again for two minutes.

From the acetonitrile phase 30 – 40 mL were transferred into a 50 mL graduated cylinder containing 10 mL volume of anhydrous sodium sulfate. The cylinder was closed with a glass stopper and shaken well to remove water.

From the clear supernatant 20 mL were transferred to a 100 mL round-bottomed flask and evaporated to dryness on a rotary vacuum evaporator. Elution mixture 1 (2 mL)

was added to the residue and any material adhering to the glass wall was re-suspended by means of an ultrasound sonification bath.

#### 4.8.3.6 Clean-Up

Envi-Carb™ tubes were equilibrated with each 5 mL elution mixture 1, amino SPE tubes with each 3 mL elution mixture 1.

The sample extract derived from 4.8.3.4 was applied onto the Envi-Carb™ packing. The flask was rinsed with 2 mL elution mixture 1 and the rinse applied onto the tube packing. The column was then rinsed with additional 3 mL elution mixture 1. All eluates up to this point were discarded.

The amino exchange tube was placed under the Envi-Carb™ tube. Quinoxifen was eluted with three portions of 3 mL elution mixture 2, collecting the eluate in a 50 mL round-bottomed flask. The solvent was evaporated with a vacuum rotary evaporator ( $\approx 45$  °C water bath temperature) to  $\approx 1$  mL.

#### 4.8.4 Preparation of Samples for Gas Chromatographic Analysis

##### 4.8.4.1 Sample Extracts with Low Expected Quinoxifen Concentrations

Internal standard (chlorobicyclen, 10  $\mu$ L of 2  $\mu$ g/mL solution in toluene) and toluene (to adjust the volume to 1 – 2 mL) was added directly to the sample extract in the 50 mL flask. The flask was swirled and the extract transferred to a GC vial.

##### 4.8.4.2 Sample Extracts with High Expected Quinoxifen Concentrations

The residue obtained from 4.8.3.6 was transferred to volumetric flasks (5 mL or 10 mL). The 50 mL flask which contained the extract was rinsed several times with toluene, and the toluene added into the volumetric flask. The volume was adjusted to mark with toluene and the flask shaken.

From this solution, 1 mL (or 500  $\mu$ L plus 500  $\mu$ L toluene) was transferred into a GC vial containing internal standard (chlorobicyclen, 10  $\mu$ L of 2  $\mu$ g/mL solution in toluene).



#### 4.8.5 Gas Chromatographic Analysis

Gas chromatograph:	Hewlett-Packard HP 5890 Series II with autosampler HP 7673A	
Column:	Chrompack CP-Sil 5 CB (equivalent to DB-1), 30 m x 0.25 mm i.d., 0.42 µm film thickness	
Carrier gas:	hydrogen, 100 kPa	
Injection:	1 µL splitless at 250 °C	
Temperature program:	80 °C, hold 0.5 min, 20 °C/min to 290°C, hold 3 min	
Detector:	ECD, 300 °C (nitrogen as make-up gas)	
Retention time:	quinoxifen	9.4 min
	chlorobicyclen (internal standard)	8.1 min

At the beginning of the sequence, a calibration curve was prepared by injecting quinoxifen standards. Injections of samples were interspersed with injections of standards to provide a continuous check on the instrument calibration.

#### 4.8.6 Calculation of Residues

Residues were calculated by the following equation:

$$R = c \cdot \frac{V_{\text{end}}}{f \cdot W}$$

R residue (mg/kg)

c quinoxifen concentration in final extract, as calculated from the peak areas of the sample by means of a calibration curve (µg/mL)

V<sub>end</sub> final volume of extract (mL)  
equals 1 mL for extracts treated according to 4.8.4.1

W sample weight for analysis (25.0 g or 12.5 g)

f aliquot factor in sample work-up (20 mL of 100 mL = 0.2)



## 5 Deviations from the Protocol Supplement

The study was performed according to the protocol RF98-200 (DowAgroSciences) dated 15/05/98, the protocol supplement 98251/G1-FPHO (GAB/IFU, dated 17/06/98), the SOPs of GAB/IFU, the protocol supplement 98368/01-RHO (GAB/IFU, dated 23/10/98), the protocol supplements RF 0498, RF 0598 and RF0698 (LBP, dated 16/06/98), and the three amendments to the protocol and protocol supplements dated 31/05/99, respectively, with the following deviations:

- Step 3.3.4 of protocol supplement: The sample weight for dried hop cones was reduced to 12.5 g instead of 25.0 g.
- Step 3.3.5: In the cleanup procedure, the volume of the third rinse step with elution mixture 1 was reduced to 3 mL (protocol supplement: 5 mL).
- Step 3.3.5: The sample extract after cleanup was not evaporated to dryness, but only to a volume of  $\approx$  1 mL. Internal standard was added directly to this final extract or to a 1 mL aliquot after adjusting to a given volume with toluene.
- Step 3.3.7: The retention time of chlorobicyclen internal standard was 8.1 min (typing error).

This report reflects the conduct of this study. All information mentioned in the amendments is described in this report. No facts are known which might adversely influence the validity of the study.

## 6 Results

### 6.9 Method Validation

In the present study, a modified version of a published multiresidue method was used. This extraction and cleanup procedure has been found to be suitable for monitoring up to 200 pesticides in fruits and vegetables (FILLION et al., 1995). Sample throughput and purity of the final extracts exceed the established DFG S19 multiresidue method.

#### 6.9.7 Recovery

The recovery was tested by fortification of untreated samples of hop cones with quinoxifen analytical standard prior to extraction with acetonitrile. The results are listed in Table 20 and Table 21.

Table 20: Recovery of quinoxifen from fresh hop cones

Fortified sample	Analysis	Added (mg/kg)	Found (mg/kg)	Recovery (%)
RF 98-200-D-1	04/11/98	0.01	0.015	150
RF 98-200-D-1	04/11/98	0.01	0.007	70
RF 98-200-B1	06/11/98	0.02	0.017	85
RF 98-200-B1	06/11/98	0.02	0.014	70
RF 98-200-B1	06/11/98	0.02	0.018	90
RF 98-200-D-1	03/11/98	0.50	0.450	90
RF 98-200-B-1	03/11/98	0.50	0.363	73
RF 98-200-A-1	05/11/98	1.00	0.908	91
RF 98-200-C-1	05/11/98	1.00	0.933	93
			Mean ± RSD	85 ± 11 <sup>1)</sup>

<sup>1)</sup> without results from 0.01 mg fortification level

Table 21: Recovery of quinoxifen from dried hop cones

Fortified sample	Analysis	Added (mg/kg)	Found (mg/kg)	Recovery (%)
RF 98-200-A-13	06/11/98	0.02	0.021	105
RF 98-200-A-13	06/11/98	0.02	0.020	100
RF 98-200-A-13	05/11/98	0.50	0.464	93
			Mean ± RSD	99 ± 6

### 6.9.8 Detection Limit, Blanks and Quantitation Limit

The detection limit was 0.006 mg/kg as estimated from the signal-to-noise ratio (S/N = 5:1) of a 0.02 mg/kg recovery sample.

Interfering peaks at the retention times of quinoxifen and chlorobicyclen (internal standard) were not detectable.

The quantitation limit was defined as the lowest fortification level with a recovery between 70 % and 110 %, with a relative standard deviation not exceeding 20 % and blanks not exceeding 30 %. These criteria are fulfilled for the 0.02 mg/kg fortification level (mean recovery 82 %  $\pm$  13 % RSD for fresh hop cones, 103 %  $\pm$  3 % RSD for dried hop cones).

### 6.9.9 Detector Response

The calibration curve used for the current study is shown in Figure 2 in the appendix. The detector response was best described second order within the range from 0.02  $\mu$ g/mL to 1.0  $\mu$ g/mL.

### 6.9.10 Precision

The overall analytical precision was determined by triplicate analysis of a sample containing quinoxifen above the quantitation limit. The results (Table 22) indicate that the precision is in the range of the relative standard deviation obtained from fortified samples. This proves that the laboratory sample was homogeneous.

Table 22: Precision of quinoxifen determination

Sample ID	Analysis	Residue (mg/kg)
RF 98-200-A-3	05/11/98	0.53
RF 98-200-A-3	05/11/98	0.44
RF 98-200-A-3	05/11/98	0.44
	Mean $\pm$ SD	0.47 $\pm$ 0.05
	RSD	11 %

## 6.10 Results from Residue Analysis

The results from residue analysis are summarised in Table 23 to Table 26. No residues of quinoxifen were detected in the control samples. Residues in the treated samples taken at 7 DALA ranged between 0.44 mg/kg and 1.00 mg/kg. At 35 DALA residues were maximum 0.05 mg/kg. Residues in dried hops were maximum 0.07 mg/kg.

Table 23: Results from residue analysis of hop cones, trial RF 98-200-A

Sample Code	Treated	Timing	Sampling	Extraction + Cleanup	Quinoxifen (mg/kg)
RF 98-200-A-1	no	n/a	28/07/98	03/11/98	n.d.
RF 98-200-A-3	yes	7 DALA	28/07/98	05/11/98	0.53 / 0.44 / 0.44
RF 98-200-A-5	yes	14 DALA	04/08/98	05/11/98	0.12
RF 98-200-A-7	yes	21 DALA	11/08/98	04/11/98	< LOQ
RF 98-200-A-9	yes	27 DALA	17/08/98	04/11/98	0.03
RF 98-200-A-11	no	n/a	25/08/98	03/11/98	n.d.
RF 98-200-A-13	no	n/a	26/08/98	03/11/98	n.d.
RF 98-200-A-15	yes	35 DALA	25/08/98	04/11/98	0.03
RF 98-200-A-17	yes	36 DALA	26/08/98	04/11/98	0.04

DALA: days after last treatment, n.d.: not detectable, < LOQ: below quantitation limit, n/a: not applicable  
GC analysis of all samples was performed in one sequence started on 05/11/98 and finished on 06/11/98.

Table 23: Results from residue analysis of hop cones, trial RF 98-200-B

Sample Code	Treated	Timing	Sampling	Extraction + Cleanup	Quinoxifen (mg/kg)
RF 98-200-B-1	no	n/a	28/07/98	03/11/98	n.d.
RF 98-200-B-3	yes	7 DALA	28/07/98	05/11/98	0.53 / 0.53
RF 98-200-B-5	yes	14 DALA	04/08/98	05/11/98	0.10
RF 98-200-B-7	yes	21 DALA	11/08/98	04/11/98	0.05
RF 98-200-B-9	yes	27 DALA	17/08/98	04/11/98	< LOQ
RF 98-200-B-11	no	n/a	25/08/98	03/11/98	n.d.
RF 98-200-B-13	no	n/a	26/08/98	03/11/98	n.d.
RF 98-200-B-15	yes	35 DALA	25/08/98	04/11/98	< LOQ
RF 98-200-B-17	yes	36 DALA	26/08/98	04/11/98	< LOQ

DALA: days after last treatment, n.d.: not detectable, < LOQ: below quantitation limit, n/a: not applicable  
GC analysis of all samples was performed in one sequence started on 05/11/98 and finished on 06/11/98.

Table 24: Results from residue analysis of hop cones, trial RF 98-200-C

Sample Code	Treated	Timing	Sampling	Extraction + Cleanup	Quinoxifen (mg/kg)
RF 98-200-C-1	no	n/a	28/07/98	04/11/98	n.d.
RF 98-200-C-3	yes	7 DALA	28/07/98	03/11/98 04/11/98	0.50 0.38
RF 98-200-C-5	yes	14 DALA	04/08/98	05/11/98	0.12
RF 98-200-C-7	yes	21 DALA	11/08/98	04/11/98	0.03
RF 98-200-C-9	yes	27 DALA	17/08/98	04/11/98	0.03
RF 98-200-C-11	no	n/a	25/08/98	03/11/98	n.d.
RF 98-200-C-13	no	n/a	26/08/98	03/11/98	n.d.
RF 98-200-C-15	yes	35 DALA	25/08/98	04/11/98	0.04
RF 98-200-C-17	yes	36 DALA	26/08/98	04/11/98 06/11/98	0.07 0.07

DALA: days after last treatment, n.d.: not detectable, < LOQ: below quantitation limit, n/a: not applicable  
GC analysis of all samples was performed in one sequence started on 05/11/98 and finished on 06/11/98.

Table 26: Results from residue analysis of hop cones, trial RF 98-200-D

Sample Code	Treated	Timing	Sampling	Extraction + Cleanup	Quinoxifen (mg/kg)
RF 98-200-D-1	no	n/a	31/07/98	03/11/98	n.d.
RF 98-200-D-3	yes	7 DALA	31/07/98	04/11/98	1.01 / 0.98
RF 98-200-D-5	yes	14 DALA	07/08/98	05/11/98	0.31
RF 98-200-D-7	yes	21 DALA	14/08/98	04/11/98	0.09
RF 98-200-D-9	yes	28 DALA	21/08/98	04/11/98	0.19
RF 98-200-D-11	no	n/a	28/08/98	03/11/98	n.d.
RF 98-200-D-13	no	n/a	28/08/98	03/11/98	n.d.
RF 98-200-D-15	yes	35 DALA	28/08/98	04/11/98	0.05
RF 98-200-D-17	yes	35 DALA	28/08/98	04/11/98	0.05

DALA: days after last treatment, n.d.: not detectable, < LOQ: below quantitation limit, n/a: not applicable  
GC analysis of all samples was performed in one sequence started on 05/11/98 and finished on 06/11/98.

## 7 Calculation

Based on the residue values detected in the analysed samples MRL levels can be calculated. Calculation was done using according BBA guideline part IV, 3-6 (1990) using the following formulas:

$$\text{Formula 1: } \text{MRL} = 2 \cdot R_{(0.75)}$$

MRL: calculated maximum residue level

$R_{(0.75)}$ : 75 % quantil of residues

$$\text{Formula 2: } R_{(0.75)} = (1 - G) \cdot R_{(J)} + G \cdot R_{(J+1)}$$

$$\text{Formula 3: } (n + 1) \cdot P = J + G$$

n: number of residue values

P: quantil/100 %; for this calculation 0.75

J: non broken number of  $(n+1) \cdot P$

G: broken rest of  $(n+1) \cdot P$

$R_{(J)}$ : Residue at position J

$R_{(J+1)}$ : Residue at position J+1

The procedure described above was chosen because of the small number of residue trials (only 4 trials). Based on these formulas and the results of all 4 trials the MRLs given in Table 26 were calculated.

Table 26: Calculated MRLs for all sampling dates.

Date (DALA)	J	G	R(0.75)	MRL
7	3	0.75	0.883 mg/kg	1.765 mg/kg
14	3	0.75	0.263 mg/kg	0.525 mg/kg
21	3	0.75	0.080 mg/kg	0.160 mg/kg
28	3	0.75	0.150 mg/kg	0.300 mg/kg
35	3	0.75	0.048 mg/kg	0.095 mg/kg
35 (dried hops)	3	0.75	0.065 mg/kg	0.130 mg/kg

## 8 Discussion and Conclusions

The residue study took place 1998 at four locations in Germany. The trials were located at Tett nang (Baden-Württemberg, Southern Germany) and in the Hallertau (Bavaria, Southern Germany). Both areas are well known and representative hops growing regions. The test compound was applied as often as recommended by the sponsor and with the highest recommended rate.

For interpretation of the residues, the following points should be considered:

- The applications were done with the demanded rates. The actual applied rates were within the range specified in the protocol.
- All samples were taken as planned and frozen within 1 day in the latest.
- Until shipment samples were stored at temperatures less than - 18 °C all the time. During sample shipment temperatures remained below - 18 °C.
- Shipment duration to the analytical laboratory was maximum 2 days. All samples arrived in the laboratory in good conditions and frozen.
- Non treated and treated samples were handled strictly separately.

Therefore it can be concluded, that no adverse effects influence the sample integrity and that the samples generated within the field part of this study are suited to predict maximum residue levels (MRLs) for the use of the test substances in hops.

The residue analysis showed that the control samples contained no residues of quinoxifen. This supports the validity of the study. Limit of detection (0.006 mg/kg) and limit of quantitation (0.02 mg/kg) as well as the recovery rate (82 % ± 13 % for fresh hops and 103 % ± 3 % for dried hops) were suitable to detect residues with the demanded accuracy and sensitivity.

Residues were between 0.44 mg/kg and 1.00 mg/kg 7 days after application. The 7 DALA residues in the trials conducted in the Hallertau were all in the same magnitude of order. This demonstrates the good repeatability of applications and comparability of hops growing systems in that region. The highest initial (7 DALA) residues were observed in the trial at Tett nang. This might be attributed to the following differences between the trials at Tett nang and the Hallertau:

- higher water volumes at Tett nang
- different training systems (single wires at Tett nang and double wires at Hallertau)
- different nozzles used for the applications at Tett nang and Hallertau
- different varieties at Tett nang (“Spalter”) and Hallertau (“Hallertauer Tradition”).

Until harvest the residues declined to maximum 0.05 mg/kg in fresh hops and maximum 0.07 mg/kg in dried hops. The differences between the trial sites were minor. Thus it can be concluded that residue decline was comparably fast at all sites.



The small differences between residues in fresh hops and dried hops demonstrate the drying does not lead to a concentration of residues.

Based on the residues determined in the harvest samples a MRL of 0.095 mg/kg for fresh hops and 0.130 mg/kg for dried hops at harvest was determined. However, it has to be considered that these MRLs are based on the results of only four trials.

## 9 Archiving

This study was allocated the study code 98251/G1-FPHO. The final report was prepared in two original signed copies. For the periods demanded by the principles of GLP the following documents and materials will be archived:

- Authorised copy of the study protocol, protocol supplements, amendments, original raw data or authorised copy of the raw data, comments of the sponsor on the draft report and one original signed copy of the final report.
- All documentation generated by the Quality Assurance Unit of GAB/IFU.
- A sample of the test substance used in trial RF98-200-D and of the analytical reference substance.

All documents and materials will be stored in the archives of Arbeitsgemeinschaft GAB Biotechnologie GmbH & IFU Umweltanalytik GmbH. The premises for storing the documents and materials are settled according to the principles of Good Laboratory Practice in the organisation of the testing facility.

## 10 References

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## 11 Appendix

### 11.1 Weather Data

Table 27: Weather conditions at trial RF 98-200-A, RF 98-200-B and RF 98-200-C

Location of the weather station: Hüll  
 Meters above sea-level: 440  
 Distance to the test site: 5 to 15 km  
 Origin of the weather data: Bayerische Landesanstalt für Bodenkultur und Pflanzenbau

Long-term averages, 1951-1980			
Month/Period	Temperature avg. [°C]	Precipitation [mm]	Sunshine [h]
May	12	86	207
June	16	106	220
July	17	108	240
August	16	68	218
Conditions during the trial			
May	13.8	49.2	243.6
June	16.8	151.6	237.5
July	17.1	67.3	159.6
August	17.2	33.3	234.4
A <sub>1</sub>	16.7	0.0	8.8
A <sub>1</sub> - A <sub>2</sub>	18.4	50.6	71.4
A <sub>2</sub>	15.8	1.4	0.7
A <sub>2</sub> - A <sub>3</sub>	16.0	49.6	86.0
A <sub>3</sub>	24.3	1.4	12.9
A <sub>3</sub> -S <sub>1</sub>	19.1	11.2	34.6
S <sub>1</sub>	16.7	0.0	3.8
S <sub>1</sub> - S <sub>2</sub>	18.2	14.3	30.4
S <sub>2</sub>	18.4	0.1	1.2
S <sub>2</sub> - S <sub>3</sub>	19.6	0.0	74.5
S <sub>3</sub>	23.3	0.0	13.0
S <sub>3</sub> - S <sub>4</sub>	19.7	0.5	51.6
S <sub>4</sub>	20.9	0.0	12.3
S <sub>4</sub> - S <sub>5</sub>	16.4	18.0	33.6
S <sub>5</sub>	13.3	0.1	8.9

A = Application, S = Sampling; index = number of T or S;

Table 28: Weather conditions at trial RF 98-200-D

Location of the weather station: Eriskirch  
 Meters above sea-level: 410  
 Distance to the test site: 7 km  
 Origin of the weather data: Deutscher Wetterdienst Offenbach

Long-term averages. 1951-1980 <sup>1)</sup>			
Month/Period	Temperature avg. [°C]	Precipitation [mm]	Sunshine [h]
May	13	96	211
June	17	121	226
July	19	133	245
August	18	120	219
Conditions during the trial			
June	17.8	113.5	228.2
July	18.9	80.2	171.0
August	18.6	62.5	218.6
A <sub>1</sub>	18.7	0.0	10.6
A <sub>1</sub> – A <sub>2</sub>	17.0	39.8	41.0
A <sub>2</sub>	18.3	0.2	4.2
A <sub>2</sub> – A <sub>3</sub>	20.4	19.4	94.9
A <sub>3</sub>	20.8	0.0	3.8
A <sub>3</sub> – S <sub>1</sub>	19.3	22.3	35.0
S <sub>1</sub>	17.2	0.0	0.6
S <sub>1</sub> – S <sub>2</sub>	18.4	19.7	29.1
S <sub>2</sub>	19.1	0.0	11.4
S <sub>2</sub> – S <sub>3</sub>	23.0	1.6	57.5
S <sub>3</sub>	18.0	0.0	9.9
S <sub>3</sub> – S <sub>4</sub>	21.1	0.4	50.2
S <sub>4</sub>	17.4	13.2	0.3
S <sub>4</sub> – S <sub>5</sub>	15.6	27.6	28.8
S <sub>5</sub>	12.4	0.0	8.4

A=Treatment, S = Sampling; index = number of T or S;

<sup>1)</sup>Weather station Friedrichshafen, approx. 3 km distance to Eriskirch

n.a.\*: not available, will be given in the final report



### Calibration Curve

Fit Analysis Output For Method File: "T:\DATA6\98368RHO\QUINOX.MTH"

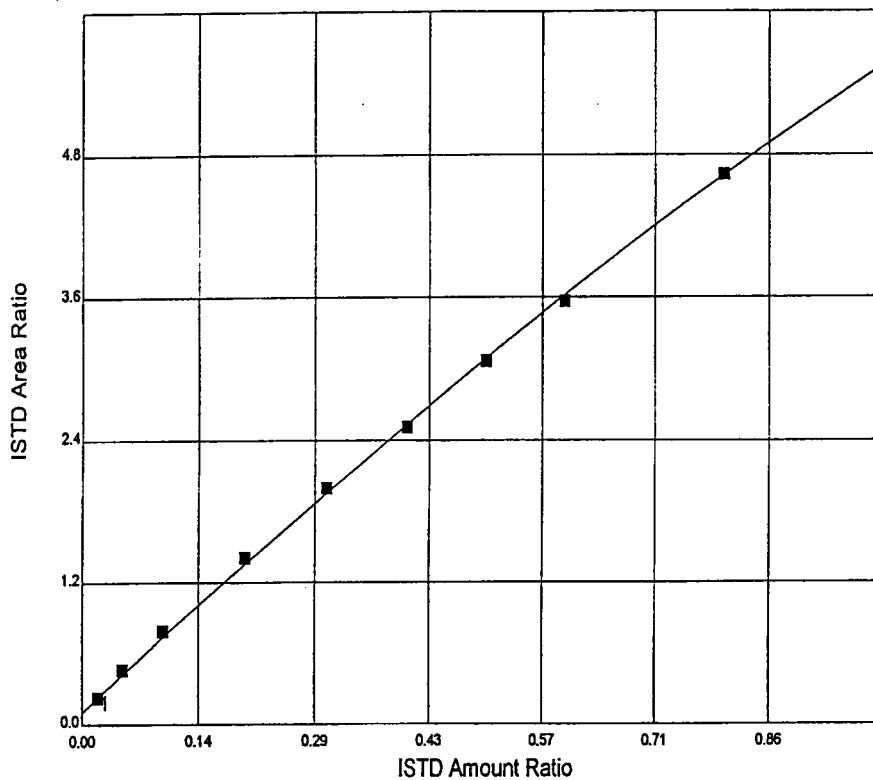
Component Name: "Quinoxifen"

Date: 06.11.1998 Time: 08:46

Curve Parameters:

Curve #1 : 2nd Order - Incl Origin  
 Weighting Factor = 1.0 (No Weighting)  $r^2 = 0.999309$   
 Calibration Curve =  $(0.103105) + (6.481106)X + (-1.034111)X^2$

### Quinoxifen



Level Name	Observed X-Value	Calculated X-Value	Delta	%Diff.	Observed Y-Value	Calculated Y-Value	Delta	%Diff.
0.02	0.020000	0.019472	0.000528	2.713	0.229	0.232	-0.003	-1.465
0.05	0.050000	0.055849	-0.005849	-10.472	0.461	0.425	0.037	8.777
0.1	0.100000	0.107688	-0.007688	-7.139	0.789	0.741	0.048	6.502
0.2	0.200000	0.209182	-0.009182	-4.389	1.414	1.358	0.056	4.096
0.3	0.300000	0.307120	-0.007120	-2.318	1.996	1.954	0.042	2.132
0.4	0.400000	0.396154	0.003846	0.971	2.508	2.530	-0.022	-0.860
0.5	0.500000	0.495859	0.004141	0.835	3.062	3.085	-0.023	-0.732
0.6	0.600000	0.589305	0.010695	1.815	3.563	3.619	-0.056	-1.582
0.8	0.800000	0.800848	-0.000848	-0.106	4.630	4.626	0.004	0.088
1	1.000000	1.004577	-0.004577	-0.456	5.570	5.550	0.020	0.364

Figure 2: Calibration curve for quinoxifen



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## 11.2 Chromatograms

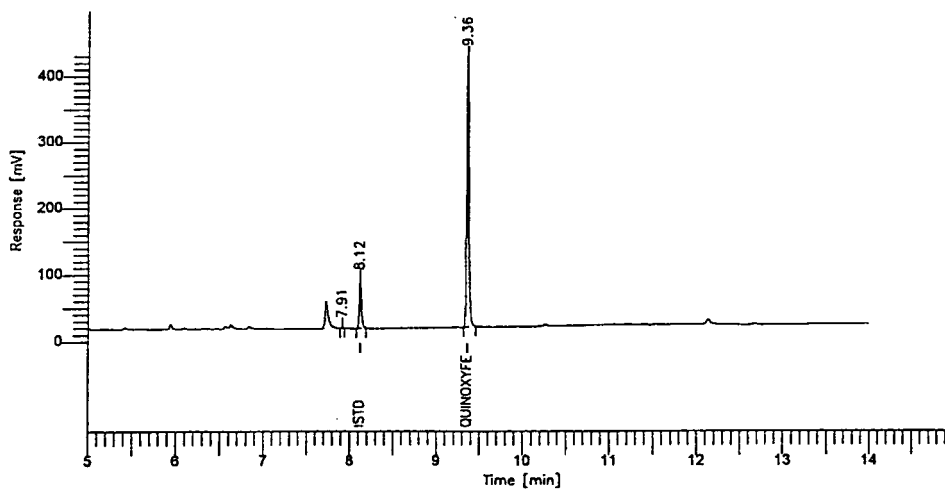
Software Version: 4.0<4J28>  
 Sample Name : S1  
 Sample Number: 1 µg/ml  
 Operator : me  
 Time : 06.11.1998 09:30  
 Study : 98368/01-RHO

Instrument : HP5890-17.2  
 AutoSampler :  
 Rack/Vial : 0/0  
 Channel : A  
 A/D mV Range : 2000

Interface Serial # : 9136560286  
 Data Acquisition Time: 05.11.1998 17:11  
 Delay Time : 5.00 min.  
 End Time : 14.00 min.  
 Sampling Rate : 6.2500 pts/sec

Raw Data File : T:\DATA6\98368RHO\QUI1011.RAW  
 Result File : T:\DATA6\98368RHO\QUI1011.RST  
 Inet Method : T:\DATA6\98368RHO\QUINCOX from T:\DATA6\98368RHO\QUI1011.RST  
 Proc Method : T:\DATA6\98368RHO\QUINCOX from T:\DATA6\98368RHO\QUI1011.RST  
 Calib Method : T:\DATA6\98368RHO\QUINCOX from T:\DATA6\98368RHO\QUI1011.RST  
 Sequence File : T:\DATA6\98368RHO\QUI1.SEQ

Sample Volume : 1.0000 µl  
 Sample Amount : 1.0000  
 Area Reject : 0.000000  
 Dilution Factor : 1.00



Time [min]	Area (µV·s)	Component Name	Amount (µg/ml)	Dilution factor	Final vol (ml)	Aliquot factor	Weight (g)	Residue (mg/kg)
8.12	129530	ISTD	0.000	1	1	1	1.0	0.0000
9.36	721519	Quinoxifen	1.009	1	1	1	1.0	1.0095

Figure 3: Chromatogram of a standard containing 1 µg/mL quinoxifen



```

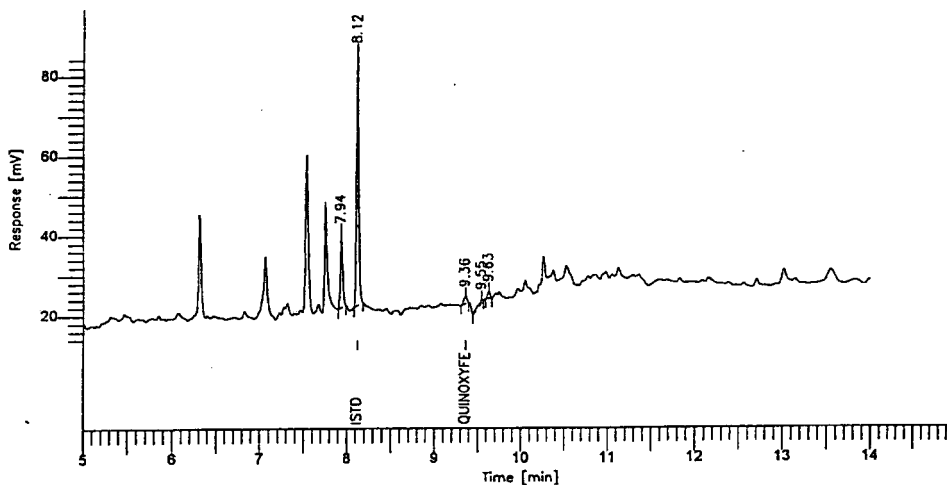
Software Version: 4.0<4J28>
Sample Name : RF98-200A-13           Time : 06.11.1998 09:42
Sample Number: 859-98                Study : 98368/01-RHO
Operator : me

Instrument : HP5890-17.2             Channel : A      A/D mV Range : 2000
AutoSampler :
Rack/Vial : 0/0

Interface Serial # : 9136560286     Data Acquisition Time: 05.11.1998 19:48
Delay Time : 5.00 min.
End Time : 14.00 min.
Sampling Rate : 6.2500 pts/sec

Raw Data File : T:\DATA6\98368RHO\QUI1019.RAW
Result File : T:\DATA6\98368RHO\QUI1019.RST
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Proc Method : T:\DATA6\98368RHO\QUINOX from T:\DATA6\98368RHO\QUI1019.RST
Calib Method : T:\DATA6\98368RHO\QUINOX from T:\DATA6\98368RHO\QUI1019.RST
Sequence File : T:\DATA6\98368RHO\QUI11.SEQ

Sample Volume : 1.0000 µl           Area Reject : 0.000000
Sample Amount : 12.5000             Dilution Factor : 1.00
    
```



Time [min]	Area [µV·s]	Component Name	Amount [µg/ml]	Dilution factor	Final vol [ml]	Aliquot Weight factor	Weight [g]	Residue [mg/kg]
8.12	111570	ISTD	0.000	1	1	5	12.5	0.0000
9.36	4659	Quinoxifen	-0.009	1	1	5	12.5	-0.0038
								-0.0038

Figure 4: Chromatogram of an extract from an untreated sample of dried hop cones (RF 98-200-A-13)



```

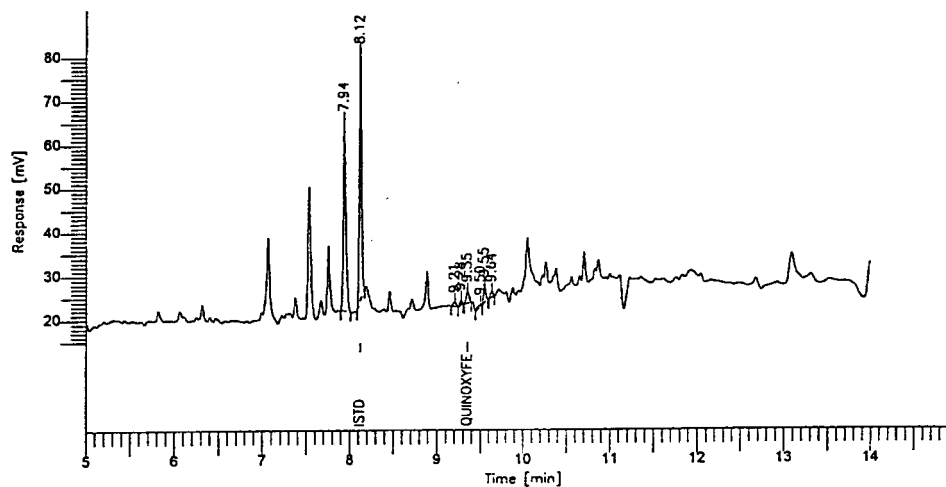
Software Version: 4.0<4J28>
Sample Name : RF98-200B-1
Sample Number: 862-98
Operator : me
Time : 06.11.1998 09:45
Study : 98368/01-RHO

Instrument : HP5890-17.2
AutoSampler :
Rack/Vial : 0/0
Channel : A
A/D mV Range : 2000

Interface Serial # : 9136560286
Data Acquisition Time: 05.11.1998 21:26
Delay Time : 5.00 min.
End Time : 14.00 min.
Sampling Rate : 6.2500 pts/sec

Raw Data File : T:\DATA6\98368RHO\QUI1024.RAW
Result File : T:\DATA6\98368RHO\QUI1024.RST
Inst Method : T:\DATA6\98368RHO\QUINOX from T:\DATA6\98368RHO\QUI1024.RST
Proc Method : T:\DATA6\98368RHO\QUINOX from T:\DATA6\98368RHO\QUI1024.RST
Calib Method : T:\DATA6\98368RHO\QUINOX from T:\DATA6\98368RHO\QUI1024.RST
Sequence File : T:\DATA6\98368RHO\QUI1.SEQ

Sample Volume : 1.0000 µl
Sample Amount : 25.0000
Area Reject : 0.000000
Dilution Factor : 1.00
    
```



Time (min)	Area (µV·s)	Component Name	Amount (pg/ml)	Dilution factor	Final vol (µl)	Aliquot factor	Weight (g)	Residue (mg/kg)
8.12	98082	ISTD	0.000	1	1	5	25.0	0.0000
9.35	6101	Quinoxifen	-0.006	1	1	5	25.0	-0.0013

Figure 5: Chromatogram of an extract from an untreated sample of hop cones (RF 98-200-B1)



```

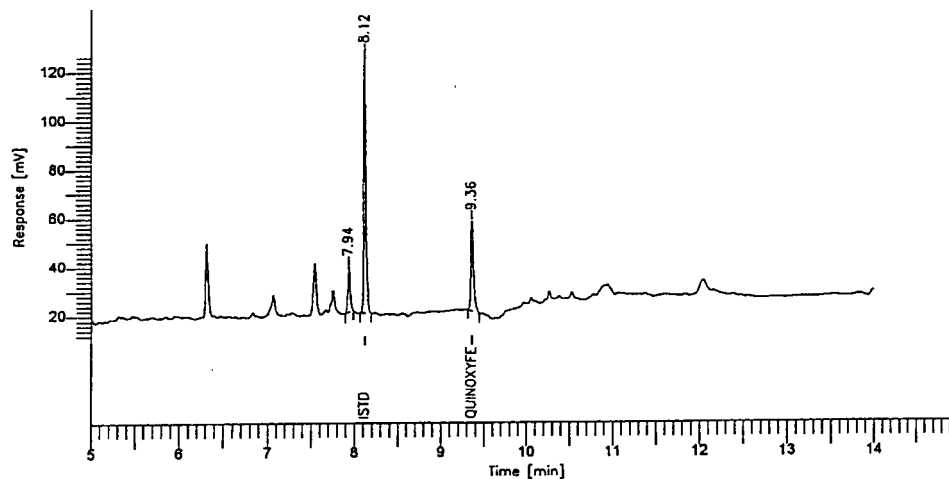
Software Version: 4.0<4J28>
Sample Name : hop2-0.02
Sample Number: recovery
Operator : me
Time : 06.11.1998 09:40
Study : 98368/01-RHO

Instrument : HP5890-17.2
AutoSampler :
Rack/Vial : 0/0
Channel : A A/D mV Range : 2000

Interface Serial # : 9136560286 Data Acquisition Time: 05.11.1998 18:49
Delay Time : 5.00 min.
End Time : 14.00 min.
Sampling Rate : 6.2500 pts/sec

Raw Data File : T:\DATA6\98368RHO\QUI1016.RAW
Result File : T:\DATA6\98368RHO\QUI1016.RST
Inst Method : T:\DATA6\98368RHO\QUINOX from T:\DATA6\98368RHO\QUI1016.RST
Proc Method : T:\DATA6\98368RHO\QUINOX from T:\DATA6\98368RHO\QUI1016.RST
Calib Method : T:\DATA6\98368RHO\QUINOX from T:\DATA6\98368RHO\QUI1016.RST
Sequence File : T:\DATA6\98368RHO\QUI1.SEQ

Sample Volume : 1.0000 µl
Sample Amount : 12.5000
Area Reject : 0.000000
Dilution Factor : 1.00
    
```



Time [min]	Area [µV·s]	Component Name	Amount [µg/ml]	Dilution factor	Final vol [ml]	Aliquot factor	Weight [g]	Residue [mg/kg]
8.12	185741	ISTD	0.008	1	1	5	12.5	0.0000
9.36	79448	Quinoxifen	0.008	1	1	5	12.5	0.0282
								0.0282

Figure 6: Chromatogram of an extract from an untreated sample of dried hop cones fortified with 0.02 mg/kg quinoxifen



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```

Software Version: 4.0<4J28>
Sample Name : hop4-0.02
Sample Number: recovery
Operator : me
Time : 06.11.1998 14:58
Study : 98368/01-RHO

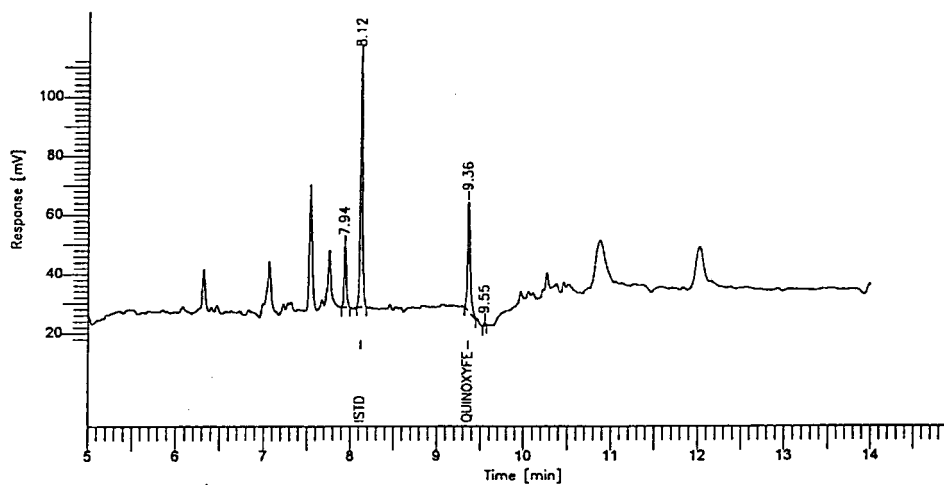
Instrument : HP5890-17.2
AutoSampler :
Rack/Vial : 0/0
Channel : A
A/D mV Range : 2000

Interface Serial # : 9136560286
Data Acquisition Time: 06.11.1998 14:31
Delay Time : 5.00 min.
End Time : 14.00 min.
Sampling Rate : 6.2500 pts/sec

Raw Data File : T:\DATA6\98368RHO\QUI1075.RAW
Result File : T:\DATA6\98368RHO\QUI1075.RST
Inst Method : T:\DATA6\98368RHO\QUINOX from T:\DATA6\98368RHO\QUI1075.RST
Proc Method : T:\DATA6\98368RHO\QUINOX from T:\DATA6\98368RHO\QUI1075.RST
Calib Method : T:\DATA6\98368RHO\QUINOX from T:\DATA6\98368RHO\QUI1075.RST
Sequence File : T:\DATA6\98368RHO\QUI1.SEQ

Sample Volume : 1.0000 µl
Sample Amount : 25.0000
Area Reject : 0.000000
Dilution Factor : 1.00

```



Time [min]	Area [µV·s]	Component Name	Amount [µg/ml]	Dilution Factor	Final vol [ml]	Aliquot Weight [g]	Residue [mg/kg]
8.12	152104	ISTD	0.000	1	1	5 25.0	0.0000
9.36	81978	Quinoxifen	0.068	1	1	5 25.0	0.0136
							0.0136

Figure 7: Chromatogram of an extract from an untreated sample of hop cones fortified with 0.02 mg/kg quinoxifen

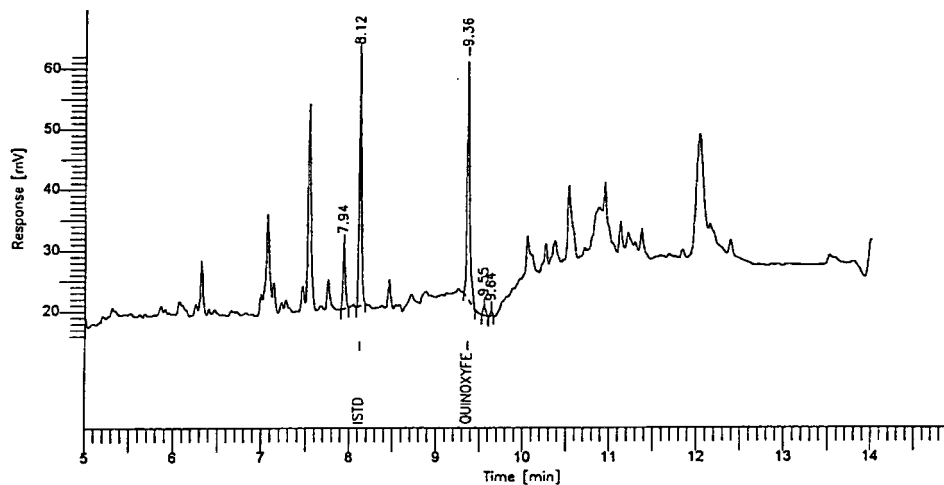
Software Version: 4.0<4J28>  
 Sample Name : RF98-200A-15 Time : 06.11.1998 09:43  
 Sample Number: 860-98 Study : 98368/01-RHO  
 Operator : me

Instrument : HPS890-17.2 Channel : A A/D mV Range : 2000  
 AutoSampler :  
 Rack/Vial : 0/0

Interface Serial # : 9136560286 Data Acquisition Time: 05.11.1998 20:08  
 Delay Time : 5.00 min.  
 End Time : 14.00 min.  
 Sampling Rate : 6.2500 pts/sec

Raw Data File : T:\DATA6\98368RHO\QUI1020.RAW  
 Result File : T:\DATA6\98368RHO\QUI1020.RST  
 Inst Method : T:\DATA6\98368RHO\QUINOX from T:\DATA6\98368RHO\QUI1020.RST  
 Proc Method : T:\DATA6\98368RHO\QUINOX from T:\DATA6\98368RHO\QUI1020.RST  
 Calib Method : T:\DATA6\98368RHO\QUINOX from T:\DATA6\98368RHO\QUI1020.RST  
 Sequence File : T:\DATA6\98368RHO\QUI1.SEQ

Sample Volume : 1.0000  $\mu$ l Area Reject : 0.000000  
 Sample Amount : 25.0000 Dilution Factor : 1.00



Time [min]	Area [ $\mu$ V $\cdot$ s]	Component Name	Amount ( $\mu$ g/ml)	Dilution factor	Final vol (ml)	Aliquot Weight factor (g)	Residue (mg/kg)
8.12	76074	ISTD	0.000	1	1	5 25.0	0.0000
9.36	86349	Quinoxifen	0.163	1	1	5 25.0	0.0327

Figure 8: Chromatogram of an extract from a treated sample of dried hop cones, residue 0.03 mg/kg



```

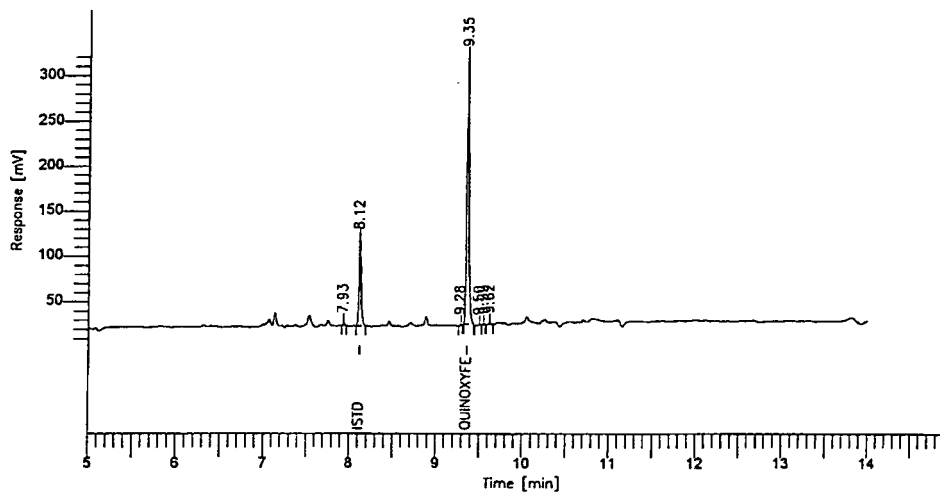
Software Version: 4.0<4J28>
Sample Name      : RF98-200C-3
Sample Number: 872-98-1
Operator       : me
Time          : 06.11.1998 10:11
Study       : 98368/01-RHO

Instrument    : HP5890-17.2
AutoSampler  :
Rack/Vial    : 0/0
Channel      : A
A/D mV Range : 2000

Interface Serial # : 9136560286
Data Acquisition Time: 06.11.1998 08:11
Delay Time      : 5.00 min.
End Time       : 14.00 min.
Sampling Rate   : 6.2500 pts/sec

Raw Data File   : T:\DATA6\98368RHO\QUI1057.RAW
Result File    : T:\DATA6\98368RHO\QUI1057.RST
Inst Method    : T:\DATA6\98368RHO\QUINOX from T:\DATA6\98368RHO\QUI1057.RST
Proc Method    : T:\DATA6\98368RHO\QUINOX from T:\DATA6\98368RHO\QUI1057.RST
Calib Method   : T:\DATA6\98368RHO\QUINOX from T:\DATA6\98368RHO\QUI1057.RST
Sequence File  : T:\DATA6\98368RHO\QUI1.SEQ

Sample Volume   : 1.0000 µl
Sample Amount   : 25.0000
Area Reject     : 0.000000
Dilution Factor : 1.00
    
```



Time [min]	Area [µV·s]	Component Name	Amount (µg/ml)	Dilution factor	Final vol (ml)	Aliquot factor	Weight (g)	Residue (mg/kg)
8.12	170094	ISTD	0.000	1	5	5	25.0	0.0000
9.35	322917	Quinoxifen	0.498	1	5	5	25.0	0.4980

Figure 9: Chromatogram of an extract from a treated sample of hop cones, residue 0.5 mg/kg



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98251/G1-FPHO

Dow AgroSciences  
 Letcombe Laboratory  
 Letcombe Regis  
 Wantage  
 Oxon, OX12 9JT  
 Telephone: 01235 772900  
 Fax: 01235 774803



### CERTIFICATE OF ANALYSIS - AD/1316

SAMPLE NAME : DE-795  
 TYPE OF MATERIAL : ANALYTICAL STANDARD  
 BATCH REFERENCE : AGR296691  
 ANALYTICAL REFERENCE : N/A

APPEARANCE

WHITE CRYSTALLINE SOLID

ASSAY

DE-795 99.8% w/w

STORAGE CONDITIONS : AMBIENT

SAMPLE EXPIRY DATE : APRIL 2002

COMMENTS : P98-085, GHE-P-7119, SUPERSEDES AD/1009

*K. L. Bay 98*

SIGNED *H. P. ...* DATE 2 April 98 SIGNED *K. L. Bay* DATE 2 April 98

*Approval*

*Approval*

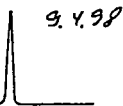
Dow AgroSciences Limited Registered Office: Letchmore Court, Brand Street, Hitchin, Herts, SG5 1HZ. Registered Number 238102 England

Figure 10: Certificate of analysis for quinoxifen reference substance



# Gravimetric Certificate

Dr. Ehrenstorfer



Reference Materials for  
Residue Analysis

## Product Identification

111700 Chlorbicyclen  
 CA 1,2,3,4,7,7-Hexachloro-5,6-bis(chloromethyl)-2-norbomene  
 IUPAC 1,2,3,4,7,7-Hexachloro-5,6-bis(chloromethyl)-8,9,10-trinorbom-2-ene  
 Formula C<sub>9</sub>H<sub>6</sub>Cl<sub>8</sub>  
 Mol.Weight 397.77  
 CAS No. 2550-75-6

Expiry Date 01.03.2001  
 Lot Number 80312IO  
 Store at 20 °C in the dark

Please Note: The expiry date is valid under recommended storage conditions only

## Gravimetric Data

Product Name	Lot. No.	Purity	Weight (mg)
Chlorbicyclen	60208	99.6 %	2.512

Concentration (mg/l): 10.0

Tolerance of the weighing procedure and the dilution error add to a maximum of +/- 0.5 %

## Solvent Information

Iso-Octane                      Lot: 27698                      Exact Quantity (ml): 250

## Analytical Data

Method 1 GC/MSD                      Column DB-5, 30 m, ID 0.25 mm  
 Inj. Volume (µl) 5                      Temperature (°C) 120-280 / 280

Method 2                      Column  
 Inj. Volume (µl)                      Flow (ml/min.)

Eluent A  
 Eluent B  
 Gradient  
 Comment

Please Note: Results are based on a minimum of five determinations  
 Data has been verified by second lot peak area comparison

Certified 13.03.1998  
 by DR. KRAWIELITZKI




Labor Dr. Ehrenstorfer-Schäfers · Bgm.-Schlosser-Str. 6 A · D 86199 Augsburg · Germany  
 The information herein is believed to be correct, but is provided without warranty of any kind.

ISO 9001

Figure 11: Certificate of analysis for chlorbicyclen internal standard



### 11.3 GLP Certificates of the Testing Facilities



**MINISTERIUM FÜR UMWELT UND VERKEHR  
BADEN-WÜRTTEMBERG**

**GLP-Bescheinigung**

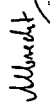

<p><b>Bescheinigung</b></p> <p>Hiermit wird bestätigt, daß die Prüfeinrichtung</p> <p>in 75223 Niefern-Oschelbronn Eulinger Straße 24 der Arbeitsgemeinschaft GAB/IFU GmbH</p> <p>am 22.07.1996 und 12.05.1997</p>	<p><b>Certificate</b></p> <p>It is hereby certified that the test facility</p> <p>in 75223 Niefern-Oschelbronn Eulinger Straße 24 of Arbeitsgemeinschaft GAB/IFU GmbH</p> <p>on 22.07.1996 and 12.05.1997</p>
--	---

Prüfkategorie 1  
Prüfkategorie 4  
Prüfkategorie 5  
Prüfkategorie 6

Prüfungen zur Bestimmung der physikalisch-chemischen Eigenschaften und Gehaltsbestimmungen  
Cytotoxikologische Prüfungen zur Bestimmung der Auswirkungen auf aquatische und terrestrische Organismen  
Prüfungen zum Verhalten im Boden, im Wasser und in der Luft; Prüfungen zur Bioakkumulation und zur Metabolisierung  
Prüfungen zur Bestimmung von Rückständen

Das entspricht den Kategorien der Allgemeinen Verwaltungsverordnung zum Verfahren der behördlichen Überwachung der Einhaltung der Guten Laborpraxis (ChemVwV-GLP) vom 15. Mai 1997.

Stuttgart, den 03.11.1997

  
  
 Dr. Albrecht

Seite 1/2

von der für die Überwachung zuständigen Behörde über die Einhaltung der Grundsätze der Guten Laborpraxis inspiziert worden ist.

Es wird hiermit bestätigt, daß folgende Prüfungen in dieser Prüfeinrichtung nach den Grundsätzen der Guten Laborpraxis durchgeführt werden.


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was inspected by the competent authority regarding compliance with the Principles of Good Laboratory Practice.

It is hereby certified that studies in this test facility are conducted in compliance with the Principles of Good Laboratory Practice.

Stuttgart, den 03.11.1997

page 1/2

Kontakt:  **Ministerium für Umwelt und Verkehr**  
 70173 Stuttgart  
 Telefon 07141 158-0  
 Telefax 07141 158-1000  
 Telex 07141 158-1000  
 GAB/IFU  
 70173 Stuttgart

Stuttgart, den 03.11.1997

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
Kontakt:  **Ministerium für Umwelt und Verkehr**  
 70173 Stuttgart  
 Telefon 07141 158-0  
 Telefax 07141 158-1000  
 Telex 07141 158-1000  
 GAB/IFU  
 70173 Stuttgart

Figure 12: GLP-certificate of GAB/IFU