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Dimoxystrobin

DAPA Collaborative Study R-196-80-08

CIPAC 4672/R, small scale study

COLLABORATIVE STUDY OF A HIGH RESOLUTION GAS CHROMATOGRAPHIC ANALYSIS OF DIMOXYSTROBIN TECHNICAL MATERIAL AND FORMULATED PRODUCTS

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1. Participants (alphabetical order)

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Dr. Fries	BASF SE Limburgerhof, Deutschland
Dr. Haustein	CURRENTA GmbH & Co OHG Dormagen, Deutschland
Dr. Kettner	Syngenta Crop Protection Münchwilen, Schweiz
B. Patrian	FAW Wädenswil Wädenswil, Schweiz
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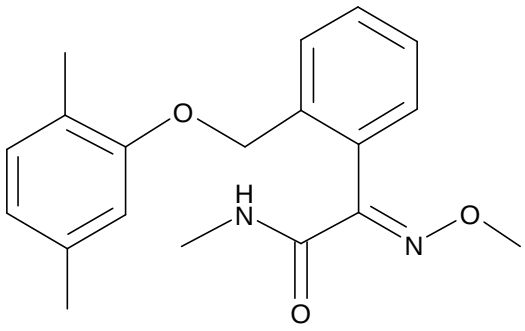
2. Introduction

Chemical name: (E)-o-(2,5-dimethylphenoxymethyl)-2-methoxyimino-N-methylphenylacetamide
Common name: Dimoxystrobin
CAS-Nr.: 149961-52-4
Chemical structure:



RMM: 326.39 g/mol
Empirical formula: $C_{19}H_{22}N_2O_3$
Indication: Fungicide

3. Samples

The following test samples were sent to the participants in November, 2008:

1.	Dimoxystrobin, analytical standard	997 g/kg
2.	Dimoxystrobin, technical material TC 1	c. 999 g/kg
3.	Dimoxystrobin, technical material TC 2	c. 995 g/kg
4.	Dimoxystrobin, suspension concentrate SC I	c. 183 g/kg
5.	Dimoxystrobin, suspension concentrate SC II	c. 400 g/l
6.	Dimoxystrobin, suspo-emulsion SE	c. 333 g/l

4. Method

4.1 Scope

Testing of a specific chromatographic method (GC) to determine Dimoxystrobin in formulations (SC, SE) and in technical material (TC).

4.2 Procedure

A solution of the sample (acetone) is analyzed by using a high resolution gas chromatographic procedure that employs an internal standard (1,1,2,2-tetra-phenylethylene). The separation is achieved by using a DB-1 (30 m, 0.32 mm, 0.25 µm) capillary column, temperature programmed. Dimoxystrobin is detected using a flame ionisation detector (FID) and quantified by comparing the specific response ratio of the samples with that of standards of known qualities.
Each sample was analyzed by two independent determinations on two days (each sample was determined by double injection). The determination of content was calculated by the mean values of the response factors, which were taken from the calibration solutions that enclose the samples.

5. Deviations from the analytical method reported by the participants

Lab 1:	different columns tried, without success
Lab 2:	Injection volume: 1 µl, split ratio 40:1
Lab 3:	no comments
Lab 4:	Column: HP-1
Lab 5:	Column: DB-1, 30 m, 0.25 mm, 0.25 µm
Lab 6:	Column: DB-1, 30 m, 0.25 mm, 0.25 µm 1.5 ml/min constant flow; injection volume: 0.2 µl, split ratio: 20:1, temperature program: 0.5 mins 60 °C up to 270 °C with 20 °C/min and hold for 9.5 mins
Lab 7:	Column: ZB1 Zebron, 30 m, 0.32 mm, 0.25 µm

6. Remarks reported by the participants

Lab 1: We could not perform this inter-laboratory comparison, because of the age of our GLC-system a constant column flow was not applicable. To solve this problem we tried to use different columns and temperature programs, but without success. Constant flow technology seems to be essential to separate the peak of the active ingredient from the one of the internal standard.
Result: This method seems to be not applicable for GLC-systems without constant column flow technology.

Lab 2: Analysis sequence used was as per accompanying info sheet R-196-80-08 Dimoxystrobin and also the e-mail from Michael Siebecker: (calibration1, TC1, TC1, calibration2, TC2, TC2, calibration1, SC1, SC1, calibration2, SC2, SC2, calibration1, SE, SE, calibration2). Therefore areas of Dimoxystrobin and Istd for only single Injections of Calib. 1 and 2 entered into results tables.

Lab 3: no further remarks

Lab 4: no further remarks

Lab 5: the same sample and calibration solutions are used for both days

Lab 6: no further remarks

Lab 7: For each day two sequences were measured, all sequences were: C1, TCI, TCI, C2, TCII, TCII, C1, SCI, SCI, C2, SCII, SCII, C1, SE, SE, C2.

7. Results and Discussion

The statistical evaluation is based on that outlined in DIN ISO 5725. The formulae used for calibration of reproducibility and repeatability are listed in section 8 of this report.
The results of six labs participated in the collaborative study have been taken into account for the statistical evaluation. Analytical measurement of one lab failed.
In Tables 1 to 5 the individual results were summarized.

In lab 4, outliers were identified according to Dixon-test for TC I, SC II and SE.
In lab 4, also a straggler was identified according to Dixon-Test for TC II.
In lab 6, a straggler was identified according to Cochran-Test for TC I.

7.1 Table 1: Summery of the individual results: Dimoxystrobin TC I

Lab	Mean Value of 2 doses		Mean Value	Spread
	Day 1 g/kg	Day 2 g/kg	y_i g/kg	w_i g/kg
1	1002.1	999.2	1000.7	2.9
2	997.3	995.5	996.4	1.8
3	1000.1	998.5	999.3	1.6
4	1016.6	1020.8	1018.7	4.2
5	1002.4	1001.9	1002.2	0.5
6	1008.3	995.9	1002.1	12.4

7.2 Table 2: Summery of the individual results: Dimoxystrobin TC II

Lab	Mean Value of 2 doses		Mean Value	Spread
	Day 1 g/kg	Day 2 g/kg	y_i g/kg	w_i g/kg
1	1000.8	996.7	998.8	4.1
2	1006.7	995.7	1001.2	11.0
3	992.7	992.4	992.6	0.3
4	1020.8	1028.3	1024.6	7.5
5	1002.6	1005.6	1004.1	3.0
6	1000.6	1006.2	1003.4	5.6

7.3 Table 3: Summery of the individual results: Dimoxystrobin SC I

Lab	Mean Value of 2 doses		Mean Value	Spread
	Day 1 g/kg	Day 2 g/kg	y_i g/kg	w_i g/kg
1	121.0	119.8	120.4	1.2
2	124.1	125.8	125.0	1.7
3	122.9	122.8	122.9	0.1
4	126.5	127.4	127.0	0.9
5	122.8	122.8	122.8	0.0
6	124.8	123.9	124.4	0.9

7.4 Table 4: Summery of the individual results: Dimoxystrobin SC II

Lab	Mean Value of 2 doses		Mean Value	Spread
	Day 1 g/kg	Day 2 g/kg	g/kg	g/kg
1	181.3	182.1	181.7	0.8
2	181.4	181.1	181.3	0.3
3	180.8	179.6	180.2	1.2
4	190.3	189.0	189.7	1.3
5	180.5	181.6	181.1	1.1
6	178.2	180.3	179.3	2.1

7.5 Table 5: Summery of the individual results: Dimoxystrobin SE

Lab	Mean Value of 2 doses		Mean Value	Spread
	Day 1 g/kg	Day 2 g/kg	g/kg	g/kg
1	126.5	128.8	127.7	2.3
2	127.5	127.1	127.3	0.4
3	127.1	127.5	127.3	0.4
4	131.4	129.5	130.5	1.9
5	128.3	126.8	127.6	1.5
6	127.9	127.1	127.5	0.8

7.6 Table 6: Repeatability and Reproducibility (all results included)

sample	# of labs	# of values	mean value g/kg	RSD %	RSD_H %	$r_{(95)}$ g/kg	$R_{(95)}$ g/kg
Dimoxystrobin TC I	6	12	1003.2	0.83	2.00	11.02	23.40
Dimoxystrobin TC II	6	12	1004.1	1.12	2.00	12.38	31.63
Dimoxystrobin SC I	6	12	123.7	1.85	2.74	1.97	6.41
Dimoxystrobin SC II	6	12	182.2	2.09	2.58	2.49	10.67
Dimoxystrobin SE	6	12	128.0	1.11	2.73	2.81	3.97

7.7 Table 7: Repeatability and Reproducibility (outliers excluded)

sample	# of labs	# of values	mean value g/kg	RSD %	RSD_H %	$r_{(95)}$ g/kg	$R_{(95)}$ g/kg
Dimoxystrobin TC I	5	10	1000.1	0.39	2.00	12.07	10.84
Dimoxystrobin TC II	6	12	1004.1	1.12	2.00	12.38	31.63
Dimoxystrobin SC I	6	12	123.7	1.85	2.74	1.97	6.41
Dimoxystrobin SC II	5	10	180.7	0.66	2.59	2.73	3.33
Dimoxystrobin SE	5	10	127.5	0.62	2.73	3.08	2.22

The outliers according to Dixon test were removed.

RSD_H = Horwitz-function = $2^{\cdot 1-0.5\log C}$
C = concentration of the analyte as decimal number

8. Statistical formulae

y_i = mean of the various laboratories
w_i = spread of the individual values
L = number of labs

$$T_1 = \sum_{i=1}^{p} y_i$$

$$T_2 = \sum_{i=1}^{p} y_i^2$$

$$T_3 = \sum_{i=1}^{p} w_i^2$$

Repeatability and reproducibility were calculated as follows:

$$S_r^2 = \frac{T_3}{2p}$$

$$S_L^2 = \frac{pT_2 - T_1^2}{p(p-1)} - \frac{Sr^2}{2}$$

$$S_R^2 = S_L^2 + S_r^2$$

$$r(95) = 2.8 \cdot \sqrt{S_r^2}$$

$$R(95) = 2.8 \cdot \sqrt{S_R^2}$$

9. Summary of the results

9.1 Summary of the results of all laboratories

	TC I	TC II	SC I	SC II	SE
x	1003.2	1004.1	123.7	182.2	128.0
L	6	6	6	6	6
S_r	3.94	4.42	0.70	0.89	1.00
S_R	8.36	11.30	2.29	3.81	1.42
RSD_r	0.39	0.44	0.57	0.49	0.79
RSD_R	0.83	1.12	1.85	2.09	1.11
r	11.02	12.38	1.97	2.49	2.81
R	23.40	31.63	6.41	10.67	3.97
$RSD_{R(Hor)}$	2.00	2.00	2.74	2.58	2.73

where:

x = average

L = number of laboratories

S_r = repeatability standard deviation

S_R = reproducibility standard deviation = $\sqrt{(S_r^2 + S_L^2)}$

RSD_r = repeatability relative standard deviation (S_r/xE100)

RSD_R = reproducibility relative standard deviation (S_R/xE100)

r = repeatability (S_rE2.8)

R = reproducibility (S_RE2.8)

RSD_R(Hor) = Horwitz value calculated from: $2^{(1-0.5\log c)}$

where c = the concentration of the analyte as a decimal fraction

values given in units of g/kg!

9.2 Summary of the results after elimination of outlier values

	TC I	TC II	SC I	SC II	SE
x	1000.1	1004.1	123.7	180.7	127.5
L	5	6	6	5	5
S_r	4.31	4.42	0.70	0.97	1.10
S_R	3.87	11.30	2.29	1.19	0.79
RSD_r	0.43	0.44	0.57	0.54	0.86
RSD_R	0.39	1.12	1.85	0.66	0.62
r	12.07	12.38	1.97	2.73	3.08
R	10.84	31.63	6.41	3.33	2.22
$RSD_{R(Hor)}$	2.00	2.00	2.74	2.59	2.73

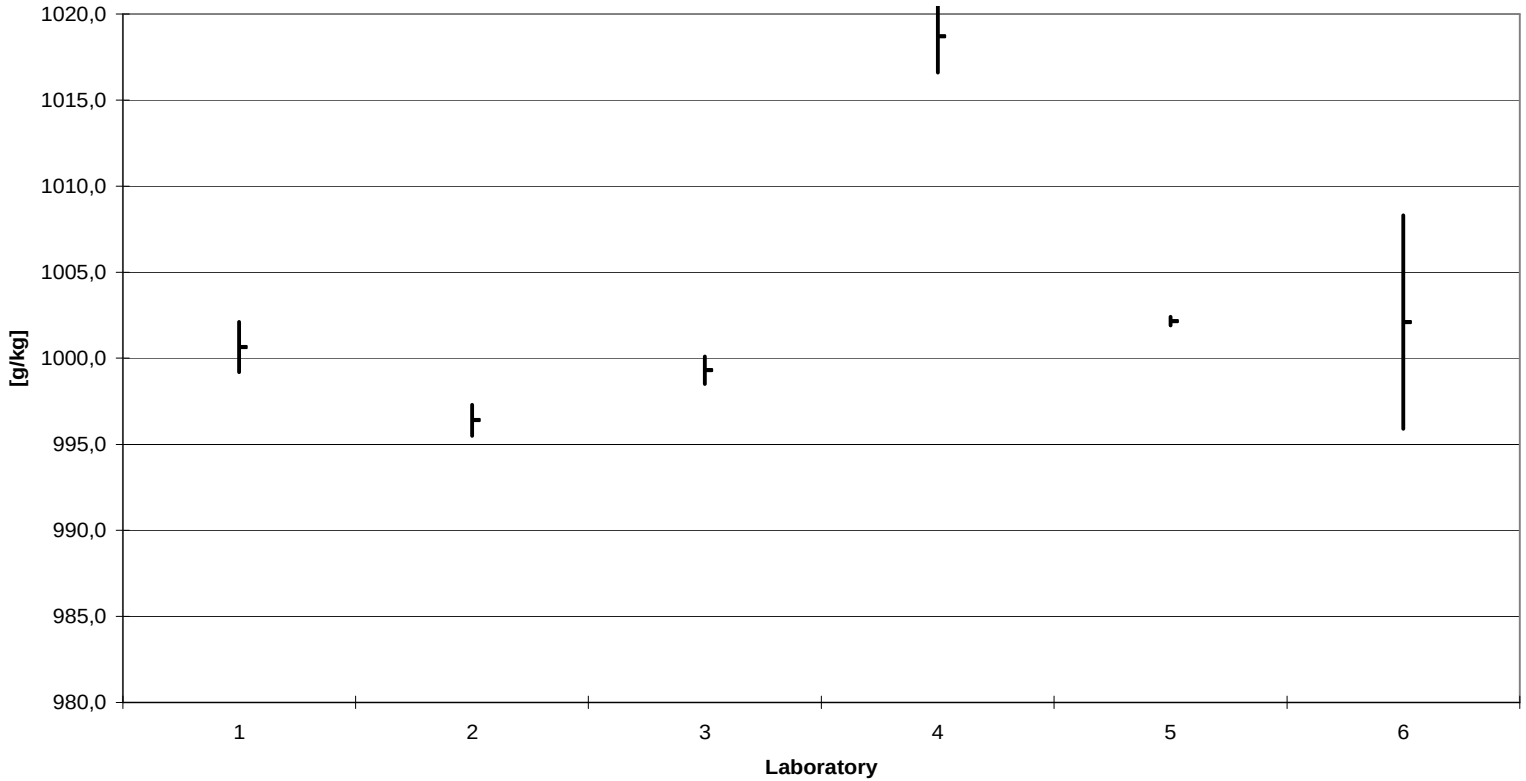
9.3 Summary of the results after elimination of outlier and straggler values

	TC I	TC II	SC I	SC II	SE
x	1000.1	1000.0	123.7	180.7	127.5
L	5	5	6	5	5
S_r	4.31	4.84	0.70	0.97	1.10
S_R	3.87	5.78	2.29	1.19	0.79
RSD_r	0.43	0.48	0.57	0.54	0.86
RSD_R	0.39	0.58	1.85	0.66	0.62
r	12.07	13.56	1.97	2.73	3.08
R	10.84	16.19	6.41	3.33	2.22
$RSD_{R(Hor)}$	2.00	2.00	2.74	2.59	2.73

10. Statistics

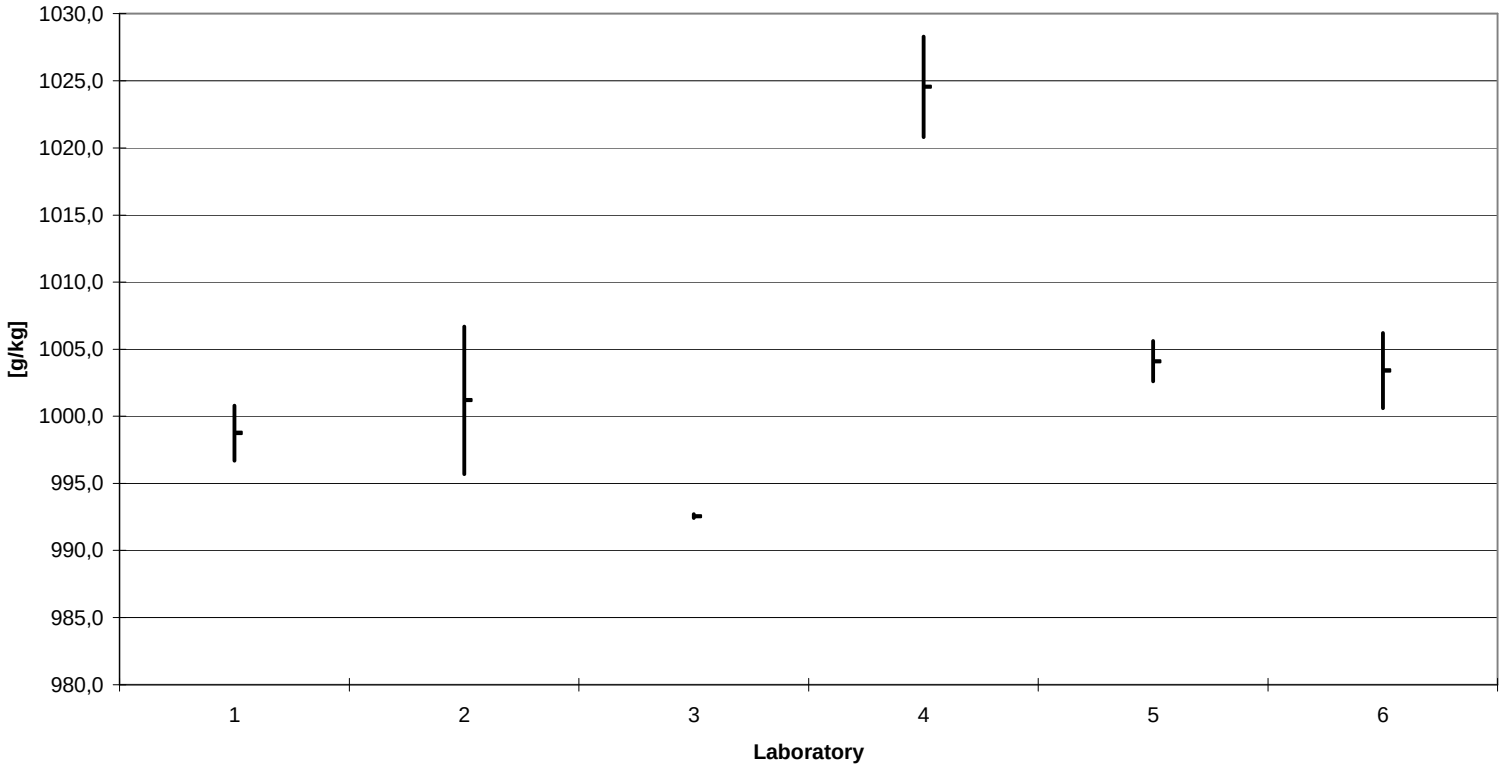
10.1 Summary of the individual results: Dimoxystrobin TC I

Table 1: Results Dimoxystrobin TC I



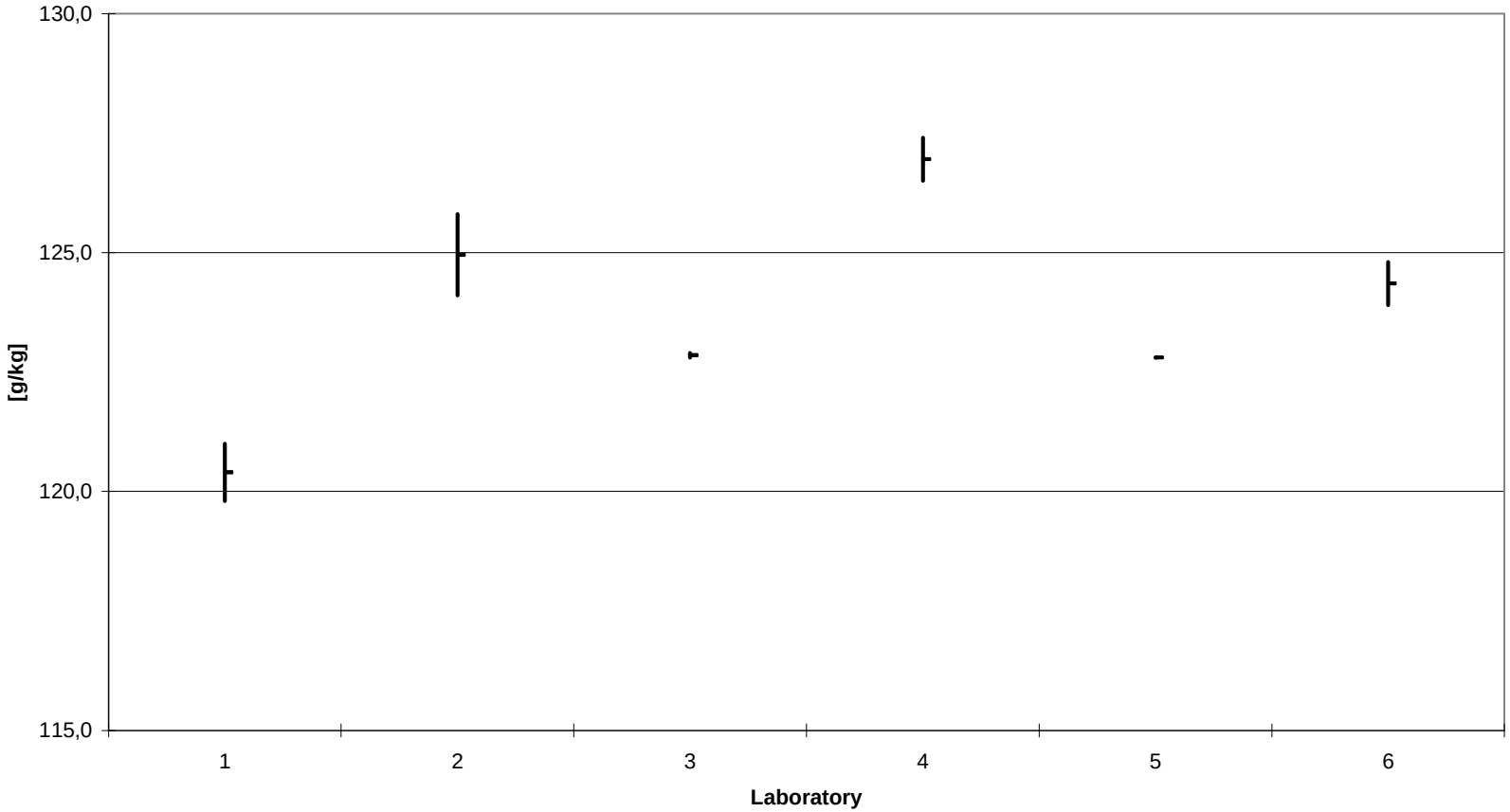
10.2 Summary of the individual results: Dimoxystrobin TC II

Table 2: Results Dimoxystrobin TC II



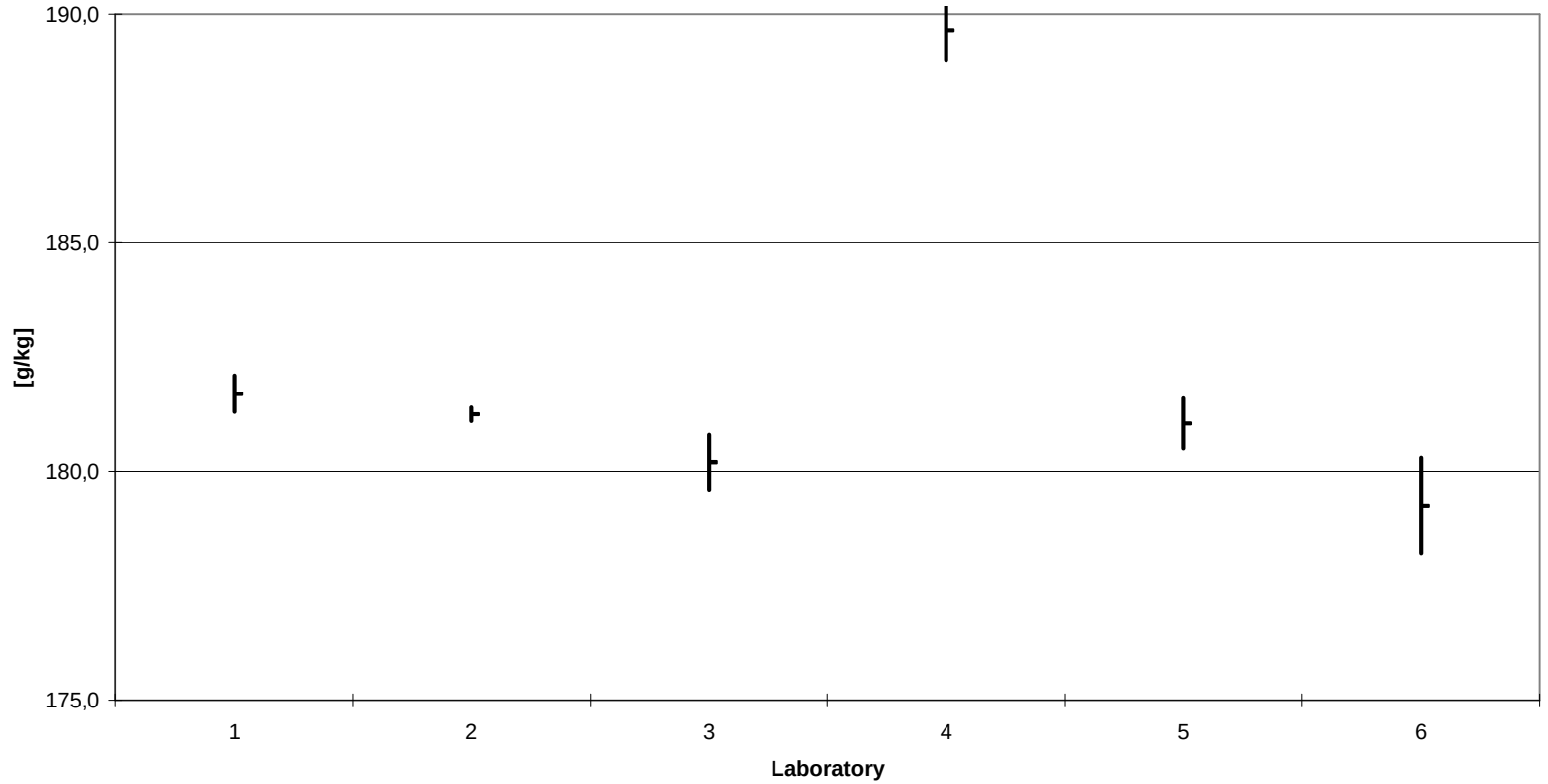
10.2 Summary of the individual results: Dimoxystrobin SC I

Table 3: Results Dimoxystrobin SC I



10.4 Summary of the individual results: Dimoxystrobin SC II

Table 4: Results Dimoxystrobin SC II



10.5 Summary of the individual results: Dimoxystrobin SE

Table 5: Results Dimoxystrobin SE