



The Chemical Company

**BASF SE**

Crop Protection Division

BASF SE ▪ 67114 Limburgerhof, Germany

## **Dimoxystrobin**

**CIPAC collaborative trial**

**CIPAC 4711/R, full scale study**

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

BASF SE  
Global Research Crop Protection  
Dr. Jürgen Fries  
APR/DP – Li 721  
67117 Limburgerhof  
Germany

Presented at the CIPAC meeting in Ljubljana, Slovenia  
June, 2010

Pages: 30

## Table of contents

	Page
<b>1. List of Participants .....</b>	<b>4</b>
<b>2. General Information on Dimoxystrobin .....</b>	<b>5</b>
<b>3. Samples.....</b>	<b>5</b>
<b>4. Study Procedure Instructions .....</b>	<b>6</b>
<b>5. Analytical Method.....</b>	<b>6</b>
<b>6. Deviations from the Analytical Method reported by the Participants .....</b>	<b>7</b>
<b>7. Remarks reported by the Participants.....</b>	<b>9</b>
<b>8. Results and Discussion.....</b>	<b>11</b>
8.1    Table 1: Summery of the individual results: Dimoxystrobin TC I .....	12
8.2    Table 2: Summery of the individual results: Dimoxystrobin TC II .....	13
8.3    Table 3: Summery of the individual results: Dimoxystrobin SC I .....	14
8.4    Table 4: Summery of the individual results: Dimoxystrobin SC II .....	15
8.5    Table 5: Summery of the individual results: Dimoxystrobin SE.....	16
8.6    Table 6: Repeatability and Reproducibility (all results included) .....	17
8.7    Table 7: Repeatability and Reproducibility (outliers excluded) .....	17
8.8    Table 8: Repeatability and Reproducibility (outliers and stragglers excluded) .....	17
<b>9. Statistical Formulae .....</b>	<b>18</b>
<b>10. Summary of the Results: Tables .....</b>	<b>19</b>
10.1    Table 9: Summary of the results of all laboratories .....	19
10.2    Table 10: Summary of the results after elimination of outliers (Dixon-test).....	20
10.3    Table 11: Summary of the results after elimination of outliers and stragglers .....	20
<b>11. Summary of the Results: Figures.....</b>	<b>21</b>
11.1    Figure 1: Dimoxystrobin TC I (all laboratories) .....	21
11.2    Figure 2: Dimoxystrobin TC I (after elimination of outliers).....	22

11.3	Figure 3: Dimoxystrobin TC II (all laboratories) .....	23
11.4	Figure 4: Dimoxystrobin TC II (after elimination of outliers).....	24
11.5	Figure 5: Dimoxystrobin SC I (all laboratories) .....	25
11.6	Figure 6: Dimoxystrobin SC I (after elimination of outliers and stragglers) .....	26
11.7	Figure 7: Dimoxystrobin SC II (all laboratories) .....	27
11.8	Figure 8: Dimoxystrobin SC II (after elimination of outliers and stragglers) .....	28
11.9	Figure 9: Dimoxystrobin SE (all laboratories) .....	29
11.10	Figure 10: Dimoxystrobin SE (after elimination of outliers and stragglers) .....	30

## 1. List of Participants

26 laboratories located in 22 countries worldwide took part at the collaborative study (in randomized order)

ORGANIZATION	NAME	COUNTRY
Kmetijski Institut Slovenije Agricultural Institute of Slovenia, Ljubljana	Ana Gregorcic	Slovenia
Quality Control of Pesticides Formulation National Direction of Plant Protection Ministry Agriculture, Panama	Brenda Checa	Panama
Wallon Agricultural Research Centre, Gembloux	Albert Bernes	Belgium
Forschungsanstalt Agroscope Changins-Wädenswil ACW, Wädenswil	Bruno Patrian	Switzerland
EPA Chemistry Laboratory of Beltsville at Ft. Meade ALCHIMEX, Bucharest	Adrian Burns	USA
Laboratory of Physical and Chemical Examination of Pesticides Benaki Phytopathological Institute, Athens	Cornel Grecu	Romania
Bayer Crop Science Aktiengesellschaft, Monheim	Eleni Karassali	Greece
Technical Center for Safety of Industrial Products of Tianjin, Tianjin	Erika Seidel	Germany
IPESA SA, Buenos Aires	Gang Lv	P.R. China
Pesticide Control Laboratory Backweston Laboratory Campus, Backweston	Hector di Loreto	Argentina
Central Laboratory for Chemical Testing and Control, Sofia	Jim Garvey	Ireland
JAI Research Foundation, Gujarat	Nikolinka Jivkova	Bulgaria
Central Control and Testing Institute in Agriculture, Bratislava	S.Y. Pandey	India
CHEMINOVA A/S, Harboøre	Juliana Schlosserova	Slovakia
Pesticides Analytical Laboratories Department of Agriculture, Nicosia	Kamilla Klausen	Denmark
Plant Protection and Soil Conservation Directorate, Velence	Anna Kouppari	Cyprus
Lajos Benke	Hungary	
Laboratorio Arbitral Agroalimentario, Madrid	Luis Manso Martinez	Spain
CURRENTA GmbH, Dormagen	Michael Haustein	Germany
Agricultural Production Science Research Development Office, Bangkok	Nunchana Luetrakool	Thailand
State Phytosanitary Administration, Brno	Olga Novakova	Czech Rep.
Maryland Department of Agriculture, Annapolis	Tom Phillips	USA
BASF Corporation, RTP Raleigh	Tacheng Hsieh	USA
RIKILT-Institute of Food Safety, Wageningen	Theo de Rijk	Netherlands
BASF SE, Ludwigshafen	Wolfgang Schäfer	Germany
Laboratoire Officiel d'Analyses et de Recherches Chimiques LOARC, Casablanca	Ahmed Zouaoui	Maroc

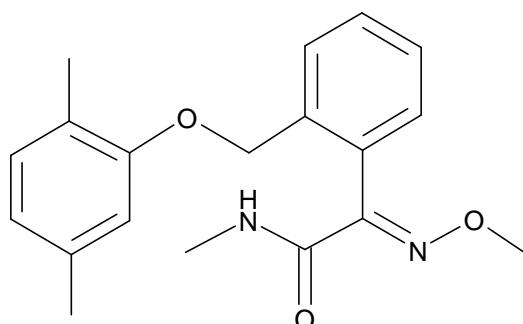
## 2. General Information on Dimoxystrobin

Chemical name: (E)-o-(2,5-dimethylphenoxymethyl)-2-methoxyimino-N-methylphenylacetamide

Common name: Dimoxystrobin

CAS-no.: 149961-52-4

Chemical structure:



RMM: 326.39 g/mol

Empirical formula: C<sub>19</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub>

Indication: Fungicide

Formulations: Suspension Concentrate

Suspo-emulsion

## 3. Samples

The following test samples were provided to the participants in October, 2009:

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

Together with the samples of the collaborative trial study procedure instructions were forwarded to the participants.

#### 4. Study Procedure Instructions

TC1, TC2, SC 1, SC 2 and SE can be stored at ambient temperature (typically +25°C) or cooler.

The study design is based on two series of determinations performed at two different days. Please prepare two calibration solutions for each day of determination. Each sample is weighed once and analyzed once (twofold injection), and the procedure is repeated at a later date using calibration solutions C1 and C2 freshly prepared. Bracketing calibration is suggested.

Once the performance of the GC-system has been checked by five consecutive injections of e.g. calibration solution C1 the sequence of injections to be followed is given as: C1, TC1, TC1, C2, TC2, TC2, C1, SC1, SC1 and so on. Please refer to the result tables 1 and 2 attached for details about the complete injection sequence.

Typical examples of chromatograms are given in the method provided.

Tabulate all your results, (please consider the purity of the analytical standard) deviations of the method and any comments you may have on the result sheets provided, including details of your analytical equipment used and your chromatographic parameters.

#### 5. Analytical Method

##### 5.1 Scope

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

##### 5.2 Procedure

A solution of the sample (acetone) is analyzed by using a high resolution gas chromatographic procedure that employs an internal standard (e.g. 1,1,2,2-tetraphenylethylene). 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.

**6. Deviations from the Analytical Method reported by the Participants**

- Lab 1: column: HP-1
- Lab 2: column: BP-1, 30 m x 0.22 mm, 0.25 µm, injection volume: 1 µl,  
split ratio: 1:10, temperature program: 3 min 120°C to 260°C at 20°C/min  
and hold for 8 min.
- Lab 3: column: DB-1, 30 m x 0.32 mm, 1.0 µm, injection volume: 0.2 µl,  
constant column flow: 2.5 ml/min, split ratio: 1:20,  
temperature program: 0.5 min 80°C to 270°C at 20°C/min  
and hold for 9.5 min.
- Lab 4: no deviations
- Lab 5: column: HP-1
- Lab 6: column: VF-1ms, 15 m x 0.25 mm, 0.25 µm, injection volume: 1 µl,  
constant column flow: 1 ml/min, split ratio: 1:50,  
temperature program: 0.5 min 60°C up to 260°C at 20°C/min  
and hold for 9.5 min.
- Lab 7: column: HP-1, 25 m x 0.2 mm, 0.33 µm, injection volume: 1 µl
- Lab 8: column: DB-1, 30 m x 0.53 mm, 1.5 µm, injection volume: 0.2 µl,  
constant column flow: 5.1 ml/min.
- Lab 9: carrier gas: N<sub>2</sub> instead of He, PTEE filter, acetone p.a. instead of acetone  
GC grade
- Lab 10: column: DB-1, 30 m x 0.25 mm, 0.25 µm, injection volume: 0.5 µl,  
split ratio: 1:50
- Lab 11: column: HP-1
- Lab 12: column: TR-1, 30 m x 0.25 mm, 0.25 µm, constant column flow:  
1.56 ml/min, Istd.: dibutyl-phthalate
- Lab 13: carrier gas: N<sub>2</sub> instead of He, Istd.: dibutyl-phthalate, filter: 0.45 µm,
- Lab 14: column: Rtx-CLP, 30 m x 0.25 mm, 0.25 µm, injection volume: 1 µl
- Lab 15: no deviations
- Lab 16: column: HP-5
- Lab 17: column: CP-Sil 13CB, 25 m x ? mm, 0.20 µm, injection volume: 1 µl,  
constant column flow: 1.5 ml/min, split ratio: 1:50,  
carrier gas: H<sub>2</sub> instead of He, Istd.: triphenyl phosphate
- Lab 18: column: HP-5, 30 m x 0.32 mm, 0.25 µm, constant column flow:  
1.8 ml/min, carrier gas: N<sub>2</sub> instead of He

- Lab 19: injection volume: 1 µl
- Lab 20: column: CP-Sil 5CB, 30 m x 0.32 mm, 0.25 µm, injection volume: 1 µl,  
split ratio: 1:100
- Lab 21: no deviations
- Lab 22: column: DB-1, 30 m x 0.25 mm, 0.25 µm
- Lab 23: column: DB-5, 30 m x 0.32 mm, 0.50 µm
- Lab 24: column: Rtx-1ms, 30 m x 0.25 mm, 0.25 µm, injection volume: 0.2 µl,  
constant column flow: 3.0 ml/min.
- Lab 25: column: Rtx-5, 30 m x 0.25 mm, 0.25 µm, injection volume: 1 µl,  
constant column flow: 1.5 ml/min.
- Lab 26: column: HP-1, 25 m x 0.32 mm, 0.25 µm, constant column flow:  
1 ml/min, carrier gas: N<sub>2</sub> instead of He, split ratio: 1:10,  
injection volume: 1 µl

## 7. Remarks reported by the Participants

- Lab 1: no further remarks
- Lab 2: no further remarks
- Lab 3: temperature program adapted in case of higher film thickness
- Lab 4: 2<sup>nd</sup> day: calculation mistake in the excel sheet. Correct lines are attached
- Lab 5: no further remarks
- Lab 6: no further remarks
- Lab 7: no further remarks
- Lab 8: SC and SE formulations: it was left 30 min in the ultrasonic bath
- Lab 9: bad solubility of the Istd. in THF. Therefore Istd. dissolved in THF + sonification (ultrasonic bath). Recommodation: to weight samples in duplicate
- Lab 10: no further remarks
- Lab 11: no further remarks
- Lab 12: no further remarks
- Lab 13: the TC II, the crystals are different colors (yellow clearly and white), when adding 20 ml of acetone in the flask with the sample SC II it was formed like a gel mass
- Lab 14: instead of a FID-system a GC/MS-system was used, based on MS-identification we were able to identify all mentioned compounds, quantification of Dimoxystrobin m/z 205, quantification of Tetraphenylethylene m/z 332
- Lab 15: 3 small modifications: 0.5 g Istd. diluted to 50 ml with THF, sonification was needed to dissolve the Istd., filters used to filter the formulations prior to injection, the concentrations for the 3 formulations provided were in g/l, but the spreadsheet results were shown in g/kg as per proposed method
- Lab 16: weight of Istd. In table of 1<sup>st</sup> day and 2<sup>nd</sup> day is 1 g not 1 mg
- Lab 17: no further remarks
- Lab 18: no further remarks
- Lab 19: no further remarks
- Lab 20: no further remarks
- Lab 21: no further remarks
- Lab 22: no further remarks
- Lab 23: no further remarks

Lab 24: no further remarks

Lab 25: manual injection

Lab 26: no further remarks

## 8. Results and Discussion

The data from each of the laboratories were reviewed to determine if there were any problems with analysis procedure used, chromatography or reporting results, which might affect the analysis results. The changes / deviations and observations which are noted will not be expected to affect the analysis results significantly.

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 9 of this report.

All laboratories which offered to participate in the collaborative trial and got samples for analyzing sent a complete set of data to the organizer of the trial. These total set of data have been taken into account for the statistical evaluation.

In tables 1 to 5 the individual data set received from all participants are listed in detail.

In tables 9 to 11 the calculated results of all participants are summarized.

- If the results of all laboratories have been taken into account for the statistical evaluation, i.e. all stragglers and outliers according to Dixon-Test and Cochran-Test are left in the evaluation and no data are rejected, the Horwitz-criterion will be not fulfilled (table 9).
- After excluding the outliers according to Dixon-test, the Horwitz-criterion is not fulfilled (table 10).
- The Horwitz-criterion will be fulfilled, if outliers as well as stragglers are excluded (table 11).

**Overview:** outliers and stragglers identified and allocated to the participant

Sample / Lab ID no.	Outlier Dixon (D)	Straggler Dixon (d)	Outlier Cochran (C)	Straggler Cochran (c)
TC I	21	none	21	none
TC II	21	none	21	none
SC I	23	8, 13, 21	21	none
SC II	23	2, 8, 21, 24	21	none
SE	21, 23	8, 14	21	none

***We would like to propose the analytical method for Dimoxystrobin to become provisional***

## Acknowledgements

The author wishes to thank all the laboratories and their staff who participated in this study

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

Laboratory	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	1027.6	1023.1	1025.4	4.5
2	986.0	985.8	985.9	0.2
3	1019.4	1021.7	1020.6	2.3
4	991.9	998.2	995.1	6.3
5	993.4	994.9	994.2	1.5
6	990.7	990.7	990.7	0.0
7	1004.8	997.7	1001.3	7.1
8	996.9	991.1	994.0	5.8
9	1001.9	1008.0	1005.0	6.1
10	990.6	1002.7	996.7	12.1
11	1010.7	1001.1	1005.9	9.6
12	988.4	996.8	992.6	8.4
13	980.9	999.6	990.3	18.7
14	989.4	988.0	988.7	1.4
15	1012.6	1005.8	1009.2	6.8
16	1004.8	1004.6	1004.7	0.2
17	996.5	994.8	995.7	1.7
18	1008.1	996.7	1002.4	11.4
19	987.2	997.4	992.3	10.2
20	993.7	1002.7	998.2	9.0
21	1002.7	1460.7	1231.7	458.0
22	1003.6	1001.1	1002.4	2.5
23	980.1	982.3	981.2	2.2
24	986.0	987.2	986.6	1.2
25	1005.0	995.5	1000.3	9.5
26	989.1	980.2	984.7	8.9

## 8.2 Table 2: Summery of the individual results: Dimoxystrobin TC II

<b>Laboratory</b>	<b>Mean Value of 2 Doses</b>		<b>Mean Value</b>	<b>Spread</b>
	<b>Day 1</b> <b>g/kg</b>	<b>Day 2</b> <b>g/kg</b>	<b>y<sub>i</sub></b> <b>g/kg</b>	<b>w<sub>i</sub></b> <b>g/kg</b>
1	1028.5	1029.8	1029.2	1.3
2	978.3	978.0	978.2	0.3
3	1015.1	1021.7	1018.4	6.6
4	997.5	992.8	995.2	4.7
5	997.7	996.8	997.3	0.9
6	977.1	976.1	976.6	1.0
7	991.0	997.7	994.4	6.7
8	989.9	983.6	986.8	6.3
9	983.9	1012.3	998.1	28.4
10	978.3	988.4	983.4	10.1
11	1002.9	1002.7	1002.8	0.2
12	987.1	994.7	990.9	7.6
13	1014.0	998.1	1006.1	15.9
14	980.4	977.8	979.1	2.6
15	995.9	1008.3	1002.1	12.4
16	990.8	977.3	984.1	13.5
17	997.3	992.4	994.9	4.9
18	998.4	988.7	993.6	9.7
19	995.7	992.3	994.0	3.4
20	995.0	1002.0	998.5	7.0
21	989.6	1460.0	1224.8	470.4
22	998.4	1000.4	999.4	2.0
23	963.6	950.7	957.2	12.9
24	975.0	975.0	975.0	0.0
25	1014.3	1003.5	1008.9	10.8
26	981.5	979.6	980.6	1.9

## 8.3 Table 3: Summery of the individual results: Dimoxystrobin SC I

<b>Laboratory</b>	<b>Mean Value of 2 Doses</b>		<b>Mean Value</b>	<b>Spread</b>
	<b>Day 1</b> <b>g/kg</b>	<b>Day 2</b> <b>g/kg</b>	<b>y<sub>i</sub></b> <b>g/kg</b>	<b>w<sub>i</sub></b> <b>g/kg</b>
1	126.8	128.1	127.5	1.3
2	133.9	133.9	133.9	0.0
3	129.1	126.9	128.0	2.2
4	125.5	124.3	124.9	1.2
5	127.4	127.4	127.4	0.0
6	123.8	123.3	123.6	0.5
7	124.6	124.9	124.8	0.3
8	138.7	139.5	139.1	0.8
9	125.3	126.4	125.9	1.1
10	123.8	123.8	123.8	0.0
11	127.7	126.9	127.3	0.8
12	125.3	125.4	125.4	0.1
13	137.0	135.0	136.0	2.0
14	133.1	132.8	133.0	0.3
15	126.0	127.7	126.9	1.7
16	123.2	126.2	124.7	3.0
17	125.6	125.4	125.5	0.2
18	123.2	122.2	122.7	1.0
19	125.3	124.4	124.9	0.9
20	127.7	126.8	127.3	0.9
21	126.2	180.0	153.1	53.8
22	125.6	125.4	125.5	0.2
23	88.8	85.4	87.1	3.4
24	132.9	133.0	133.0	0.1
25	119.9	121.5	120.7	1.6
26	124.4	123.1	123.8	1.3

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

<b>Laboratory</b>	<b>Mean Value of 2 Doses</b>		<b>Mean Value</b>	<b>Spread</b>
	<b>Day 1</b> <b>g/kg</b>	<b>Day 2</b> <b>g/kg</b>	<b>y<sub>i</sub></b> <b>g/kg</b>	<b>w<sub>i</sub></b> <b>g/kg</b>
1	182.6	182.3	182.5	0.3
2	201.7	201.9	201.8	0.2
3	182.0	182.3	182.2	0.3
4	175.5	177.5	176.5	2.0
5	178.0	175.3	176.7	2.7
6	173.4	172.9	173.2	0.5
7	176.3	174.6	175.5	1.7
8	191.1	194.2	192.7	3.1
9	175.7	178.0	176.9	2.3
10	175.7	178.4	177.1	2.7
11	180.4	179.1	179.8	1.3
12	174.2	176.0	175.1	1.8
13	183.8	176.4	180.1	7.4
14	171.4	177.2	174.3	5.8
15	177.1	179.0	178.1	1.9
16	171.9	174.5	173.2	2.6
17	175.9	176.5	176.2	0.6
18	176.5	174.6	175.6	1.9
19	177.0	176.3	176.7	0.7
20	179.3	177.3	178.3	2.0
21	169.1	240.5	204.8	71.4
22	176.6	176.0	176.3	0.6
23	114.6	111.4	113.0	3.2
24	199.6	200.2	199.9	0.6
25	168.5	177.3	172.9	8.8
26	174.5	174.3	174.4	0.2

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

<b>Laboratory</b>	<b>Mean Value of 2 Doses</b>		<b>Mean Value</b>	<b>Spread</b>
	<b>Day 1</b> <b>g/kg</b>	<b>Day 2</b> <b>g/kg</b>	<b>y<sub>i</sub></b> <b>g/kg</b>	<b>w<sub>i</sub></b> <b>g/kg</b>
1	128.8	131.0	129.9	2.2
2	132.0	132.2	132.1	0.2
3	133.2	132.3	132.8	0.9
4	128.1	126.1	127.1	2.0
5	129.4	129.6	129.5	0.2
6	124.2	123.7	124.0	0.5
7	127.6	128.6	128.1	1.0
8	138.5	139.0	138.8	0.5
9	126.2	130.9	128.6	4.7
10	127.7	128.0	127.9	0.3
11	131.7	130.0	130.9	1.7
12	127.9	127.2	127.6	0.7
13	130.5	124.6	127.6	5.9
14	138.5	139.6	139.1	1.1
15	129.0	127.5	128.3	1.5
16	127.2	126.9	127.1	0.3
17	128.9	128.6	128.8	0.3
18	126.2	125.0	125.6	1.2
19	128.6	127.2	127.9	1.4
20	128.1	130.0	129.1	1.9
21	127.6	184.3	156.0	56.7
22	124.7	124.2	124.5	0.5
23	111.2	106.6	108.9	4.6
24	132.9	133.2	133.1	0.3
25	126.1	124.0	125.1	2.1
26	124.5	125.5	125.0	1.0

## 8.6 Table 6: Repeatability and Reproducibility (all results included)

sample	# of labs	# of values	mean value g/kg	RSD %	RSD <sub>H</sub> %	r <sub>(95)</sub> g/kg	R <sub>(95)</sub> g/kg
Dimoxystrobin TC I	26	52	1006.7	6.47	2.00	178.43	182.35
Dimoxystrobin TC II	26	52	1001.9	6.64	2.00	183.55	186.36
Dimoxystrobin SC I	26	52	126.7	9.26	2.73	21.05	32.87
Dimoxystrobin SC II	26	52	177.8	9.85	2.59	28.36	49.03
Dimoxystrobin SE	26	52	129.3	7.37	2.72	22.39	26.69

## 8.7 Table 7: Repeatability and Reproducibility (outliers excluded)

sample	# of labs	# of values	mean value g/kg	RSD %	RSD <sub>H</sub> %	r <sub>(95)</sub> g/kg	R <sub>(95)</sub> g/kg
Dimoxystrobin TC I	25	50	997.7	1.11	2.00	14.79	31.15
Dimoxystrobin TC II	25	50	993.0	1.57	2.00	18.51	43.78
Dimoxystrobin SC I	25	50	128.3	6.76	2.73	21.43	24.29
Dimoxystrobin SC II	25	50	180.4	6.49	2.59	28.90	32.79
Dimoxystrobin SE	24	48	129.1	3.09	2.72	3.79	11.18

## 8.8 Table 8: Repeatability and Reproducibility (outliers and stragglers excluded)

sample	# of labs	# of values	mean value g/kg	RSD %	RSD <sub>H</sub> %	r <sub>(95)</sub> g/kg	R <sub>(95)</sub> g/kg
Dimoxystrobin TC I	25	50	997.7	1.11	2.00	14.79	31.15
Dimoxystrobin TC II	25	50	993.0	1.57	2.00	18.51	43.78
Dimoxystrobin SC I	22	44	126.4	2.66	2.73	2.28	9.40
Dimoxystrobin SC II	21	42	176.7	1.77	2.59	6.37	8.77
Dimoxystrobin SE	22	44	128.2	2.12	2.72	3.93	7.62

The outliers according to Dixon test were removed.

$$RSD_H = \text{Horwitz-function} = 2^{1-0.5\log C}$$

C = concentration of the analyte as decimal number

## 9. Statistical Formulae

$y_i$  = mean of the various laboratories

$w_i$  = spread of the individual values

$L$  = number of labs

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

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

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

Repeatability and reproducibility were calculated as follows:

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

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

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

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

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

## 10. Summary of the Results: Tables

### 10.1 Table 9: Summary of the results of all laboratories

	TC I	TC II	SC I	SC II	SE
x	1006.7	1001.9	126.7	177.8	129.3
L	26	26	26	26	26
S <sub>r</sub>	63.72	65.55	7.52	10.13	8.00
S <sub>R</sub>	65.12	66.56	11.74	17.51	9.53
RSD <sub>r</sub>	6.33	6.54	5.93	5.70	6.18
RSD <sub>R</sub>	6.47	6.64	9.26	9.85	7.37
r	178.43	183.55	21.05	28.36	22.39
R	182.35	186.36	32.87	49.03	26.69
RSD <sub>R(Hor)</sub>	2.00	2.00	2.73	2.59	2.72

where:

x = average

L = number of laboratories

S<sub>r</sub> = repeatability standard deviation

S<sub>R</sub> = reproducibility standard deviation =  $\sqrt{(S_r^2 + S_L^2)}$

RSD<sub>r</sub> = repeatability relative standard deviation (S<sub>r</sub>/xE100)

RSD<sub>R</sub> = reproducibility relative standard deviation (S<sub>R</sub>/xE100)

r = repeatability (S<sub>r</sub>E2.8)

R = reproducibility (S<sub>R</sub>E2.8)

RSD<sub>R(Hor)</sub> = 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!

## 10.2 Table 10: Summary of the results after elimination of outliers (Dixon-test)

	<b>TC I</b>	<b>TC II</b>	<b>SC I</b>	<b>SC II</b>	<b>SE</b>
<b>x</b>	997.7	993.0	128.3	180.4	129.1
<b>L</b>	25	25	25	25	24
<b>S<sub>r</sub></b>	5.28	6.61	7.65	10.32	1.35
<b>S<sub>R</sub></b>	11.12	15.64	8.68	11.71	3.99
<b>RSD<sub>r</sub></b>	0.53	0.67	5.96	5.72	1.05
<b>RSD<sub>R</sub></b>	<b>1.11</b>	<b>1.57</b>	<b>6.76</b>	<b>6.49</b>	<b>3.09</b>
<b>r</b>	14.79	18.51	21.43	28.90	3.79
<b>R</b>	31.15	43.78	24.29	32.79	11.18
<b>RSD<sub>R(Hor)</sub></b>	2.00	2.00	2.72	2.59	2.72

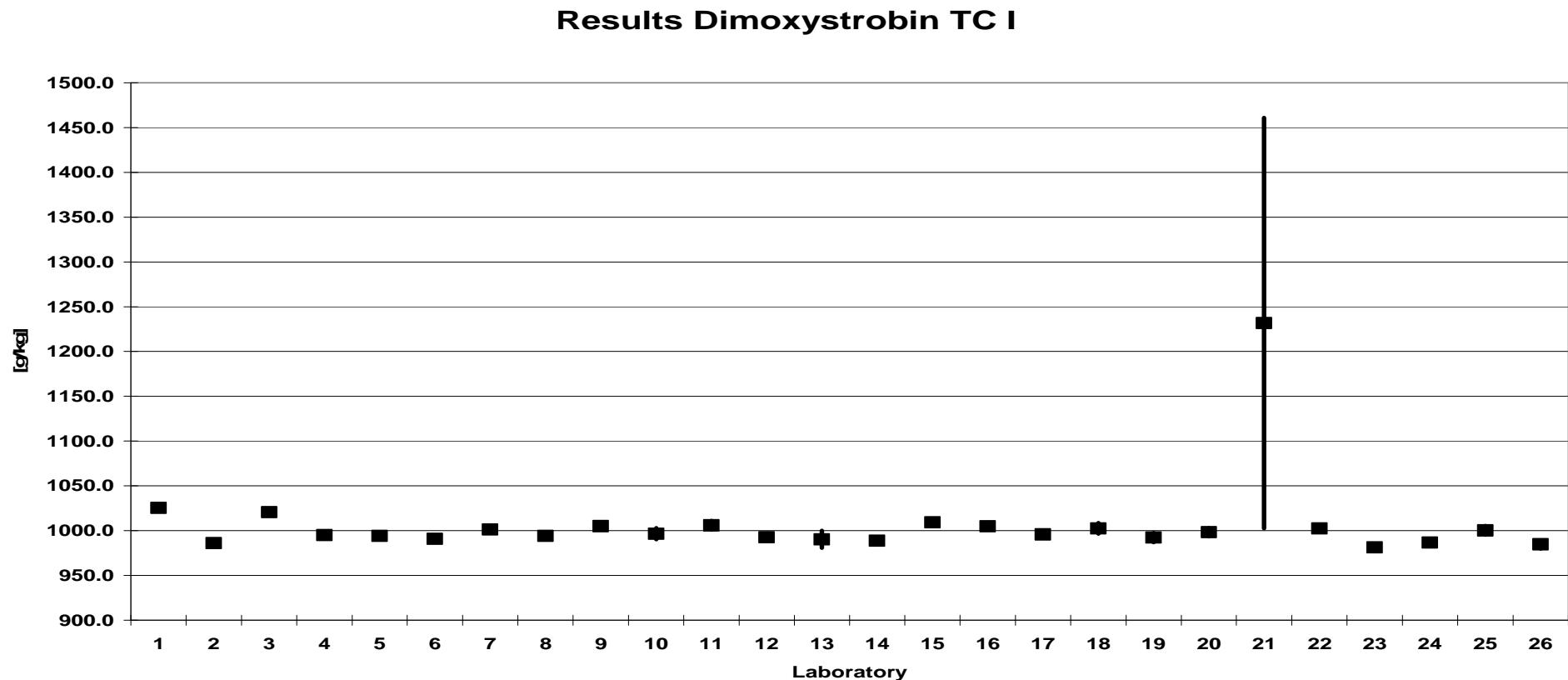
## 10.3 Table 11: Summary of the results after elimination of outliers and stragglers

	<b>TC I</b>	<b>TC II</b>	<b>SC I</b>	<b>SC II</b>	<b>SE</b>
<b>x</b>	997.7	993.0	126.4	176.7	128.2
<b>L</b>	25	25	22	21	22
<b>S<sub>r</sub></b>	5.28	6.61	0.81	2.27	1.40
<b>S<sub>R</sub></b>	11.12	15.64	3.36	3.13	2.72
<b>RSD<sub>r</sub></b>	0.53	0.67	0.64	1.29	1.09
<b>RSD<sub>R</sub></b>	<b>1.11</b>	<b>1.57</b>	<b>2.66</b>	<b>1.77</b>	<b>2.12</b>
<b>r</b>	14.79	18.51	2.28	6.37	3.93
<b>R</b>	31.15	43.78	9.40	8.77	7.62
<b>RSD<sub>R(Hor)</sub></b>	2.00	2.00	2.73	2.60	2.72

## 11. Summary of the Results: Figures

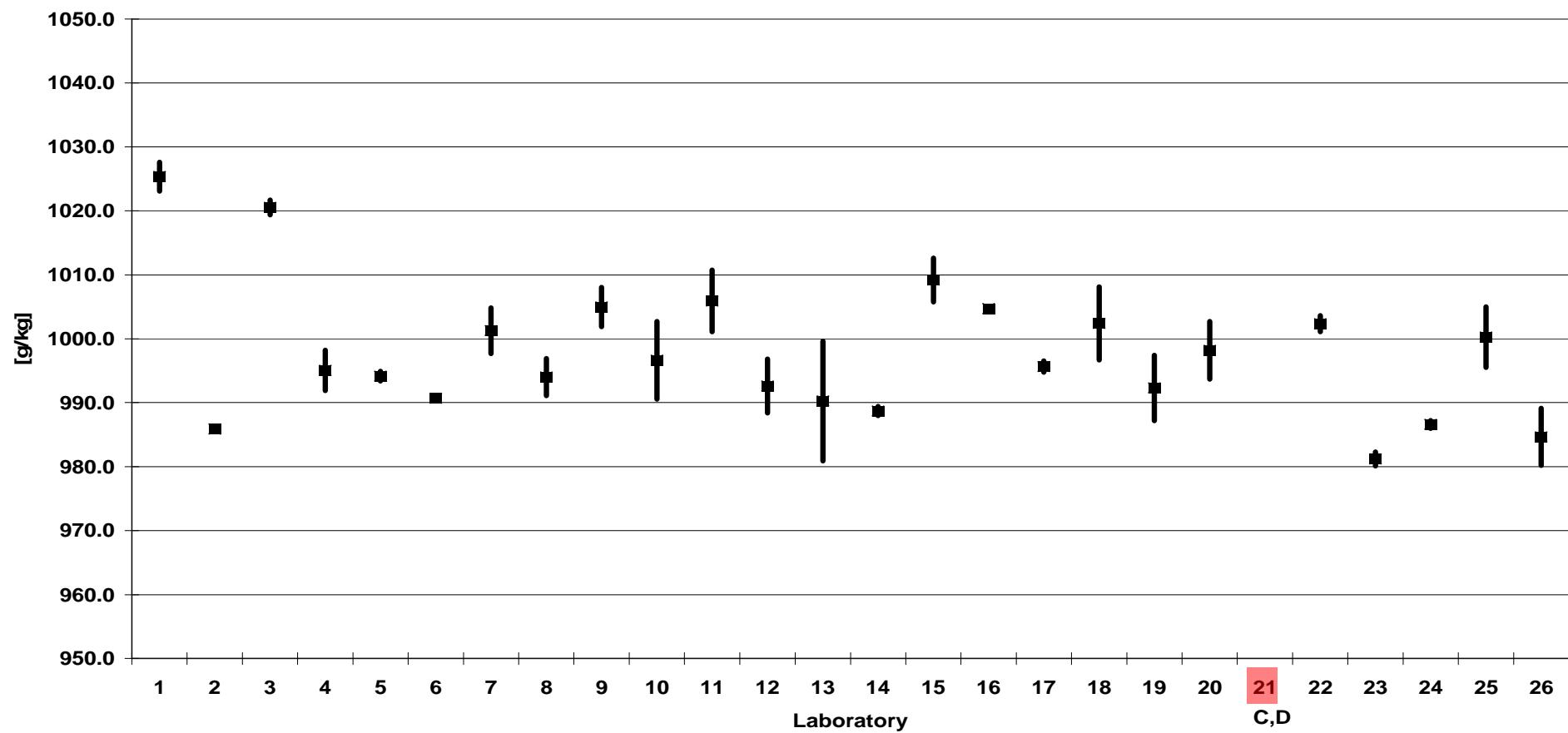
**Note:** Outliers (Dixon (D), Cochran (C)) and Stragglers (Dixon (d), Cochran (c)) are marked in the figures.  
Analytical data of a lab being identified as an outlier value as well as a straggler value are marked in red

11.1 Figure 1: Dimoxystrobin TC I (all laboratories)

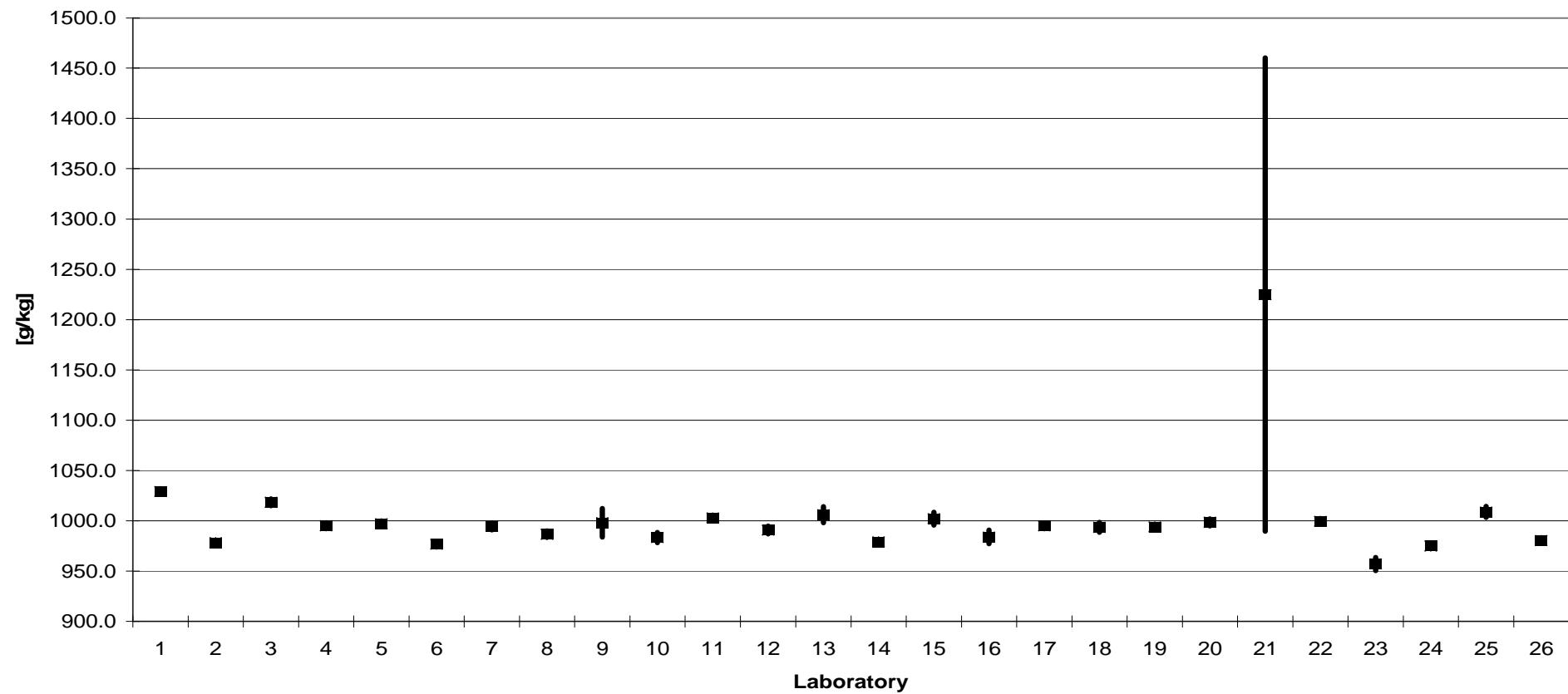


11.2 Figure 2: Dimoxystrobin TC I (after elimination of outliers)

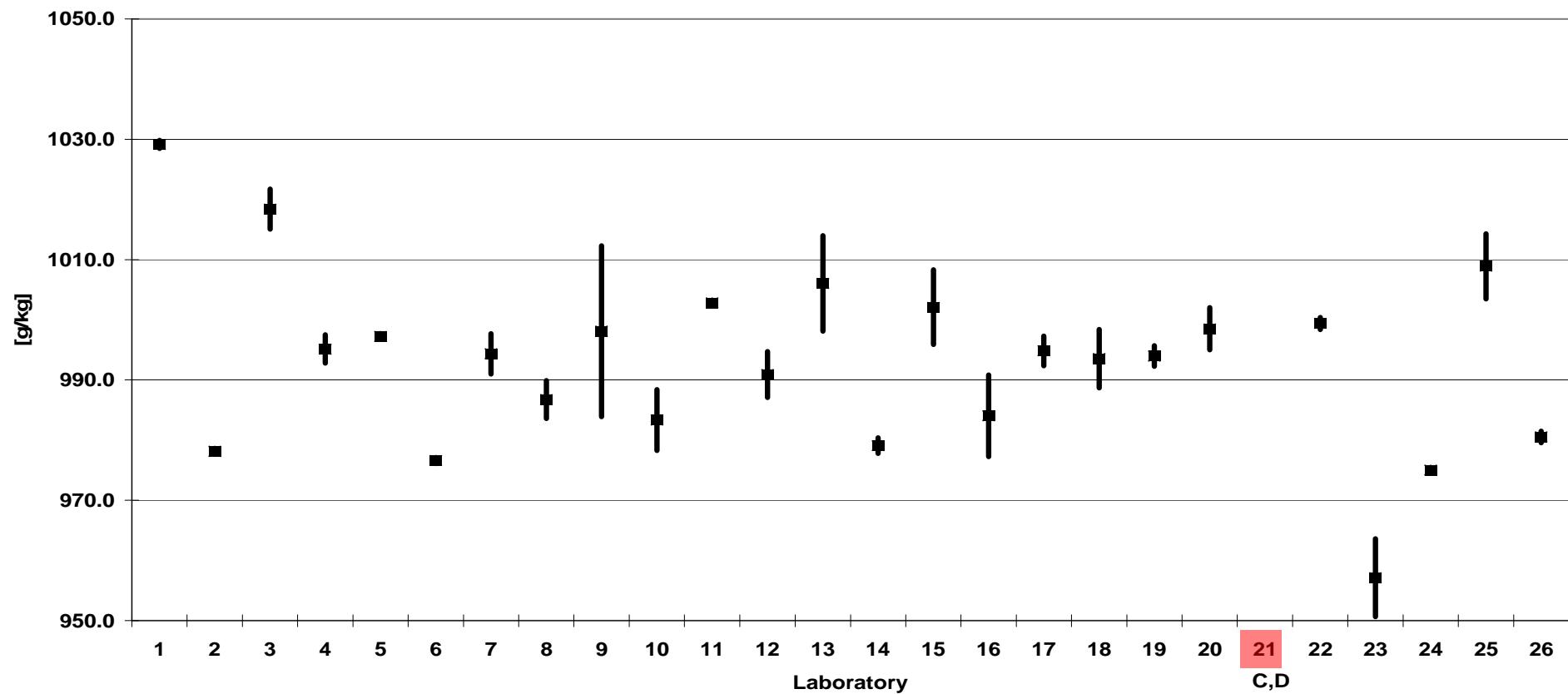
### Results Dimoxystrobin TC I



## 11.3 Figure 3: Dimoxystrobin TC II (all laboratories)

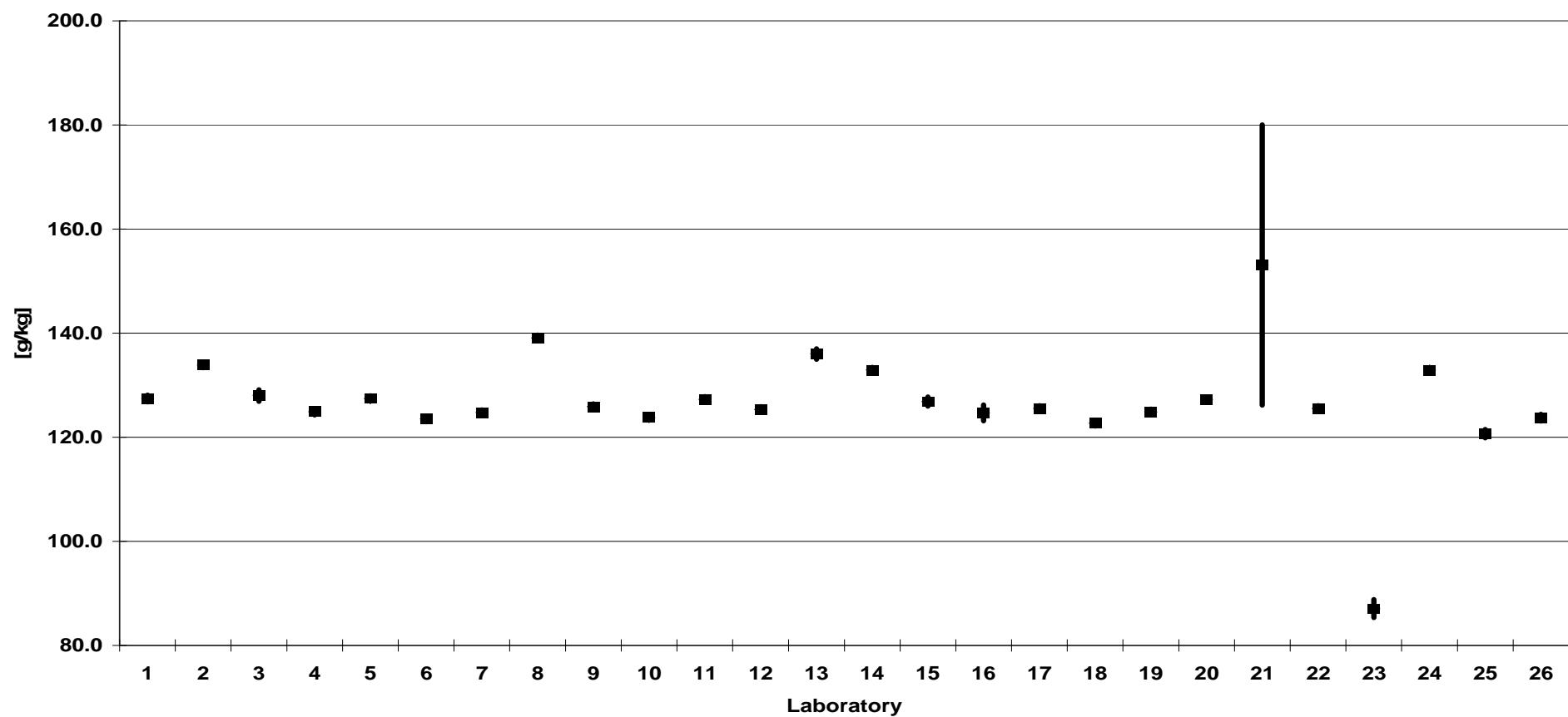
**Results Dimoxystrobin TC II**

11.4 Figure 4: Dimoxystrobin TC II (after elimination of outliers)

**Results Dimoxystrobin TC II**

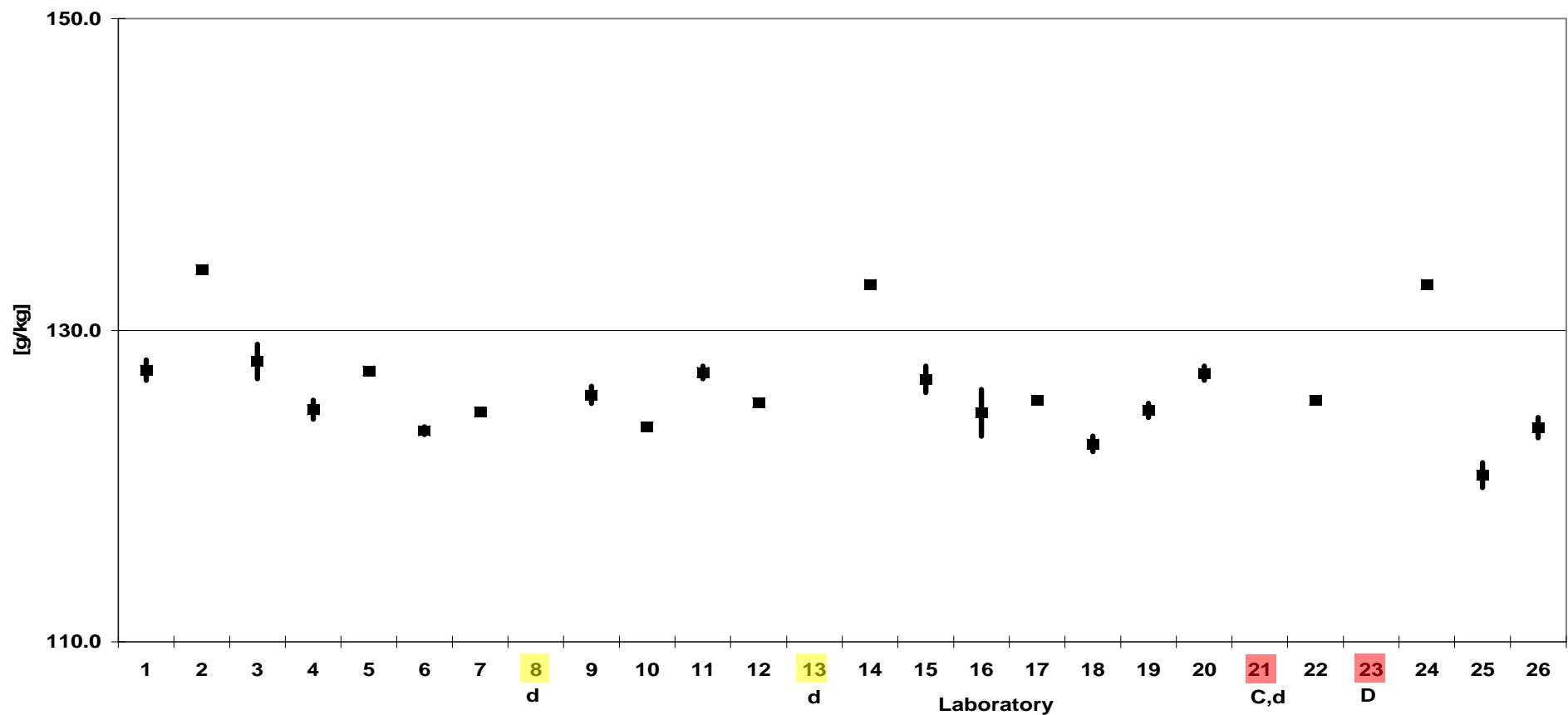
11.5 Figure 5: Dimoxystrobin SC I (all laboratories)

### Results Dimoxystrobin SC I



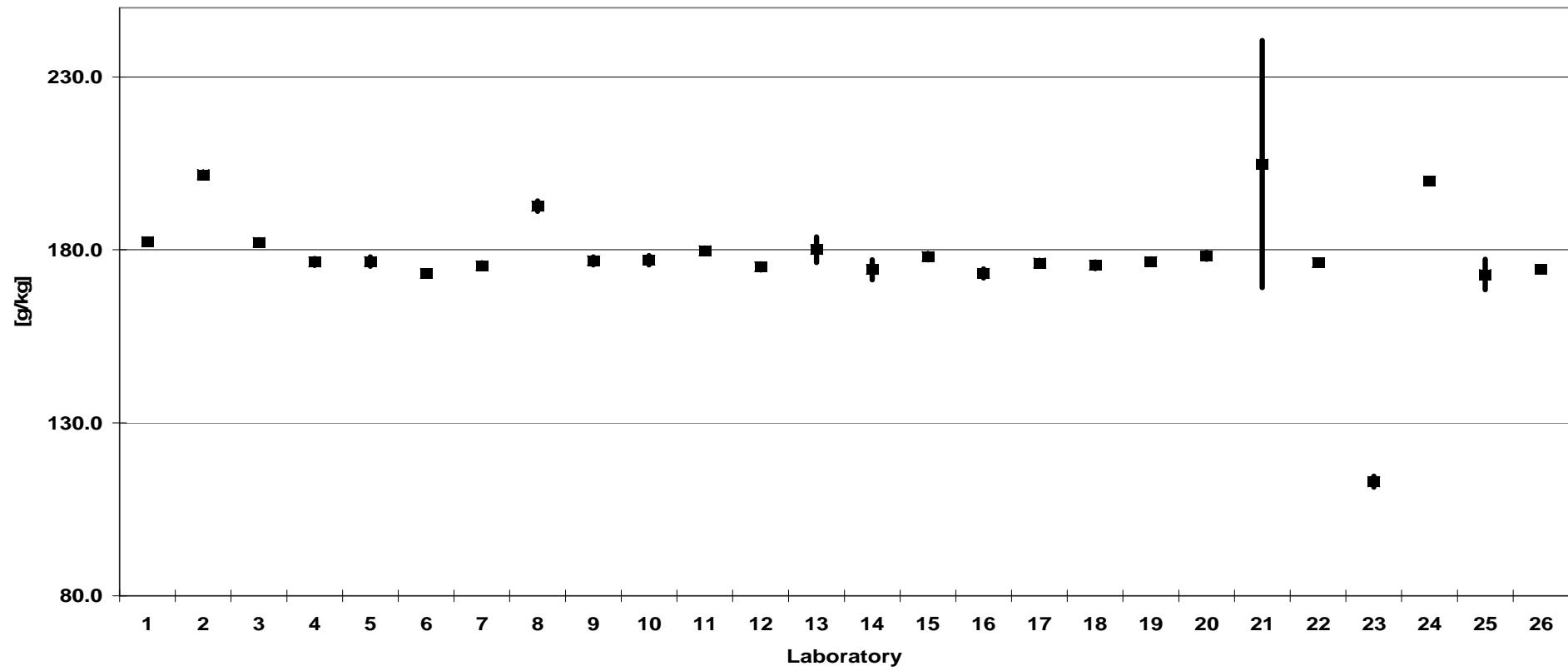
11.6 Figure 6: Dimoxystrobin SC I (after elimination of outliers and stragglers)

### Results Dimoxystrobin SC I



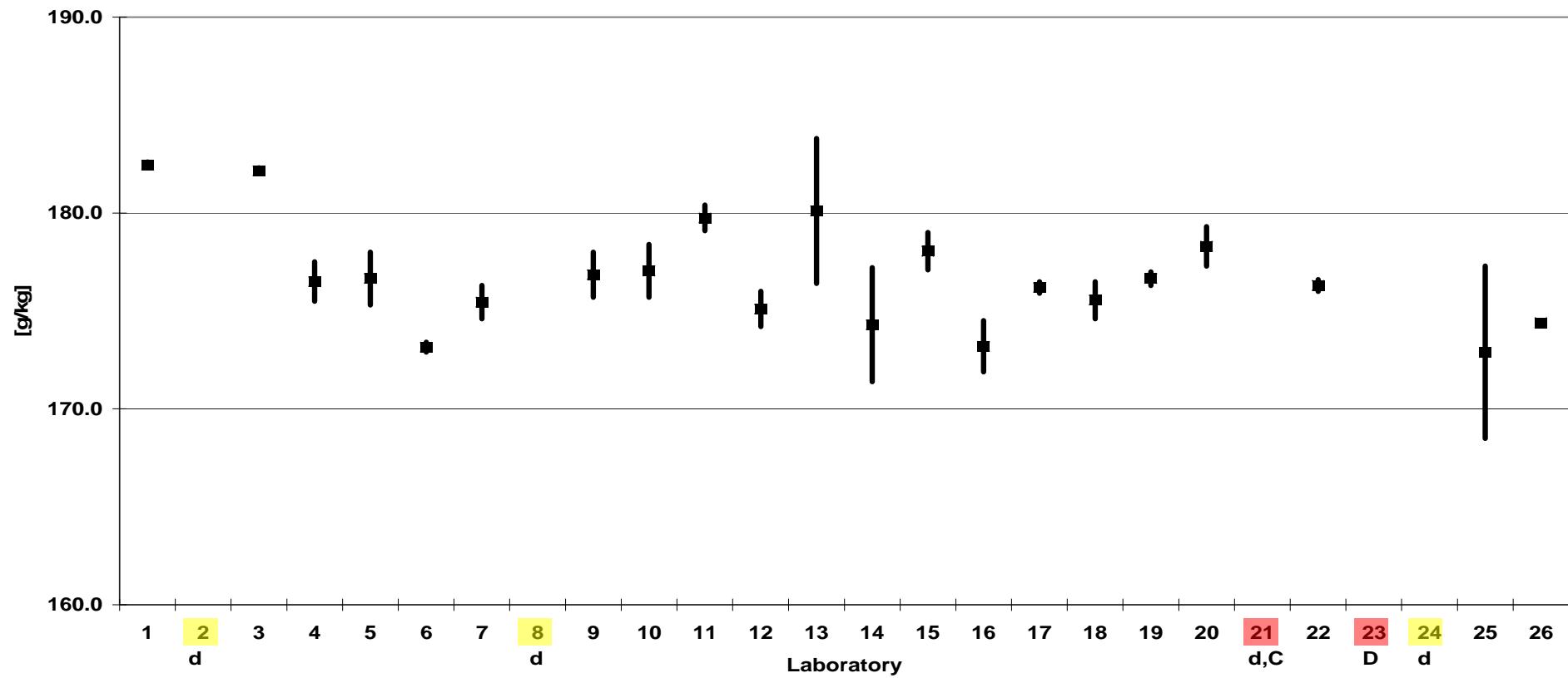
11.7 Figure 7: Dimoxystrobin SC II (all laboratories)

### Results Dimoxystrobin SC II



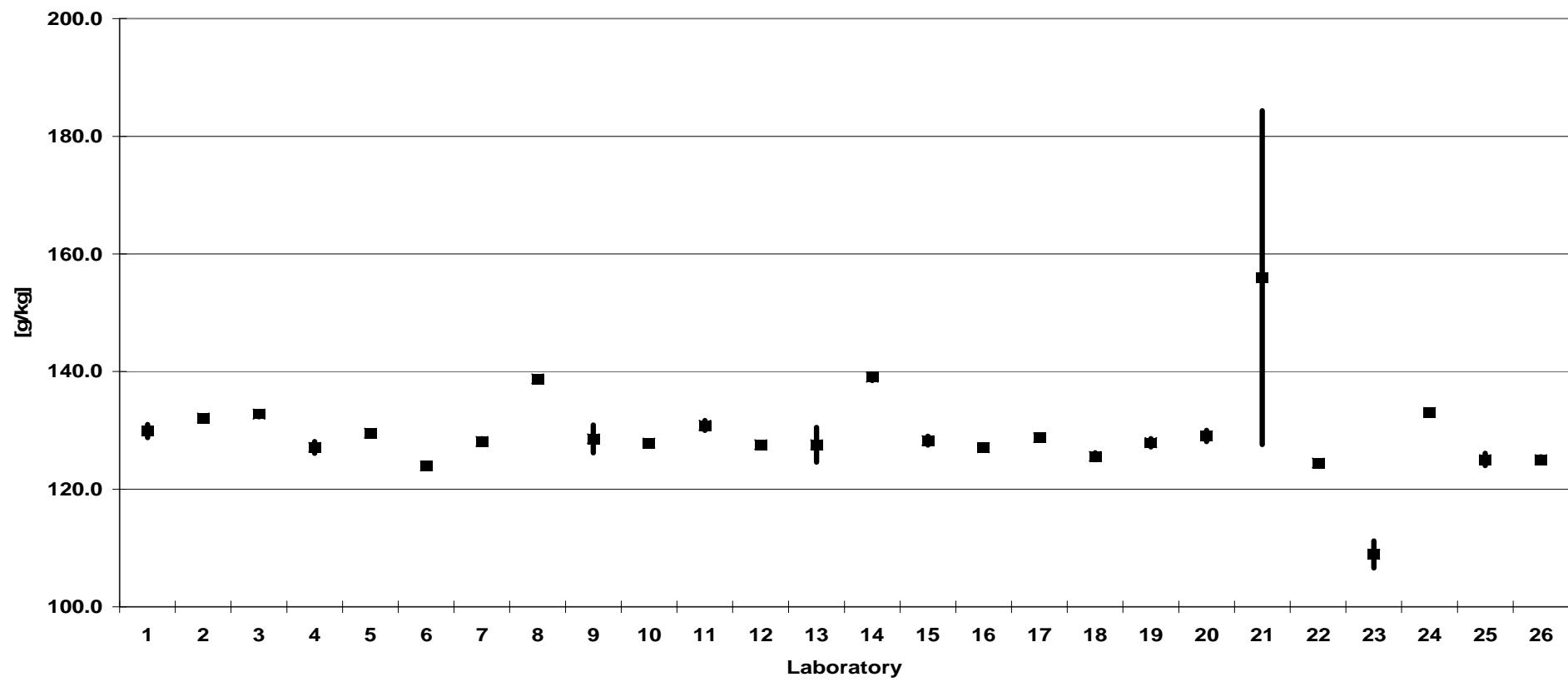
11.8 Figure 8: Dimoxystrobin SC II (after elimination of outliers and stragglers)

### Results Dimoxystrobin SC II



11.9 Figure 9: Dimoxystrobin SE (all laboratories)

### Results Dimoxystrobin SE



11.10 Figure 10: Dimoxystrobin SE (after elimination of outliers and stragglers)

**Results Dimoxystrobin SE**