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Crop Protection Division
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# Chlorfenapyr

## CIPAC collaborative trial

## CIPAC 4826/R, full scale study

# COLLABORATIVE STUDY OF A HIGH PERFORMANCE LIQUID CHROMATOGRAPHIC ANALYSIS OF CHLORFENAPYR TECHNICAL MATERIAL AND FORMULATED PRODUCTS

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Presented at the CIPAC meeting in Dublin, Ireland

June, 2012

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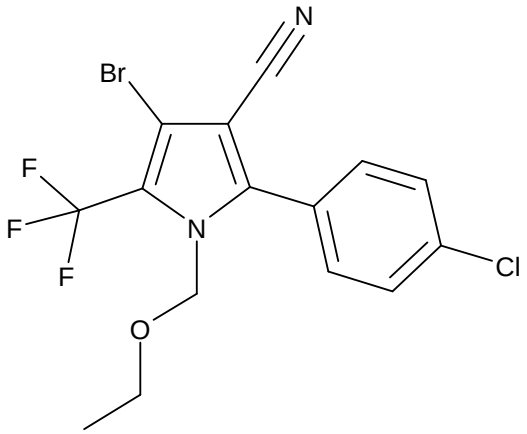
## 1. List of Participants

20 laboratories located in 14 countries worldwide took part at the collaborative study (in alphabetic order)

| ORGANIZATION | NAME | COUNTRY |
|---|---|---|
| Agence Federale pour la Securite de la Chaine Alimetaire, Section Phyto / Residus, Liege | Fabian Etienne Thewissen | Belgium |
| Agricultural Product Quality Testing Center in Jiangsu Province, Nanjing | Huimin Tang | China |
| Analysis & Certification Department FACT, Seodun-dong Gwonseon-gu Suwon | Kim Sang Chion | Korea |
| BASF Corporation, RTP Raleigh | Tacheng Hsieh | USA |
| BASF SE, Ludwigshafen | Christoph Grote | Germany |
| Bayer Crop Science Aktiengesellschaft, Frankfurt | Michael Cichy | Germany |
| Bureau of Cosmetics and Hazardous Substances, Ministry of Public Health, Nonthaburi | Kultida Siriwat | Thailand |
| Central Control and Testing Institute in Agriculture, Bratislava | Juliana Schlosserova | Slovak Republic |
| Currenta GmbH & Co. KG., Dormagen | Michael Haustein | Germany |
| Federal Office of Consumer Protection and Food Safety, Dept. Plant Protection Products | Claudia Vinke | Germany |
| International Institute of Biotechnology and Toxicology (IIBAT), Chennai, Tamil Nadu | Atmakuru Ramesh | India |
| Kansas Dept. Of Agriculture Laboratories, Topeka | Oliver O. Bennett Jr. | USA |
| Laboratorio Arbitral Agroalimentario, Madrid | Luis Manso Martinez | Spain |
| Laboratorio Nacional De Salud, Barcena Villa Nueva | Carmen Castillo | Guatemala |
| Laboratory for Quality Control of Pesticides, Central Phytosanitary Laboratory, Voluntari | Nicoleta Predescu | Romania |
| National Center for the Quality Supervision and Test of Pesticide | Tiechun Chen | China |
| Pesticide Control Laboratory<br>Backweston Laboratory Campus, Backweston | Jim Garvey | Ireland |
| Quality Control of Pesticides Formulation<br>National Direction of Plant Protection<br>Ministry Agriculture, Ciudad de Panama | Brenda Checa | Panama |
| RIKILT Institute of Food Safety, Wageningen | Theo C. de Rijk | Netherlands |
| Walloon Agricultural Research Centre<br>Agriculture and Natural Environment Department, Gembloux | Vanessa Lecocq | Belgium |

## 2. General Information on Chlorfenapyr

Chemical name: 4-bromo-2-(4-chlorophenyl)-1-(ethoxymethyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile (IUPAC)
Common name: Chlorfenapyr
CAS-no.: 122453-73-0
Chemical structure:




RMM: 407.6 g/mol
Empirical formula: $C_{15}H_{11}BrClF_3N_2O$
Indication: Insecticide
Formulations: Suspension Concentrates

## 3. Samples

The following test samples were provided to the participants in April, 2011:

| | |
|---|---|
| Chlorfenapyr, analytical standard | 996 g/kg |
| Chlorfenapyr, technical material TC I | c. 990 g/kg |
| Chlorfenapyr, technical material TC II | c. 990 g/kg |
| Chlorfenapyr, suspension concentrate SC I | c. 100 g/kg |
| Chlorfenapyr, suspension concentrate SC II | c. 200 g/kg |

Together with the samples of the collaborative trial study procedure instructions (section 4, page 6) were forwarded to the participants.

## 4. Study Procedure Instructions

TC1, TC2, SC 1 and SC 2 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 HPLC-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

Chlorfenapyr is determined by high performance liquid chromatography on a reversed phase column (isocratic elution with flush gradient) with UV-detection using the external standard method.

5.2 Procedure

A solution of the sample dissolved in acetonitrile is analyzed using a high performance liquid chromatographic procedure. The separation is achieved using a stainless steel reversed phase column, e. g. 50 mm x 4.6 mm, size diameter 2.7 µm or equivalent with a mobile phase of acetic acid (0.5 ml/l) / acetonitrile (isocratic conditions). Detection is done by an UV-detector at 300 nm, calculation with external standard.

5.3 List of analytical columns used by participants

| | |
|---|---|
| Halo C18, 50 mm x 4.6 mm (2.7 µm) | recommended by organizer |
| Synergi 4µm Fusion-RP80A, 50 mm x 4.6 mm (4 µm) | |
| Kintex XB C18, 100 mm x 4.6 (2.6 µm) | |
| Poroshell 120 EC-C18, 50 mm x 4.6 mm (2.7 µm) | |
| Halo C8, 50 mm x 2.1 mm (2.7 µm) | |
| BDS Hypersil C18, 50 mm x 4.6 mm (2.4 µm) | |
| Poroshell 120 SB-C18, 50 mm x 4.6 mm (2.7 µm) | |
| Symmetry C18, 50 mm x 4.6 mm (2.7 µm) | |
| Zorbax SB-C18, 30 mm x 2.1 mm (3.5 µm) | |
| LiChrosorb RP-18 | |
| Zorbax Eclipse XDB-C18, 250 mm x 4.6 mm | |

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

| | |
|---|---|
| Lab. 1 | column: Synergi 4 µm Fusion-RP80A, 50 mm x 4.6 mm (4 µm)<br>mobile phase: 35% water / 65% $CH_3CN$ / 0.05% v/v acetic acid (0 – 3.5 min.)<br>Filtration: Nylon filters (0.2 µm); column temperature: 25°C |
| Lab. 2 | column: KINTEX XB C18, 100 mm x 4.6 mm (2.6 µm)<br>flow: 1.8 ml/min, column temperature: 35°C, injection volume: 10 µl |
| Lab. 3 | no deviations found |
| Lab. 4 | column: Poroshell 120 EC-C18, 50 mm x 4.6 mm (2.7 µm) |
| Lab. 5 | column: HALO C 8, 50 mm x 2.1 mm (2.7 µm),<br>mobile phase: 47% water / 53% $CH_3CN$ / 0.05% v/v acetic acid;<br>Flow: 1 ml/min; injection volume: 10 µl, column temperature: 22.6°C |
| Lab. 6 | no deviations |
| Lab. 7 | column: BDS HYPERSIL C18, 50 mm x 4.6 mm (2.4 µm) |
| Lab. 8 | flow: 1.8 ml/min. |
| Lab. 9 | no deviations |
| Lab. 10 | column: Poroshell 120 SB-C-18, 50 mm x 4.6 mm (2.7 µm) |
| Lab. 11 | column: Symmetry C18, 150 mm x 3 mm (5 µm)<br>mobile phase: 30% water / 70% $CH_3CN$ / 0.05% v/v acetic acid (0 – 4 min.)<br>flow: 1.2 ml/min, injection volume: 20 µl, column temperature: 25°C |
| Lab. 12 | no deviations |
| Lab. 13 | column: Kinetex C18 100A, 100 mm x 4.6 mm (2.6 µm), column temp.: 30°C |
| Lab. 14 | column: Zorbax SB-C18, 30 mm x 2.1 mm (3.5 µm), Flow: 1 ml/min.<br>temp. 25°C; A: $CH_3COOH$ in $CH_3CN$ (0.5ml/L), B: $CH_3COOH$ in $H_2O$ (0.5ml/L). |
| Lab. 15 | SC I and SC II filtered using 0.45 µm filters |
| Lab. 16 | no deviations |
| Lab. 17 | no deviations |
| Lab. 18 | column: LiChrosorb RP-18 (5 µm) with LiChroCART 125-4 HPLC Cartridge<br>column temperature: 25°C. Filter: 0.45 µm Nylon. Chlorfenapyr mean content<br>calculated by height. Gradient: flushing and conditioning times changed |
| Lab. 19 | column: Poroshell 120 EC-C18, 50 mm x 4.6 mm (2.7 µm)<br>column temperature: 25°C. Gradient: flushing and conditioning times changed |
| Lab. 20 | column: Zorbax Elipse XDB-C18, 250 mm x 4.6 mm<br>mobile phase: 30% water 70% $CH_3CN$ / 0.05% v/v acetic acid (0-10 min.)<br>column temperature: 30°C, flow: 1.5 ml/min. Gradient: flushing and<br>conditioning times changed |

## 7. Remarks reported by the Participants

| | |
|---|---|
| Lab. 1 | C1 and C2 are prepared in acetonitrile, C3 and C4 are prepared in water (5 ml) and acetonitrile. There is no need to prepare separate calibration solutions to analyze TC and SC, calibration solutions can be prepared in acetonitrile only. Detection at 260 nm is more specific and gives better signal to noise ratio than detection at 300 nm. |
| Lab. 2 | no remarks |
| Lab. 3 | no remarks found |
| Lab. 4 | both calibrations prepared in 50 ml acetonitrile! Samples are double weighted. |
| Lab. 5 | I was surprised to be using the “strong solvent” as the solvent for samples and standards. My use of 10 µl injectioned might have flooded the shell part of the packing. |
| Lab. 6 | no remarks |
| Lab. 7 | no remarks |
| Lab. 8 | no remarks |
| Lab. 9 | 1) The code for the calibration solution for TC and SC sample should be difference. 2) The original table for reporting has only one row for standard 'C1' of TC II sample it's should have a row for standard of SC I and SC II. |
| Lab. 10 | no remarks |
| Lab. 11 | The mobile phase is modified in order to prevent the formation of bubbles |
| Lab. 12 | TC samples didn’t need to be filtered. 0.45µm filter used instead of 2µm. |
| Lab. 13 | no remarks |
| Lab. 14 | no remarks |
| Lab. 15 | Filtration of SC I und SC II |
| Lab. 16 | Filtration of SC I and SC II. What is the reason to use gradient elution. There were no other peaks than for the active substance in the chromatogramms. What is the reason to prepare the calibration solution different depending on analysis of TC or SC. It was not clearly stated which kind of calibration solution should be used. |
| Lab. 17 | no remarks |
| Lab. 18 | Retention Time about 4.6 minutes. |
| Lab. 19 | As shown in the results, your proposed tests is good enough for the analysis. I have two suggestions while performed this experiment. First, this method requires an accurate instrument, for example, more reliable HPLC system and Chemical balance. Second, all step of experiment (injector, sampler, column oven, PDA) should be managed at specific temperature, 25°C. |
| Lab. 20 | no remarks |

## 8. 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 9 (page 15) of this report.

Twenty-two labs worldwide offered to participate in the collaborative trial and got samples from the organizer of the collaborative trial. Twenty of them sent a complete data set of results back to the organizer. These results have been taken into account for the statistical evaluation.

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 analyses results. The changes, deviations and observations which were noted will not be expected to affect the analyses results significantly.

The results are summarized in table 1 to table 9 (pp. 10 – 17) and figure 1 to figure 8 (pp. 18 – 25).

If the results of twenty laboratories participated in the collaborative trial are 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 fulfilled in case of TC I, TC II, SC I and not fulfilled in case of SC II (table 7).
The Horwitz criterion is improved for TC I after elimination of one outlier according Cochran (Lab 5) and one outlier according Dixon (Lab 17).
The Horwitz criterion is improved for TC II after elimination of one straggler according Dixon (Lab 17).
The Horwitz criterion is improved for SC I after elimination of one outlier according Cochran (Lab 12) and one straggler according Dixon (Lab. 17).
The Horwitz criterion is fulfilled for SC II after elimination of one outlier according Cochran (Lab. 5), one straggler according Dixon (Lab. 5) and two outliers according Dixon (Lab 11 and Lab 17).
If in calculation procedure outliers and stragglers are all excluded, the value of the $\%RSD_R$ will be well below the calculated acceptable $\%RSD_R$ based on the Horwitz curve (table 8).
The Horwitz criterion is also fulfilled for TC I, TC II, SC I and SC II after exclusion of the whole data set given by 'Lab 17' (table 9).

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

| Sample no. | Lab ID no.<br>Identification of outliers and stragglers |
|---|---|
| TC I | 5, 17 |
| TC II | 17 |
| SC I | 12, 17 |
| SC II | 5, 11, 17 |

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

**Acknowledgements**
The organizer wishes to thank all laboratories and their staff who participated in this study.

8.1 Table 1: Summary of the individual results: Chlorfenapyr 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 | 1 007.2 | 996.3 | 1001.8 | 10.9 |
| 2 | 989.2 | 973.9 | 981.5 | 15.3 |
| 3 | 995.6 | 996.0 | 995.8 | 0.4 |
| 4 | 997.1 | 998.2 | 997.6 | 1.0 |
| 5 | 1 026.9 | 990.6 | 1008.7 | 36.4 |
| 6 | 995.7 | 998.8 | 997.2 | 3.0 |
| 7 | 996.2 | 996.5 | 996.4 | 0.3 |
| 8 | 1 012.8 | 994.9 | 1003.9 | 17.9 |
| 9 | 980.9 | 984.1 | 982.5 | 3.2 |
| 10 | 1 006.9 | 1 013.7 | 1010.3 | 6.8 |
| 11 | 1 011.5 | 993.2 | 1002.4 | 18.3 |
| 12 | 987.7 | 998.9 | 993.3 | 11.1 |
| 13 | 992.0 | 994.4 | 993.2 | 2.4 |
| 14 | 1 000.2 | 992.7 | 996.5 | 7.5 |
| 15 | 998.0 | 998.7 | 998.4 | 0.7 |
| 16 | 995.7 | 999.0 | 997.3 | 3.3 |
| 17 | 942.8 | 941.9 | 942.4 | 0.9 |
| 18 | 1 011.6 | 1 004.7 | 1008.2 | 6.9 |
| 19 | 993.6 | 991.5 | 992.6 | 2.1 |
| 20 | 989.9 | 991.6 | 990.7 | 1.7 |

8.2 Table 2: Summary of the individual results: Chlorfenapyr TC II

| 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 | 991.5 | 994.9 | 993.2 | 3.4 |
| 2 | 985.2 | 973.6 | 979.4 | 11.6 |
| 3 | 996.4 | 995.0 | 995.7 | 1.4 |
| 4 | 991.7 | 991.6 | 991.6 | 0.1 |
| 5 | 995.0 | 1015.9 | 1005.4 | 20.9 |
| 6 | 990.0 | 985.0 | 987.5 | 5.1 |
| 7 | 991.2 | 990.6 | 990.9 | 0.5 |
| 8 | 996.9 | 990.1 | 993.5 | 6.8 |
| 9 | 970.8 | 979.1 | 975.0 | 8.4 |
| 10 | 1002.3 | 1004.9 | 1003.6 | 2.6 |
| 11 | 989.2 | 991.6 | 990.4 | 2.4 |
| 12 | 983.3 | 990.5 | 986.9 | 7.1 |
| 13 | 988.5 | 991.3 | 989.9 | 2.8 |
| 14 | 989.7 | 983.6 | 986.7 | 6.1 |
| 15 | 993.6 | 992.3 | 992.9 | 1.3 |
| 16 | 988.8 | 994.0 | 991.4 | 5.2 |
| 17 | 953.0 | 951.8 | 952.4 | 1.2 |
| 18 | 1001.0 | 1017.8 | 1009.4 | 16.8 |
| 19 | 987.2 | 987.3 | 987.3 | 0.1 |
| 20 | 983.1 | 991.5 | 987.3 | 8.5 |

8.3 Table 3: Summary of the individual results: Chlorfenapyr SC 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 | 102.9 | 102.9 | 102.9 | 0.1 |
| 2 | 102.2 | 102.8 | 102.5 | 0.6 |
| 3 | 104.3 | 104.5 | 104.4 | 0.2 |
| 4 | 102.8 | 103.3 | 103.0 | 0.5 |
| 5 | 108.7 | 105.9 | 107.3 | 2.8 |
| 6 | 103.8 | 103.2 | 103.5 | 0.6 |
| 7 | 100.6 | 102.4 | 101.5 | 1.9 |
| 8 | 103.8 | 103.9 | 103.8 | 0.1 |
| 9 | 100.5 | 99.9 | 100.2 | 0.6 |
| 10 | 105.0 | 105.0 | 105.0 | 0.0 |
| 11 | 105.6 | 105.7 | 105.7 | 0.1 |
| 12 | 103.2 | 108.3 | 105.7 | 5.1 |
| 13 | 103.2 | 102.8 | 103.0 | 0.3 |
| 14 | 104.6 | 102.4 | 103.5 | 2.2 |
| 15 | 103.2 | 103.8 | 103.5 | 0.6 |
| 16 | 103.3 | 104.1 | 103.7 | 0.8 |
| 17 | 97.6 | 97.6 | 97.6 | 0.0 |
| 18 | 101.5 | 101.5 | 101.5 | 0.0 |
| 19 | 103.4 | 103.6 | 103.5 | 0.2 |
| 20 | 104.0 | 103.5 | 103.7 | 0.5 |

8.4 Table 4: Summary of the individual results: Chlorfenapyr SC II

| 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 | 213.5 | 213.3 | 213.4 | 0.2 |
| 2 | 210.8 | 208.2 | 209.5 | 2.6 |
| 3 | 215.3 | 215.0 | 215.2 | 0.3 |
| 4 | 211.9 | 212.9 | 212.4 | 1.0 |
| 5 | 232.8 | 212.8 | 222.8 | 20.0 |
| 6 | 214.7 | 214.8 | 214.7 | 0.1 |
| 7 | 210.6 | 210.3 | 210.4 | 0.3 |
| 8 | 214.4 | 213.6 | 214.0 | 0.7 |
| 9 | 208.9 | 206.3 | 207.6 | 2.6 |
| 10 | 216.5 | 217.4 | 217.0 | 0.9 |
| 11 | 201.3 | 200.7 | 201.0 | 0.6 |
| 12 | 213.2 | 211.6 | 212.4 | 1.6 |
| 13 | 213.8 | 213.7 | 213.8 | 0.1 |
| 14 | 215.2 | 212.4 | 213.8 | 2.8 |
| 15 | 215.0 | 216.6 | 215.8 | 1.7 |
| 16 | 212.6 | 215.1 | 213.9 | 2.5 |
| 17 | 200.2 | 200.0 | 200.1 | 0.3 |
| 18 | 209.7 | 210.1 | 209.9 | 0.5 |
| 19 | 213.6 | 214.4 | 214.0 | 0.8 |
| 20 | 214.0 | 213.4 | 213.7 | 0.6 |

8.5 Table 5: Repeatability and Reproducibility (all results included)

| sample | # of labs | # of values | mean value g/kg | $RSD_R$ % | $RSD_H$ % | $r_{(95)}$ g/kg | $R_{(95)}$ g/kg |
|---|---|---|---|---|---|---|---|
| Chlorfenapyr TC I | 20 | 40 | 994.5 | 1.56 | 2.00 | 22.78 | 43.43 |
| Chlorfenapyr TC II | 20 | 40 | 989.5 | 1.26 | 2.00 | 15.46 | 34.89 |
| Chlorfenapyr SC I | 20 | 40 | 103.3 | 2.14 | 2.81 | 2.97 | 6.19 |
| Chlorfenapyr SC II | 20 | 40 | 212.3 | 2.64 | 2.53 | 9.26 | 15.66 |

8.6 Table 6: Repeatability and Reproducibility (outliers and stragglers excluded)

| sample | # of labs | # of values | mean value g/kg | $RSD_R$ % | $RSD_H$ % | $r_{(95)}$ g/kg | $R_{(95)}$ g/kg |
|---|---|---|---|---|---|---|---|
| Chlorfenapyr TC I | 18 | 36 | 996.6 | 0.86 | 2.00 | 16.99 | 24.03 |
| Chlorfenapyr TC II | 19 | 38 | 991.5 | 0.92 | 2.00 | 15.85 | 25.53 |
| Chlorfenapyr SC I | 18 | 36 | 103.4 | 1.67 | 2.81 | 2.07 | 4.82 |
| Chlorfenapyr SC II | 17 | 34 | 213.0 | 1.21 | 2.52 | 2.93 | 7.24 |

Outliers and stragglers according to Dixon test and Cochran test were removed.

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

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

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

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

Repeatability and reproducibility were calculated as follows:

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

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

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

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

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

## 10. Summary of the Results

10.1 Table 7: Summary of the results of all laboratories included in calculation

| | TC I | TC II | SC I | SC II |
|---|---|---|---|---|
| **x** | 994.5 | 989.5 | 103.3 | 212.3 |
| **L** | 20 | 20 | 20 | 20 |
| **$S_r$** | 8.14 | 5.52 | 1.06 | 3.31 |
| **$S_R$** | 15.51 | 12.46 | 2.21 | 5.59 |
| **$RSD_r$** | 0.82 | 0.56 | 1.03 | 1.56 |
| **$RSD_R$** | 1.56 | 1.26 | 2.14 | 2.64 |
| **r** | 22.78 | 15.46 | 2.97 | 9.26 |
| **R** | 43.43 | 34.89 | 6.19 | 15.66 |
| **$RSD_{R(Hor)}$** | 2.00 | 2.00 | 2.81 | 2.53 |

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 ($S_r$E2.8)

R = reproducibility ($S_R$E2.8)

$RSD_R$(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!

10.2 Table 8: Summary of the results after elimination of outlier and straggler values

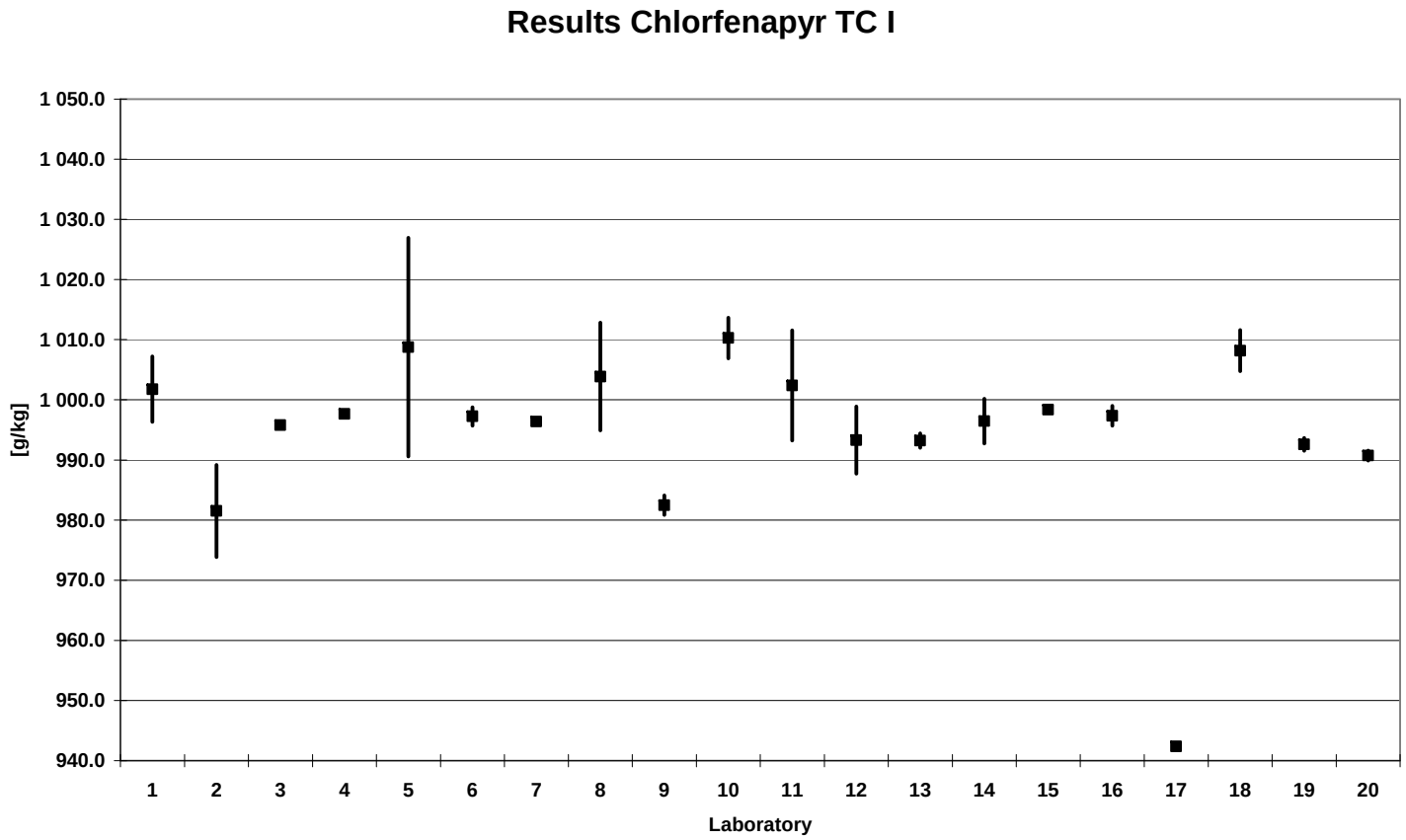
| | TC I | TC II | SC I | SC II |
|---|---|---|---|---|
| **x** | 996.6 | 991.5 | 103.4 | 213.0 |
| **L** | 18 | 19 | 18 | 17 |
| **$S_r$** | 6.07 | 5.66 | 0.74 | 1.05 |
| **$S_R$** | 8.58 | 9.12 | 1.72 | 2.58 |
| **$RSD_r$** | 0.61 | 0.57 | 0.72 | 0.49 |
| **$RSD_R$** | 0.86 | 0.92 | 1.67 | 1.21 |
| **r** | 16.99 | 15.85 | 2.07 | 2.93 |
| **R** | 24.03 | 25.53 | 4.82 | 7.24 |
| **$RSD_{R(Hor)}$** | 2.00 | 2.00 | 2.81 | 2.52 |

10.3 Table 9: Summary of the results after exclusion of the data of ‘Lab 17’

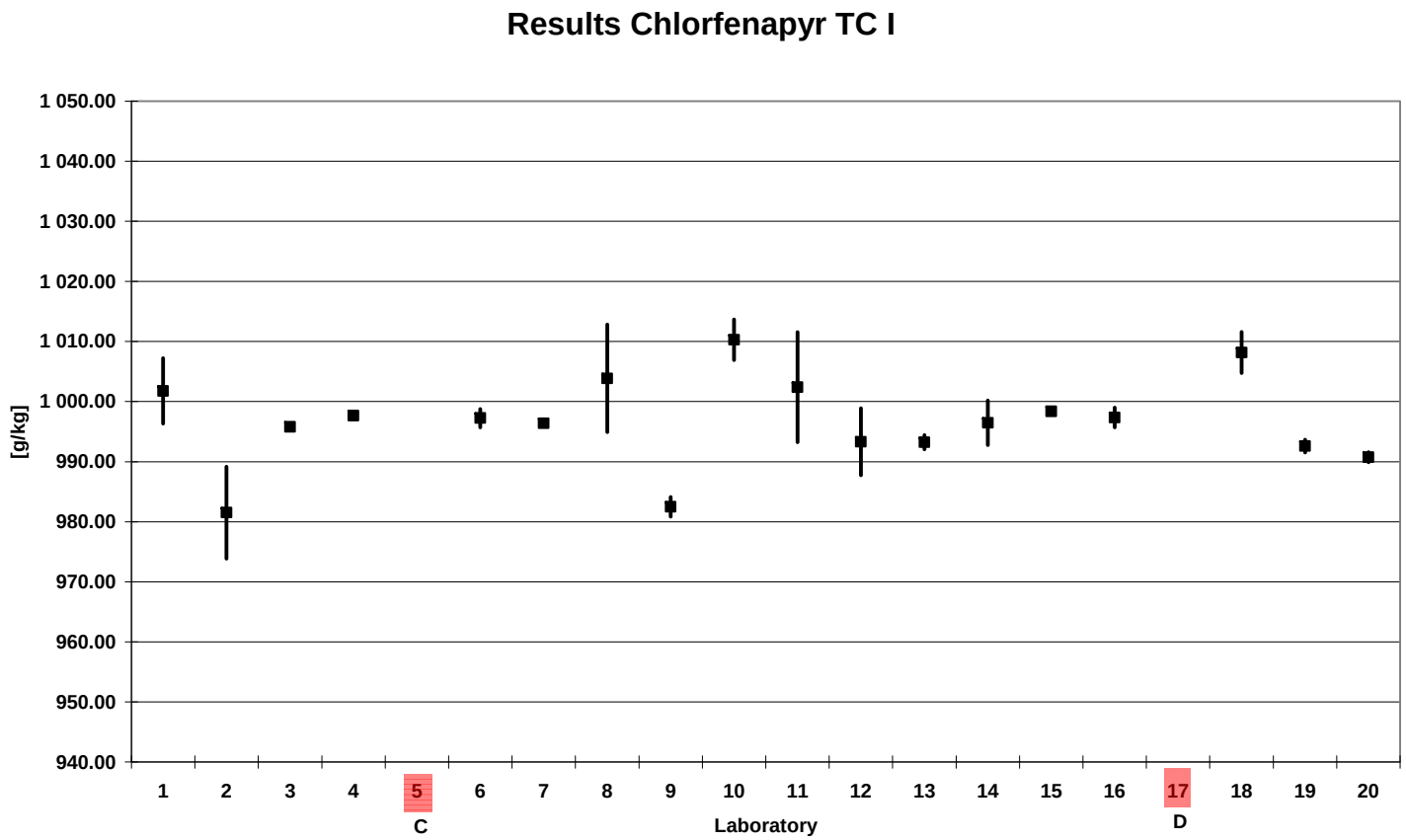
| | TC I | TC II | SC I | SC II |
|---|---|---|---|---|
| **x** | 997.3 | 991.5 | 103.6 | 212.9 |
| **L** | 19 | 19 | 19 | 19 |
| **$S_r$** | 8.35 | 5.66 | 1.09 | 3.39 |
| **$S_R$** | 9.73 | 9.12 | 1.81 | 4.93 |
| **$RSD_r$** | 0.84 | 0.57 | 1.05 | 1.59 |
| **$RSD_R$** | 0.98 | 0.92 | 1.75 | 2.32 |
| **r** | 23.37 | 15.85 | 3.05 | 9.50 |
| **R** | 27.25 | 25.53 | 5.08 | 13.82 |
| **$RSD_{R(Hor)}$** | 2.00 | 2.00 | 2.81 | 2.52 |

## 11. Statistics

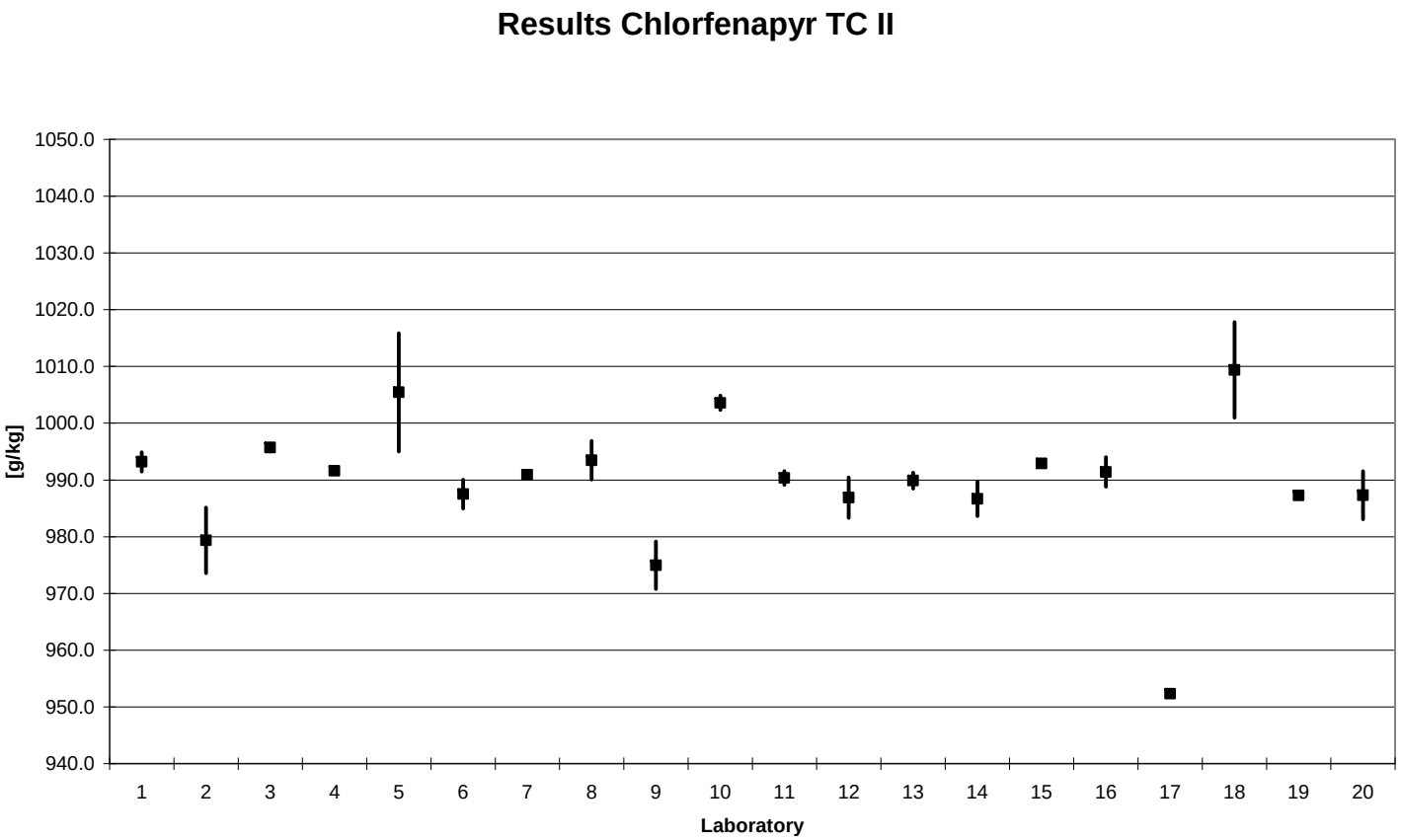
11.1 Figure 1: Summary of the individual results: Chlorfenapyr TC I (all laboratories)



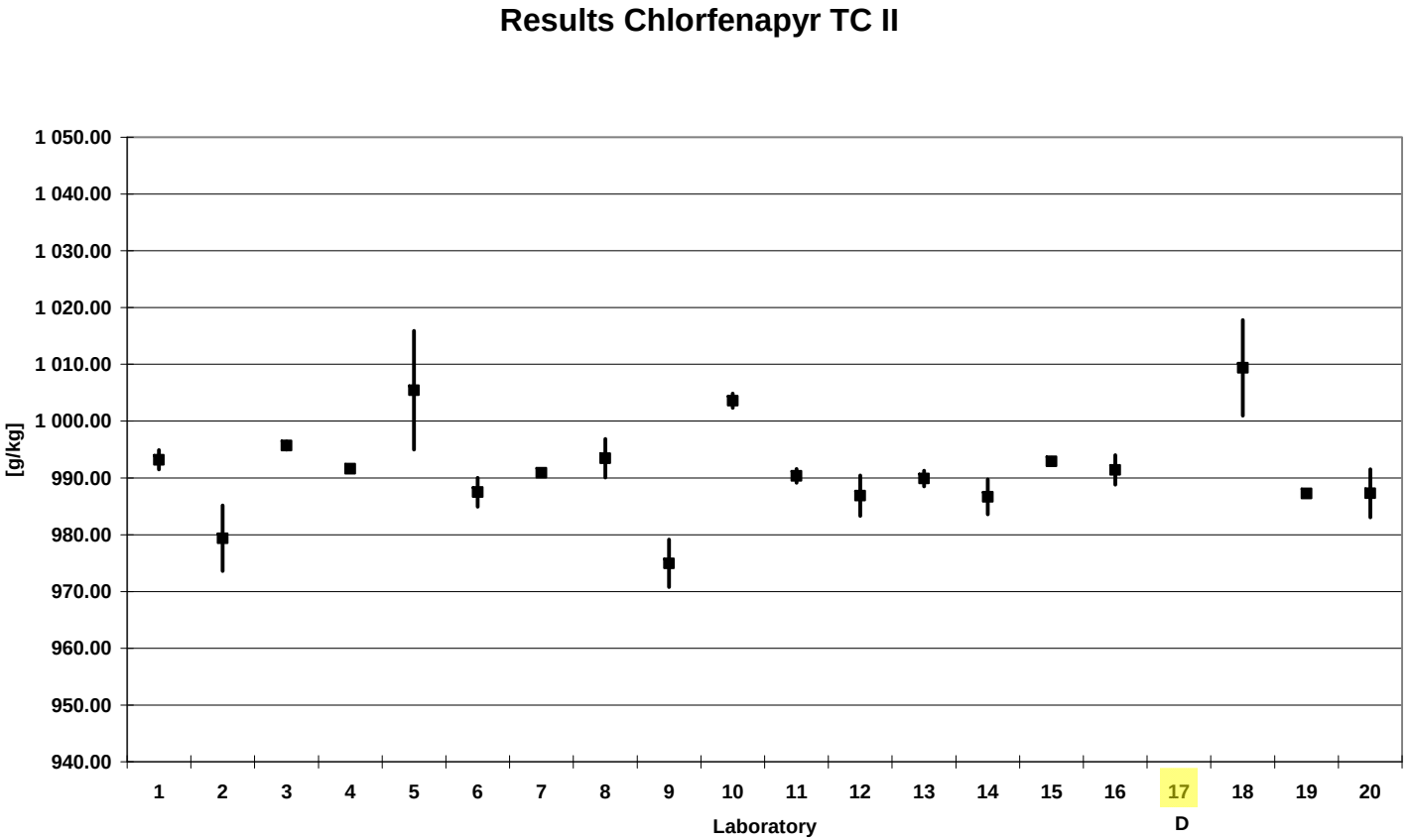
11.2 Figure 2: Summary of the individual results: Chlorfenapyr TC I (after elimination of straggler and outlier values)



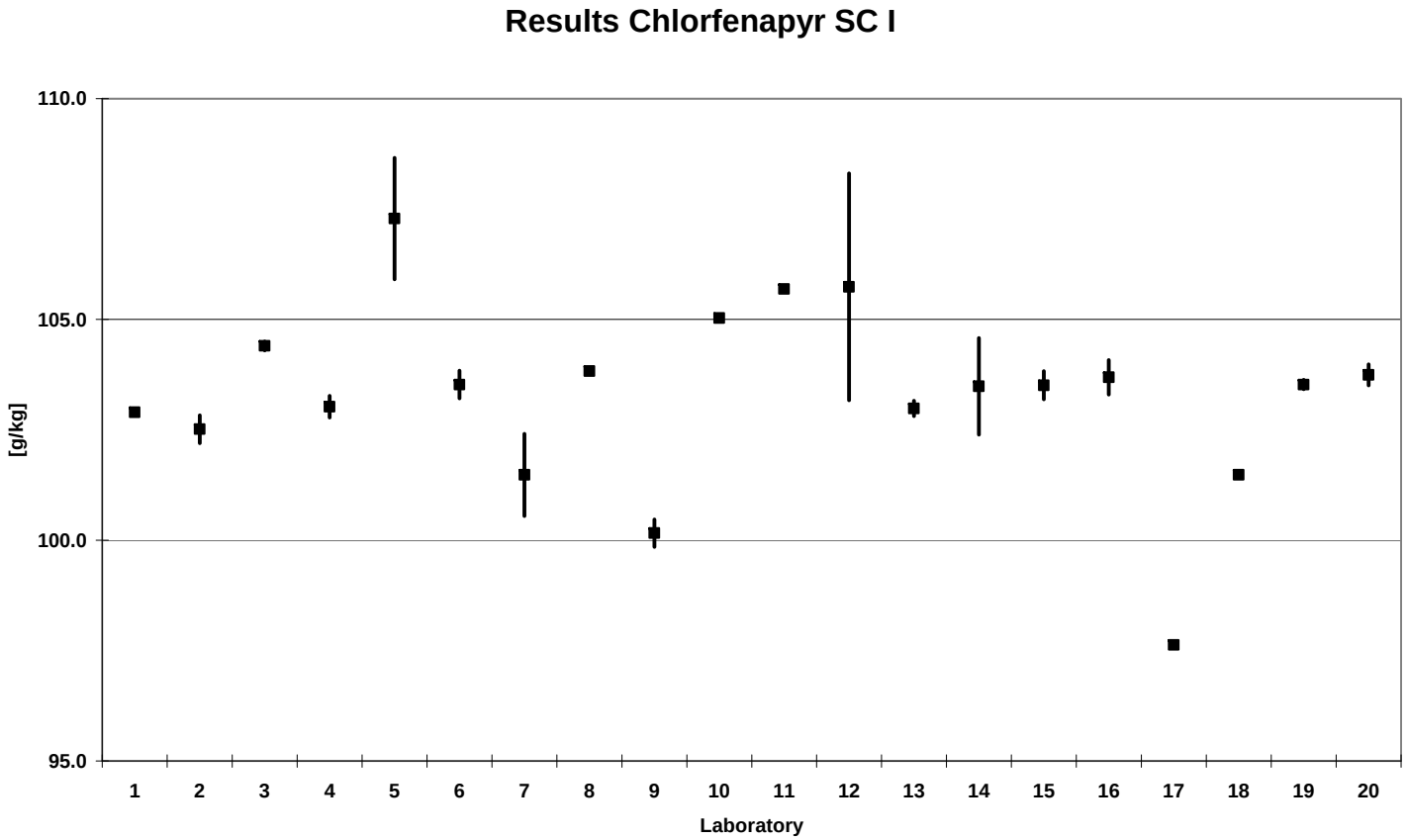
11.3 Figure 3: Summary of the individual results: Chlorfenapyr TC II (all laboratories)



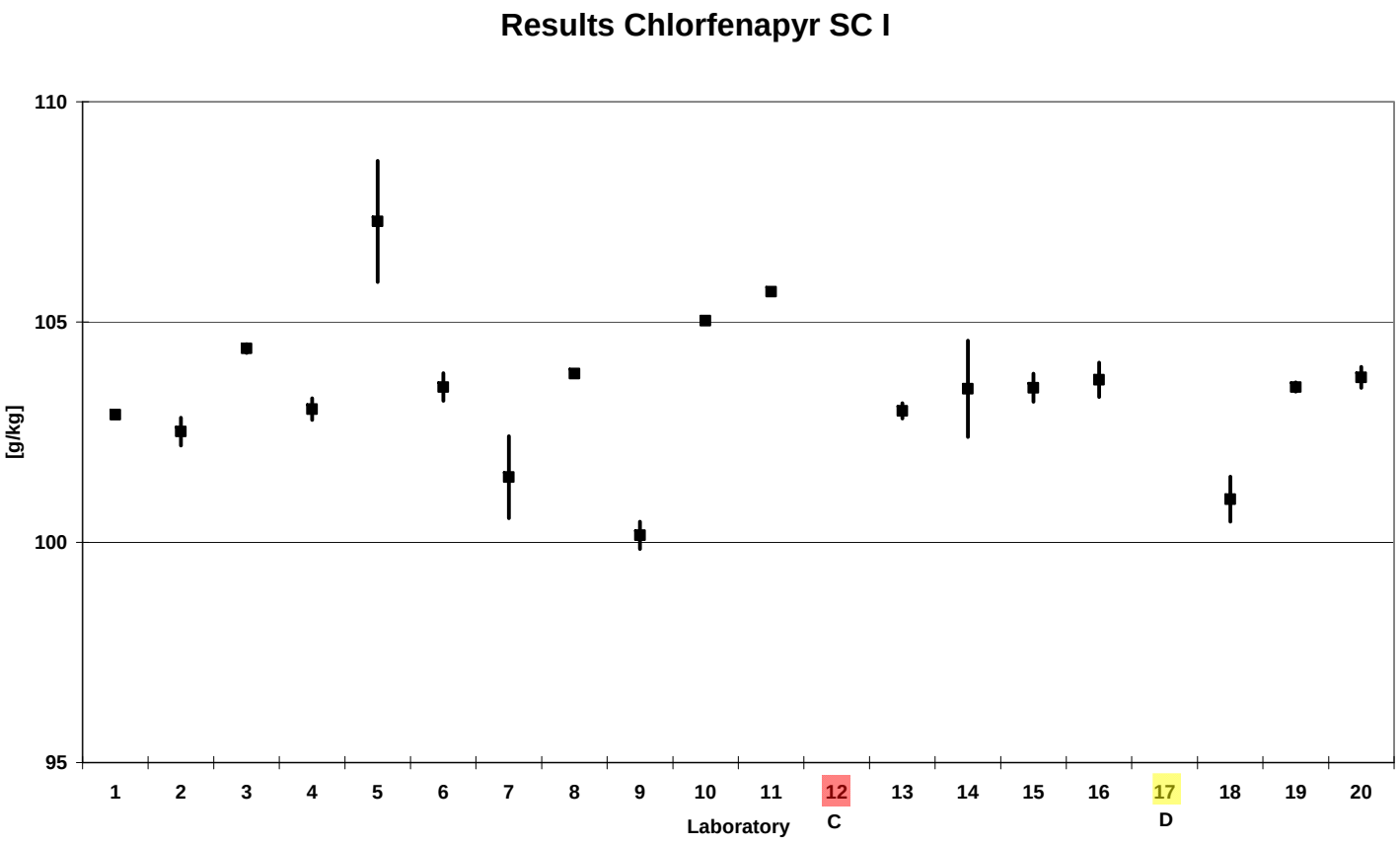
11.4 Figure 4: Summary of the individual results: Chlorfenapyr TC II (after elimination of straggler and outlier values)



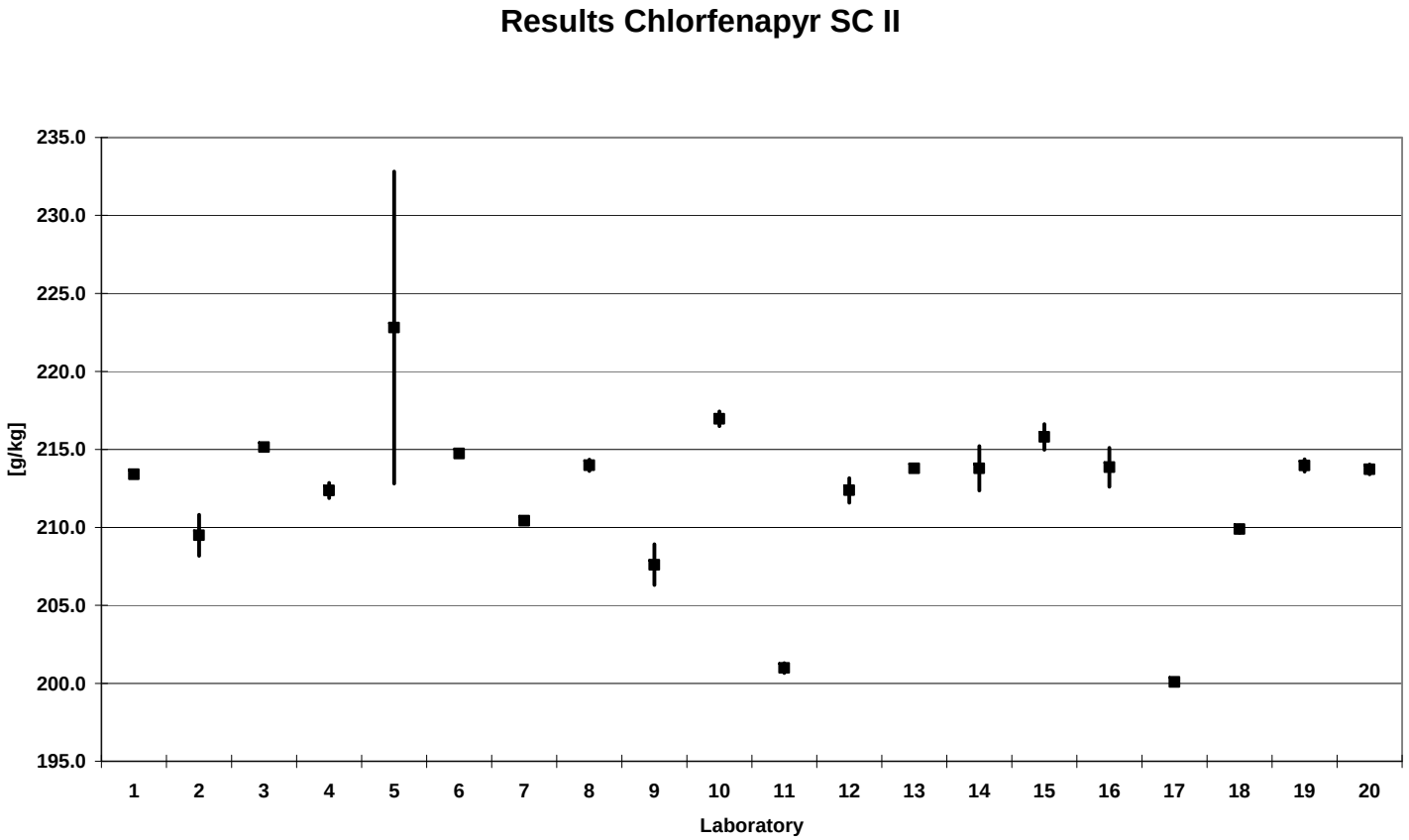
11.5 Figure 5: Summary of the individual results: Chlorfenapyr SC I (all laboratories)



11.6 Figure 6: Summary of the individual results: Chlorfenapyr SC I (after elimination of straggler and outlier values)



11.7 Figure 7: Summary of the individual results: Chlorfenapyr SC II (all laboratories)



11.8 Figure 8: Summary of the individual results: Chlorfenapyr SC II (after elimination of straggler and outlier values)