# ESPAC

Report 5009/R

On

Chlorantraniliprole

Small Scale Collaborative Trial
For the
Determination of Chlorantraniliprole A.I. and Formulations
Using HPLC with Internal and External Standard Calibration

Report to **CIPAC**
On behalf of
**ESPAC**

June 2015

## Contents

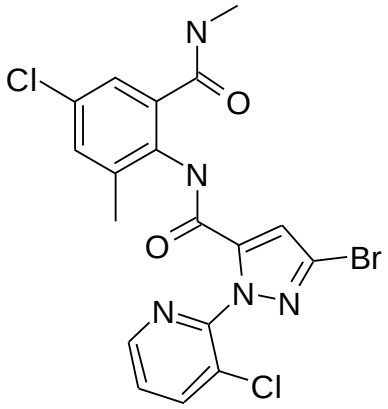
# 1. Participants

| | |
|---|---|
| Theo de Rijk | Akkermaalsbos 2 (Building 123)<br>6708 WB Wageningen<br>The Netherlands |
| Olga Nováková | CENTRAL INSTITUTE FOR SUPERVISING AND TESTING IN AGRICULTURE<br>National Reference Laboratory<br>Department of Testing Plant Protection Products<br>Zemedelska 1a, 613 00<br>Brno, Czech Republic |
| Joe Moreland | Dow AgroSciences, A2P R&D, Phyto Plant,<br>B.P. 20, 8,Route de Herrlisheim,<br>67410<br>Drusenheim, France |
| Lajos Benke | National Food Chain Safety Office, Directorate of Plant Protection<br>Soil Conservation and Agri-environment<br>Pesticide Analytical Laboratory<br>Ország út 23<br>2481-Velence<br>Hungary |
| Jim Garvey, Denis Carr | Pesticide Control Laboratory<br>Backweston Laboratory Campus<br>Backweston<br>Youngs Cross<br>Celbridge<br>Co. Kildare<br>Ireland |
| Olivier Pigeon | Walloon Agricultural Research Centre (CRA-W);<br>Agriculture and Natural Environment Department (D3)<br>Plant Protection Products and Biocides Physico-chemistry and Residues Unit (U10), Carson Building<br>Rue du Bordia, 11, B-5030<br>Gembloux, Belgium |

Participants are listed in alphabetical order by company/laboratory name whereas laboratory numbers were assigned randomly.

## 2. Active ingredient, general information

**CHLORANTRANILIPROLE**
**794**




| | |
|---|---|
| *ISO Common name* | Chlorantraniliprole |
| *Chemical name* | 3-bromo-4'-chloro-1-(3-chloro-2-pyridyl)-2'-methyl-6'-(methylcarbamoyl)pyrazole-5-carboxanilide (IUPAC)<br><br>3-Bromo-N-[4-chloro-2-methyl-6-[(methylamino)carbonyl]phenyl]-1-(3-chloro-2-pyridinyl)-1H-pyrazole-5-carboxamide (CAS 500008-45-7) |
| *Empirical formula* | $C_{18}H_{14}BrCl_2N_5O_2$ |
| *RMM* | 483.15 |
| *CAS No.* | 500008-45-7 |

## 3. Samples

One technical material and four samples of formulations were sent to the participants, these are listed below. Participants in the trial also received an analytical standard with a purity of 99.9% and an HPLC column if needed.

1. DPX-E2Y45 Technical
2. Formulation 1: Chlorantraniliprole 625 FS
3. Formulation 2: Chlorantraniliprole 35 Wettable Granule (WG)
4. Formulation 3: Chlorantraniliprole 200 g/L Suspension Concentrate (SC)
5. Formulation 4: Chlorantraniliprole 50 g/L Suspension Concentrate (SC)

## 4. Method

*4.1 Scope*

The HPLC method to determine the active ingredient, Chlorantraniliprole, in technical grade active ingredient and in formulations was evaluated by six laboratories.

*4.2 Principle*

Chlorantraniliprole is determined by reversed phase high performance liquid chromatography using UV detection at 270 nm using internal and external standard calibration.

*4.3 Procedure*

See attached method for details.

Fig 1a A typical chromatogram of Chlorantraniliprole Technical material and internal standard.

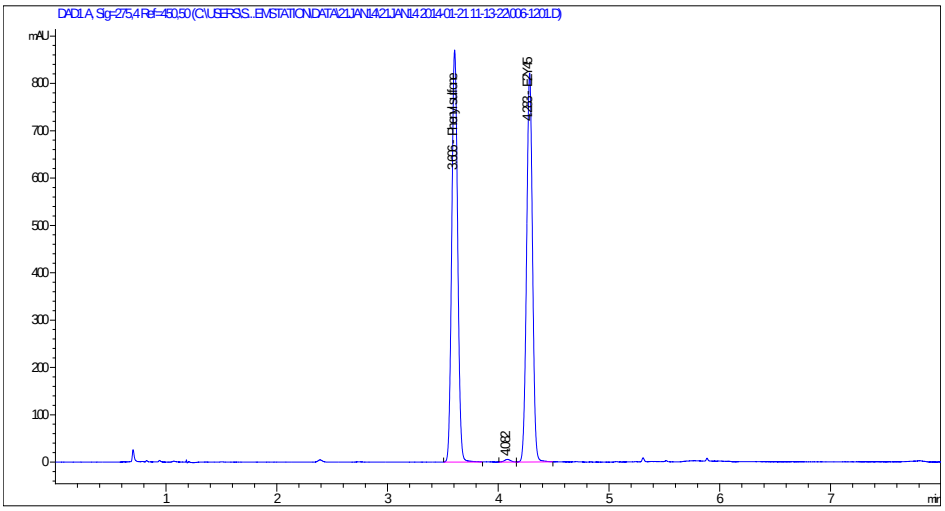
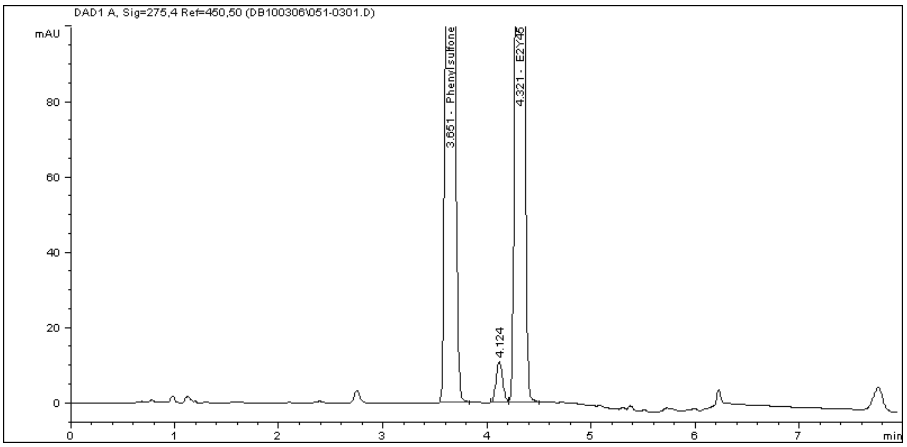


Fig 1 b A typical example of a formulation chromatogram showing Chlorantraniliprole 50 g/L SC solution and internal standard.




## 5. Comments from the Participants.

The following comments were received from the study participants, responses are given as appropriate.

Laboratory 1 Some problems with the HPLC equipment Waters Alliance between the Day 1 and the Day 2; we had to use another apparatus for the Day 2 (Agilent 1100).

Laboratory 2

a. Why do you use so week buffer solution in the method? Isn´t enough only acidified water (for example with H3PO4) to pH = 3.00? pKa of chlorantraniliprole is 10.88.
   Response: We use the buffer to help with the peak shape and resolution of the critical pair, acidified water is not adequate for this in all cases.

b. Why is THF used for sample and standard preparation? Isn´t better for example MeOH? We should avoid with all problems with THF properties.
   Response: Chlorantraniliprole is more soluble in THF than it is in MeOH.

c. We have problem with system pressure. If mobile phase would be 40 % ACN:60 % pH3,0 H2O and eluent flow rate is 2,0 ml/min, the system pressure is than much higher than recommended, 4000 PSI. Can you tell us the value of pressure which you usually have in your system in the same chromatographic conditions? (We checked our HPLC system without column and the pressure is O.K. The high pressure must be due to chromatographic conditions.)
   Response: We use Agilent 1100 and 1290 systems with these conditions successfully, our maximum pressure on this instrument is 400 bar, we typically run between 250 and 270 bars of pressure. This is close to the 4000 psi.

Laboratory 3 No comments.

Laboratory 4 The measurement was carried out using external standard calibration method.

Laboratory 5 Included results using a Kinetix® column. Same sample preparations were used as for the original trial.

Laboratory 6 Changed the Excel reporting template.

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## 6. Evaluation and Discussion

*6.1 Screening for valid data*

The statistical evaluation was carried out according to the guidelines in the CIPAC document "Guideline for CIPAC collaborative studies Procedure for Assessment of Performance of Analytical Methods. The data was tested for outliers firstly using Cochran's test on the within laboratory variance and then using Grubbs test on laboratory means to test the between laboratory variance. The tests were carried out at the alpha levels of 0.01 for outliers and 0.05 for stragglers.

Internal Standard Calibration

There were Cochran stragglers from Lab 4 for the analysis of the technical material and the 625 FS; and one Cochran straggler and outlier from Lab 2 for the 50 g/L (5SC) formulation.

When the results for the Kinetix® column were evaluated as a separate lab, only the one Cochran straggler and outlier from Lab 2 for the 50 g/L (5SC) formulation remained.

External Standard Calibration

Lab 2 was a Cochran straggler and outlier for the technical and all formulations with the external standard calibration method. The internal standard calibration method had corrected for the systematic error from this laboratory as given above. In addition, Lab 3 was a Cochran straggler and outlier for the 200 g/L (20 SC); Lab 4 was a Grubb straggler for the 50 g/L (5SC).

Again, when the results for the Kinetix® column were evaluated as a separate lab, one Cochran straggler and outlier from Lab 2 for the 50 g/L (5SC) formulation remained. Also, the results for this column were a Cochran straggler and outlier for the 200 g/L (20 SC) formulation.

No data was excluded from the initial evaluation.

*6.2 Determination of active ingredient content.*

The results obtained for laboratories 1 – 6 are given in Tables 1-3 and Fig's 1 – 6.

Using the internal standard calibration method, the technical material and all of the formulations meet the Horowitz criteria. This is also the case if the second column is included.

Using the external standard calibration method, the method passed the Horowitz criteria for three formulations: the 35 WG, wettable granule, and the 50 g/L, and the 20 and 5 SC, soluble concentrates. When the second column data was included, these same three formulations passed the Horowitz criteria.

# Table 1. Internal and External Standard Results with and without additional HPLC column

*Internal Standard Calibration Used*

| | Tech 1 | | | | | | 625 FS (50 wgt %) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Lab | Day 1 | | Day 2 | | Mean | s | Day 1 | | Day 2 | | Mean | s |
| 1 | 961.5 | 959.2 | 973.0 | 975.9 | 967.4 | 8.3 | 503.8 | 507.0 | 514.8 | 513.5 | 509.8 | 5.2 |
| 2 | 975.9 | 977.7 | 974.9 | 978.8 | 976.8 | 1.8 | 515.6 | 514.9 | 520.1 | 515.7 | 516.6 | 2.4 |
| 3 | 978.1 | 980.3 | 990.3 | 984.1 | 983.2 | 5.3 | 519.4 | 518.5 | 518.4 | 514.6 | 517.7 | 2.1 |
| 4 | **986.3** | **987.2** | **101.16** | **100.95** | **998.7** | **13.8** | **515.4** | **517.7** | **528.6** | **532.0** | **523.4** | **8.1** |
| 5 | 962.6 | 965.6 | 974.0 | 968.7 | 967.7 | 4.9 | 506.9 | 506.4 | 508.9 | 509.2 | 507.9 | 1.4 |

**Cochran's stragglers**
**Cochran outliers**
**Grubb's straggler**
**Grubb's outlier**

| | 35 WG | | | | | | 200 g/L (20 SC) | | | | | | 5 g/L (5 SC) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Lab | Day 1 | | Day 2 | | Mean | s | Day 1 | | Day 2 | | Mean | s | Day 1 | | Day 2 | | Mean | s |
| 1 | 353.0 | 364.0 | 356.6 | 359.1 | 358.2 | 4.6 | 182.7 | 183.1 | 185.0 | 185.8 | 184.2 | 1.5 | 51.0 | 51.0 | 51.5 | 51.6 | 51.3 | 0.3 |
| 2 | 356.6 | 356.3 | 355.0 | 355.8 | 355.9 | 0.7 | 185.3 | 185.4 | 186.3 | 185.3 | 185.6 | 0.5 | **51.6** | **51.7** | **51.5** | **42.8** | **49.4** | **0.44** |
| 3 | 358.2 | 359.5 | 349.6 | 355.9 | 355.8 | 4.4 | 186.5 | 189.0 | 183.8 | 185.1 | 186.1 | 2.2 | 51.7 | 52.1 | 51.4 | 51.2 | 51.6 | 0.4 |
| 4 | 361.8 | 361.5 | 363.1 | 367.5 | 363.5 | 2.8 | 186.2 | 186.2 | 190.4 | 189.2 | 188.0 | 2.1 | 51.9 | 51.9 | 52.8 | 53.1 | 52.4 | 0.6 |
| 5 | 353.0 | 351.7 | 344.0 | 350.9 | 349.9 | 4.0 | 182.9 | 182.8 | 182.6 | 183.4 | 182.9 | 0.3 | 50.9 | 50.8 | 50.8 | 50.8 | 50.8 | 0.05 |

*External Standard Calibration Used*

| | Tech 1 | | | | | | 625 FS (50 wgt %) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Lab | Day 1 | | Day 2 | | Mean | s | Day 1 | | Day 2 | | Mean | s |
| 1 | 965.8 | 963.3 | 978.4 | 972.1 | 972.1 | 8.8 | 508.9 | 510.2 | 518.6 | 517.2 | 513.7 | 4.9 |
| 2 | **1053.9** | **1076.9** | **966.4** | **101.84** | **1018.4** | **55.2** | **569.8** | **571.7** | **526.3** | **514.8** | **545.7** | **2.94** |
| 3 | 973.6 | 963.2 | 978.4 | 970.7 | 970.7 | 6.7 | 521.6 | 510.5 | 515.3 | 514.3 | 515.4 | 4.6 |
| 4 | 958.3 | 955.9 | 958.3 | 957.7 | 957.6 | 1.1 | 511.2 | 513.9 | 515.5 | 512.4 | 513.3 | 1.9 |
| 5 | 989.7 | 991.6 | 1013.5 | 1008.7 | 1000.9 | 1.2 | 516.3 | 516.9 | 529.1 | 534.0 | 524.1 | 8.9 |
| 6 | 956.6 | 966.7 | 965.2 | 966.2 | 965.9 | 0.7 | 509.9 | 509.5 | 505.1 | 504.5 | 507.3 | 2.8 |

**Cochran's stragglers**
**Cochran outliers**
**Grubb's straggler**
**Grubb's outlier**

| | 35 WG | | | | | | 200 g/L (20 SC) | | | | | | 5 g/L (5 SC) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Lab | Day 1 | | Day 2 | | Mean | s | Day 1 | | Day 2 | | Mean | s | Day 1 | | Day 2 | | Mean | s |
| 1 | 355.3 | 354.9 | 358.1 | 360.9 | 357.3 | 2.8 | 183.2 | 183.1 | 185.6 | 185.8 | 184.4 | 1.5 | 51.3 | 51.1 | 51.7 | 51.7 | 51.5 | 0.03 |
| **2** | **394.7** | **391.2** | **355.4** | **363.0** | **376.1** | **19.8** | **203.8** | **204.3** | **188.8** | **185.9** | **195.7** | **9.7** | **56.9** | **57.0** | **52.1** | **52.3** | **54.6** | **0.27** |
| 3 | 356.1 | 356.5 | 347.4 | 354.2 | 353.6 | 4.2 | **190.4** | **198.1** | **184.7** | **183.9** | **189.3** | **6.6** | 51.0 | 53.0 | 51.3 | 50.9 | 51.6 | 0.10 |
| 4 | 355.1 | 354.5 | 359.1 | 357.8 | 356.6 | 2.2 | 183.6 | 183.5 | 184.5 | 185.7 | 184.3 | 1.0 | **49.2** | **48.8** | **50.3** | **50.2** | **4.96** | **0.07** |
| 5 | 360.9 | 358.6 | 363.1 | 367.5 | 362.5 | 3.8 | 185.9 | 184.8 | 188.0 | 185.8 | 186.1 | 1.3 | 51.5 | 51.6 | 52.7 | 52.8 | 52.2 | 0.07 |
| 6 | 356.3 | 355.6 | 355.3 | 354.0 | 355.3 | 1.0 | 182.3 | 181.8 | 182.0 | 183.0 | 182.3 | 0.5 | 51.3 | 50.8 | 51.0 | 51.5 | 5.12 | 0.03 |

*Internal Standard Calibration Used with Additional Column*

| | Tech 1 | | | | | | 625 FS (50 wgt %) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Lab | Day 1 | | Day 2 | | Mean | s | Day 1 | | Day 2 | | Mean | s |
| 1 | 961.5 | 959.2 | 973.0 | 975.9 | 967.4 | 8.3 | 503.8 | 507.0 | 514.8 | 513.5 | 509.8 | 5.2 |
| 2 | 975.9 | 977.7 | 974.9 | 978.8 | 976.8 | 1.8 | 515.6 | 514.9 | 520.1 | 515.7 | 516.6 | 2.4 |
| 3 | 978.1 | 980.3 | 990.3 | 984.1 | 983.2 | 5.3 | 519.4 | 518.5 | 518.4 | 514.6 | 517.7 | 2.1 |
| 4 | 986.3 | 987.2 | 1011.6 | 1009.5 | 998.7 | 13.8 | 515.4 | 517.7 | 528.6 | 532.0 | 523.4 | 8.1 |
| 5 | 996.7 | 995.2 | 1019.1 | 1018.2 | 1007.3 | 13.1 | 517.6 | 521.6 | 531.6 | 533.2 | 526.0 | 7.6 |
| 6 | 962.6 | 965.6 | 974.0 | 968.7 | 967.7 | 4.9 | 506.9 | 506.4 | 508.9 | 509.2 | 507.9 | 1.4 |

| | 35 WG | | | | | | 200 g/L (20 SC) | | | | | | 5 g/L (5 SC) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Lab | Day 1 | | Day 2 | | Mean | s | Day 1 | | Day 2 | | Mean | s | Day 1 | | Day 2 | | Mean | s |
| 1 | 353.0 | 364.0 | 356.6 | 359.1 | 358.2 | 4.6 | 182.7 | 183.1 | 185.0 | 185.8 | 184.2 | 1.5 | 51.0 | 51.0 | 51.5 | 51.6 | 51.3 | 0.3 |
| 2 | 356.6 | 356.3 | 355.0 | 355.8 | 355.9 | 0.7 | 185.3 | 185.4 | 186.3 | 185.3 | 185.6 | 0.5 | **51.6** | **51.7** | **51.5** | **42.8** | **49.4** | **0.44** |
| 3 | 358.2 | 359.5 | 349.6 | 355.9 | 355.8 | 4.4 | 186.5 | 189.0 | 183.8 | 185.1 | 186.1 | 2.2 | 51.7 | 52.1 | 51.4 | 51.2 | 51.6 | 0.4 |
| 4 | 361.8 | 361.5 | 363.1 | 367.5 | 363.5 | 2.8 | 186.2 | 186.2 | 190.4 | 189.2 | 188.0 | 2.1 | 51.9 | 51.9 | 52.8 | 53.1 | 52.4 | 0.6 |
| 5 | 364.1 | 364.8 | 370.7 | 371.5 | 367.8 | 3.9 | 186.5 | 187.1 | 189.6 | 190.3 | 188.4 | 1.9 | 52.1 | 52.1 | 52.7 | 52.9 | 52.5 | 0.4 |
| 6 | 353.0 | 351.7 | 344.0 | 350.9 | 349.9 | 4.0 | 182.9 | 182.8 | 182.6 | 183.4 | 182.9 | 0.3 | 50.9 | 50.8 | 50.8 | 50.8 | 50.8 | 0.05 |

**Cochran's stragglers**
**Cochran outliers**
**Grubb's straggler**
**Grubb's outlier**

*External Standard Calibration Used with Additional Column*

| | Tech 1 | | | | | | 625 FS (50 wgt %) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Lab | Day 1 | | Day 2 | | Mean | s | Day 1 | | Day 2 | | Mean | s |
| 1 | 965.8 | 963.3 | 978.4 | 972.1 | 972.1 | 8.8 | 508.9 | 510.2 | 518.6 | 517.2 | 513.7 | 4.9 |
| 2 | **1053.9** | **1076.9** | **966.4** | **101.84** | **1018.4** | **55.2** | **569.8** | **571.7** | **526.3** | **514.8** | **545.7** | **2.94** |
| 3 | 973.6 | 963.2 | 978.4 | 970.7 | 970.7 | 6.7 | 521.6 | 510.5 | 515.3 | 514.3 | 515.4 | 4.6 |
| 4 | 958.3 | 955.9 | 958.3 | 957.7 | 957.6 | 1.1 | 511.2 | 513.9 | 515.5 | 512.4 | 513.3 | 1.9 |
| 5 | 989.7 | 991.6 | 1013.5 | 1008.7 | 1000.9 | 1.2 | 516.3 | 516.9 | 529.1 | 534.0 | 524.1 | 8.9 |
| 6 | 997.2 | 997.0 | 1015.0 | 1008.3 | 1004.4 | 8.8 | 520.7 | 524.3 | 531.8 | 533.2 | 527.5 | 6.0 |
| 7 | 956.6 | 966.7 | 965.2 | 966.2 | 965.9 | 0.7 | 509.9 | 509.5 | 505.1 | 504.5 | 507.3 | 2.8 |

| | 35 WG | | | | | | 200 g/L (20 SC) | | | | | | 5 g/L (5 SC) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Lab | Day 1 | | Day 2 | | Mean | s | Day 1 | | Day 2 | | Mean | s | Day 1 | | Day 2 | | Mean | s |
| 1 | 355.3 | 354.9 | 358.1 | 360.9 | 357.3 | 2.8 | 183.2 | 183.1 | 185.6 | 185.8 | 184.4 | 1.5 | 51.3 | 51.1 | 51.7 | 51.7 | 51.5 | 0.3 |
| **2** | **394.7** | **391.2** | **355.4** | **363.0** | **376.1** | **19.8** | **203.8** | **204.3** | **188.8** | **185.9** | **195.7** | **9.7** | **56.9** | **57.0** | **52.1** | **52.3** | **54.6** | **2.7** |
| 3 | 356.1 | 356.5 | 347.4 | 354.2 | 353.6 | 4.2 | 190.4 | 198.1 | 184.7 | 183.9 | 189.3 | 6.6 | 51.0 | 53.0 | 51.3 | 50.9 | 51.6 | 1.0 |
| 4 | 355.1 | 354.5 | 359.1 | 357.8 | 356.6 | 2.2 | 183.6 | 183.5 | 184.5 | 185.7 | 184.3 | 1.0 | 49.2 | 48.8 | 50.3 | 50.2 | 4.96 | 0.7 |
| 5 | 360.9 | 358.6 | 363.1 | 367.5 | 362.5 | 3.8 | 185.9 | 184.8 | 188.0 | 185.8 | 186.1 | 1.3 | 51.5 | 51.6 | 52.7 | 52.8 | 52.2 | 0.7 |
| 6 | 366.6 | 368.4 | 370.7 | 371.5 | 369.3 | 2.2 | **187.6** | **188.7** | **147.5** | **190.22** | **178.5** | **20.7** | 5.21 | 5.22 | 5.27 | 5.29 | 5.25 | 0.4 |
| 7 | 356.3 | 355.6 | 355.3 | 354.0 | 355.3 | 1.0 | 182.3 | 181.8 | 182.0 | 183.0 | 182.3 | 0.5 | 51.3 | 50.8 | 51.0 | 51.5 | 5.12 | 0.3 |

## Table 2. Summary of statistical evaluation using Internal Standard

| | Tech | 625 FS (50%) | 35 WG | 200 g/L | 50 g/L | 50 g/L * |
|---|---|---|---|---|---|---|
| x (g/kg) | 978.8 | 515.1 | 356.7 | 185.4 | 51.1 | 51.5 |
| L | 5 | 5 | 5 | 5 | 5 | 4 |
| $s_r$ | 8.54 | 2.70 | 1.20 | 0.28 | 0.38 | 0.02 |
| $s_L$ | 12.34 | 2.56 | 2.01 | 0.22 | 0.02 | 0.04 |
| $s_R$ | 15.01 | 3.72 | 2.34 | 0.36 | 0.38 | 0.04 |
| $RSD_r$ | 0.87 | 0.52 | 0.34 | 0.15 | 0.75 | 0.04 |
| $RSD_R$ | 1.53 | 0.72 | 0.66 | 0.19 | 0.75 | 0.08 |
| r | 24.2 | 7.6 | 3.4 | 0.8 | 1.1 | 0.06 |
| R | 42.4 | 10.5 | 6.6 | 1.0 | 1.1 | 0.12 |
| $RSD_{R(Hor)}$ | 2.01 | 2.21 | 2.34 | 2.58 | 3.13 | 3.13 |

* Outliers Removed

## Table 3. Summary of statistical evaluation using External Standard

| | Tech | 625 FS | 35 WG | 200 g/L | 50 g/L |
|---|---|---|---|---|---|
| x (g/kg) | 980.9 | 519.9 | 360.2 | 187.0 | 51.8 |
| L | 6 | 6 | 6 | 6 | 6 |
| $s_r$ | 77.46 | 23.07 | 9.99 | 3.10 | 0.21 |
| $s_L$ | 9.50 | 7.02 | 1.79 | 0.73 | 0.15 |
| $s_R$ | 78.04 | 24.12 | 10.15 | 3.19 | 0.26 |
| $RSD_r$ | 7.90 | 4.44 | 2.77 | 1.66 | 0.41 |
| $RSD_R$ | 7.96 | 4.64 | 2.82 | 1.71 | 0.50 |
| r | 219.1 | 65.24 | 28.3 | 8.8 | 0.59 |
| R | 220.7 | 68.21 | 28.7 | 9.0 | 0.74 |
| $RSD_{R(Hor)}$ | 2.01 | 2.21 | 2.33 | 2.57 | 3.12 |

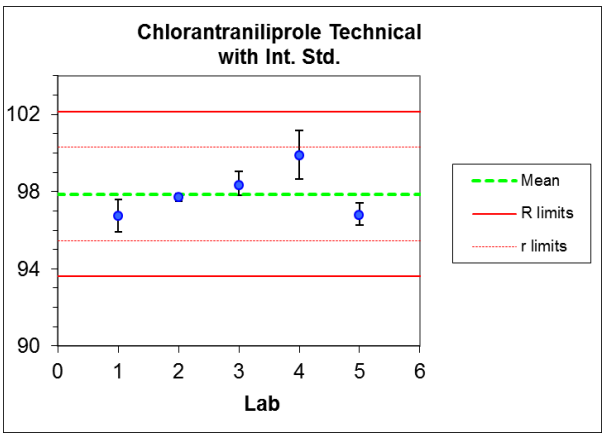
## Table 4. Summary of statistical evaluation using External Standard No Outliers

| | Tech | 625 FS | 35 WG | 200 g/L | 50 g/L |
|---|---|---|---|---|---|
| x (g/kg) | 973.4 | 514.7 | 357.1 | 184.3 | 51.1 |
| L | 5 | 5 | 5 | 4 | 5 |
| $s_r$ | 6.32 | 2.91 | 0.85 | 0.13 | 0.04 |
| $s_L$ | 32.36 | 2.07 | 0.66 | 0.18 | 0.07 |
| $s_R$ | 32.97 | 3.57 | 1.08 | 0.22 | 0.08 |
| $RSD_r$ | 0.65 | 0.57 | 0.24 | 0.07 | 0.07 |
| $RSD_R$ | 3.39 | 0.69 | 0.30 | 0.12 | 0.15 |
| r | 17.9 | 8.20 | 2.4 | 0.4 | 0.11 |
| R | 93.2 | 20.10 | 3.1 | 0.6 | 0.22 |
| $RSD_{R(Hor)}$ | 2.01 | 2.21 | 2.34 | 2.58 | 3.13 |

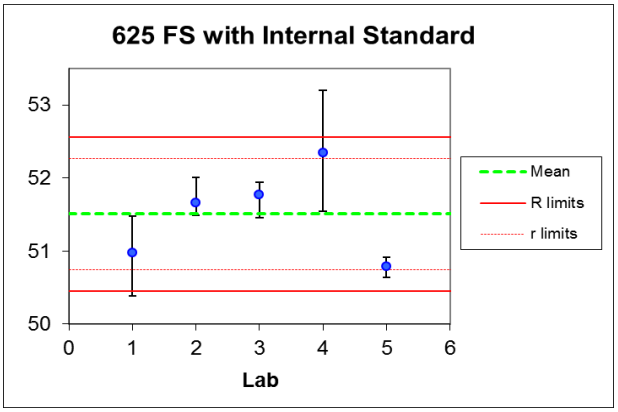
**Key for Tables 2, 3 and 4.**

| | | |
|---|---|---|
| Xm | = | Overall sample mean |
| L | = | Number of laboratories |
| Sr | = | Repeatability standard deviation |
| RSDr | = | Relative repeatability standard deviation |
| r | = | Repeatability limit |
| SR | = | Reproducibility standard deviation |
| RSDR | = | Relative reproducibility standard deviation |
| R | = | Reproducibility limit |
| SL | = | "pure" between laboratory standard deviation |
| RSDR (Hor) | = | Relative reproducibility standard deviation (Horowitz equation) |

## Figure 2. Chlorantraniliprole Technical




## Figure 3. 625 FS, Flowable Suspension for Seeds, 50% by weight




## Figure 4. 35 WG, Wettable Granule

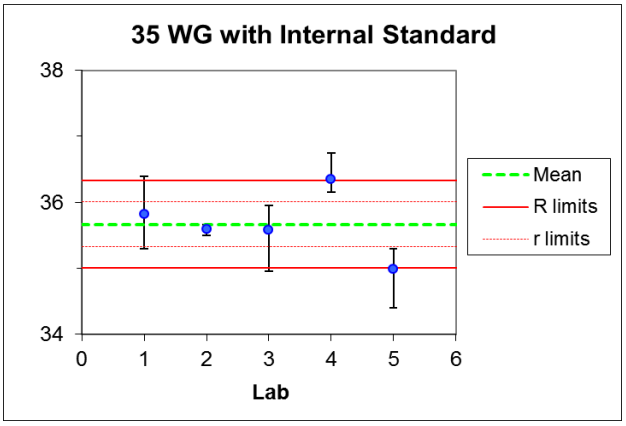


**Figure 5. 200 g/L, 20 SC, Soluble Concentrate**

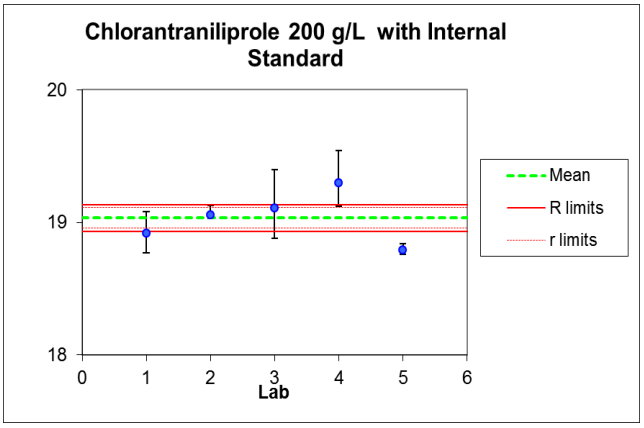
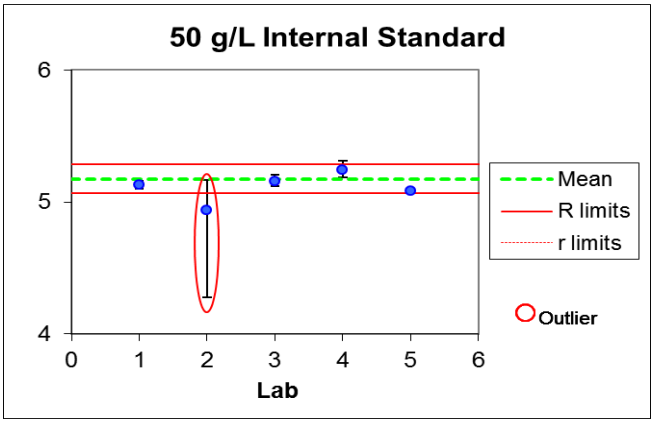



**Figure 6. 50 g/L, 5 SC, Soluble Concentrate**



## 7. Conclusion

Six laboratories received samples for this collaborative trial and all of these laboratories submitted results. Five of these six laboratories used both internal and external calibration methods. After the initial evaluation, the calculated Reproducibility Standard Deviation ($RSD_R$) meets the Horowitz criteria for both the Technical Active Ingredient and all four of the formulations examined using the internal standard calibration method. When a second column was employed using the same HPLC conditions and internal standard calibration and these results were treated as an additional laboratory in the calculations, the calculated Reproducibility Standard Deviation ($RSD_R$) also meets the Horowitz criteria for both the Technical Active Ingredient and all four of the formulations examined.

For the external standard calibration, six laboratories evaluated the method. After the initial evaluation, the calculated Reproducibility Standard Deviation ($RSD_R$) meets the Horowitz criteria for three of the four formulations examined, the 35WG, the 20 SC and the 5SC. When a second column was employed using the same HPLC conditions and external standard calibration, these results were treated as an additional laboratory in the calculations and the calculated Reproducibility Standard Deviation ($RSD_R$) also met the Horowitz criteria for the same three formulations.

When the outliers were removed from the calculations, all of the formulation materials passed the Horowitz using external standard calibration. The technical material results still did not.

On the basis of these results ESPAC recommends that this method using the internal standard calibration proceed to a full scale trial.