BROFLANILIDE (No. 994)

CIPAC Collaborative Trial

CIPAC Collaborative Trial on the Determination of Broflanilide
in Broflanilide Technical and Formulation
by High Performance Liquid Chromatography

By
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1. INTRODUCTION

1.1 Scope

The results of the full scale CIPAC collaborative trial for broflanilide technical material and broflanilide wettable powder are reported.

1.2 Samples

Five test samples and one analytical standard were sent to the participants;

1) broflanilide technical material (TC-1)
2) broflanilide technical material (TC-2)
3) broflanilide wettable powder (WP-1)
4) broflanilide wettable powder (WP-2)
5) broflanilide wettable powder (WP-3)

Broflanilide analytical standard, purity: 99.9 %

1.3 Participants

In August 2018, Information Sheet No. 315 was sent out by the CIPAC Secretary.
We sent samples to 23 laboratories and received examination results from all the laboratories—
Participants are listed in alphabetical sequence.

Isabelle Monisse	AFSCA (Belgium)
Veronika Kmecl	AGRICULTURAL INSTITUTE OF SLOVENIA (KMETIJSKI INSTITUT ŠLOVENIJE) (Slovenia)
Astrid Bächli	Agroscope (Switzerland)
Olivera Gogic	Center for Ecotoxicological Research Podgorica (Montenegro)
Frantisek Csicsay	Central Control and Testing Institute in Agriculture (Slovakia)
Kevin King	Clarke Mosquito Control (USA)
F. Güdel	CURRENTA GmbH&Co OHG, ANT-PDA3, A559 (Germany)
Ivan Orgei	FRANDESA Co. LTD (Belarus)
Ana B. Estebanez	Laboratorio Arbitral Agroalimentario (Spain)
Eva Jacobsen	Laboratory of chemistry and microbiology, Danish Technological Institute (Denmark)
Volodymyr Mykhaylov	Laboratory of pesticides analytical chemistry of L.I. Medved's Reseach Center of Preventive Toxicology,

	Food and Chemical Safety, Ministry of Health, Ukraine (Ukraine)
Juliana Pereira, Estela Bonilha	Lanagro/SP (Brazil)
Ahmad Rezvani	Maryland Department of Agriculture, State Chemist Section (USA)
Kaiwei Shi	National Center for Pesticide Quality Supervision and Inspection (Beijing), Institute for the Control of Agrochemicals, Ministry of Agriculture and Rural Affairs, P. R. China (China)
Márió Molnár	National Food Chain Safety Office, Pesticide Analytical National Reference Laboratory, Velence (Hungary)
Ileana Ionica	National Phytosanitary Laboratory (Romania)
Denis Carr	Pesticides Control Laboratory (Ireland)
Meilinda Pramleonita	PT Agricon-Indonesia (Indonesia)
Cornel Grecu	Quality Control Laboratory (Romania)
Kailas Gore, Satish Patel	RALLIS INDIA LIMITED (India)
Ovsanna Tshakatyan	Republican Veterinary-Sanitary and Phyto-Sanitary Centre of Laboratory Services SNCO (Armenia)
Yukiko Koma	The Institute of Environmental Toxicology (Japan)
Régis De Bruyne, Laurent Soquette	Walloon Agricultural Research Centre (CRA-W) Agriculture and Natural Environment Department (D3) Plant Protection Products and Biocides Physico-chemistry and Residues Unit (U10) (Belgium)

2. ANALYTICAL METHOD

2.1 Outline of Method

Broflanilide is determined by reversed phase high performance liquid chromatography using UV detection at 254 nm and external standardization as stated in CIPAC/5213/m.

2.2 Program of Work

We requested the collaborators to:

1) conduct duplicate determinations on two different days for each of five

samples;

2) inject each sample solution in duplicate and calculate the mean value;

3) check the response factors before determination;

4) check linearity before determination;

5) describe high performance liquid chromatography operating conditions in detail.

3. REMARKS OF PARTICIPANTS

3.1 Analytical Conditions

Lab. No.*	High Performance Liquid Chromatography Integrator	Column	Mobile phase	Column temp. (℃) / Injection volume(µl)	Flow rate (ml/min) / Retention time(min)
Proposed Method		250 x 4.6 mm (i.d.) Waters XSelect CSH C_{18}, 5 µm	Acetonitrile – Water, 65 + 35 (v/v)	40	1.0
				20	11.5
1	Agilent 1260 Infinity II ChemStation	250 x 4.6 mm (i.d.) Waters XBridge C_{18}, 5 µm	Acetonitrile – Water, 65 + 35 (v/v)	40	0.92
				20	11.6
2	Thermo Ultimate 3000 Chromeleon Version 7.2.7	250 x 4.6 mm (i.d.) Inertsil 5 ODS-2 5 µm	Acetonitrile – Water, 65 + 35 (v/v)	40	1.2
				20	11.8
3	PerkinElmer Altus Empower 3	250 x 4.6 mm (i.d.) Phenomenex Prodigy ODS3, 5 µm	Acetonitrile – Water, 65 + 35 (v/v)	40	1.0
				5	14.4
4	Waters UPLC Acquity Empower	250 x 4.6 mm (i.d.) Waters XSelect CSH C_{18}, 5 µm	Acetonitrile – Water, 65 + 35 (v/v)	40	1.0
				20	11.6
5	Shimadzu Prominence LabSolutions	250 x 4.6 mm (i.d.) Cosmosil C18, 5 µm	Acetonitrile – Water, 65 + 35 (v/v)	40	1.0
				20	13.0
6	Dionex Chromeleon	250 x 4.6 mm (i.d.) Zorbax SB C18, 5 µm	Acetonitrile – Water, 65 + 35 (v/v)	40	1.2
				20	12.0

7	Agilent 1100 Series Agilent ChemStation for LC 3D systems	250 x 4.6 mm (i.d.) Zorbax SB C18, 5 µm	Acetonitrile – Water, 65 + 35 (v/v)	40 20	1.0 13.0
8	Shimadzu Nexera XR with SPD-20A Shimadzu LC Solution	250 x 4.6 mm (i.d.) Waters XSelect CSH C_{18}, 5 µm	Acetonitrile – Water, 65 + 35 (v/v)	40 20	1.0 11.2
9	Agilent 1260 Infinity series Chemstation	250 x 4.6 mm (i.d.) Inertsil ODS-3V 5 µm	Acetonitrile – Water, 65 + 35 (v/v)	40 20	1.0 16.6
10	Shimadzu LC-20AD Prominence Shimadzu LabSolutions	250 x 4.6 mm (i.d.) Zorbax Eclipse XDB-C18, 5µm	Acetonitrile – Water, 65 + 35 (v/v)	40 20	1.0 unknown
11	Agilent 1260 Infinity II Chromeleon 6.80	250 x 4.6 mm (i.d.) Waters XSelect CSH C_{18}, 5 µm	Acetonitrile – Water, 65 + 35 (v/v)	40 20	1.0 11.7
12	Agilent Infinity 1200 Open Lab CDS ChemStation	250 x 4.6 mm (i.d.) Zorbax Eclipse Plus C18, 5µm	Acetonitrile – Water, 65 + 35 (v/v)	40 20	1.1 11.8
13	Dionex UltiMate 3000 Chromeleon 6.88	250 x 4.6 mm (i.d.) Zorbax Eclipse XDB-C18 5µm	Acetonitrile – Water, 65 + 35 (v/v)	40 20	1.0 13.1
14	Agilent 1260 Infinity Chemstation	250 x 4.6 mm (i.d.) Luna C18(2) 5µm	Acetonitrile – Water, 65 + 35 (v/v)	40 20	1.0 15.3
15	Agilent 1200 Series Agilent, Chemstation	250 x 4.6 mm (i.d.) Phenomenex, Gemini C18, 5µm	Acetonitrile – Water, 65 + 35 (v/v)	40 20	1.0 11.7
16	Thermo UltiMate 3000 Chromeleon Version 7.2.9	250 x 4.6 mm (i.d.) Kromasil 100-5C18, 5µm	Acetonitrile – Water, 65 + 35 (v/v)	40 5	1.4 11.6
17	Agilent 1100 Series Agilent ChemStation for LC 3D	250 x 4.6 mm (i.d.) Phenomenex Luna C18 (2) , 5 µm	Acetonitrile – Water, 65 + 35 (v/v)	40 20	1.0 15.6
18	Waters Acquity UPLC H-Class Series Waters Empower 3	250 x 4.6 mm (i.d.) Waters XSelect CSH C_{18}, 5 µm	Acetonitrile – Water, 65 + 35 (v/v)	40 10	1.0 11.5

19	Shimadzu 20 AD Shimadzu LabSolutions	250 x 4.6 mm (i.d.) Hypersil ODS 5µm	Acetonitrile – Water, 65 + 35 (v/v)	40	0.9
				20	11.4
20	Thermo UltiMate 3000 Chromeleon (Cobra Wizard)	250 x 4.0 mm (i.d.) Purospher, 5um	Acetonitrile – Water, 65 + 35 (v/v)	40	1.0
				20	11.6
21	UPLC Hclass Waters Empower 3	100 x 2.1mm (i.d) Kinetex Evo C18 2.6µm	Acetonitrile – Water, 65 + 35 (v/v)	40	0.3
				1	unknown
22	Agilent 1100 Series Chemstation	250 x 4.6 mm (i.d.) Zorbax Eclipse XDB-C18, 5µm	Acetonitrile – Water, 65 + 35 (v/v)	40	1.0
				20	13.2
23	Agillent 1260 Infinity ChemStation for LC 3D Systems	250 x 4.6 mm (i.d.) Zorbax SB-C18 5µm	Acetonitrile – Water, 65 + 35 (v/v)	40	1.0
				20	12.5

*Laboratory numbers in the result tables were assigned in the sequence of results receipt.

3.2 Remarks

Several participants provided comments about the method performance and made a note of any deviations from the method.

Lab.1:

- Flow rate was changed to 0.92 ml/min to adjust the retention time to 11.5 min.

Lab.2:

- C3: There were some particles left after shaking, therefore 15s in ultrasonic bath. Since C3 and C4 deviated finally too much, new calibrations (C5 and C6) were prepared
- We used 0.20 µm RC (regenerated cellulose) filter (instead of 0.45 µm filter).
- Flow 1.2 ml/min (instead of 1.0 ml/min), RT: 11.84 min.

Lab.3:

- Reduced injection volume to 5 µl.

Lab.9:

- We have used comparable HPLC column, but retention time of broflanilide is 16.6 min. As per test method shared with us retention time should be 11.5 min. No change in the test parameters.

Lab.10:

- I have placed the calibration and technical concentrate solutions in ultrasonic

bath for about 1 min.

Lab.11:

- WP-formulations are filtrated by Chromafil Xtra 0.45 µm filters to clarify the sample solutions.

Lab.12:

- Flow rate was changed to 1.1 ml/min. In the WP sample preparation the flasks were placed in the ultrasonic bath for about 15 min.

Lab.16:

- I injected just 5 µl because is the maximum volume that can be injected with this type of autosampler.

Lab.18:

- The injection volume was set at 10 µl because the HPLC is not able to inject a greater volume.

Lab.19:

- Flow rate was changed to 0.90 ml/min to adjust the retention time about to 11.4 min.

Lab.21:

- I observe variations between 2 test samples of the same sample, despite great attention to the homogenization of the sample before sampling. The system suitability was done on the 2nd day.

Lab.22:

- Calibration solution and sample preparation: 25mg broflanilide was weighed into 50ml volumetric flasks.

4. RESULTS AND DISCUSSION

The samples were sent to twenty three laboratories and all of them returned results. All results reported by the 23 laboratories were statistically evaluated. The statistical evaluations were carried out according to ISO 5725. Summary and detailed statistical evaluations are shown in Tables 1 and 2-1 to 2-5. The results of statistical evaluations are displayed in Figures 1-5.

TC-1

The variance of Lab.5, 10, 14, 21 was identified as an outlier by Cochran's test. The mean of Lab.20, 21 was identified as an outlier by Grubbs's test. These data were retained because there were no reasons to remove them.

TC-2

The variance of Lab.10, 14, 21 was identified as an outlier by Cochran's test. The mean of Lab.21 was identified as a straggler by Grubbs's test. The mean of Lab.4, 20 was identified as an outlier by Grubbs's test. These data were retained because there were no reasons to remove them.

WP-1

The variance of Lab.10, 14, 20 was identified as an outlier by Cochran's test. The mean of Lab.20 was identified as an outlier by Grubbs's test. These data were retained because there were no reasons to remove them.

WP-2

The variance of Lab.10 was identified as an outlier by Cochran's test. The mean of Lab.20 was identified as an outlier by Grubbs's test. These data were retained because there were no reasons to remove them.

WP-3

The variance of Lab.20 was identified as an outlier by Cochran's test. The mean of Lab.20 was identified as an outlier by Grubbs's test. These data were retained because there were no reasons to remove them.

5. CONCLUSION

All data of 23 different laboratories, who participated in this full scale CIPAC collaborative trial, have been used for the statistical evaluation.

The values of RSD_R (reproducibility relative standard deviation) were less than Horwitz's value even if outliers on Cochran's and Grubbs's tests were included.

The proposed method is considered to be appropriate for the determination of broflanilide in technical material and wettable powder.

JAPAC proposes that the method is accepted as a provisional CIPAC method.

Table 1 Summary of statistical evaluation of broflanilide large scale collaborative study (full set of 23 participants)

	TC-1	TC-2	WP-1	WP-2	WP-3
Average (g/kg)	997.0	996.9	500.3	501.8	499.9
Number of laboratories	23	23	23	23	23
Repeatability standard deviation (S_r)	12	17	4.0	3.8	4.1
"Pure" between laboratory standard variation (S_L)	11	8.2	6.4	7.3	7.6
Reproducibility standard deviation (S_R)	17	19	7.5	8.2	8.7
Repeatability (r)	35	47	11	11	12
Reproducibility (R)	47	52	21	23	24
RSD_r	1.2	1.7	0.80	0.77	0.83
RSD_R	1.7	1.9	1.5	1.6	1.7
Horwitz's value	2.0	2.0	2.2	2.2	2.2
HorRat value (reference)	0.85	0.94	0.68	0.74	0.78

Table 2-1 Broflanilide Technical-1 (full set of 23 participants)

Lab		Analytical data (n=4)		Yi	Yi^2	Si	Si^2
1	Day1	1002.5	999.5				
	Day2	1000.6	997.2	999.95	999900.00	2.213	4.897
2	Day1	992.2	990.4				
	Day2	990.2	989.9	990.68	981436.96	1.037	1.076
3	Day1	998.5	992.2				
	Day2	988.0	986.1	991.20	982477.44	5.494	30.180
4	Day1	998.8	996.3				
	Day2	1004.9	1007.0	1001.75	1003503.06	5.030	25.297
5	Day1	997.8	1002.3				**
	Day2	986.5	967.4	988.50	977132.25	15.558	242.047
6	Day1	992.9	992.4				
	Day2	995.4	994.9	993.90	987837.21	1.472	2.167
7	Day1	994.8	991.2				
	Day2	992.7	991.2	992.48	985006.63	1.704	2.902
8	Day1	993.1	991.5				
	Day2	998.0	993.3	993.98	987986.30	2.802	7.849
9	Day1	996.7	995.7				
	Day2	999.7	993.4	996.38	992763.14	2.612	6.823
10	Day1	1014.9	1017.8				**
	Day2	991.0	990.3	1003.50	1007012.25	14.888	221.647
11	Day1	997.7	994.0				
	Day2	994.2	996.3	995.55	991119.80	1.771	3.137
12	Day1	989.9	991.4				
	Day2	994.5	996.5	993.08	986197.96	2.980	8.883
13	Day1	997.7	998.2				
	Day2	993.7	992.1	995.43	990870.93	2.995	8.969
14	Day1	988.5	950.1				**
	Day2	1048.5	1023.7	1002.70	1005407.29	42.845	1835.680
15	Day1	999.4	996.9				
	Day2	999.3	1003.5	999.78	999550.05	2.739	7.503
16	Day1	1000.8	993.4				
	Day2	996.3	992.8	995.83	991667.43	3.652	13.336
17	Day1	994.9	995.2				
	Day2	996.5	996.4	995.75	991518.06	0.819	0.670
18	Day1	988.2	1000.8				
	Day2	986.1	1000.5	993.90	987837.21	7.842	61.500
19	Day1	996.5	999.0				
	Day2	987.6	995.0	994.53	989079.98	4.903	24.036
20	Day1	1038.2	1059.4	**			
	Day2	1063.1	1041.8	1050.63	1103812.89	12.448	154.963
21	Day1	1006.8	994.3	**			**
	Day2	962.7	942.4	976.55	953649.90	29.372	862.723
22	Day1	980.8	988.7				
	Day2	989.6	995.4	988.63	977379.39	6.002	36.029
23	Day1	998.8	998.5				
	Day2	994.3	994.9	996.63	993261.39	2.354	5.543
S1 SUM	Yi =			22931.25			
S2 SUM	Yi^2 =				22866407.52		
S3 SUM	Si^2 =						3567.853

p = 23 n = 4 ** Regarded as a statistical outlier

1) Cochran's test (p=23, n=4)

$C = Si^2 max / S3$ = 0.5145 > 0.197 (p=23, n=4, 5%), > 0.238 (p=23, n=4, 1%)

2) Grubbs's test (p=23, n=4)

Yi min = 976.55 Yi max = 1050.63 Y = S1/p = 997.01

Y - Yi min = 20.46 Yi max - Y = 53.61 S = 12.972

lower = (Y - Yi min)/S = 1.5773 < 2.781 (p=23, 5%)

upper = (Yi max - Y)/S = 4.1331 > 2.781 (p=23, 5%) , > 3.087 (p=23, 1%)

3) Calculation of r and R

Mean; Y = S1 / p = 997.01

S_r^2 = S3 / p = 155.124 S_r = 12.455

$S_L^2 = [(pS2-S1^2)/p(p-1)]-(S_r^2/n)$ = 129.492 S_L = 11.379

$S_R^2 = S_r^2 + S_L^2$ = 284.617 S_R = 16.871

$r = 2.8 \times S_r$ =	34.874
$R = 2.8 \times S_R$ =	47.238
$RSD_r = (S_r / mean) \times 100$ =	1.249
$RSD_R = (S_R / mean) \times 100$ =	1.692

Horwitz's value = $2 ^{[1 - 0.5 \times \log (Y / 1000)]}$ = 2.001

RSD_r and RSD_R < 2.00 (Horwitz's value)

HorRat value = RSD_R/Horwitz's value = 0.85

Table 2-2 Broflanilide Technical-2 (full set of 23 participants)

Lab		Analytical data (n=4)		Yi	Yi^2	Si	Si^2
1	Day1	998.3	999.4				
	Day2	997.7	998.5	998.48	996952.33	0.704	0.496
2	Day1	992.7	998.6				
	Day2	984.5	985.2	990.25	980595.06	6.691	44.763
3	Day1	994.5	989.6				
	Day2	998.6	990.8	993.38	986793.89	4.060	16.483
4	Day1	1007.5	1007.4	**			
	Day2	1011.8	1012.4	1009.78	1019645.55	2.696	7.269
5	Day1	998.1	1005.9				
	Day2	995.1	988.0	996.78	993560.40	7.412	54.942
6	Day1	994.9	993.7				
	Day2	994.8	995.9	994.83	989676.78	0.900	0.809
7	Day1	996.7	994.4				
	Day2	990.8	990.3	993.05	986148.30	3.042	9.257
8	Day1	991.0	999.6				
	Day2	989.3	999.9	994.95	989925.50	5.587	31.217
9	Day1	996.5	992.2				
	Day2	1000.0	992.4	995.28	990572.33	3.721	13.849
10	Day1	1022.3	1013.8				**
	Day2	987.4	1009.8	1008.33	1016719.31	14.892	221.769
11	Day1	997.8	997.9				
	Day2	1000.2	996.6	998.13	996253.52	1.504	2.263
12	Day1	988.8	992.7				
	Day2	1001.8	993.6	994.23	988483.35	5.463	29.842
13	Day1	998.4	999.9				
	Day2	999.1	999.2	999.15	998300.72	0.614	0.377
14	Day1	1003.3	1001.6				**
	Day2	980.7	1059.9	1011.38	1022879.39	33.943	1152.129
15	Day1	1009.6	1003.9				
	Day2	997.1	982.3	998.23	996453.15	11.782	138.823
16	Day1	996.6	994.7				
	Day2	991.2	996.3	994.70	989428.09	2.478	6.140
17	Day1	980.1	1009.4				
	Day2	996.0	991.3	994.20	988433.64	12.131	147.167
18	Day1	994.0	1002.2				
	Day2	989.9	993.4	994.88	989776.27	5.207	27.116
19	Day1	999.5	1003.9				
	Day2	994.5	992.9	997.70	995405.29	4.999	24.987
20	Day1	1014.6	1010.5	**			
	Day2	1038.7	1052.0	1028.95	1058738.10	19.771	390.897
21	Day1	988.6	1001.2	*			**
	Day2	865.1	990.4	961.33	924145.76	64.391	4146.183
22	Day1	986.1	978.5				
	Day2	991.2	990.2	986.50	973182.25	5.772	33.313
23	Day1	995.3	996.1				
	Day2	995.4	993.1	994.98	989975.25	1.300	1.689
S1 SUM	Yi =			22929.40			
S2 SUM	Yi^2 =				22862044.22		
S3 SUM	Si^2 =						6501.778

p = 23 n = 4 * Regarded as a statistical straggler, ** Regarded as a statistical outlier

1) Cochran's test (p=23, n=4)

$C = Si^2 max / S3$ = 0.6377 > 0.197 (p=23, n=4, 5%), > 0.238 (p=23, n=4, 1%)

2) Grubbs's test (p=23, n=4)

Yi min = 961.33 Yi max = 1028.95 Y = S1/p = 996.93

Y - Yi min = 35.61 Yi max - Y = 32.02 S = 11.731

lower = (Y - Yi min)/S = 3.0352 > 2.781 (p=23, 5%) , < 3.087 (p=23, 1%)

upper = (Yi max - Y)/S = 2.7295 < 2.781 (p=23, 5%)

3) Calculation of r and R

Mean; Y = S1 / p = 996.93

S_r^2 = S3 / p = 282.686 S_r = 16.813

$S_L^2 = [(pS2-S1^2)/p(p-1)]-(S_r^2/n)$ = 66.943 S_L = 8.182

$S_R^2 = S_r^2 + S_L^2$ = 349.629 S_R = 18.698

$r = 2.8 \times S_r$ =	47.077
$R = 2.8 \times S_R$ =	52.355
$RSD_r = (S_r / mean) \times 100$ =	1.687
$RSD_R = (S_R / mean) \times 100$ =	1.876

Horwitz's value = $2 \wedge [1 - 0.5 \times \log (Y / 1000)]$ = 2.001

RSD_r and RSD_R < 2.00 (Horwitz's value)

HorRat value = RSD_R/Horwitz's value = 0.94

Table 2-3 Broflanilide Wettable Powder-1 (full set of 23 participants)

Lab		Analytical data (n=4)		Yi	Yi^2	Si	Si^2
1	Day1	502.2	502.7				
	Day2	500.4	499.6	501.23	251226.50	1.466	2.149
2	Day1	491.0	490.0				
	Day2	491.1	494.8	491.73	241793.48	2.109	4.449
3	Day1	499.4	494.4				
	Day2	498.2	497.5	497.38	247381.89	2.133	4.549
4	Day1	503.2	507.3				
	Day2	498.5	503.1	503.03	253034.15	3.596	12.929
5	Day1	498.0	502.5				
	Day2	501.9	503.7	501.53	251527.33	2.466	6.082
6	Day1	499.5	498.1				
	Day2	499.1	498.5	498.80	248801.44	0.622	0.387
7	Day1	499.1	496.1				
	Day2	495.9	496.8	496.98	246984.15	1.468	2.156
8	Day1	499.0	501.0				
	Day2	499.1	498.7	499.45	249450.30	1.047	1.097
9	Day1	500.0	498.4				
	Day2	497.6	499.8	498.95	248951.10	1.147	1.317
10	Day1	507.2	511.6				**
	Day2	492.7	503.4	503.73	253738.88	8.078	65.249
11	Day1	499.6	499.1				
	Day2	500.9	499.4	499.75	249750.06	0.794	0.630
12	Day1	494.9	494.6				
	Day2	496.6	496.5	495.65	245668.92	1.047	1.097
13	Day1	501.2	501.8				
	Day2	500.9	501.1	501.25	251251.56	0.387	0.150
14	Day1	503.9	502.5				**
	Day2	497.4	512.8	504.15	254167.22	6.408	41.057
15	Day1	500.0	503.4				
	Day2	502.5	501.0	501.73	251727.98	1.517	2.302
16	Day1	499.3	498.7				
	Day2	500.9	501.1	500.00	250000.00	1.183	1.400
17	Day1	507.1	498.9				
	Day2	500.5	499.9	501.60	251602.56	3.726	13.880
18	Day1	499.6	500.4				
	Day2	495.2	494.9	497.53	247531.13	2.879	8.289
19	Day1	502.3	501.0				
	Day2	502.3	495.0	500.15	250150.02	3.488	12.163
20	Day1	529.9	538.8	**			**
	Day2	508.1	528.4	526.30	276991.69	12.973	168.287
21	Day1	494.3	491.8				
	Day2	487.5	492.7	491.58	241645.98	2.907	8.449
22	Day1	495.4	495.0				
	Day2	488.5	492.9	492.95	242999.70	3.163	10.003
23	Day1	503.5	502.4				
	Day2	500.7	500.9	501.88	251878.52	1.323	1.749
S1 SUM	Yi =			11507.28			
S2 SUM	Yi^2 =				5758254.56		
S3 SUM	Si^2 =						369.821

p = 23 n = 4 ** Regarded as a statistical outlier

1) Cochran's test (p=23, n=4)

$C = Si^2 max / S3$ = 0.4550 > 0.197 (p=23, n=4, 5%), > 0.238 (p=23, n=4, 1%)

2) Grubbs's test (p=23, n=4)

Yi min = 491.58 Yi max = 526.30 Y = S1/p = 500.32

Y - Yi min = 8.74 Yi max - Y = 25.98 S = 6.665

lower = (Y - Yi min)/S = 1.3115 < 2.781 (p=23, 5%)

upper = (Yi max - Y)/S = 3.8986 > 2.781 (p=23, 5%) , > 3.087 (p=23, 1%)

3) Calculation of r and R

Mean; Y = S1 / p =	500.32	
S_r^2 = S3 / p =	16.079	S_r = 4.010
$S_L^2 = [(pS2-S1^2)/p(p-1)]-(S_r^2/n)$ =	40.401	S_L = 6.356
$S_R^2 = S_r^2 + S_L^2$ =	56.480	S_R = 7.515

$r = 2.8 \times S_r$ =	11.228
$R = 2.8 \times S_R$ =	21.043
$RSD_r = (S_r / mean) \times 100$ =	0.801
$RSD_R = (S_R / mean) \times 100$ =	1.502

Horwitz's value = $2 \wedge [1 - 0.5 \times \log (Y / 1000)]$ = 2.220

RSD_r and RSD_R < 2.22 (Horwitz's value)

HorRat value = RSD_R/Horwitz's value = 0.68

Table 2-4 Broflanilide Wettable Powder-2 (full set of 23 participants)

Lab		Analytical data (n=4)		Yi	Yi^2	Si	Si^2
1	Day1	505.2	504.7				
	Day2	501.4	501.2	503.13	253134.77	2.119	4.489
2	Day1	497.8	484.8				
	Day2	499.5	497.3	494.85	244876.52	6.766	45.777
3	Day1	490.4	506.2				
	Day2	499.0	498.5	498.53	248527.18	6.459	41.716
4	Day1	504.2	499.9				
	Day2	501.8	498.5	501.10	251101.21	2.470	6.100
5	Day1	506.6	505.7				
	Day2	503.0	502.7	504.50	254520.25	1.944	3.780
6	Day1	499.7	498.7				
	Day2	499.6	499.2	499.30	249300.49	0.455	0.207
7	Day1	500.7	499.1				
	Day2	495.9	498.2	498.48	248477.33	2.004	4.016
8	Day1	500.6	500.4				
	Day2	501.3	500.6	500.73	250725.53	0.395	0.156
9	Day1	498.9	499.3				
	Day2	500.3	502.0	500.13	250125.02	1.382	1.909
10	Day1	511.1	509.0				**
	Day2	491.0	504.4	503.88	253890.02	9.028	81.503
11	Day1	501.5	500.7				
	Day2	501.7	502.8	501.68	251677.81	0.866	0.749
12	Day1	493.8	495.0				
	Day2	497.2	495.0	495.25	245272.56	1.418	2.010
13	Day1	503.9	501.2				
	Day2	503.1	499.9	502.03	252029.10	1.814	3.289
14	Day1	509.3	508.1				
	Day2	497.2	507.4	505.50	255530.25	5.589	31.233
15	Day1	500.7	502.3				
	Day2	502.1	501.1	501.55	251552.40	0.772	0.597
16	Day1	500.5	500.4				
	Day2	501.5	500.9	500.83	250825.68	0.499	0.249
17	Day1	498.5	504.4				
	Day2	502.2	502.8	501.98	251978.90	2.496	6.229
18	Day1	502.2	501.5				
	Day2	495.5	495.7	498.73	248726.63	3.621	13.109
19	Day1	507.6	506.2				
	Day2	501.7	499.5	503.75	253764.06	3.790	14.363
20	Day1	534.0	541.4	**			
	Day2	528.7	526.8	532.73	283795.93	6.537	42.729
21	Day1	485.4	491.8				
	Day2	498.3	494.8	492.58	242630.13	5.471	29.936
22	Day1	499.3	494.6				
	Day2	495.8	495.6	496.33	246338.51	2.052	4.209
23	Day1	503.1	504.5				
	Day2	505.6	503.3	504.13	254142.02	1.162	1.349
S1 SUM	Yi =			11541.63			
S2 SUM	Yi^2 =				5792942.26		
S3 SUM	Si^2 =						339.704

p = 23 n = 4 ** Regarded as a statistical outlier

1) Cochran's test (p=23, n=4)

$C = Si^2 max / S3$ = 0.2399 > 0.197 (p=23, n=4, 5%), > 0.238 (p=23, n=4, 1%)

2) Grubbs's test (p=23, n=4)

Yi min = 492.58 Yi max = 532.73 Y = S1/p = 501.81

Y - Yi min = 9.23 Yi max - Y = 30.92 S = 7.513

lower = (Y - Yi min)/S = 1.2291 < 2.781 (p=23, 5%)

upper = (Yi max - Y)/S = 4.1147 > 2.781 (p=23, 5%) , > 3.087 (p=23, 1%)

3) Calculation of r and R

Mean; Y = S1 / p =	501.81	
S_r^2 = S3 / p =	14.770	S_r = 3.843
$S_L^2 = [(pS2-S1^2)/p(p-1)]-(S_r^2/n)$ =	52.759	S_L = 7.264
$S_R^2 = S_r^2 + S_L^2$ =	67.529	S_R = 8.218

$r = 2.8 \times S_r$ =	10.761
$R = 2.8 \times S_R$ =	23.009
$RSD_r = (S_r / mean) \times 100$ =	0.766
$RSD_R = (S_R / mean) \times 100$ =	1.638

Horwitz's value = $2 \wedge [1 - 0.5 \times \log (Y / 1000)]$ = 2.219

RSD_r and RSD_R < 2.22 (Horwitz's value)

HorRat value = RSD_R/Horwitz's value = 0.74

Table 2-5 Broflanilide Wettable Powder-3 (full set of 23 participants)

Lab		Analytical data (n=4)		Yi	Yi^2	Si	Si^2
1	Day1	501.7	502.3				
	Day2	499.1	498.6	500.43	250425.18	1.846	3.409
2	Day1	487.5	495.3				
	Day2	495.5	495.1	493.35	243394.22	3.903	15.237
3	Day1	495.4	492.6				
	Day2	488.5	494.4	492.73	242777.93	3.046	9.276
4	Day1	501.5	502.6				
	Day2	496.9	497.9	499.73	249725.08	2.752	7.576
5	Day1	512.8	495.6				
	Day2	500.4	497.1	501.48	251477.18	7.812	61.022
6	Day1	498.0	498.1				
	Day2	496.5	497.9	497.63	247630.64	0.754	0.569
7	Day1	494.7	495.6				
	Day2	491.3	493.9	493.88	243912.52	1.852	3.429
8	Day1	500.7	499.7				
	Day2	499.1	499.8	499.83	249825.03	0.660	0.436
9	Day1	499.1	496.1				
	Day2	499.1	500.0	498.58	248577.03	1.704	2.902
10	Day1	512.3	509.9				
	Day2	501.2	502.1	506.38	256415.64	5.555	30.862
11	Day1	500.5	498.9				
	Day2	501.4	500.3	500.28	250275.08	1.034	1.069
12	Day1	493.8	502.3				
	Day2	492.4	495.8	496.08	246090.41	4.378	19.169
13	Day1	500.9	495.4				
	Day2	500.9	496.8	498.50	248502.25	2.830	8.007
14	Day1	506.2	501.6				
	Day2	510.7	506.0	506.13	256162.52	3.716	13.809
15	Day1	500.0	504.8				
	Day2	498.4	495.1	499.58	249575.18	4.037	16.296
16	Day1	497.1	498.4				
	Day2	500.7	499.3	498.88	248876.27	1.515	2.296
17	Day1	502.5	497.2				
	Day2	501.2	498.5	499.85	249850.02	2.428	5.897
18	Day1	499.5	498.7				
	Day2	489.3	491.9	494.85	244876.52	5.032	25.317
19	Day1	503.3	504.0				
	Day2	495.1	494.6	499.25	249250.56	5.093	25.937
20	Day1	546.3	528.7	**			**
	Day2	523.3	530.9	532.30	283343.29	9.864	97.307
21	Day1	493.9	500.3				
	Day2	485.5	497.4	494.28	244307.78	6.409	41.069
22	Day1	494.0	493.3				
	Day2	495.2	495.5	494.50	244530.25	1.030	1.060
23	Day1	499.4	501.1				
	Day2	499.4	500.7	500.15	250150.02	0.881	0.777
S1 SUM	Yi =			11498.58			
S2 SUM	Yi^2 =				5749950.58		
S3 SUM	Si^2 =						392.727

p = 23 n = 4 ** Regarded as a statistical outlier

1) Cochran's test (p=23, n=4)

$C = Si^2$ max / S3 = 0.2478 > 0.197 (p=23, n=4, 5%), > 0.238 (p=23, n=4, 1%)

2) Grubbs's test (p=23, n=4)

Yi min = 492.73 Yi max = 532.30 Y = S1/p = 499.94

Y - Yi min = 7.21 Yi max - Y = 32.36 S = 7.907

lower = (Y - Yi min)/S = 0.9122 < 2.781 (p=23, 5%)

upper = (Yi max - Y)/S = 4.0928 > 2.781 (p=23, 5%) , > 3.087 (p=23, 1%)

3) Calculation of r and R

Mean; Y = S1 / p = 499.94

S_r^2 = S3 / p = 17.075 S_r = 4.132

$S_L^2 = [(pS2-S1^2)/p(p-1)]-(S_r^2/n)$ = 58.253 S_L = 7.632

$S_R^2 = S_r^2 + S_L^2$ = 75.329 S_R = 8.679

r = 2.8 x S_r =	11.570
R = 2.8 x S_R =	24.302
$RSD_r = (S_r / mean) \times 100$ =	0.827
$RSD_R = (S_R / mean) \times 100$ =	1.736

Horwitz's value = $2 ^{[1 - 0.5 \times \log (Y / 1000)]}$ = 2.220

RSD_r and RSD_R < 2.22 (Horwitz's value)

HorRat value = RSD_R/Horwitz's value = 0.78

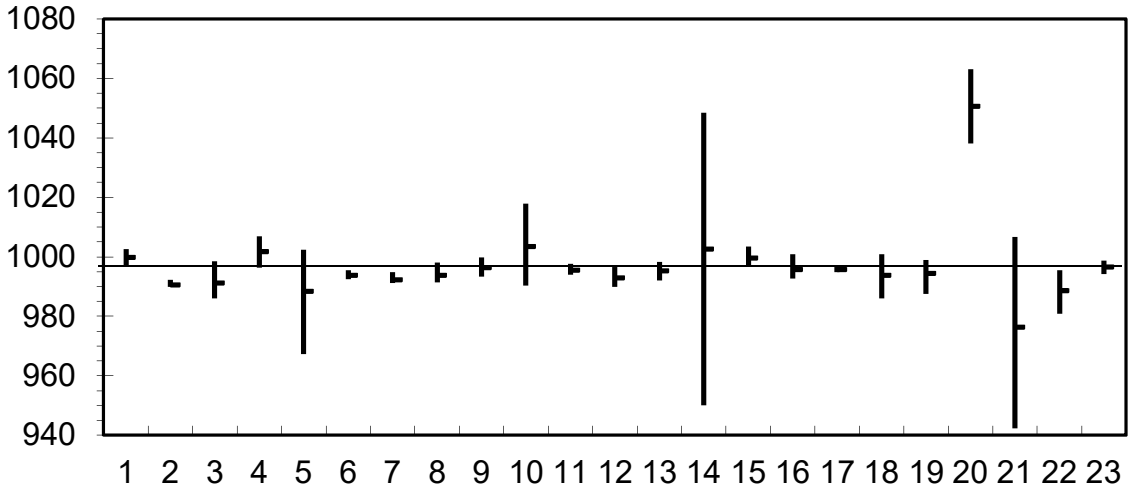

Figure 1 Broflanilide Technical (TC-1) (full set of 23 participants)

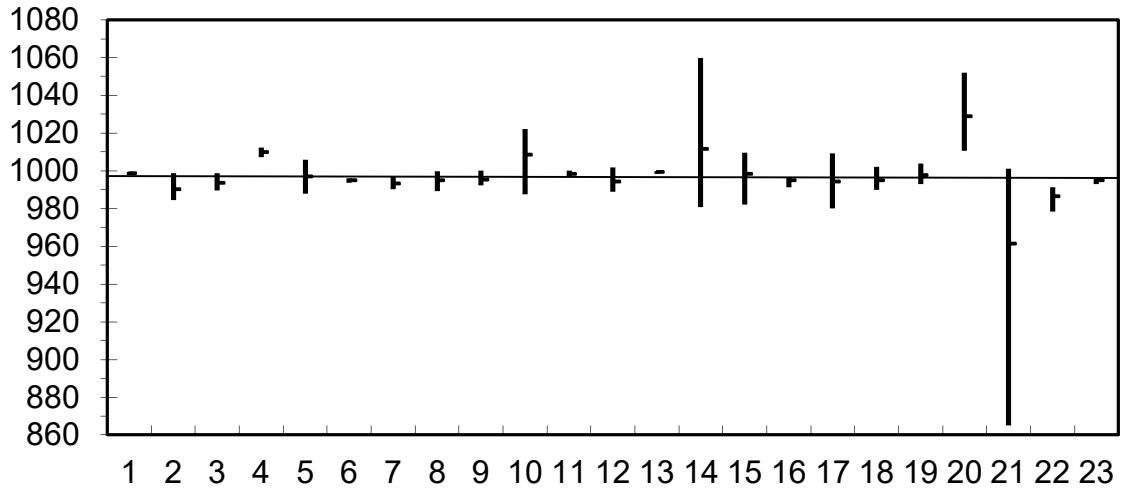

Figure 2 Broflanilide Technical (TC-2) (full set of 23 participants)

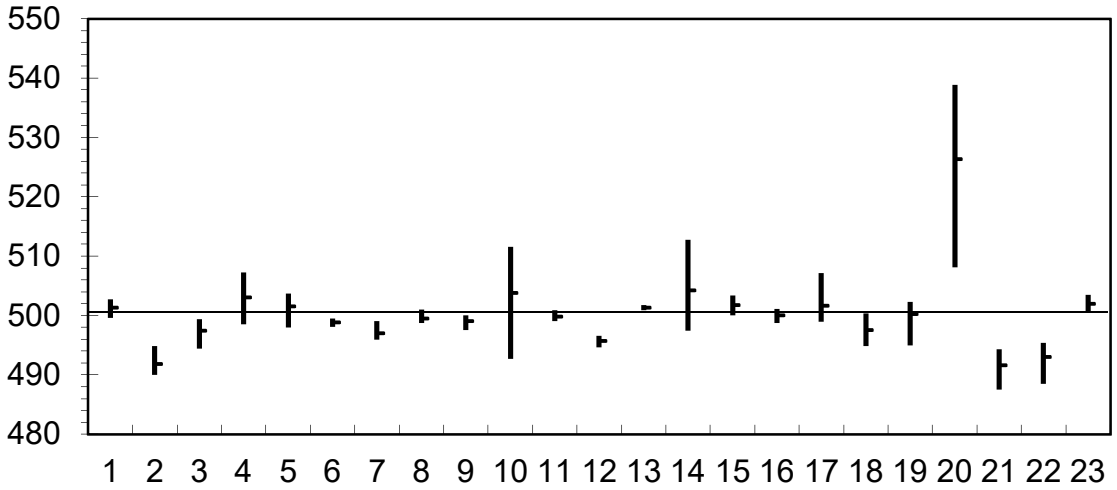

Figure 3 Broflanilide 50%Wettable Powder (WP-1) (full set of 23 participants)

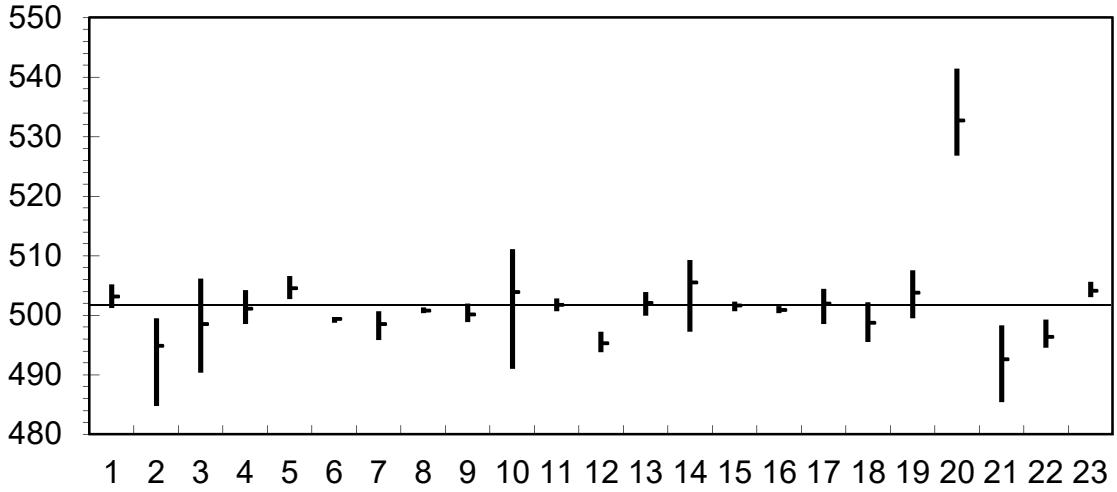

Figure 4 Broflanilide 50%Wettable Powder (WP-2) (full set of 23 participants)

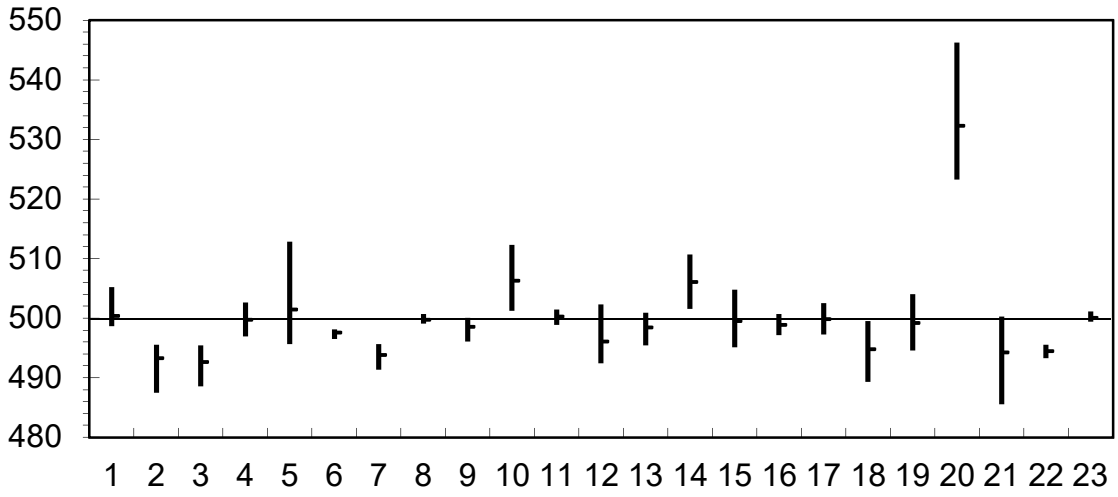

Figure 5 Broflanilide 50%Wettable Powder (WP-3) (full set of 23 participants)

6. REFERENCE

A separate evaluation was carried out with the elimination of outliers. The summary and detailed statistical evaluations are showed in Tables 3 and 4-1 to 4-5. The results of statistical evaluations are displayed in Figures 6-10.

The discussion on outliers and stragglers is as follows:

Elimination of outliers:

TC-1: Lab. 5, 10, 14, 20, 21 eliminated

The variance of Lab.18 was identified as a straggler by Cochran's test.

TC-2: Lab. 4, 10, 14, 20, 21 eliminated

The variance of Lab.17 was identified as a straggler by Cochran's test. The mean of Lab.22 was identified as a straggler by Grubbs's test.

WP-1: Lab. 10, 14, 20 eliminated

No outliers and stragglers were identified by Cochran's and Grubbs's test.

WP-2: Lab. 10, 20 eliminated

The variance of Lab.2 was identified as a straggler by Cochran's test.

WP-3: Lab. 20 eliminated

The variance of Lab.5 was identified as a straggler by Cochran's test.

Table 3 Summary of statistical evaluation of broflanilide large scale collaborative study (after elimination of outliers)

	TC-1	TC-2	WP-1	WP-2	WP-3
Average (g/kg)	995.0	995.0	498.7	500.2	498.5
Number of laboratories	18	18	20	21	22
Repeatability standard deviation (S_r)	3.7	5.7	2.2	3.2	3.7
"Pure" between laboratory standard variation (S_L)	2.7	1.2	3.2	3.0	3.2
Reproducibility standard deviation (S_R)	4.6	5.8	3.9	4.4	4.8
Repeatability (r)	10	16	6.1	9.0	10
Reproducibility (R)	13	16	11	12	14
RSD_r	0.38	0.57	0.44	0.64	0.74
RSD_R	0.47	0.58	0.78	0.88	1.0
Horwitz's value	2.0	2.0	2.2	2.2	2.2
HorRat value (reference)	0.23	0.29	0.35	0.39	0.44

Table 4-1 Broflanilide Technical-1 (after elimination of outliers)

Lab		Analytical data (n=4)		Yi	Yi^2	Si	Si^2
1	Day1	1002.5	999.5				
	Day2	1000.6	997.2	999.95	999900.00	2.213	4.897
2	Day1	992.2	990.4				
	Day2	990.2	989.9	990.68	981436.96	1.037	1.076
3	Day1	998.5	992.2				
	Day2	988.0	986.1	991.20	982477.44	5.494	30.180
4	Day1	998.8	996.3				
	Day2	1004.9	1007.0	1001.75	1003503.06	5.030	25.297
6	Day1	992.9	992.4				
	Day2	995.4	994.9	993.90	987837.21	1.472	2.167
7	Day1	994.8	991.2				
	Day2	992.7	991.2	992.48	985006.63	1.704	2.902
8	Day1	993.1	991.5				
	Day2	998.0	993.3	993.98	987986.30	2.802	7.849
9	Day1	996.7	995.7				
	Day2	999.7	993.4	996.38	992763.14	2.612	6.823
11	Day1	997.7	994.0				
	Day2	994.2	996.3	995.55	991119.80	1.771	3.137
12	Day1	989.9	991.4				
	Day2	994.5	996.5	993.08	986197.96	2.980	8.883
13	Day1	997.7	998.2				
	Day2	993.7	992.1	995.43	990870.93	2.995	8.969
15	Day1	999.4	996.9				
	Day2	999.3	1003.5	999.78	999550.05	2.739	7.503
16	Day1	1000.8	993.4				
	Day2	996.3	992.8	995.83	991667.43	3.652	13.336
17	Day1	994.9	995.2				
	Day2	996.5	996.4	995.75	991518.06	0.819	0.670
18	Day1	988.2	1000.8				*
	Day2	986.1	1000.5	993.90	987837.21	7.842	61.500
19	Day1	996.5	999.0				
	Day2	987.6	995.0	994.53	989079.98	4.903	24.036
22	Day1	980.8	988.7				
	Day2	989.6	995.4	988.63	977379.39	6.002	36.029
23	Day1	998.8	998.5				
	Day2	994.3	994.9	996.63	993261.39	2.354	5.543
S1 SUM	Yi =			17909.38			
S2 SUM	Yi^2 =				17819392.94		
S3 SUM	Si^2 =						250.794

p = 18 n = 4 * Regarded as a statistical straggler

1) Cochran's test (p=18, n=4)

$C = Si^2 max / S3$ = 0.2452 > 0.240 (p=18, n=4, 5%), < 0.288 (p=18, n=4, 1%)

2) Grubbs's test (p=18, n=4)

Yi min = 988.63 Yi max = 1001.75 Y = S1/p = 994.97

Y - Yi min = 6.34 Yi max - Y = 6.78 S = 3.314

lower = (Y - Yi min)/S = 1.9134 < 2.651 (p=18, 5%)

upper = (Yi max - Y)/S = 2.0475 < 2.651 (p=18, 5%)

3) Calculation of r and R

Mean; Y = S1 / p = 994.97

$S_r^2 = S3 / p$ = 13.933 S_r = 3.733

$S_L^2 = [(pS2-S1^2)/p(p-1)]-(S_r^2/n)$ = 7.497 S_L = 2.738

$S_R^2 = S_r^2 + S_L^2$ = 21.430 S_R = 4.629

$r = 2.8 \times S_r$ =	10.452
$R = 2.8 \times S_R$ =	12.962
$RSD_r = (S_r / mean) \times 100$ =	0.375
$RSD_R = (S_R / mean) \times 100$ =	0.465

Horwitz's value = $2 ^{[1 - 0.5 \times \log (Y / 1000)]}$ = 2.002

RSD_r and RSD_R < 2.00 (Horwitz's value)

HorRat value = RSD_R/Horwitz's value = 0.23

Table 4-2 Broflanilide Technical-2 (after elimination of outliers)

Lab		Analytical data (n=4)		Yi	Yi^2	Si	Si^2
1	Day1	998.3	999.4				
	Day2	997.7	998.5	998.48	996952.33	0.704	0.496
2	Day1	992.7	998.6				
	Day2	984.5	985.2	990.25	980595.06	6.691	44.763
3	Day1	994.5	989.6				
	Day2	998.6	990.8	993.38	986793.89	4.060	16.483
5	Day1	998.1	1005.9				
	Day2	995.1	988.0	996.78	993560.40	7.412	54.942
6	Day1	994.9	993.7				
	Day2	994.8	995.9	994.83	989676.78	0.900	0.809
7	Day1	996.7	994.4				
	Day2	990.8	990.3	993.05	986148.30	3.042	9.257
8	Day1	991.0	999.6				
	Day2	989.3	999.9	994.95	989925.50	5.587	31.217
9	Day1	996.5	992.2				
	Day2	1000.0	992.4	995.28	990572.33	3.721	13.849
11	Day1	997.8	997.9				
	Day2	1000.2	996.6	998.13	996253.52	1.504	2.263
12	Day1	988.8	992.7				
	Day2	1001.8	993.6	994.23	988483.35	5.463	29.842
13	Day1	998.4	999.9				
	Day2	999.1	999.2	999.15	998300.72	0.614	0.377
15	Day1	1009.6	1003.9				
	Day2	997.1	982.3	998.23	996453.15	11.782	138.823
16	Day1	996.6	994.7				
	Day2	991.2	996.3	994.70	989428.09	2.478	6.140
17	Day1	980.1	1009.4				*
	Day2	996.0	991.3	994.20	988433.64	12.131	147.167
18	Day1	994.0	1002.2				
	Day2	989.9	993.4	994.88	989776.27	5.207	27.116
19	Day1	999.5	1003.9				
	Day2	994.5	992.9	997.70	995405.29	4.999	24.987
22	Day1	986.1	978.5	*			
	Day2	991.2	990.2	986.50	973182.25	5.772	33.313
23	Day1	995.3	996.1				
	Day2	995.4	993.1	994.98	989975.25	1.300	1.689
S1 SUM	Yi =			17909.65			
S2 SUM	Yi^2 =				17819916.12		
S3 SUM	Si^2 =						583.532

p = 18 n = 4 * Regarded as a statistical straggler

1) Cochran's test (p=18, n=4)

$C = Si^2 max / S3$ = 0.2522 > 0.240 (p=18, n=4, 5%), < 0.288 (p=18, n=4, 1%)

2) Grubbs's test (p=18, n=4)

Yi min = 986.50 Yi max = 999.15 Y = S1/p = 994.98

Y - Yi min = 8.48 Yi max - Y = 4.17 S = 3.093

lower = (Y - Yi min)/S = 2.7421 > 2.651 (p=18, 5%) , < 2.932 (p=18, 1%)

upper = (Yi max - Y)/S = 1.3481 < 2.651 (p=18, 5%)

3) Calculation of r and R

Mean; Y = S1 / p = 994.98

S_r^2 = S3 / p = 32.418 S_r = 5.694

$S_L^2 = [(pS2-S1^2)/p(p-1)]-(S_r^2/n)$ = 1.461 S_L = 1.209

$S_R^2 = S_r^2 + S_L^2$ = 33.879 S_R = 5.821

$r = 2.8 \times S_r$ =	15.942
$R = 2.8 \times S_R$ =	16.298
$RSD_r = (S_r / mean) \times 100$ =	0.572
$RSD_R = (S_R / mean) \times 100$ =	0.585

Horwitz's value = $2 \wedge [1 - 0.5 \times \log (Y / 1000)]$ = 2.002

RSD_r and RSD_R < 2.00 (Horwitz's value)

HorRat value = RSD_R/Horwitz's value = 0.29

Table 4-3 Broflanilide Wettable Powder-1 (after elimination of outliers)

Lab		Analytical data (n=4)		Yi	Yi^2	Si	Si^2
1	Day1	502.2	502.7				
	Day2	500.4	499.6	501.23	251226.50	1.466	2.149
2	Day1	491.0	490.0				
	Day2	491.1	494.8	491.73	241793.48	2.109	4.449
3	Day1	499.4	494.4				
	Day2	498.2	497.5	497.38	247381.89	2.133	4.549
4	Day1	503.2	507.3				
	Day2	498.5	503.1	503.03	253034.15	3.596	12.929
5	Day1	498.0	502.5				
	Day2	501.9	503.7	501.53	251527.33	2.466	6.082
6	Day1	499.5	498.1				
	Day2	499.1	498.5	498.80	248801.44	0.622	0.387
7	Day1	499.1	496.1				
	Day2	495.9	496.8	496.98	246984.15	1.468	2.156
8	Day1	499.0	501.0				
	Day2	499.1	498.7	499.45	249450.30	1.047	1.097
9	Day1	500.0	498.4				
	Day2	497.6	499.8	498.95	248951.10	1.147	1.317
11	Day1	499.6	499.1				
	Day2	500.9	499.4	499.75	249750.06	0.794	0.630
12	Day1	494.9	494.6				
	Day2	496.6	496.5	495.65	245668.92	1.047	1.097
13	Day1	501.2	501.8				
	Day2	500.9	501.1	501.25	251251.56	0.387	0.150
15	Day1	500.0	503.4				
	Day2	502.5	501.0	501.73	251727.98	1.517	2.302
16	Day1	499.3	498.7				
	Day2	500.9	501.1	500.00	250000.00	1.183	1.400
17	Day1	507.1	498.9				
	Day2	500.5	499.9	501.60	251602.56	3.726	13.880
18	Day1	499.6	500.4				
	Day2	495.2	494.9	497.53	247531.13	2.879	8.289
19	Day1	502.3	501.0				
	Day2	502.3	495.0	500.15	250150.02	3.488	12.163
21	Day1	494.3	491.8				
	Day2	487.5	492.7	491.58	241645.98	2.907	8.449
22	Day1	495.4	495.0				
	Day2	488.5	492.9	492.95	242999.70	3.163	10.003
23	Day1	503.5	502.4				
	Day2	500.7	500.9	501.88	251878.52	1.323	1.749
S1 SUM	Yi =			9973.10			
S2 SUM	Yi^2 =				4973356.77		
S3 SUM	Si^2 =						95.228

p = 20 n = 4

1) Cochran's test (p=20, n=4)

$C = Si^2 max / S3$ = 0.1458 < 0.221 (p=20, n=4, 5%)

2) Grubbs's test (p=20, n=4)

Yi min = 491.58 Yi max = 503.03 Y = S1/p = 498.66

Y - Yi min = 7.08 Yi max - Y = 4.37 S = 3.407

lower = (Y - Yi min)/S = 2.0779 < 2.709 (p=20, 5%)

upper = (Yi max - Y)/S = 1.2825 < 2.709 (p=20, 5%)

3) Calculation of r and R

Mean; Y = S1 / p = 498.66

S_r^2 = S3 / p = 4.761 S_r = 2.182

$S_L^2 = [(pS2-S1^2)/p(p-1)]-(S_r^2/n)$ = 10.420 S_L = 3.228

$S_R^2 = S_r^2 + S_L^2$ = 15.181 S_R = 3.896

$r = 2.8 \times S_r$ =	6.110
$R = 2.8 \times S_R$ =	10.910
$RSD_r = (S_r / mean) \times 100$ =	0.438
$RSD_R = (S_R / mean) \times 100$ =	0.781

Horwitz's value = $2 ^{[1 - 0.5 \times \log (Y / 1000)]}$ = 2.221

RSD_r and RSD_R < 2.22 (Horwitz's value)

HorRat value = RSD_R/Horwitz's value = 0.35

Table 4-4 Broflanilide Wettable Powder-2 (after elimination of outliers)

Lab		Analytical data (n=4)		Yi	Yi^2	Si	Si^2
1	Day1	505.2	504.7				
	Day2	501.4	501.2	503.13	253134.77	2.119	4.489
2	Day1	497.8	484.8				*
	Day2	499.5	497.3	494.85	244876.52	6.766	45.777
3	Day1	490.4	506.2				
	Day2	499.0	498.5	498.53	248527.18	6.459	41.716
4	Day1	504.2	499.9				
	Day2	501.8	498.5	501.10	251101.21	2.470	6.100
5	Day1	506.6	505.7				
	Day2	503.0	502.7	504.50	254520.25	1.944	3.780
6	Day1	499.7	498.7				
	Day2	499.6	499.2	499.30	249300.49	0.455	0.207
7	Day1	500.7	499.1				
	Day2	495.9	498.2	498.48	248477.33	2.004	4.016
8	Day1	500.6	500.4				
	Day2	501.3	500.6	500.73	250725.53	0.395	0.156
9	Day1	498.9	499.3				
	Day2	500.3	502.0	500.13	250125.02	1.382	1.909
11	Day1	501.5	500.7				
	Day2	501.7	502.8	501.68	251677.81	0.866	0.749
12	Day1	493.8	495.0				
	Day2	497.2	495.0	495.25	245272.56	1.418	2.010
13	Day1	503.9	501.2				
	Day2	503.1	499.9	502.03	252029.10	1.814	3.289
14	Day1	509.3	508.1				
	Day2	497.2	507.4	505.50	255530.25	5.589	31.233
15	Day1	500.7	502.3				
	Day2	502.1	501.1	501.55	251552.40	0.772	0.597
16	Day1	500.5	500.4				
	Day2	501.5	500.9	500.83	250825.68	0.499	0.249
17	Day1	498.5	504.4				
	Day2	502.2	502.8	501.98	251978.90	2.496	6.229
18	Day1	502.2	501.5				
	Day2	495.5	495.7	498.73	248726.63	3.621	13.109
19	Day1	507.6	506.2				
	Day2	501.7	499.5	503.75	253764.06	3.790	14.363
21	Day1	485.4	491.8				
	Day2	498.3	494.8	492.58	242630.13	5.471	29.936
22	Day1	499.3	494.6				
	Day2	495.8	495.6	496.33	246338.51	2.052	4.209
23	Day1	503.1	504.5				
	Day2	505.6	503.3	504.13	254142.02	1.162	1.349
S1 SUM	Yi =			10505.03			
S2 SUM	Yi^2 =				5255256.32		
S3 SUM	Si^2 =						215.473

p = 21 n = 4 * Regarded as a statistical straggler

1) Cochran's test (p=21, n=4)

$C = Si^2 max / S3$ = 0.2124 > 0.212 (p=21, n=4, 5%), < 0.255 (p=21, n=4, 1%)

2) Grubbs's test (p=21, n=4)

Yi min = 492.58 Yi max = 505.50 Y = S1/p = 500.24

Y - Yi min = 7.66 Yi max - Y = 5.26 S = 3.392

lower = (Y - Yi min)/S = 2.2595 < 2.733 (p=21, 5%)

upper = (Yi max - Y)/S = 1.5509 < 2.733 (p=21, 5%)

3) Calculation of r and R

Mean; Y = S1 / p = 500.24

S_r^2 = S3 / p = 10.261 S_r = 3.203

$S_L^2 = [(pS2-S1^2)/p(p-1)]-(S_r^2/n)$ = 8.941 S_L = 2.990

$S_R^2 = S_r^2 + S_L^2$ = 19.201 S_R = 4.382

$r = 2.8 \times S_r$ =	8.969
$R = 2.8 \times S_R$ =	12.269
$RSD_r = (S_r / mean) \times 100$ =	0.640
$RSD_R = (S_R / mean) \times 100$ =	0.876

Horwitz's value = $2 ^{[1 - 0.5 \times \log (Y / 1000)]}$ = 2.220

RSD_r and RSD_R < 2.22 (Horwitz's value)

HorRat value = RSD_R/Horwitz's value = 0.39

Table 4-5 Broflanilide Wettable Powder-3 (after elimination of outliers)

Lab		Analytical data (n=4)		Yi	Yi^2	Si	Si^2
1	Day1	501.7	502.3				
	Day2	499.1	498.6	500.43	250425.18	1.846	3.409
2	Day1	487.5	495.3				
	Day2	495.5	495.1	493.35	243394.22	3.903	15.237
3	Day1	495.4	492.6				
	Day2	488.5	494.4	492.73	242777.93	3.046	9.276
4	Day1	501.5	502.6				
	Day2	496.9	497.9	499.73	249725.08	2.752	7.576
5	Day1	512.8	495.6				*
	Day2	500.4	497.1	501.48	251477.18	7.812	61.022
6	Day1	498.0	498.1				
	Day2	496.5	497.9	497.63	247630.64	0.754	0.569
7	Day1	494.7	495.6				
	Day2	491.3	493.9	493.88	243912.52	1.852	3.429
8	Day1	500.7	499.7				
	Day2	499.1	499.8	499.83	249825.03	0.660	0.436
9	Day1	499.1	496.1				
	Day2	499.1	500.0	498.58	248577.03	1.704	2.902
10	Day1	512.3	509.9				
	Day2	501.2	502.1	506.38	256415.64	5.555	30.862
11	Day1	500.5	498.9				
	Day2	501.4	500.3	500.28	250275.08	1.034	1.069
12	Day1	493.8	502.3				
	Day2	492.4	495.8	496.08	246090.41	4.378	19.169
13	Day1	500.9	495.4				
	Day2	500.9	496.8	498.50	248502.25	2.830	8.007
14	Day1	506.2	501.6				
	Day2	510.7	506.0	506.13	256162.52	3.716	13.809
15	Day1	500.0	504.8				
	Day2	498.4	495.1	499.58	249575.18	4.037	16.296
16	Day1	497.1	498.4				
	Day2	500.7	499.3	498.88	248876.27	1.515	2.296
17	Day1	502.5	497.2				
	Day2	501.2	498.5	499.85	249850.02	2.428	5.897
18	Day1	499.5	498.7				
	Day2	489.3	491.9	494.85	244876.52	5.032	25.317
19	Day1	503.3	504.0				
	Day2	495.1	494.6	499.25	249250.56	5.093	25.937
21	Day1	493.9	500.3				
	Day2	485.5	497.4	494.28	244307.78	6.409	41.069
22	Day1	494.0	493.3				
	Day2	495.2	495.5	494.50	244530.25	1.030	1.060
23	Day1	499.4	501.1				
	Day2	499.4	500.7	500.15	250150.02	0.881	0.777
S1 SUM	Yi =			10966.28			
S2 SUM	Yi^2 =				5466607.29		
S3 SUM	Si^2 =						295.421

p = 22 n = 4 * Regarded as a statistical straggler

1) Cochran's test (p=22, n=4)

$C = Si^2 max / S3$ = 0.2066 > 0.204 (p=22, n=4, 5%), < 0.246 (p=22, n=4, 1%)

2) Grubbs's test (p=22, n=4)

Yi min = 492.73 Yi max = 506.38 Y = S1/p = 498.47

Y - Yi min = 5.74 Yi max - Y = 7.91 S = 3.655

lower = (Y - Yi min)/S = 1.5709 < 2.758 (p=22, 5%)

upper = (Yi max - Y)/S = 2.1634 < 2.758 (p=22, 5%)

3) Calculation of r and R

Mean; Y = S1 / p = 498.47

S_r^2 = S3 / p = 13.428 S_r = 3.664

$S_L^2 = [(pS2-S1^2)/p(p-1)]-(S_r^2/n)$ = 10.004 S_L = 3.163

$S_R^2 = S_r^2 + S_L^2$ = 23.432 S_R = 4.841

$r = 2.8 \times S_r$ =	10.260
$R = 2.8 \times S_R$ =	13.554
$RSD_r = (S_r / mean) \times 100$ =	0.735
$RSD_R = (S_R / mean) \times 100$ =	0.971

Horwitz's value = 2 ^[1 - 0.5 x log (Y / 1000)] = 2.221

RSD_r and RSD_R < 2.22 (Horwitz's value)

HorRat value = RSD_R/Horwitz's value 0.44

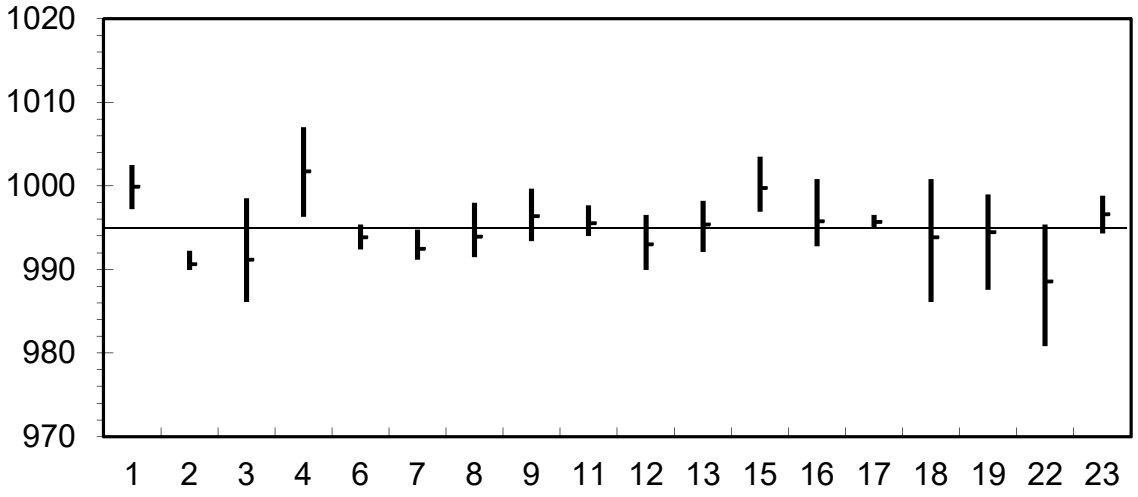

Figure 6 Broflanilide Technical (TC-1) (after elimination of outliers)

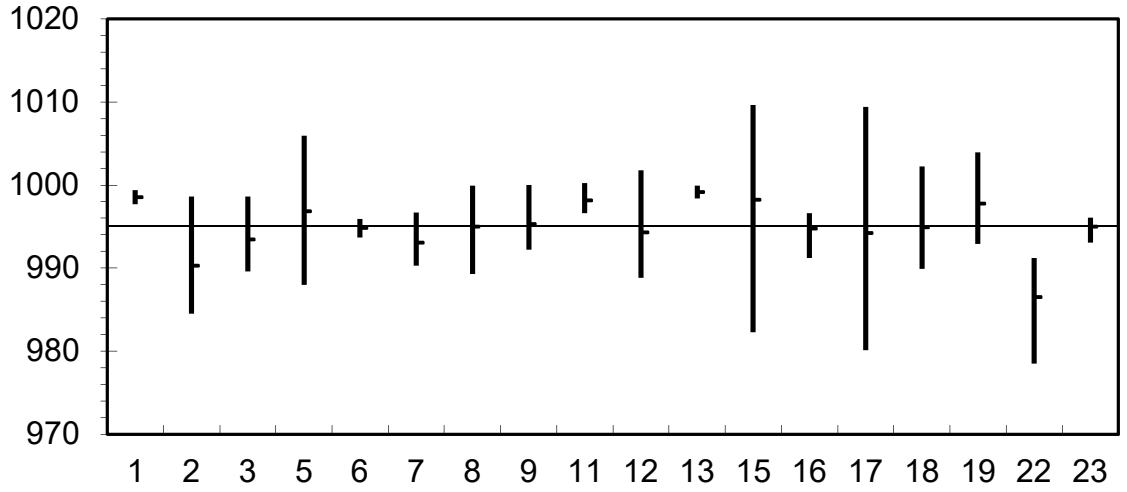

Figure 7 Broflanilide Technical (TC-2) (after elimination of outliers)

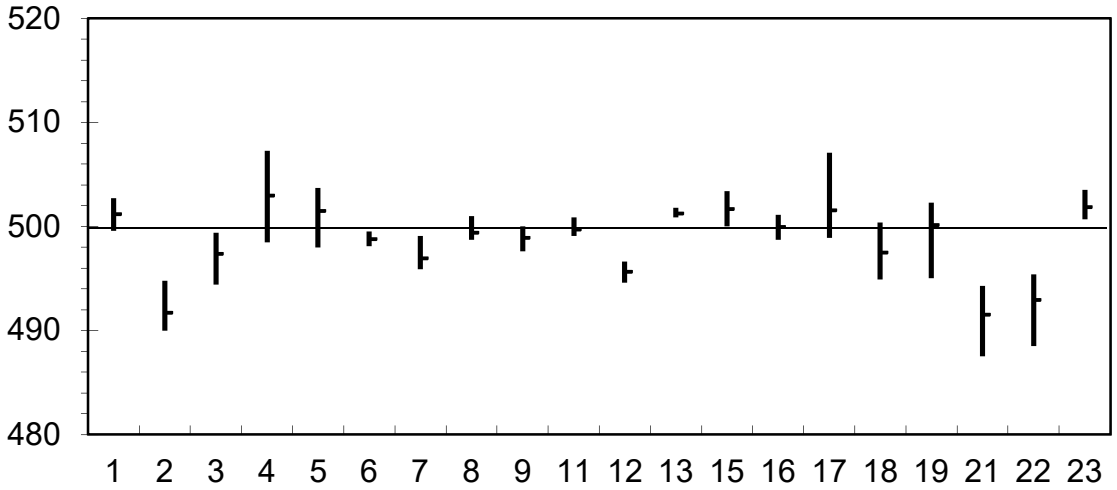

Figure 8 Broflanilide 50%Wettable Powder (WP-1) (after elimination of outliers)

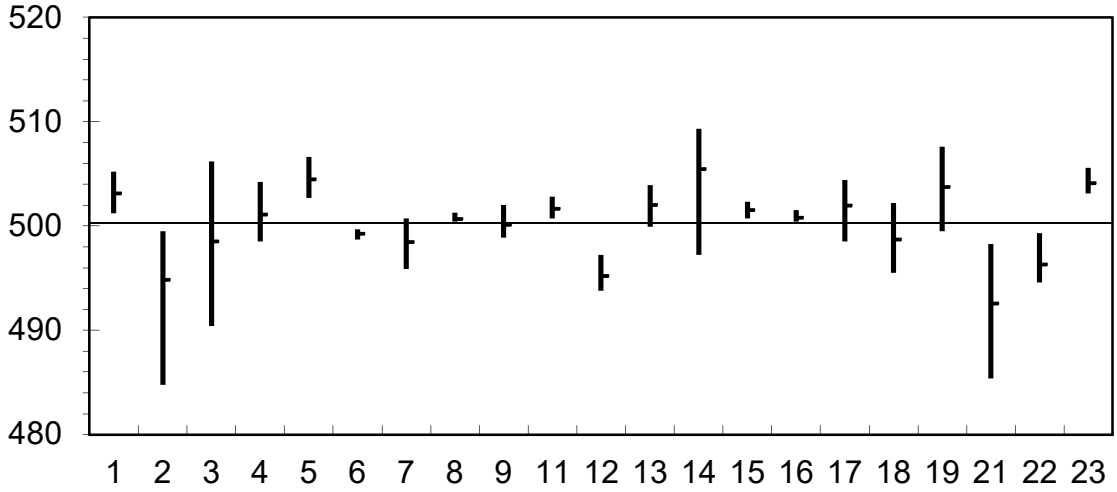

Figure 9 Broflanilide 50%Wettable Powder (WP-2) (after elimination of outliers)

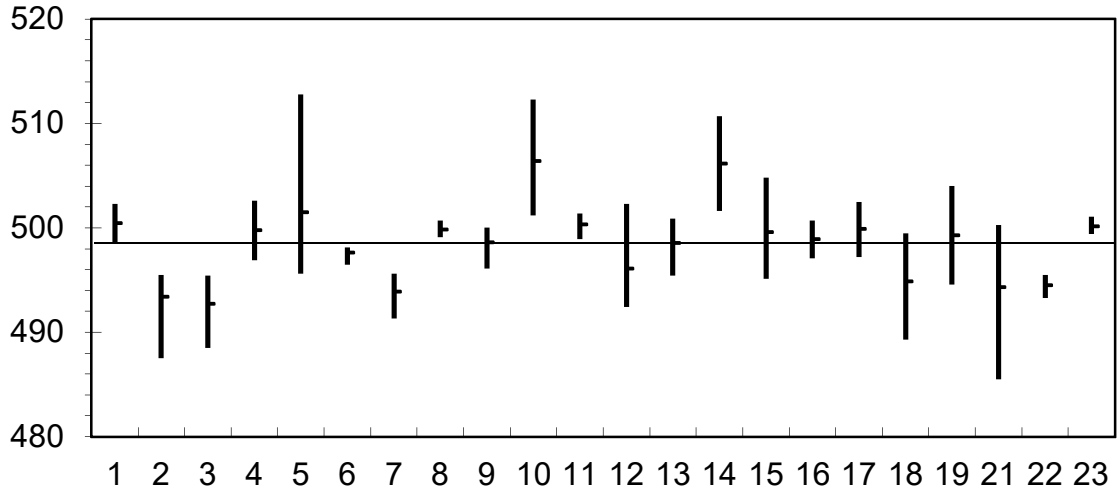

Figure 10 Broflanilide 50%Wettable Powder (WP-3) (after elimination of outliers)