FLUMIOXAZIN (No.578)
CIPAC Collaborative Trial

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

by
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1. INTRODUCTION

1.1 Scope

The results of the CIPAC collaborative trial for flumioxazin technical product and flumioxazin wettable powder are reported.

1.2 Samples

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

1.3 Participants

Ahmed Zouaoui	Official Laboratory of Chemical Analysis and Research L.O.A.R.C Service Pesticides (Morocco)
Ana Gregorčič	Kmetijski inštitut Slovenije (Slovenia)
Andrew Plumb	The Food and Environment Research Agency (UK)
Bruno Patrian	Agroscope Changins-Wädenswil (Switzerland)
Elizabeth de Aguila	Laboratorio Control de Calidad de Plaguicidas MAG-OIRSA (El Salvador)
Helen Karasali and George Balayiannis	Benaki Phytopathological Institute, Laboratory of Chemical Control of Pesticides (Greece)
Jim Garvey	Pesticide Control Laboratory (Ireland)
Lajos Benke	Agricultural Office of County Fejér, Plant Protection and Soil Conservation Directorate (Hungary)

Luis Manso	Laboratorio Arbitral Agroalimentario, Ministerio de Agricultura, Pescay Alimentacion (Spain)
Nicoleta Predescu	Central Phytosanitary Laboratory, Laboratory for Quality Control of Pesticides (Romania)
Nunchana Luetrakool	Pesticide Research Group, Agricultural production Science Research Development Office (Thailand)
Olga Novakova	State Phytosanitary Administration Pesticides Testing Laboratory (Czech)
Susan Marais	Pesticide Analytical Technology cc (South Africa)
Vanessa Lecocq	Walloon Agricultural Research Centre (CRA-W), Pesticides Research Department (Belgium)
Volodymyr Mykhaylov	Institute of Ecohygiene and Toxicology (ECOHYNTOX) (Ukraine)

2. ANALYTICAL METHOD

2.1 Outline of Method

Flumioxazin in the test samples is determined by reversed phase high performance liquid chromatography using an ODS column, UV detection at 288 nm and external standardization as stated in CIPAC/4763/m.

2.2 Program of Work

We requested the collaborators to:

1) conduct duplicate determinations on two different days for each sample;
2) inject each sample solution in duplicate and calculate the mean value;
3) check linearity before the determination;
4) describe operating conditions in detail; and
5) attach the calibration curve and all chromatograms for each sample.

3. REMARKS OF PARTICIPANTS

3.1 Analytical Conditions

The analytical conditions of the collaborators are summarized in Table 1.

3.2 Remarks

- Lab.1
  - Column temperature of 25C was used on Day 1. Correct column temperature of 40C was used on Day 2.
  - HYPERSIL C18 , 4.6mm i.d. × 150mm, 5um used instead of Phenomenex Gemini column.

- Lab.2
  - We used column Zorbax ODS because it was not possible to obtain the suggested for you.
  - We followed the study such as you suggested.

- Lab.3
  - We deviate from the method in the following: In our lab we use only 50ml volumetric flasks (instead of the 100ml flasks prescribed in your method) and therefore we adapted the weighed masses accordingly.
  - Instrument conditions to produce a retention time of approximately 5 min, will give a better peak shape with separation of impurities.

- Lab.4
  - A 150 x 3.0 mm(i.d.) column has been used (the only Gemini 5µ C18 available), because of that, mobile phase and flow rate have been modified.

- Lab.5
  - We followed the supplied method except for concentration of standards and samples because of the mistake in the instruction. We used 50 mL volumetric flasks instead of 100 mL volumetric flasks. Approximate sampling weight values for calibration solution 50mg, TC 50 mg and WP 100 mg were diluted to volume 50 mL with acetonitrile.
  - We used bracketing and calculated mean area value from 2 injections of calibration solution CB (CD as well), as you can see in worksheets and enclosed chromatograms.

- Lab.8
  - Acetonitrile analytical reagent grade was used for preparation of solutions instead of HPLC grade.
  - The volumetric flasks were filled up to volume at 20°C ± 1°C instead of at room temperature.
  - Peak symmetry was not good using the defined chromatographic parameters.
  - It would be preferable to inject 5 µL instead of 10 µL in order to prevent the overloading of the column and/or of the detector.

- Lab.10
  - Retention time is slightly shorter (9.7 mins) than given in method (11.4 mins).
  - Did not feel it was necessary to adjust flow rate to obtain closer match in retention time.

- Lab.12
  - We expand the solution time in the ultrasonic bath to 30 minutes. With 10 minutes, we get quite different results between the two weights of the same sample.

- Lab.14
  - The purities of the samples TC1 and TC3 on the package are different from those in instruction sheet.
  - Dates of analysis are spaced for technical reasons.

4. RESULTS AND DISCUSSION

Fifteen data sets were obtained from fifteen participants. Summary and detailed statistical evaluations are shown in Tables 2 and 3-1 to 3-5. The statistical evaluations were carried out according to ISO 5725.
The discussion on stragglers and outliers is as follows:

- TC-1

  The variance of Lab. 14 was identified as an outlier. The data were retained because there were no reasons to remove them.

- TC-2

  The variance of Lab. 14 was identified as an outlier. The data were retained because there were no reasons to remove them.

- TC-3

  The variance of Lab. 14 was identified as an outlier. The data were retained because there were no reasons to remove them.

- WP-1

  There were no stragglers or outliers. However, the RSD_r and RSD_R values obtained were quite big compared to other samples. This was found to be derived from inhomogeneity of the sample, and the sample subjected to the trial was thought to be inadequate. Therefore, the results for WP-1 should be deleted.

- WP-2

  The variance of Lab. 14 was identified as an outlier. The data were retained because there were no reasons to remove them.

5. CONCLUSION

For all samples except WP-1, the values of RSD_R (reproducibility relative standard deviation) were smaller than those calculated by Horwitz's equation. The sample WP-1 was considered to be inadequate. Therefore, the proposed method is considered appropriate for the determination of flumioxazin in technical product and wettable powder.
JAPAC proposes that the method be accepted as a provisional CIPAC method.

Table 1 Summary of Analytical Conditions

Lab	Liquid chromatograph	Column	Mobile phase	Flow rate (ml/min)	Injection volume (µl)	Column temp. (°C)
Proposed Method		Phenomenex Gemini 5µ C18 (4.6 mm ID × 250 mm, 5 µm)	acetonitrile - water, 50 + 50 (v/v)	1.0	10	40
1	Agilent 1100 series	Hypersil C18 (4.6 mm ID × 150 mm, 5 µm)	acetonitrile - water, 50 + 50 (v/v)	0.75	10	25 /Day 1 40 /Day 2
2	Agilent 1100 series	Zorbax C18 (4.6 mm ID × 250 mm, 5 µm)	acetonitrile - water, 50 + 50 (v/v)	1.0	10	40
3	Agilent 1200 series	Zorbax Eclipse C18 (4.6 mm ID × 150 mm, 5 µm)	acetonitrile - water, 50 + 50 (v/v)	0.8	10	40
4	Agilent 1100 series	Phenomenex Gemini 5µ C18 (3.0 mm ID × 150 mm, 5 µm)	acetonitrile - water, 40 + 60 (v/v)	0.8	10	40
5	Waters Alliance 2695	Phenomenex Gemini 5µ C18 (4.6 mm ID × 250 mm, 5 µm)	acetonitrile - water, 50 + 50 (v/v)	1.0	10	40
6	Agilent 1200 series	LiChrosher 100RP-18 (4.6 mm ID × 250 mm, 5 µm)	acetonitrile - water, 50 + 50 (v/v)	1.0	10	40
7	Shimadzu UFLC	Phenomenex Luna C18 (4.6 mm ID × 250 mm, 5 µm)	acetonitrile - water, 50 + 50 (v/v)	1.0	10	40
8	Agilent 1200 series	Phenomenex Gemini 5µ C18 (4.6 mm ID × 250 mm, 5 µm)	acetonitrile - water, 50 + 50 (v/v)	1.0	10	40
9	Dionex HPLC system	Zorbax SB-C18 (4.6 mm ID × 250 mm, 5 µm)	acetonitrile - water, 50 + 50 (v/v)	1.0	5	40

Table 1 Summary of Analytical Conditions (continued)

Lab	Liquid chromatograph	Column	Mobile phase	Flow rate (ml/min)	Injection volume (µl)	Column temp. (°C)
Proposed Method		Phenomenex Gemini 5µ C18 (4.6 mm ID × 250 mm, 5 µm)	acetonitrile - water, 50 + 50 (v/v)	1.0	10	40
10	Agilent 1050 series	Zorbax Eclipse XDB-C18 (4.6 mm ID × 250 mm, 5 µm)	acetonitrile - water, 50 + 50 (v/v)	1	10	40
11	Dalian Elite Scientific Instruments	Supelcosil LC18-DB (4.6 mm ID × 250 mm, 5 µm)	acetonitrile - water, 50 + 50 (v/v)	1.0	5	40
12	Dionex Summit	Nucleosil C18 (4.0 mm ID × 250 mm, 5 µm)	acetonitrile - water, 45 + 55 (v/v)	1.0	10	40
13	Varian Prostar	Phenomenex Gemini 5µ C18 (4.6 mm ID × 250 mm, 5 µm)	acetonitrile - water, 50 + 50 (v/v)	1	10	40
14	Agilent 1100 series	Varian Chromsep C18 (4.6 mm ID × 250 mm, 5 µm)	acetonitrile - water, 50 + 50 (v/v)	1.00	10	40
15	Agilent 1100 series	LiChrosher 100RP-18 (4.0 mm ID × 250 mm, 5 µm)	acetonitrile - water, 50 + 50 (v/v)	1.0	10	40

Table 1 Summary of Statistical Evaluation of Flumioxazin CIPAC Collaborative Study

	TC-1	TC-2	TC-3	WP-1	WP-2
Average (g/kg)	992.47	992.60	992.84	512.17	515.88
Number of labs.	15	15	15	15	15
Repeatability standard deviation (S_r)	3.660	5.762	7.129	4.116	3.237
"Pure" between laboratory standard variation (S_L)	5.106	4.791	7.226	12.768	2.345
Reproducibility standard deviation (S_R)	6.283	7.494	10.151	13.415	3.997
Repeatability (r)	10.248	16.134	19.961	11.525	9.064
Reproducibility (R)	17.592	20.983	28.423	37.562	11.192
RSD_r	0.369	0.580	0.718	0.804	0.627
RSD_R	0.633	0.755	1.022	2.619	0.775
Horwitz's value	2.002	2.002	2.002	2.212	2.210

Table 3-1 Flumioxazin Technical -1

Lab		Analytical data (n=4)		Yi	$(Yi)^2$	Si	Si^2
1	Day1	997.3	995.3				
	Day2	994.5	994.6	995.43	990880.88	1.300	1.690
2	Day1	1000.6	997.7				
	Day2	997.4	995.0	997.68	995365.38	2.294	5.262
3	Day1	988.8	992.2				
	Day2	989.5	989.6	990.03	980159.40	1.493	2.229
4	Day1	989.6	991.9				
	Day2	986.5	987.9	988.98	978081.44	2.326	5.410
5	Day1	979.9	984.4				
	Day2	975.3	978.9	979.63	959674.94	3.746	14.033
6	Day1	994.2	994.0				
	Day2	993.3	994.4	993.98	987996.24	0.479	0.229
7	Day1	993.9	995.3				
	Day2	995.0	993.2	994.35	988731.92	0.975	0.951
8	Day1	989.7	991.4				
	Day2	996.8	994.8	993.18	986406.51	3.215	10.336
9	Day1	990.4	992.4				
	Day2	991.2	991.9	991.48	983032.59	0.869	0.755
10	Day1	985.7	987.7				
	Day2	991.8	995.4	990.15	980397.02	4.324	18.697
11	Day1	996.8	997.7				
	Day2	1001.2	996.5	998.05	996103.80	2.161	4.670
12	Day1	1000.2	1006.0				
	Day2	999.7	997.1	1000.75	1001500.56	3.755	14.100
13	Day1	995.6	992.2				
	Day2	998.7	997.6	996.03	992075.76	2.855	8.151
14	Day1	975.1	993.7				**
	Day2	975.4	992.8	984.25	968748.06	10.400	108.160
15	Day1	993.9	994.6				
	Day2	994.6	989.4	993.13	986307.20	2.505	6.275
S1 SUM	Yi =			14887.10			
S2 SUM	Yi^2 =				14775461.70		
S3 SUM	Si^2 =						200.948

p = 15

1) Cochran's test (p=15, n=4)

C = Si^2max / S3 = 0.538 > 0.276 (p=15, n=4, 5%)
> 0.332 (p=15, n=4, 1%)

Outlier Lab 14 was included in the following evaluation.

2) Grubbs' test (p=15, n=4)

Yi(min) = 979.63 Yi(max) = 1000.75 Y = S1/p 992.47
S = 5.626

Y - Yi(min) = 12.84
Yi(max) - Y = 8.28
lower = [Y-Yi(min)]/S = 2.283 < 2.681 (p=15, 5%)
upper = [Yi(max)-Y]/S = 1.471 < 2.681 (p=15, 5%)

3) Calculation of r and R

Mean; Y = S1 / p =	992.47	
Sr^2 = S3 / p =	13.397	Sr = 3.660
$SL^2 = [(pS2-S1^2)/p(p-1)]-(Sr^2/n)$ =	26.075	SL = 5.106
$SR^2 = Sr^2 + SL^2$ =	39.472	SR = 6.283

r = 2.8 x Sr =	10.248
R = 2.8 x SR =	17.592
RSDr = (Sr / mean) x 100 =	0.369
RSDR = (SR / mean) x 100 =	0.633

Horwitz's Value = 2 ^[1 - 0.5 x log(Y / 1000)] = 2.002

<u>RSDr and RSDR < 2.002 (Horwitz's Value)</u>

Table 3-2 Flumioxazin Technical -2

Lab		Analytical data (n=4)		Yi	$(Yi)^2$	Si	Si^2
1	Day1	995.7	1000.8				
	Day2	994.1	992.9	995.88	991776.97	3.478	12.096
2	Day1	1004.8	1002.2				
	Day2	999.0	992.7	999.68	999360.10	5.220	27.248
3	Day1	990.5	991.1				
	Day2	988.1	992.4	990.53	981149.68	1.801	3.244
4	Day1	989.4	991.4				
	Day2	988.2	987.3	989.08	978279.25	1.773	3.144
5	Day1	982.3	980.4				
	Day2	975.4	977.0	978.78	958010.29	3.142	9.872
6	Day1	999.9	992.0				
	Day2	991.5	990.5	993.48	987002.51	4.328	18.732
7	Day1	996.0	995.7				
	Day2	994.0	996.8	995.63	991279.10	1.179	1.390
8	Day1	997.4	991.1				
	Day2	1001.9	1008.3	999.68	999360.10	7.258	52.679
9	Day1	992.1	993.5				
	Day2	993.8	994.4	993.45	986942.90	0.975	0.951
10	Day1	984.4	987.9				
	Day2	993.4	990.2	988.98	978081.44	3.793	14.387
11	Day1	997.6	990.4				
	Day2	988.5	987.2	990.93	981942.26	4.640	21.530
12	Day1	992.8	996.7				
	Day2	1011.7	996.5	999.43	998860.32	8.377	70.174
13	Day1	989.6	990.6				
	Day2	992.1	993.7	991.50	983072.25	1.791	3.208
14	Day1	987.1	1006.7				**
	Day2	984.6	967.8	986.55	973280.90	15.934	253.892
15	Day1	997.2	995.8				
	Day2	996.6	992.0	995.40	990821.16	2.338	5.466
S1 SUM	Yi =			14888.98			
S2 SUM	Yi^2 =				14779219.23		
S3 SUM	Si^2 =						498.013

p = 15

1) Cochran's test (p=15, n=4)

C = Si^2max / S3 = 0.510 > 0.276 (p=15, n=4, 5%)

> 0.332 (p=15, n=4, 1%)

Outlier Lab 14 was included in the following evaluation.

2) Grubbs' test (p=15, n=4)

Yi(min) = 978.78 Yi(max) = 999.68 Y = S1/p 992.60

S = 5.746

Y - Yi(min) = 13.82

Yi(max) - Y = 7.08

lower = [Y-Yi(min)]/S = 2.405 < 2.681 (p=15, 5%)

upper = [Yi(max)-Y]/S = 1.232 < 2.681 (p=15, 5%)

3) Calculation of r and R

Mean; Y = S1 / p =	992.60	
Sr^2 = S3 / p =	33.201	Sr = 5.762
$SL^2 = [(pS2-S1^2)/p(p-1)]-(Sr^2/n)$ =	22.952	SL = 4.791
$SR^2 = Sr^2 + SL^2$ =	56.153	SR = 7.494

r = 2.8 x Sr =	16.134
R = 2.8 x SR =	20.983
RSDr = (Sr / mean) x 100 =	0.580
RSDR = (SR / mean) x 100 =	0.755

Horwitz's Value = 2 ^[1 - 0.5 x log(Y / 1000)] = 2.002

RSDr and RSDR < 2.002 (Horwitz's Value)

Table 3-3 Flumioxazin Technical -3

Lab		Analytical data (n=4)		Yi	$(Yi)^2$	Si	Si^2
1	Day1	996.6	992.3				
	Day2	994.5	997.5	995.23	990482.75	2.320	5.382
2	Day1	1001.5	997.0				
	Day2	999.5	989.5	996.88	993769.73	5.250	27.563
3	Day1	989.0	990.2				
	Day2	991.1	990.2	990.13	980357.42	0.862	0.743
4	Day1	994.6	994.1				
	Day2	994.5	995.4	994.65	989328.62	0.545	0.297
5	Day1	974.7	974.8				
	Day2	965.6	982.4	974.38	949416.38	6.872	47.224
6	Day1	995.6	997.3				
	Day2	995.0	997.3	996.30	992613.69	1.180	1.392
7	Day1	996.2	996.7				
	Day2	997.8	998.4	997.28	994567.40	1.005	1.010
8	Day1	995.9	992.4				
	Day2	989.9	999.1	994.33	988692.15	4.024	16.193
9	Day1	995.8	996.6				
	Day2	996.9	995.1	996.10	992215.21	0.812	0.659
10	Day1	996.2	991.2				
	Day2	995.4	995.9	994.68	989388.30	2.340	5.476
11	Day1	1001.9	996.6				
	Day2	999.7	998.3	999.13	998260.76	2.243	5.031
12	Day1	1004.3	994.9				
	Day2	1016.3	997.4	1003.23	1006470.43	9.580	91.776
13	Day1	990.0	993.7				
	Day2	992.5	995.0	992.80	985651.84	2.128	4.528
14	Day1	994.7	983.3				**
	Day2	979.0	940.6	974.40	949455.36	23.487	551.639
15	Day1	995.9	991.8				
	Day2	992.7	992.2	993.15	986346.92	1.870	3.497
S1 SUM	Yi =			14892.67			
S2 SUM	Yi^2 =				14787016.96		
S3 SUM	Si^2 =						762.410

p = 15

1) Cochran's test (p=15, n=4)

$C = Si^2max / S3 =$ 0.724 > 0.276 (p=15, n=4, 5%)
> 0.332 (p=15, n=4, 1%)

Outlier Lab 14 was included in the following evaluation.

2) Grubbs' test (p=15, n=4)

Yi(min) = 974.38 Yi(max) = 1003.23 Y = S1/p 992.84
S = 8.362

Y - Yi(min) = 18.46
Yi(max) - Y = 10.39
lower = [Y-Yi(min)]/S = 2.208 < 2.681 (p=15, 5%)
upper = [Yi(max)-Y]/S = 1.242 < 2.681 (p=15, 5%)

3) Calculation of r and R

Mean; Y = S1 / p =	992.84	
$Sr^2 = S3 / p =$	50.827	Sr = 7.129
$SL^2 = [(pS2-S1^2)/p(p-1)]-(Sr^2/n) =$	52.220	SL = 7.226
$SR^2 = Sr^2 + SL^2 =$	103.048	SR = 10.151

r = 2.8 x Sr =	19.961
R = 2.8 x SR =	28.423
RSDr = (Sr / mean) x 100 =	0.718
RSDR = (SR / mean) x 100 =	1.022

Horwitz's Value = 2 ^[1 - 0.5 x log(Y / 1000)] = 2.002

RSDr and RSDR < 2.002 (Horwitz's Value)

Table 3-4 Flumioxazin Wettable Powder-1

Lab		Analytical data (n=4)		Yi	$(Yi)^2$	Si	Si^2
1	Day1	508.5	509.4				
	Day2	519.2	522.7	514.95	265173.50	7.084	50.183
2	Day1	507.5	512.4				
	Day2	503.5	508.2	507.90	257962.41	3.645	13.286
3	Day1	508.2	498.7				
	Day2	498.1	503.5	502.13	252134.54	4.716	22.241
4	Day1	483.8	487.2				
	Day2	485.0	485.0	485.25	235467.56	1.418	2.011
5	Day1	514.4	518.5				
	Day2	514.2	515.3	515.60	265843.36	1.992	3.968
6	Day1	530.5	531.0				
	Day2	531.1	527.5	530.03	280931.80	1.704	2.904
7	Day1	497.2	493.8				
	Day2	496.2	495.7	495.73	245748.23	1.427	2.036
8	Day1	531.9	528.9				
	Day2	529.7	528.9	529.85	280741.02	1.418	2.011
9	Day1	517.5	516.7				
	Day2	517.1	516.6	516.98	267268.32	0.411	0.169
10	Day1	491.1	496.6				
	Day2	507.6	498.8	498.53	248532.16	6.862	47.087
11	Day1	512.7	509.0				
	Day2	504.7	515.7	510.53	260640.88	4.753	22.591
12	Day1	525.4	516.8				
	Day2	520.7	526.0	522.23	272724.17	4.324	18.697
13	Day1	502.7	504.3				
	Day2	513.0	513.1	508.28	258348.56	5.552	30.825
14	Day1	523.2	520.6				
	Day2	517.0	509.9	517.68	267992.58	5.773	33.328
15	Day1	529.3	526.8				
	Day2	525.7	525.9	526.93	277655.22	1.654	2.736
S1 SUM	Yi =			7682.60			
S2 SUM	Yi^2 =				3937164.31		
S3 SUM	Si^2 =						254.073

p = 15

1) Cochran's test (p=15, n=4)

C = Si^2max / S3 = 0.198 < 0.276 (p=15, n=4, 5%)

2) Grubbs' test (p=15, n=4)

Yi(min) = 485.25 Yi(max) = 530.03 Y = S1/p 512.17
S = 12.734

Y - Yi(min) = 26.92
Yi(max) - Y = 17.86
lower = [Y-Yi(min)]/S = 2.114 < 2.681 (p=15, 5%)
upper = [Yi(max)-Y]/S = 1.402 < 2.681 (p=15, 5%)

3) Calculation of r and R

Mean; Y = S1 / p = 512.17
Sr^2 = S3 / p = 16.938 Sr = 4.116
SL^2 = [(pS2-$S1^2$)/p(p-1)]-(Sr^2/n) = 163.013 SL = 12.768
SR^2 = Sr^2 + SL^2 = 179.951 SR = 13.415

r = 2.8 x Sr =	11.525
R = 2.8 x SR =	37.562
RSDr = (Sr / mean) x 100 =	0.804
RSDR = (SR / mean) x 100 =	2.619

Horwitz's Value = 2 ^[1 - 0.5 x log(Y / 1000)] = 2.212

RSDr < 2.212 RSDR > 2.212 (Horwitz's Value)

Table 3-4 Flumioxazin Wettable Powder-2

Lab		Analytical data (n=4)		Yi	$(Yi)^2$	Si	Si^2
1	Day1	514.2	512.3				
	Day2	517.7	514.4	514.65	264864.62	2.243	5.031
2	Day1	518.0	520.3				
	Day2	515.7	520.3	518.58	268925.22	2.202	4.849
3	Day1	512.5	509.3				
	Day2	514.4	510.1	511.58	261714.10	2.323	5.396
4	Day1	519.9	519.9				
	Day2	517.7	517.9	518.85	269205.32	1.215	1.476
5	Day1	513.6	511.5				
	Day2	508.5	505.4	509.75	259845.06	3.576	12.788
6	Day1	518.1	517.7				
	Day2	516.9	518.0	517.68	267992.58	0.544	0.296
7	Day1	513.6	517.2				
	Day2	517.7	516.1	516.15	266410.82	1.827	3.338
8	Day1	522.3	515.4				
	Day2	513.8	515.5	516.75	267030.56	3.781	14.296
9	Day1	517.9	518.2				
	Day2	518.5	518.5	518.28	268614.16	0.287	0.082
10	Day1	518.7	520.2				
	Day2	519.0	517.3	518.80	269153.44	1.192	1.421
11	Day1	517.1	519.7				
	Day2	517.1	514.9	517.20	267495.84	1.963	3.853
12	Day1	517.3	516.6				
	Day2	517.3	519.7	517.73	268044.35	1.357	1.841
13	Day1	513.0	514.5				
	Day2	518.8	514.5	515.20	265431.04	2.502	6.260
14	Day1	513.1	526.3				**
	Day2	502.8	517.8	515.00	265225.00	9.798	96.001
15	Day1	511.9	512.6				
	Day2	512.1	511.3	511.98	262123.52	0.538	0.289
S1 SUM		Yi =		7738.18			
S2 SUM		Yi^2 =			3992075.63		
S3 SUM		Si^2 =					157.217

p = 15

1) Cochran's test (p=15, n=4)

$C = Si^2max / S3 =$ 0.611 > 0.276 (p=15, n=4, 5%)
> 0.332 (p=15, n=4, 1%)

Outlier Lab 14 was included in the following evaluation.

2) Grubbs' test (p=15, n=4)

Yi(min) = 509.75 Yi(max) = 518.85 Y = S1/p 515.88
S = 2.737

Y - Yi(min) = 6.13
Yi(max) - Y = 2.97
lower = [Y-Yi(min)]/S = 2.239 < 2.681 (p=15, 5%)
upper = [Yi(max)-Y]/S = 1.086 < 2.681 (p=15, 5%)

3) Calculation of r and R

Mean; Y = S1 / p =	515.88	
$Sr^2 = S3 / p =$	10.481	Sr = 3.237
$SL^2 = [(pS2-S1^2)/p(p-1)]-(Sr^2/n) =$	5.498	SL = 2.345
$SR^2 = Sr^2 + SL^2 =$	15.979	SR = 3.997

r = 2.8 x Sr =	9.064
R = 2.8 x SR =	11.192
RSDr = (Sr / mean) x 100 =	0.627
RSDR = (SR / mean) x 100 =	0.775

Horwitz's Value = 2 ^[1 - 0.5 x log(Y / 1000)] = 2.210

RSDr and RSDR < 2.21 (Horwitz's Value)

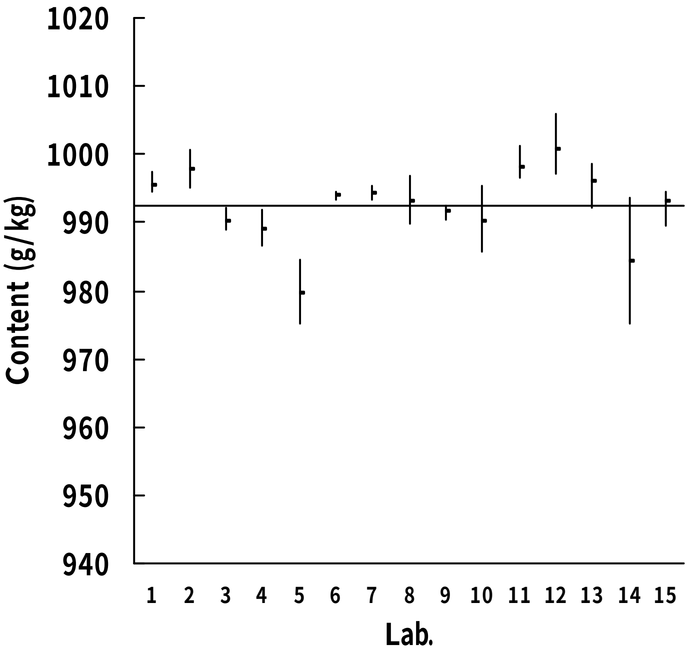

Fig. 1 Flumioxazin Technical-1

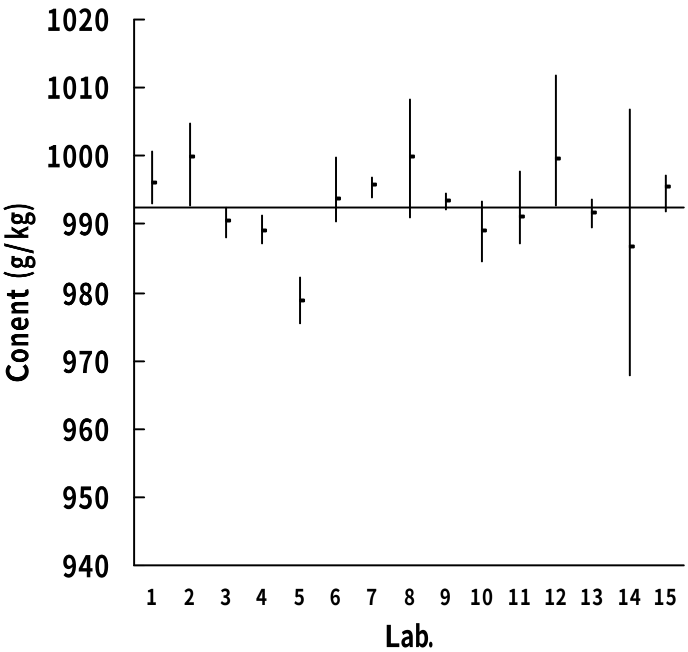

Fig. 2 Flumioxazin Technical-2

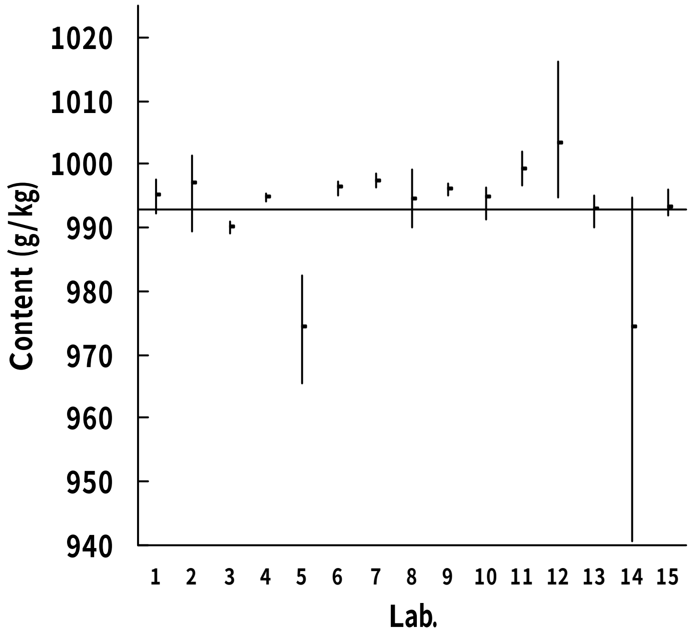

Fig. 3 Flumioxazin Technical-3

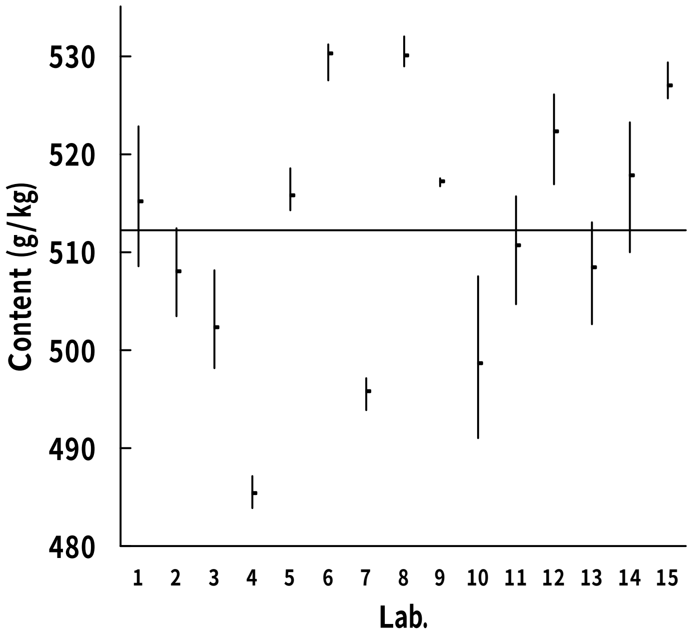

Fig. 4 Flumioxazin Wettable Powder-1

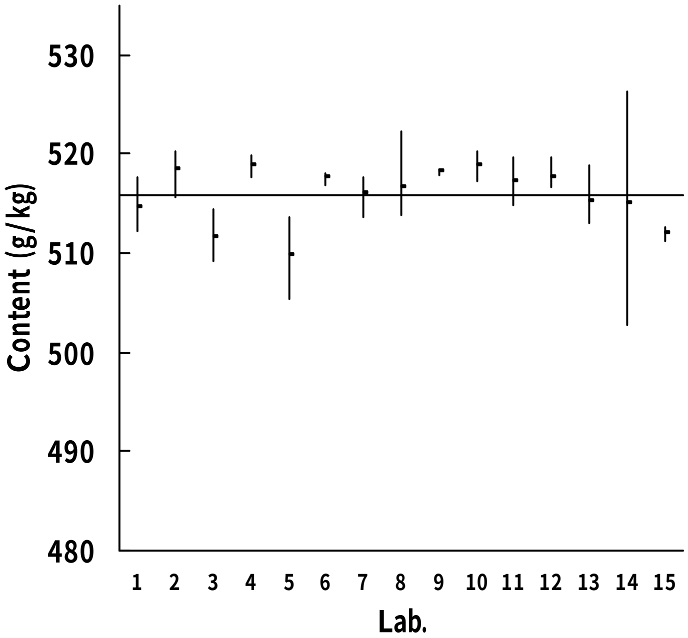

Fig. 5 Flumioxazin Wettable Powder-2