FENITROTHION (No.35)

CIPAC Collaborative Trial

CIPAC Collaborative Trial on the Determination of Fenitrothion in Fenitrothion Technical and Formulations by High Performance Liquid Chromatography

by
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1. INTRODUCTION

1.1 Scope

The results of the CIPAC collaborative trial for fenitrothion technical product, fenitrothion wettable powder, fenitrothion emulsifiable concentrate, and fenitrothion ultra-low volume liquid are reported.

1.2 Samples

1) Fenitrothion technical (TC)
2) Fenitrothion wettable powder (WP)
3) Fenitrothion emulsifiable concentrate (EC-1)
4) Fenitrothion emulsifiable concentrate (EC-2)
5) Fenitrothion ultra-low volume liquid (UL-1)
6) Fenitrothion ultra-low volume liquid (UL-2)

1.3 Participants

Carel Diepenhorst	Cerexagri B.V. (the Netherlands)
Hai-tung Feng	Taiwan Agricultural Chemical and Toxic Substances Research Institute (the Republic of China)
Helen Karasali and G. Balayiannis	Benaki Phytopathological Institute (Greece)
Jim Garvey	Pesticide Control Laboratory (Ireland)
Juliana Schlosserová	Central Control and Testing Institute in Agriculture (Slovak Republic)
Luis Manso	Laboratorio Arbitral Agroalimentario, Ministerio de Agricultura, Pescay Alimentacion (Spain)
Michael Cichy	Bayer CropScience GmbH (Germany)
Philip Jutsum	CEMAS Ltd. (UK)

See Geok Heon	Sumitomo Chemical Enviro-Agro Asia Pacific SDN BHD (Malaysia)
Steven Ha	Valent Technical Center (USA)
Teodora Iurascu	Central Laboratory for Phytosanitary Quarantine, Laboratory for Quality Control of Pesticides (Romania)
Vanessa Lecocq	Walloon Agricultural Research Centre (CRA-W), Pesticides Research Department (Belgium)
Vitali Chmil and Vladimir Michailov	Medved's Institute of Ecohygiene and Toxicology (Ukraine)
Xuejuan Wang	Institute for the Control of Agrochemicals, Hebei Province (People's Republic of China)

2. ANALYTICAL METHOD

2.1 Outline of Method

Fenitrothion in the test samples is determined by normal phase high performance liquid chromatography using a CN column, UV detection at 268 nm and external standardisation as stated in CIPAC/4602/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

Lab	Liquid chromatograph Integrator	Column	Mobile phase	Flow rate (ml/min)	Inj. volume (µl)
Proposed Method		Zorbax CN (4.6 mm ID × 25 cm, 5 µm)	*n*-Heptane - 1-Butanol, 100 + 1	1.0	10
1	Agilent 1100 Series LC/DAD Agilent Chemstation Series LC3D Version L3.01.03	Zorbax CN (4.6 mm ID × 25 cm, 5 µm)	*n*-Heptane - 1-Butanol, 100 + 1	1.0	10
2	Agilent 1100 Hpchem	Phenomenex Luna Silica(2) (4.6 mm ID × 25 cm, 5 µm)	*n*-Heptane - 2-propanol, 100 + 1	2.0	10
3	Agilent 1100 Chemstation	Zorbax CN (4.6 mm ID × 25 cm, 5 µm)	*n*-Heptane - 1-Butanol, 100 + 1	1.0	10
4	Agilent HPLC 1200 Chemstation	Zorbax CN (4.6 mm ID × 25 cm, 5 µm)	*n*-Heptane - 1-Butanol, 100 + 1	1.0	10
5	Agilent Series 1100 Dionex Chromeleon	Zorbax CN (4.6 mm ID × 25 cm, 5 µm)	*n*-Heptane - 1-Butanol, 100 + 1	1.0	10
6	Agilent 1100 Chemstation	Zorbax CN (4.6 mm ID × 25 cm, 5 µm)	*n*-Heptane - 1-Butanol, 100 + 1	1.1	10
7	Varian Prostar 240 Star software	Nucleosil CN (4.6 mm ID × 25 cm, 5 µm)	*n*-Heptane - 1-Butanol, 100 + 1	0.8	10

8	Agilent 1100 series Agilent HPLC^{3D} ChemStation (DOS series)	Macherey-Nagel CC 250/4 Nucleosil 100-5 CN (4 mm ID × 25 cm, 5 μm)	*n*-Heptane - 1-Butanol, 100 + 1	0.5	10
9	Dalian Elite Scientific Instruments WDL-95 Workstation	Nucleosil CN (4 mm ID × 25 cm, 5 μm)	*n*-Heptane - 1-Butanol, 100 + 1	0.8	5
10	Agilent 1100 Agilent HP ChemStation	Zorbax CN (4.6 mm ID × 25 cm, 5 μm)	*n*-Heptane - 1-Butanol, 100 + 1	1.0	10
11	Varian Pro Star Varian MS workstation	Lichrosorb CN (4 mm ID × 25 cm, 5 μm)	*n*-Heptane - 1-Butanol, 100 + 1	0.6	10
12	BECKMAN 126 32 Karat Software Version 5.0	Zorbax CN (4.6 mm ID × 25 cm, 5 μm)	*n*-Heptane - 1-Butanol, 100 + 1	1.0	20
13	Nomal Phase Chromatography Automatic	Waters Nova-pak CN HP (3.9 mm ID × 15 cm, 4 μm)	*n*-Heptane - 1-Butanol, 100 + 0.04	1.0	5
14	Agilent 1100 Series Chemstation	Zorbax CN (4.6 mm ID × 25 cm, 5 μm)	*n*-Heptane - 1-Butanol, 100 + 1	1.0	10

3.2 Remarks

- Lab.1
  - On Day 1, working standard solutions only were made up in heptane.
  - On day 1 an error was made with the heptane -butanol mix, 100+10 v/v was made up in error and used to dissolve the samples due to a shortage of solvent. Subsequent 1/4 dilutions were made with the

correct mobile phase (100+1). On day 2 the correct solvent mix was used.
- The run-time for a single injection seems very long.
- Samples were made up 6.3mls to 25mls instead of 5mls to 20mls as suggested by the method.

- Lab.2
  - Silica column has been used because of its better performance.
  - Mobile phase gradient has been modified to make shorter the run.
  - Less amount of standards and samples has been weighed to avoid dilutions.

- Lab.5
  - Samples were stored by room temperature.
  - Samples were not completely dissolved and filtered before injection.

- Lab.8
  - The flow rate was adapted to the column used.
  - For EC formulations, the product did not disperse well in the solvent.

- Lab.10
  - The linearity was performed on the different day from the trial. (Same instrument was used.)

- Lab.13
  - The standard and samples were weighed into 50-mL volumetric flasks.
  - The calibration solution was prepared aside from standard solution for linearity check and stabilization confirmation.

- Lab.14
  - The second analytical value of UL-1 on Day 1 was corrected to 485.9 (g/kg) from 647.8 (g/kg). This was due to preparation error.
  - For standard and sample preparation we used 50 ml volumetric flasks instead of 100 ml with sufficient sample to contain about 50 mg of fenitrothion.
  - Because of a lack of 20 ml flasks, the dilution was made by transferring 5 ml of this solution into a 25 ml volumetric flask and adding by pipette 15 ml of mobile phase.

4. RESULTS AND DISCUSSION

The samples were sent to fifteen laboratories and fourteen of them returned results. The fifteenth laboratory informed the organizer that the laboratory would not be able to perform the trial due to surgical intervention of the participant prior to the trial. Summary and detailed statistical evaluations are shown in Tables 1 and 2-1 to 2-6. The statistical evaluations were carried out according to ISO 5725.
The discussion on stragglers and outliers is as follows:

- TC
  The variance of Lab. 6 was identified as a straggler. The data were retained because there were no reasons to remove them.

- EC-1
  The variance of Lab. 4 was identified as an outlier and the mean value of Lab.5 was identified as a straggler. The data were retained because there were no reasons to remove them.

- EC-2
  The variance of Lab. 4 was identified as an outlier and the mean value of Lab.5 was identified as an outlier. The data were retained because there were no reasons to remove them.

- UL-2
  The variance of Lab. 4 was identified as an outlier. The data were retained because there were no reasons to remove them.

5. CONCLUSION

For all samples, the values of RSD_R (reproducibility relative standard deviation) were smaller than those calculated by Horwitz's equation. The proposed method is considered appropriate for the determination of fenitrothion in technical product, wettable powder, emulsifiable concentrate and ultra-low volume liquid.
JAPAC proposes that the method be accepted as a provisional CIPAC method.

Table 1 Summary of Statistical Evaluation of Fenitrothion CIPAC Collaborative Study

	TC	WP	EC-1	EC-2	UL-1	UL-2
Average (g/kg)	962.07	417.94	478.91	788.56	487.73	808.69
Number of labs.	14	14	14	14	14	14
Repeatability standard deviation (S_r)	5.839	2.956	4.891	6.264	3.728	6.182
"Pure" between laboratory standard deviation (S_L)	10.574	5.603	6.061	5.600	5.164	8.744
Reproducibility standard deviation (S_R)	12.079	6.335	7.789	8.402	6.369	10.709
Repeatability (r)	16.349	8.277	13.695	17.539	10.438	17.310
Reproducibility (R)	33.821	17.738	21.809	23.526	17.833	29.985
RSD_r	0.607	0.707	1.021	0.794	0.764	0.764
RSD_R	1.256	1.516	1.626	1.065	1.306	1.324
Horwitz's value	2.012	2.281	2.234	2.073	2.228	2.065

Table 2-1 Fenitrothion Technical

Lab		Analytical data (n=4)		Yi	$(Yi)^2$	Si	Si^2
1	Day1	963.6	968.1				
	Day2	953.6	963.6	962.23	925886.57	6.129	37.565
2	Day1	971.6	970.0				
	Day2	970.2	970.4	970.55	941967.30	0.719	0.517
3	Day1	967.5	967.4				
	Day2	967.6	971.3	968.45	937895.40	1.902	3.618
4	Day1	975.3	972.2				
	Day2	966.2	966.9	970.15	941191.02	4.355	18.966
5	Day1	939.5	948.1				
	Day2	933.4	934.1	938.78	881307.89	6.788	46.077
6	Day1	971.9	945.1				*
	Day2	947.8	954.1	954.73	911509.37	12.055	145.323
7	Day1	933.2	944.1				
	Day2	939.6	930.7	936.90	877781.61	6.090	37.088
8	Day1	964.1	966.2				
	Day2	966.7	967.7	966.18	933503.79	1.517	2.301
9	Day1	960.9	972.8				
	Day2	969.9	961.5	966.28	933697.04	5.984	35.808
10	Day1	965.6	970.2				
	Day2	963.1	966.2	966.28	933697.04	2.941	8.649
11	Day1	968.5	965.8				
	Day2	968.8	968.6	967.93	936888.48	1.422	2.022
12	Day1	975.6	970.5				
	Day2	960.8	962.5	967.35	935766.02	6.938	48.136
13	Day1	960.8	969.5				
	Day2	972.9	965.5	967.18	935437.15	5.216	27.207
14	Day1	978.0	963.0				
	Day2	962.0	961.2	966.05	933252.60	8.001	64.016
S1 SUM		Yi =		13469.04			
S2 SUM		Yi^2 =			12959781.28		
S3 SUM		Si^2 =					477.293
							p = 14

1) Cochran's test (p=14, n=4)

$C = Si^2max / S3$ = 0.304 > 0.291 (p=14, n=4, 5%)
< 0.349 (p=14, n=4, 1%)

Straggler Lab 6 was included in the following evaluation.

2) Grubbs' test (p=14, n=4)

Yi(min) = 936.90 Yi(max) = 970.55 Y = S1/p 962.07
S = 10.969

Y - Yi(min) = 25.17
Yi(max) - Y = 8.48
lower = [Y-Yi(min)]/S = 2.295 < 2.507 (p=14, 5%)
upper = [Yi(max)-Y]/S = 0.773 < 2.507 (p=14, 5%)

3) Calculation of r and R

Mean; Y = S1 / p = 962.07
$Sr^2 = S3 / p$ = 34.092 Sr = 5.839
$SL^2 = [(pS2-S1^2)/p(p-1)]-(Sr^2/n)$ = 111.803 SL = 10.574
$SR^2 = Sr^2 + SL^2$ = 145.896 SR = 12.079

r = 2.8 x Sr =	16.349
R = 2.8 x SR =	33.821
RSDr = (Sr / mean) x 100 =	0.607
RSDR = (SR / mean) x 100 =	1.256

Horwitz's Value = 2 ^[1 - 0.5 x log(Y / 1000)] = 2.012

RSDr and RSDR < 2.012 (Horwitz's Value)

Table 2-2 Fenitrothion Wettable Powder

Lab		Analytical data (n=4)		Yi	$(Yi)^2$	Si	Si^2
1	Day1	419.5	417.2				
	Day2	417.4	419.0	418.28	174958.16	1.147	1.316
2	Day1	419.9	419.5				
	Day2	421.9	421.4	420.68	176971.66	1.156	1.336
3	Day1	417.9	420.2				
	Day2	420.6	419.6	419.58	176047.38	1.190	1.416
4	Day1	426.4	423.7				
	Day2	421.9	421.3	423.33	179208.29	2.290	5.244
5	Day1	404.8	408.8				
	Day2	402.9	401.8	404.58	163684.98	3.077	9.468
6	Day1	420.3	422.4				
	Day2	422.6	415.4	420.18	176551.23	3.349	11.216
7	Day1	426.4	426.2				
	Day2	421.5	419.7	423.45	179309.90	3.373	11.377
8	Day1	421.4	421.1				
	Day2	420.3	424.8	421.90	177999.61	1.988	3.952
9	Day1	418.2	419.9				
	Day2	415.8	417.5	417.85	174598.62	1.698	2.883
10	Day1	428.1	419.2				
	Day2	418.1	417.2	420.65	176946.42	5.034	25.341
11	Day1	417.5	418.3				
	Day2	418.7	417.4	417.98	174707.28	0.629	0.396
12	Day1	408.1	401.3				
	Day2	405.5	406.5	405.35	164308.62	2.905	8.439
13	Day1	423.4	420.9				
	Day2	415.5	417.3	419.28	175795.72	3.550	12.603
14	Day1	417.5	422.6				
	Day2	410.9	421.2	418.05	174765.80	5.230	27.353
S1 SUM		Yi =		5851.14			
S2 SUM		Yi^2 =			2445853.67		
S3 SUM		Si^2 =					122.340

p = 14

1) Cochran's test (p=14, n=4)

C = Si^2max / S3 = 0.224 < 0.291 (p=14, n=4, 5%)

2) Grubbs' test (p=14, n=4)

Yi(min) = 404.58 Yi(max) = 423.45 Y = S1/p 417.94

S = 5.795

Y - Yi(min) = 13.36

Yi(max) - Y = 5.51

lower = [Y-Yi(min)]/S = 2.305 < 2.507 (p=14, 5%)

upper = [Yi(max)-Y]/S = 0.951 < 2.507 (p=14, 5%)

3) Calculation of r and R

Mean; Y = S1 / p = 417.94

Sr^2 = S3 / p = 8.739 Sr = 2.956

SL^2 = [(pS2-$S1^2$)/p(p-1)]-(Sr^2/n) = 31.398 SL = 5.603

SR^2 = Sr^2 + SL^2 = 40.137 SR = 6.335

r = 2.8 x Sr =	8.277
R = 2.8 x SR =	17.738
RSDr = (Sr / mean) x 100 =	0.707
RSDR = (SR / mean) x 100 =	1.516

Horwitz's Value = 2 ^[1 - 0.5 x log(Y / 1000)] = 2.281

RSDr and RSDR < 2.281 (Horwitz's Value)

Table 2-3 Fenitrothion Emulsifiable Concentrate-1

Lab		Analytical data (n=4)		Yi	$(Yi)^2$	Si	Si^2
1	Day1	470.6	474.9				
	Day2	476.5	480.2	475.55	226147.80	3.977	15.817
2	Day1	485.5	484.3				
	Day2	488.8	485.5	486.03	236225.16	1.935	3.744
3	Day1	482.3	483.6				
	Day2	484.9	479.8	482.65	232951.02	2.176	4.735
4	Day1	483.3	485.8				**
	Day2	473.9	460.6	475.90	226480.81	11.414	130.279
5	Day1	460.0	462.8	*			
	Day2	463.6	458.6	461.25	212751.56	2.346	5.504
6	Day1	478.4	476.2				
	Day2	477.9	482.5	478.75	229201.56	2.671	7.134
7	Day1	483.5	496.9				
	Day2	483.7	483.4	486.88	237052.13	6.684	44.676
8	Day1	479.6	464.1				
	Day2	472.7	479.3	473.93	224609.64	7.283	53.042
9	Day1	485.4	487.3				
	Day2	479.5	487.0	484.80	235031.04	3.630	13.177
10	Day1	483.2	482.7				
	Day2	487.1	475.6	482.15	232468.62	4.789	22.935
11	Day1	479.3	478.0				
	Day2	481.4	481.8	480.13	230524.82	1.791	3.208
12	Day1	486.8	480.5				
	Day2	478.0	480.4	481.43	231774.84	3.765	14.175
13	Day1	478.0	478.8				
	Day2	481.5	482.7	480.25	230640.06	2.216	4.911
14	Day1	480.1	473.6				
	Day2	473.2	473.1	475.00	225625.00	3.407	11.608
S1 SUM		Yi =		6704.70			
S2 SUM		Yi^2 =			3211484.06		
S3 SUM		Si^2 =					334.945

p = 14

1) Cochran's test (p=14, n=4)

C = Si^2max / S3 = 0.389 > 0.291 (p=14, n=4, 5%)
> 0.349 (p=14, n=4, 1%)

Outlier Lab 4 was included in the following evaluation.

2) Grubbs' test (p=14, n=4)

Yi(min) = 461.25 Yi(max) = 486.88 Y = S1/p 478.91
S = 6.536

Y - Yi(min) = 17.66
Yi(max) - Y = 7.97
lower = [Y-Yi(min)]/S = 2.701 > 2.507 (p=14, 5%)
< 2.755 (p=14, 1%)
upper = [Yi(max)-Y]/S = 1.220 < 2.507 (p=14, 5%)

Straggler Lab 5 was included in the following evaluation.

3) Calculation of r and R

Mean; Y = S1 / p = 478.91
Sr^2 = S3 / p = 23.925 Sr = 4.891
SL^2 = [(pS2-$S1^2$)/p(p-1)]-(Sr^2/n) = 36.737 SL = 6.061
SR^2 = Sr^2 + SL^2 = 60.662 SR = 7.789

r = 2.8 x Sr =	13.695
R = 2.8 x SR =	21.809
RSDr = (Sr / mean) x 100 =	1.021
RSDR = (SR / mean) x 100 =	1.626

Horwitz's Value = 2 ^[1 - 0.5 x log(Y / 1000)] = 2.234

Table 2-4 Fenitrothion Emulsifiable Concentrate-2

Lab		Analytical data (n=4)		Yi	$(Yi)^2$	Si	Si^2
1	Day1	790.3	785.4				
	Day2	784.4	788.0	787.03	619416.22	2.659	7.070
2	Day1	794.2	793.5				
	Day2	799.5	797.0	796.05	633695.60	2.753	7.579
3	Day1	786.8	780.7				
	Day2	784.5	787.2	784.80	615911.04	2.981	8.886
4	Day1	798.6	805.1				**
	Day2	788.1	769.2	790.25	624495.06	15.684	245.988
5	Day1	773.2	769.3	**			
	Day2	765.5	774.9	770.73	594024.73	4.199	17.632
6	Day1	788.0	790.9				
	Day2	790.4	799.2	792.13	627469.94	4.884	23.853
7	Day1	788.2	790.1				
	Day2	793.7	790.1	790.53	624937.68	2.298	5.281
8	Day1	786.4	770.8				
	Day2	792.7	788.0	784.48	615408.87	9.501	90.269
9	Day1	789.3	790.9				
	Day2	781.8	785.7	786.93	619258.82	4.050	16.403
10	Day1	795.3	794.6				
	Day2	791.4	790.3	792.90	628690.41	2.426	5.885
11	Day1	797.8	797.3				
	Day2	797.3	797.9	797.58	636133.86	0.320	0.102
12	Day1	789.1	791.6				
	Day2	785.2	791.0	789.23	622883.99	2.887	8.335
13	Day1	797.3	787.3				
	Day2	783.0	780.2	786.95	619290.30	7.492	56.130
14	Day1	796.4	796.9				
	Day2	784.5	783.0	790.20	624416.04	7.476	55.891
S1 SUM		Yi =		11039.79			
S2 SUM		Yi^2 =			8706032.56		
S3 SUM		Si^2 =					549.304

p = 14

1) Cochran's test (p=14, n=4)

C = Si^2max / S3 = 0.448 > 0.291 (p=14, n=4, 5%)
> 0.349 (p=14, n=4, 1%)

Outlier Lab 4 was included in the following evaluation.

2) Grubbs' test (p=14, n=4)

Yi(min) = 770.73 Yi(max) = 797.58 Y = S1/p 788.56
S = 6.416

Y - Yi(min) = 17.83
Yi(max) - Y = 9.02
lower = [Y-Yi(min)]/S = 2.778 > 2.507 (p=14, 5%)
> 2.755 (p=14, 1%)
upper = [Yi(max)-Y]/S = 1.406 < 2.507 (p=14, 5%)

Outlier Lab 5 was included in the following evaluation.

3) Calculation of r and R

Mean; Y = S1 / p = 788.56
Sr^2 = S3 / p = 39.236 Sr = 6.264
SL^2 = [(pS2-$S1^2$)/p(p-1)]-(Sr^2/n) = 31.359 SL = 5.600
SR^2 = Sr^2 + SL^2 = 70.595 SR = 8.402

r = 2.8 x Sr =	17.539
R = 2.8 x SR =	23.526
RSDr = (Sr / mean) x 100 =	0.794
RSDR = (SR / mean) x 100 =	1.065

Horwitz's Value = 2 ^[1 - 0.5 x log(Y / 1000)] = 2.073

Table 2-5 Fenitrothion Ultra-Low Volume Liquid-1

Lab		Analytical data (n=4)		Yi	$(Yi)^2$	Si	Si^2
1	Day1	484.7	490.9				
	Day2	492.8	492.8	490.30	240394.09	3.839	14.738
2	Day1	491.8	491.0				
	Day2	490.4	490.6	490.95	241031.90	0.619	0.383
3	Day1	493.3	491.8				
	Day2	494.6	490.5	492.55	242605.50	1.782	3.176
4	Day1	497.6	494.6				
	Day2	485.9	482.4	490.13	240227.42	7.151	51.137
5	Day1	480.0	481.0				
	Day2	471.8	474.6	476.85	227385.92	4.386	19.237
6	Day1	490.3	494.0				
	Day2	494.0	491.0	492.33	242388.83	1.955	3.822
7	Day1	477.9	479.9				
	Day2	472.4	480.5	477.68	228178.18	3.688	13.601
8	Day1	493.1	492.0				
	Day2	492.3	491.3	492.18	242241.15	0.746	0.557
9	Day1	492.9	499.4				
	Day2	492.0	496.9	495.30	245322.09	3.465	12.006
10	Day1	492.6	475.6				
	Day2	487.3	486.9	485.60	235807.36	7.155	51.194
11	Day1	488.2	488.6				
	Day2	488.5	487.8	488.28	238417.36	0.359	0.129
12	Day1	489.0	480.1				
	Day2	485.4	480.1	483.65	233917.32	4.355	18.966
13	Day1	487.0	486.3				
	Day2	489.4	486.2	487.23	237393.07	1.493	2.229
14	Day1	486.1	485.9				
	Day2	482.4	486.3	485.18	235399.63	1.857	3.448
S1 SUM		Yi =		6828.21			
S2 SUM		Yi^2 =			3330709.82		
S3 SUM		Si^2 =					194.623

p = 14

1) Cochran's test (p=14, n=4)

C = Si^2max / S3 = 0.263 < 0.291 (p=14, n=4, 5%)

2) Grubbs' test (p=14, n=4)

Yi(min) = 476.85 Yi(max) = 495.30 Y = S1/p 487.73

S = 5.490

Y - Yi(min) = 10.88

Yi(max) - Y = 7.57

lower = [Y-Yi(min)]/S = 1.982 < 2.507 (p=14, 5%)

upper = [Yi(max)-Y]/S = 1.379 < 2.507 (p=14, 5%)

3) Calculation of r and R

Mean; Y = S1 / p = 487.73

Sr^2 = S3 / p = 13.902 Sr = 3.728

SL^2 = [(pS2-$S1^2$)/p(p-1)]-(Sr^2/n) = 26.666 SL = 5.164

SR^2 = Sr^2 + SL^2 = 40.567 SR = 6.369

r = 2.8 x Sr =	10.438
R = 2.8 x SR =	17.833
RSDr = (Sr / mean) x 100 =	0.764
RSDR = (SR / mean) x 100 =	1.306

Horwitz's Value = 2 ^[1 - 0.5 x log(Y / 1000)] = 2.228

RSDr and RSDR < 2.228 (Horwitz's Value)

Table 2-6 Fenitrothion Ultra-Low Volume Liquid-2

Lab		Analytical data (n=4)		Yi	$(Yi)^2$	Si	Si^2
1	Day1	799.2	810.1				
	Day2	813.2	801.0	805.88	649442.57	6.827	46.608
2	Day1	815.9	814.9				
	Day2	814.2	817.8	815.70	665366.49	1.564	2.446
3	Day1	812.0	810.5				
	Day2	809.1	810.4	810.50	656910.25	1.186	1.407
4	Day1	830.1	825.9				**
	Day2	807.2	797.1	815.08	664355.41	15.578	242.674
5	Day1	799.0	797.6				
	Day2	789.9	787.4	793.48	629610.51	5.693	32.410
6	Day1	819.1	815.3				
	Day2	824.9	827.5	821.70	675190.89	5.526	30.537
7	Day1	790.1	791.6				
	Day2	789.0	799.3	792.50	628056.25	4.657	21.688
8	Day1	818.0	814.1				
	Day2	817.4	818.1	816.90	667325.61	1.892	3.580
9	Day1	814.3	816.8				
	Day2	806.4	817.0	813.63	661993.78	4.971	24.711
10	Day1	819.0	812.7				
	Day2	810.6	827.2	817.38	668110.06	7.459	55.637
11	Day1	796.3	796.8				
	Day2	797.0	797.0	796.78	634858.37	0.330	0.109
12	Day1	811.0	806.5				
	Day2	799.9	792.9	802.58	644134.66	7.898	62.378
13	Day1	810.2	808.4				
	Day2	805.5	808.3	808.10	653025.61	1.941	3.767
14	Day1	812.1	814.9				
	Day2	809.5	809.2	811.43	658418.64	2.658	7.065
S1 SUM		Yi =		11321.64			
S2 SUM		Yi^2 =			9156799.10		
S3 SUM		Si^2 =					535.017

p = 14

1) Cochran's test (p=14, n=4)

C = Si^2max / S3 = 0.454 > 0.291 (p=14, n=4, 5%)
> 0.349 (p=14, n=4, 1%)

Outlier Lab 4 was included in the following evaluation.

2) Grubbs' test (p=14, n=4)

Yi(min) = 792.50 Yi(max) = 821.70 Y = S1/p 808.69
S = 9.275

Y - Yi(min) = 16.19
Yi(max) - Y = 13.01
lower = [Y-Yi(min)]/S = 1.745 < 2.507 (p=14, 5%)
upper = [Yi(max)-Y]/S = 1.403 < 2.507 (p=14, 5%)

3) Calculation of r and R

Mean; Y = S1 / p = 808.69
Sr^2 = S3 / p = 38.216 Sr = 6.182
SL^2 = [(pS2-$S1^2$)/p(p-1)]-(Sr^2/n) = 76.463 SL = 8.744
SR^2 = Sr^2 + SL^2 = 114.679 SR = 10.709

r = 2.8 x Sr =	17.310
R = 2.8 x SR =	29.985
RSDr = (Sr / mean) x 100 =	0.764
RSDR = (SR / mean) x 100 =	1.324

Horwitz's Value = 2 ^[1 - 0.5 x log(Y / 1000)] = 2.065

RSDr and RSDR < 2.065 (Horwitz's Value)

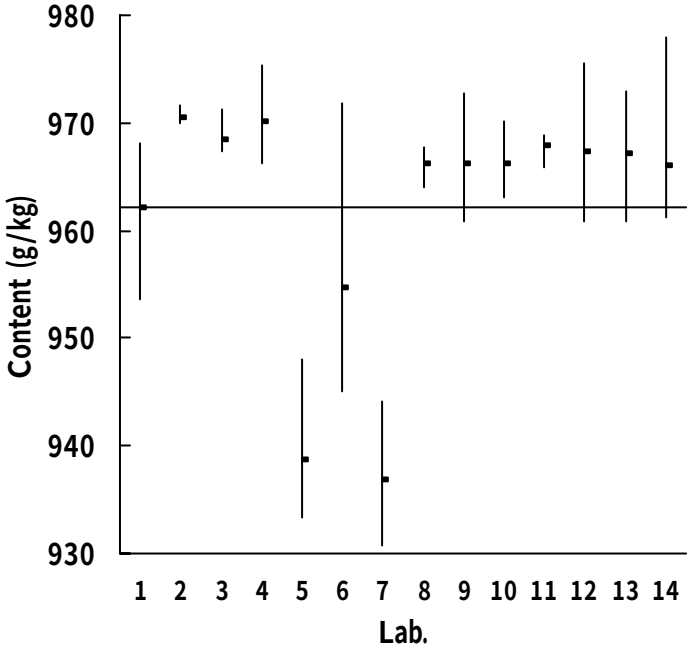

Fig. 1 Fenitrothion Technical

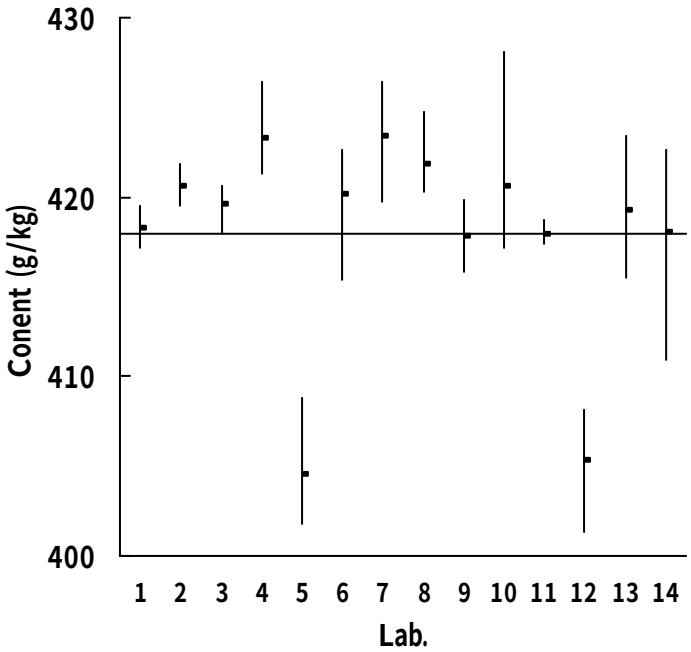

Fig. 2 Fenitrothion Wettable Powder

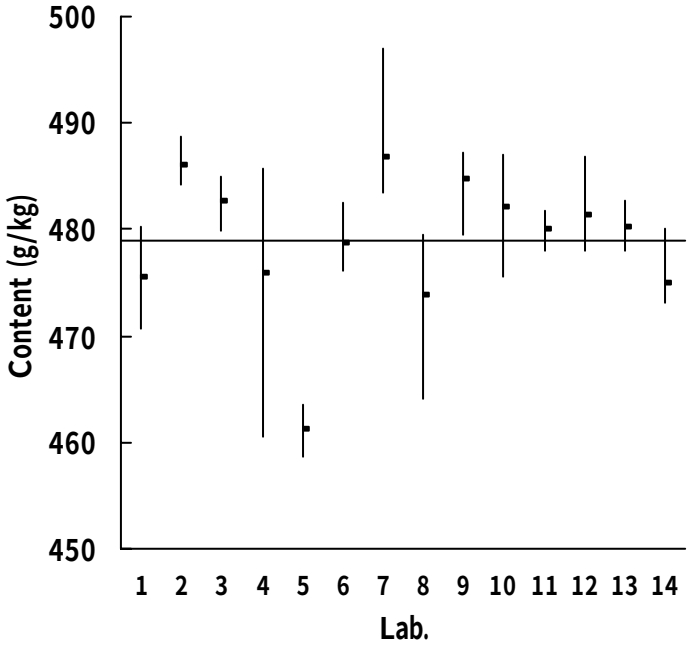

Fig. 3 Fenitrothion Emulsifiable Concentrate-1

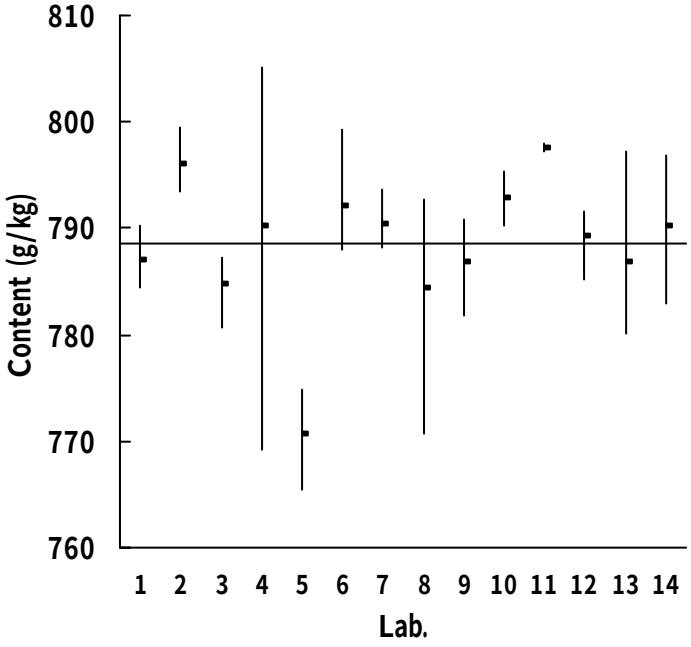

Fig. 4 Fenitrothion Emulsifiable Concentrate-2

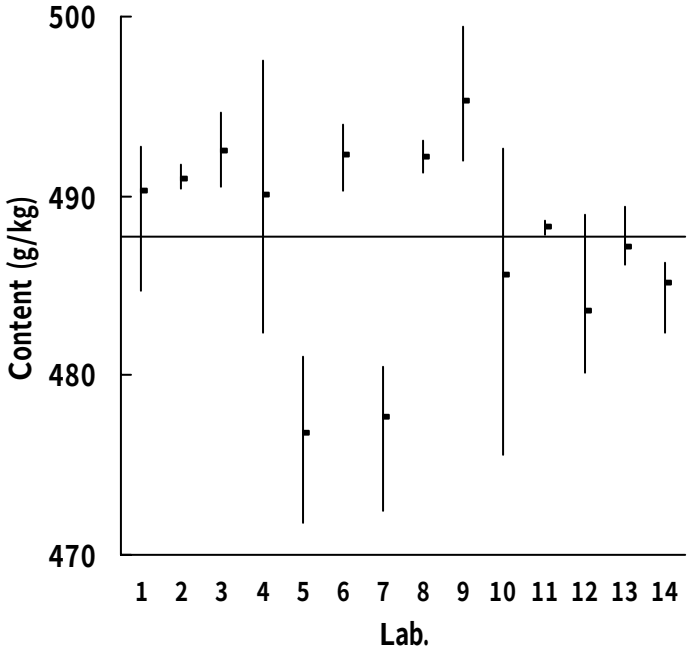

Fig. 5 Fenitrothion Ultra-Low Volume Liquid-1

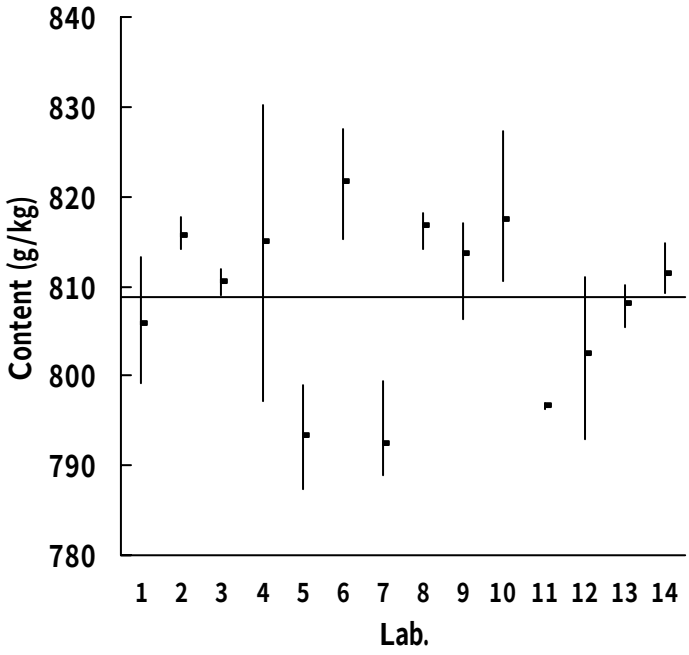

Fig. 6 Fenitrothion Ultra-Low Volume Liquid-2