METOFLUTHRIN (No.993)

Small Scale Collaborative Trial

Small Scale Collaborative Trial on the Determination of Metofluthrin in Metofluthrin Technical and Formulation by Gas Chromatography

by
Kiyoko Miyakawa
Sumitomo Chemical Co., Ltd.
Environmental Health Science Laboratory
3-1-98, Kasugade-naka, Konohanaku, Osaka
JAPAN

Table of Contents

1. INTRODUCTION

1.1 Scope

The results of the small scale collaborative trial for metofluthrin technical product and metofluthrin emulsion, oil in water are reported.

1.2 Samples

1) Metofluthrin technical (TC-1)
2) Metofluthrin technical (TC-2)
3) Metofluthrin technical (TC-3)
4) Metofluthrin emulsion, oil in water (EW-1)*
5) Metofluthrin emulsion, oil in water (EW-2)*

* The sample subjected to this trial was SumiPro, which contains metofluthrin, *d,d-trans*-cyphenothrin and piperonyl butoxide as active ingredients.

1.3 Participants

Kiyoko Miyakawa	Sumitomo Chemical Co., Ltd. Environmental Health Science Laboratory (JAPAN)
Midori Kumazawa	Sumika Chemical Analysis Service, Ltd. Osaka Laboratory (JAPAN)
Sayuri Inada	Sumika Technoservice Corporation (JAPAN)
Takashi Shiota	Taoka Chemical Analysis Center Co., Ltd. (JAPAN)

2. ANALYTICAL METHOD

2.1 Outline of Method

Metofluthrin in the test samples is determined by capillary gas chromatography using flame ionisation detection and fluoranthene as internal standard, as stated in CIPAC/5086/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	Gas chromatograph Integrator	Column	Column temp (°C)	Carrier gas (cm/sec)	Split flow (ml/min)
Proposed Method		DB-5 (0.25 mm ID × 30 m, 0.25 μm)	160	He, 30	50 for TC 10 for EW
1	Shimadzu GC-2010 Shimadzu GCsolution	DB-5 (0.25 mm ID × 30 m, 0.25 μm)	168	He, 30	50 for TC 10 for EW
2	Shimadzu GC-2010 Shimadzu GCsolution	DB-5 (0.25 mm ID × 30 m, 0.25 μm)	170	He, 30	50 for TC 10 for EW
3	Shimadzu GC-2010 Shimadzu GCsolution	DB-5 (0.25 mm ID × 30 m, 0.25 μm)	173	He, 30	49.8 for TC 10 for EW
4	Shimadzu GC-2010 Shimadzu LabSolution	DB-5 (0.25 mm ID × 30 m, 0.25 μm)	173	He, 30	50 for TC 10 for EW

3.2 Remarks

- Lab.1
  - Column temperature was set at 168°C to adjust the retention time of Metofluthrin.
  - General type of inlet liner was used (for TC and EW).
  - Black residue was found on the wool in the inlet liner after EW analysis.

- Lab.2
  - Column temperature was set at 170°C to adjust the retention time of Metofluthrin.
  - FocusLiner® was used as an inlet liner (for TC and EW).
  - Black residue was found on the wool in the inlet liner after EW analysis.
  - The response factor on the second day of EW analysis deviated by more than 1.0%, which was the criterion indicated in the protocol, and the peak shape became worse when reanalysis was started. The inlet liner was changed to new one and the reanalysis was carried out without any trouble.

- Lab.3
  - Column temperature was set at 173°C to adjust the retention time of Metofluthrin.
  - SKY® liner was used as an inlet liner (for TC and EW).
  - Black residue was found on the wool in the inlet liner after EW analysis.

- Lab.4
  - Column temperature was set at 173°C to adjust the retention time of Metofluthrin.
  - General type of inlet liner was used for TC and SKY® liner was used for EW.
  - Black residue was found on the wool in the inlet liner after EW analysis.
  - Analytical values varied widely after several injections of EW. The inlet liner was changed to new one and the reanalysis was carried out without any trouble.

FocusLiner®: manufactured by SGE Analytical Science
SKY® liner: manufactured by RESTEC

4. RESULTS AND DISCUSSION

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

- TC-1
  The analytical data of Lab. 1 was identified as a straggler. The data were retained because there were no reasons to remove them.

Several types of inlet liner were used in this trial. Although all types of inlet liner allowed the analysis of TC and EW, black residue was found on the wool in the inlet liner after EW analysis and it might have a negative impact on the analysis such as variability of factors and / or analytical values. When the factors and / or analytical values vary widely, the inlet liner should be changed to new one. Additionally, highly deactivated inlet liners such as FocusLiner® and SKY® liner are recommended.

Since response factors for EW analysis deviated from 0.6% to 1.0% in Labs. 1 to 3, the criterion of the deviation of the response factor for EW analysis should be changed from 1.0%, which was the criterion indicated in the protocol, to 2.0%.

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 metofluthrin in technical product and emulsion, oil in water.
JAPAC recommends proceeding to a large scale collaborative trial.

Table 1 Summary of Statistical Evaluation of Metofluthrin Small Scale Collaborative Study

	TC-1	TC-2	TC-3	EW-1	EW-2
Average (g/kg)	966.79	968.12	966.98	0.9620	1.0197
Number of labs.	4	4	4	4	4
Repeatability standard deviation (S_r)	1.330	2.808	1.311	0.01132	0.01018
"Pure" between laboratory standard variation (S_L)	1.355	0.757	1.189	0.01205	0.01610
Reproducibility standard deviation (S_R)	1.899	2.908	1.770	0.01653	0.01905
Repeatability (r)	3.724	7.862	3.671	0.03170	0.02850
Reproducibility (R)	5.317	8.142	4.956	0.04628	0.05334
RSD_r	0.138	0.290	0.136	1.177	0.998
RSD_R	0.196	0.300	0.183	1.718	1.868
Horwitz's value	2.010	2.010	2.010	5.690	5.640

Table 2-1 Metofluthrin TC-1						
Lab	Analytical data (n=4)		Yi	$(Yi)^2$	Si	Si^2
1 Day1	966.7	964.0	*			
Day2	965.5	962.0	964.55	930356.70	2.027	4.109
2 Day1	966.9	967.3				
Day2	967.8	969.0	967.75	936540.06	0.911	0.830
3 Day1	968.9	967.5				
Day2	966.6	967.5	967.63	936307.82	0.950	0.903
4 Day1	965.7	968.0				
Day2	968.1	967.1	967.23	935533.87	1.112	1.237
S1 SUM	Yi =		3867.16			
S2 SUM	Yi^2 =			3738738.45		
S3 SUM	Si^2 =					7.079
					p =	4

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

$C = Si^2max / S3$ = 0.580 < 0.684 (p=4, n=4, 5%)

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

Yi(min) =	964.55	Yi(max) =	967.75	Y = S1/p	966.79
				S =	1.510
Y - Yi(min) =		2.24			
Yi(max) - Y =		0.96			
lower = [Y-Yi(min)]/S =		1.484	> 1.481 (p=4, 5%)		
			< 1.496 (p=4, 1%)		
upper = [Yi(max)-Y]/S		0.636	< 1.481 (p=4, 5%)		

Straggler Lab 1 was included in the following evaluation.

3) Calculation of r and R

Mean; Y = S1 / p =	966.79		
$Sr^2 = S3 / p$ =	1.770	Sr =	1.330
$SL^2 = [(pS2-S1^2)/p(p-1)]-(Sr^2/n)$ =	1.835	SL =	1.355
$SR^2 = Sr^2 + SL^2$ =	3.605	SR =	1.899
r = 2.8 x Sr =	3.724		
R = 2.8 x SR =	5.317		
RSDr = (Sr / mean) x 100 =	0.138		
RSDR = (SR / mean) x 100 =	0.196		
Horwitz's Value = 2 ^[1 - 0.5 x log(Y / 1000)] =		2.010	

RSDr and RSDR < 2.010 (Horwitz's Value)

Table 2-2 Metofluthrin TC-2

Lab		Analytical data (n=4)		Yi	$(Yi)^2$	Si	Si^2
1	Day1	971.4	972.9				
	Day2	966.7	968.3	969.83	940570.23	2.830	8.009
2	Day1	962.4	963.9				
	Day2	971.4	966.6	966.08	933310.57	3.953	15.626
3	Day1	971.7	966.0				
	Day2	969.5	967.9	968.78	938534.69	2.419	5.852
4	Day1	966.7	966.6				
	Day2	969.6	968.3	967.80	936636.84	1.431	2.048
S1 SUM		Yi =		3872.49			
S2 SUM		Yi^2 =			3749052.33		
S3 SUM		Si^2 =					31.535

p = 4

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

$C = Si^2max / S3$ = 0.496 < 0.684 (p=4, n=4, 5%)

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

Yi(min) = 966.08 Yi(max) = 969.83 Y = S1/p 968.12
S = 1.594

Y - Yi(min) = 2.04
Yi(max) - Y = 1.71
lower = [Y-Yi(min)]/S = 1.281 < 1.481 (p=4, 5%)
upper = [Yi(max)-Y]/S = 1.071 < 1.481 (p=4, 5%)

3) Calculation of r and R

Mean; Y = S1 / p = 968.12

$Sr^2 = S3 / p$ = 7.884 Sr = 2.808

$SL^2 = [(pS2-S1^2)/p(p-1)]-(Sr^2/n)$ = 0.572 SL = 0.757

$SR^2 = Sr^2 + SL^2$ = 8.456 SR = 2.908

r = 2.8 x Sr =	7.862
R = 2.8 x SR =	8.142
RSDr = (Sr / mean) x 100 =	0.290
RSDR = (SR / mean) x 100 =	0.300

Horwitz's Value = 2 ^[1 - 0.5 x log(Y / 1000)] = 2.010

RSDr and RSDR < 2.010 (Horwitz's Value)

Table 2-3 Metofluthrin TC-3

Lab		Analytical data (n=4)		Yi	$(Yi)^2$	Si	Si^2
1	Day1	966.0	966.0				
	Day2	966.1	965.4	965.88	932924.17	0.320	0.102
2	Day1	964.9	966.6				
	Day2	964.9	967.4	965.95	933059.40	1.256	1.578
3	Day1	967.6	971.9				
	Day2	967.7	967.8	968.75	938476.56	2.102	4.418
4	Day1	968.4	966.3				
	Day2	967.1	967.6	967.35	935766.02	0.881	0.776
S1 SUM		Yi =		3867.93			
S2 SUM		Yi^2 =			3740226.15		
S3 SUM		Si^2 =					6.874

p = 4

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

C = Si^2max / S3 = 0.643 < 0.684 (p=4, n=4, 5%)

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

Yi(min) = 965.88 Yi(max) = 968.75 Y = S1/p 966.98
S = 1.359

Y - Yi(min) = 1.10
Yi(max) - Y = 1.77
lower = [Y-Yi(min)]/S = 0.811 < 1.481 (p=4, 5%)
upper = [Yi(max)-Y]/S = 1.301 < 1.481 (p=4, 5%)

3) Calculation of r and R

Mean; Y = S1 / p = 966.98
Sr^2 = S3 / p = 1.719 Sr = 1.311
SL^2 = [(pS2-$S1^2$)/p(p-1)]-(Sr^2/n) = 1.413 SL = 1.189
SR^2 = Sr^2 + SL^2 = 3.132 SR = 1.770

r = 2.8 x Sr =	3.671
R = 2.8 x SR =	4.956
RSDr = (Sr / mean) x 100 =	0.136
RSDR = (SR / mean) x 100 =	0.183

Horwitz's Value = 2 ^[1 - 0.5 x log(Y / 1000)] = 2.010

RSDr and RSDR < 2.010 (Horwitz's Value)

Table 2-4 Metofluthrin EW-1

Lab		Analytical data (n=4)		Yi	$(Yi)^2$	Si	Si^2
1	Day1	0.968	0.975				
	Day2	0.979	0.975	0.9743	0.9493	4.573E-03	2.091E-05
2	Day1	0.977	0.985				
	Day2	0.950	0.956	0.9670	0.9351	1.667E-02	2.780E-04
3	Day1	0.951	0.948				
	Day2	0.975	0.973	0.9618	0.9251	1.422E-02	2.022E-04
4	Day1	0.940	0.947				
	Day2	0.947	0.946	0.9450	0.8930	3.367E-03	1.134E-05
S1 SUM		Yi =		3.8481			
S2 SUM		Yi^2 =			3.7025		
S3 SUM		Si^2 =					5.125E-04

p = 4

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

C = Si^2max / S3 = 0.542 < 0.684 (p=4, n=4, 5%)

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

Yi(min) = 0.9450 Yi(max) = 0.9743 Y = S1/p 0.9620
S = 0.0125

Y - Yi(min) = 0.0170
Yi(max) - Y = 0.0123
lower = [Y-Yi(min)]/S = 1.367 < 1.481 (p=4, 5%)
upper = [Yi(max)-Y]/S = 0.986 < 1.481 (p=4, 5%)

3) Calculation of r and R

Mean; Y = S1 / p = 0.9620
Sr^2 = S3 / p = 1.281E-04 Sr = 0.01132
SL^2 = [(pS2-$S1^2$)/p(p-1)]-(Sr^2/n) = 1.452E-04 SL = 0.01205
SR^2 = Sr^2 + SL^2 = 2.733E-04 SR = 0.01653

r = 2.8 x Sr =	0.03170
R = 2.8 x SR =	0.04628
RSDr = (Sr / mean) x 100 =	1.177
RSDR = (SR / mean) x 100 =	1.718

Horwitz's Value = 2 ^[1 - 0.5 x log(Y / 1000)] = 5.690

RSDr and RSDR < 5.690 (Horwitz's Value)

Table 2-5 Metofluthrin EW-2

Lab		Analytical data (n=4)		Yi	$(Yi)^2$	Si	Si^2
1	Day1	1.037	1.035				
	Day2	1.039	1.037	1.0370	1.0754	1.633E-03	2.670E-06
2	Day1	1.037	1.039				
	Day2	1.015	1.015	1.0265	1.0537	1.330E-02	1.770E-04
3	Day1	0.999	1.008				
	Day2	1.027	1.031	1.0163	1.0329	1.526E-02	2.329E-04
4	Day1	1.000	0.998				
	Day2	1.000	0.997	0.9988	0.9976	1.500E-03	2.250E-06
S1 SUM		Yi =		4.0786			
S2 SUM		Yi^2 =			4.1596		
S3 SUM		Si^2 =					4.149E-04

p = 4

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

$C = Si^2max / S3$ = 0.561 < 0.684 (p=4, n=4, 5%)

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

Yi(min) = 0.9988 Yi(max) = 1.0370 Y = S1/p 1.0197
S = 0.0163

Y - Yi(min) = 0.0208
Yi(max) - Y = 0.0174
lower = [Y-Yi(min)]/S = 1.282 < 1.481 (p=4, 5%)
upper = [Yi(max)-Y]/S = 1.067 < 1.481 (p=4, 5%)

3) Calculation of r and R

Mean; Y = S1 / p = 1.0197

$Sr^2 = S3 / p$ = 1.037E-04 Sr = 0.01018

$SL^2 = [(pS2-S1^2)/p(p-1)]-(Sr^2/n)$ = 2.592E-04 SL = 0.01610

$SR^2 = Sr^2 + SL^2$ = 3.630E-04 SR = 0.01905

r = 2.8 x Sr =	0.02850
R = 2.8 x SR =	0.05334
RSDr = (Sr / mean) x 100 =	0.998
RSDR = (SR / mean) x 100 =	1.868

Horwitz's Value = 2 ^[1 - 0.5 x log(Y / 1000)] = 5.640

RSDr and RSDR < 5.640 (Horwitz's Value)

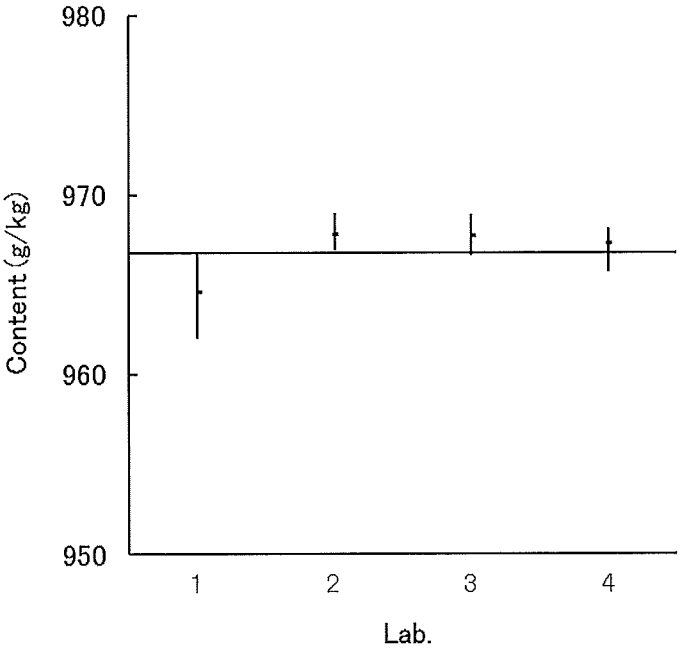

Fig. 1 Metofluthrin TC-1

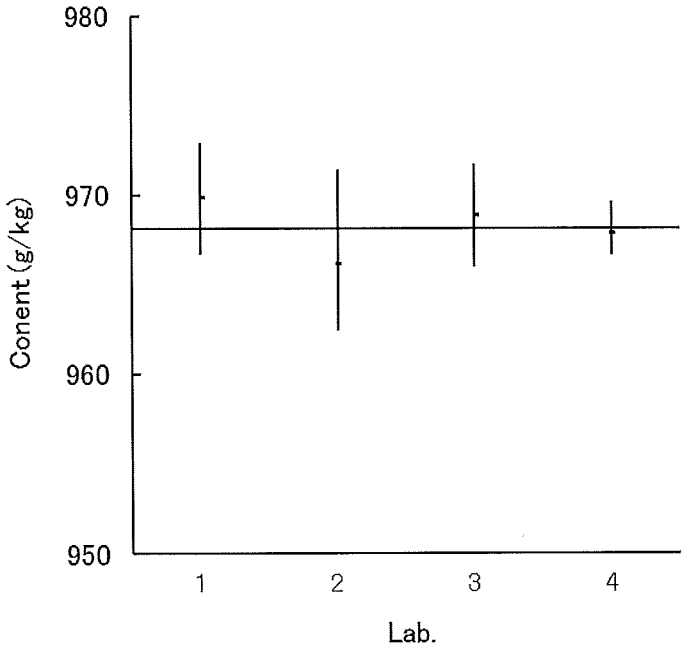

Fig. 2 Metofluthrin TC-2

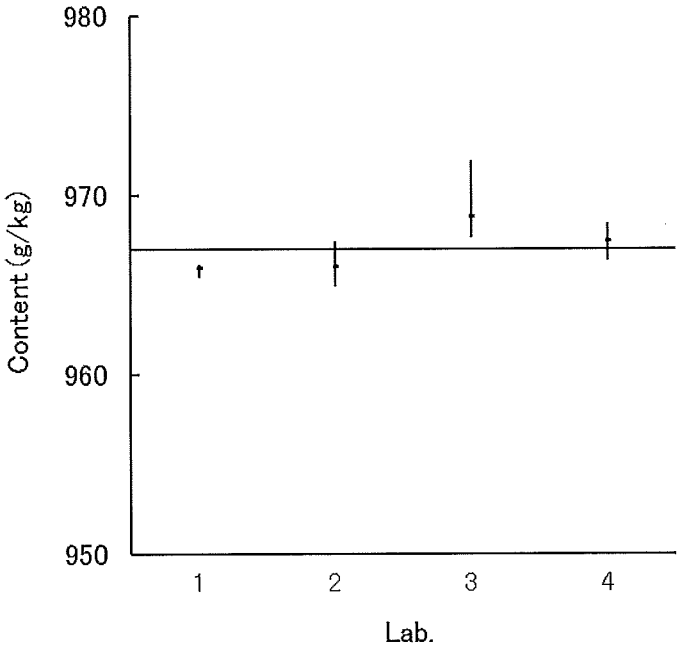

Fig. 3 Metofluthrin TC-3

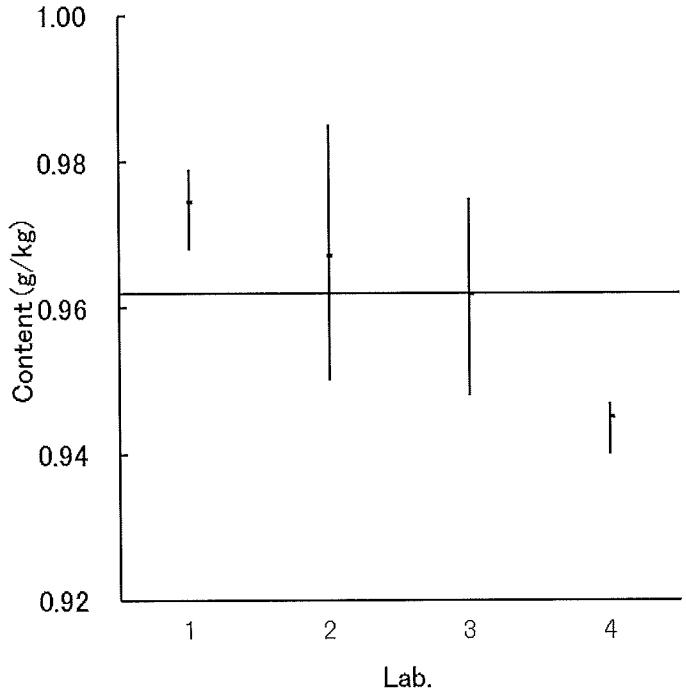

Fig. 4 Metofluthrin EW-1

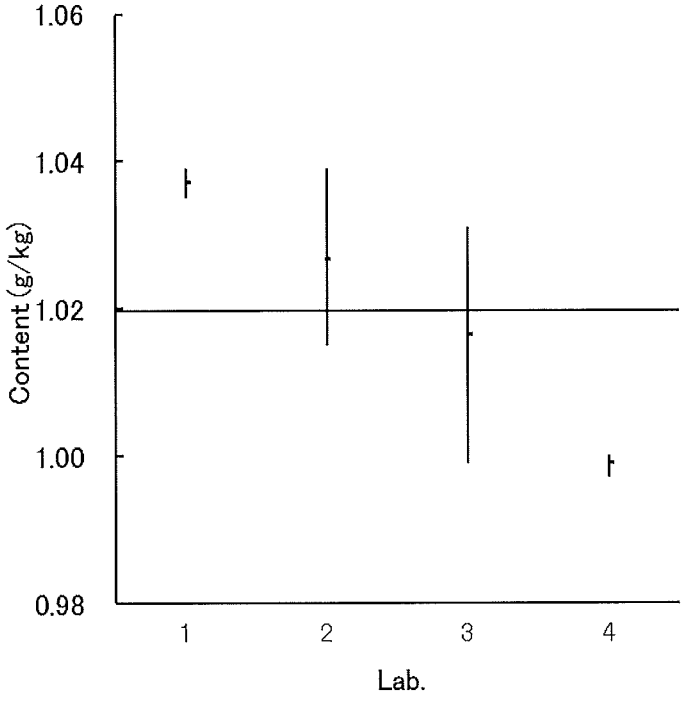

Fig. 5 Metofluthrin EW-2