CYENOPYRAFEN (No.983)

Small Scale Collaborative Trial

Small Scale Collaborative Study on the Determination of Cyenopyrafen in Cyenopyrafen Technical and Formulation by High Performance Liquid Chromatography

by
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1. INTRODUCTION

1.1 Scope

The results of the small scale collaborative trial for cyenopyrafen technical product and cyenopyrafen suspension concentrate are reported.

1.2 Samples

1) Cyenopyrafen technical (TC-1)
2) Cyenopyrafen technical (TC-2)
3) Cyenopyrafen suspension concentrate (SC-1)
4) Cyenopyrafen suspension concentrate (SC-2)
5) Cyenopyrafen suspension concentrate (SC-3)

1.3 Participants

Kazuya Maeda	Nihon Nohyaku Co., Ltd. Research center (JAPAN)
Akiko Sumi	Sumitomo Chemical Co., Ltd. (JAPAN)
Tomomi Onisi	Sumika Chemical Analysis Service, Ltd. (JAPAN)
Keiji Yokouchi	Nissan Chemical Industries, Ltd. Biological Research Laboratory (JAPAN)

2. ANALYTICAL METHOD

2.1 Outline of Method

Cyenopyrafen in the test samples is determined by reversed phase high performance liquid chromatography using an ODS column, UV detection at 280 nm and external standardization as stated in CIPAC/5038/m.

2.2 Program of Work

The collaborators were requested 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) report 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)	Column temp. (ºC)
Proposed Method		YMC Pack Pro C18 (4.6 mm ID × 250 mm, 5 µm)	Acetonitrile – Water, 80 + 20 (v/v)	1.0	40
1	Agilent 1200 Agilent ChemStation	YMC Pack Pro C18 (4.6 mm ID × 250 mm, 5 µm)	Acetonitrile – Water, 80 + 20 (v/v)	1.0	40
2	Shimadzu LC-2014A Dionex Chromeleon	Inertsil ODS-2 (4.6 mm ID × 250 mm, 5 µm)	Acetonitrile – Water, 80 + 20 (v/v)	1.0	40
3	Shimadzu 20A Labsolutions	L-column ODS (4.6 mm ID × 250 mm, 5 µm)	Acetonitrile – Water, 80 + 20 (v/v)	0.9	40
4	Shimadzu Prominence Shimadzu LC solution	SUMIPAX ODS Z-CLUE (4.6 mm ID × 250 mm, 5 µm)	Acetonitrile – Water, 80 + 20 (v/v)	1.0	40

3.2 REMARKS

- Lab.1

- WS and TC samples were easily dissolved in 80% acetonitrile. The sonication time of 3 minutes is enough.

- Lab.3

- Cyenopyrafen 30SC samples were shaken for 1 minutes by hand before sampling.
- Ekicrodisc 25CR organic solvent-based was used for filtration.

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.
No stragglers and outliers were observed.

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 to be appropriate for the determination of cyenopyrafen in technical and suspension concentrate.
JAPAC proposes to proceed with a large scale collaborative trial.

Table 1 Summary of statistical evaluation of cyenopyrafen small scale collaborative study

	TC-1	TC-2	SC-1	SC-2	SC-3
Average (g/kg)	997.10	996.24	298.33	297.75	296.34
Number of laboratories	4	4	4	4	4
Repeatability standard deviation (S_r)	3.511	3.186	1.352	1.092	1.469
"Pure" between laboratory standard variation (S_L)	2.741	3.228	2.888	1.789	2.116
Reproducibility standard deviation (S_R)	4.454	4.535	3.189	2.096	2.576
Repeatability (r)	9.831	8.920	3.785	3.058	4.115
Reproducibility (R)	12.471	12.698	8.928	5.869	7.212
RSD_r	0.352	0.320	0.453	0.367	0.496
RSD_R	0.447	0.455	1.069	0.704	0.869
Horwitz's value	2.001	2.001	2.399	2.400	2.402

Table 2-1 Cyenopyrafen Technical-1

Lab		Analytical data (n=4)		Yi	Yi^2	Si	Si^2
1	Day1	1001.7	1000.4				
	Day2	997.3	1001.5	1000.23	1000450.05	2.032	4.129
2	Day1	1002.4	1005.2				
	Day2	995.9	993.0	999.13	998250.77	5.644	31.849
3	Day1	997.7	997.7				
	Day2	994.4	994.4	996.05	992115.60	1.905	3.630
4	Day1	994.3	989.1				
	Day2	996.4	992.2	993.00	986049.00	3.114	9.700
S1 SUM	Yi =			3988.40			
S2 SUM	Yi^2 =				3976865.42		
S3 SUM	Si^2 =						49.308

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

$C = Si^2$ max / S3 = 0.646 < 0.684 (p=4, n=4, 5%)

2) Grubbs's test (P=4, n=4)

Yi min = 993.00 Yi max = 1000.23 Y = S1/p = 997.10

S = 3.255

Y - Yi min = 4.10

Yi max - Y = 3.12

lower = (Y - Yi min)/S = 1.260 < 1.481 (p=4, 5%)

upper = (Yi max - Y)/S = 0.960 < 1.481 (p=4, 5%)

3) Calculation of r and R

Mean; Y = S1 / p = 997.10

S_r^2 = S3 / p = 12.327 S_r = 3.511

$S_L^2 = [(pS2-S1^2)/p(p-1)]-(S_r^2/n)$ = 7.511 S_L = 2.741

$S_R^2 = S_r^2 + S_L^2$ = 19.838 S_R = 4.454

$r = 2.8 \times S_r$ =	9.831
$R = 2.8 \times S_R$ =	12.471
$RSD_r = (S_r / mean) \times 100$ =	0.352
$RSD_R = (S_R / mean) \times 100$ =	0.447

Horwitz's value = 2 ^[1 - 0.5 x log (Y / 1000)] = 2.001

RSD_R < 2.001 (Horwitz's value)

Table 2-2 Cyenopyrafen Technical-2

Lab		Analytical data (n=4)		Yi	Yi^2	Si	Si^2
1	Day1	998.1	999.0				
	Day2	997.5	1000.7	998.83	997651.38	1.394	1.943
2	Day1	1005.0	1002.3				
	Day2	996.0	995.9	999.80	999600.04	4.580	20.980
3	Day1	995.3	998.1				
	Day2	991.7	990.0	993.78	987588.75	3.633	13.196
4	Day1	992.7	989.6				
	Day2	994.5	993.5	992.58	985205.13	2.116	4.476
S1 SUM	Yi =			3984.98			
S2 SUM	Yi^2 =				3970045.30		
S3 SUM	Si^2 =						40.594

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

$C = Si^2$ max / S3 = 0.517 < 0.684 (p=4, n=4, 5%)

2) Grubbs's test (P=4, n=4)

Yi min = 992.58 Yi max = 999.80 Y = S1/p = 996.24

S = 3.599

Y - Yi min = 3.67

Yi max - Y = 3.56

lower = (Y - Yi min)/S = 1.019 < 1.481 (p=4, 5%)

upper = (Yi max - Y)/S = 0.988 < 1.481 (p=4, 5%)

3) Calculation of r and R

Mean; Y = S1 / p = 996.24

S_r^2 = S3 / p = 10.149 S_r = 3.186

$S_L^2 = [(pS2-S1^2)/p(p-1)]-(S_r^2/n)$ = 10.418 S_L = 3.228

$S_R^2 = S_r^2 + S_L^2$ = 20.566 S_R = 4.535

$r = 2.8 \times S_r$ =	8.920
$R = 2.8 \times S_R$ =	12.698
$RSD_r = (S_r / mean) \times 100$ =	0.320
$RSD_R = (S_R / mean) \times 100$ =	0.455

Horwitz's value = 2 ^[1 - 0.5 x log (Y / 1000)] = 2.001

RSD_R < 2.001 (Horwitz's value)

Table 2-3 Cyenopyrafen Suspension Concentrate-1

Lab		Analytical data (n=4)		Yi	Yi^2	Si	Si^2
1	Day1	299.0	297.7				
	Day2	295.8	297.0	297.38	88431.89	1.338	1.789
2	Day1	303.3	303.7				
	Day2	300.5	302.3	302.45	91476.00	1.427	2.037
3	Day1	296.6	296.9				
	Day2	293.3	294.9	295.43	87275.93	1.668	2.782
4	Day1	297.8	297.8				
	Day2	297.4	299.3	298.08	88848.71	0.838	0.703
S1 SUM	Yi =			1193.33			
S2 SUM	Yi^2 =				356032.53		
S3 SUM	Si^2 =						7.311

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

$C = Si^2$ max / S3 = 0.381 < 0.684 (p=4, n=4, 5%)

2) Grubbs's test (P=4, n=4)

Yi min = 295.43 Yi max = 302.45 Y = S1/p = 298.33

S = 2.966

Y - Yi min = 2.91

Yi max - Y = 4.12

lower = (Y - Yi min)/S = 0.980 < 1.481 (p=4, 5%)

upper = (Yi max - Y)/S = 1.389 < 1.481 (p=4, 5%)

3) Calculation of r and R

Mean; Y = S1 / p = 298.33

S_r^2 = S3 / p = 1.828 S_r = 1.352

$S_L^2 = [(pS2-S1^2)/p(p-1)]-(S_r^2/n)$ = 8.340 S_L = 2.888

$S_R^2 = S_r^2 + S_L^2$ = 10.168 S_R = 3.189

$r = 2.8 \times S_r$ =	3.785
$R = 2.8 \times S_R$ =	8.928
$RSD_r = (S_r / mean) \times 100$ =	0.453
$RSD_R = (S_R / mean) \times 100$ =	1.069

Horwitz's value = 2 ^[1 - 0.5 x log (Y / 1000)] = 2.399

RSD_R < 2.399 (Horwitz's value)

Table 2-4 Cyenopyrafen Suspension Concentrate-2

Lab		Analytical data (n=4)		Yi	Yi^2	Si	Si^2
1	Day1	297.2	295.8				
	Day2	297.6	298.3	297.23	88342.70	1.053	1.109
2	Day1	299.8	298.5				
	Day2	300.4	301.9	300.15	90090.02	1.411	1.990
3	Day1	295.5	296.8				
	Day2	295.4	294.9	295.65	87408.92	0.810	0.657
4	Day1	297.1	297.2				
	Day2	298.4	299.2	297.98	88789.10	1.008	1.016
S1 SUM	Yi =			1191.00			
S2 SUM	Yi^2 =				354630.75		
S3 SUM	Si^2 =						4.772

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

$C = Si^2 max / S3$ = 0.417 < 0.684 (p=4, n=4, 5%)

2) Grubbs's test (P=4, n=4)

Yi min = 295.65 Yi max = 300.15 Y = S1/p = 297.75

S = 1.870

Y - Yi min = 2.10

Yi max - Y = 2.40

lower = (Y - Yi min)/S = 1.123 < 1.481 (p=4, 5%)

upper = (Yi max - Y)/S = 1.283 < 1.481 (p=4, 5%)

3) Calculation of r and R

Mean; Y = S1 / p = 297.75

$S_r^2 = S3 / p$ = 1.193 S_r = 1.092

$S_L^2 = [(pS2-S1^2)/p(p-1)]-(S_r^2/n)$ = 3.201 S_L = 1.789

$S_R^2 = S_r^2 + S_L^2$ = 4.393 S_R = 2.096

$r = 2.8 \times S_r$ =	3.058
$R = 2.8 \times S_R$ =	5.869
$RSD_r = (S_r / mean) \times 100$ =	0.367
$RSD_R = (S_R / mean) \times 100$ =	0.704

Horwitz's value = 2 ^[1 - 0.5 x log (Y / 1000)] = 2.400

RSD_R < 2.400 (Horwitz's value)

Table 2-5 Cyenopyrafen Suspension Concentrate-3

Lab		Analytical data (n=4)		Yi	Yi^2	Si	Si^2
1	Day1	294.5	291.6				
	Day2	294.2	297.0	294.33	86627.21	2.208	4.876
2	Day1	300.0	296.8				
	Day2	298.9	298.9	298.65	89191.82	1.338	1.790
3	Day1	293.2	295.5				
	Day2	294.8	294.6	294.53	86744.98	0.964	0.929
4	Day1	296.9	297.1				
	Day2	298.9	298.6	297.88	88729.52	1.021	1.043
S1 SUM	Yi =			1185.38			
S2 SUM	Yi^2 =				351293.52		
S3 SUM	Si^2 =						8.637

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

$C = Si^2 max / S3$ = 0.564 < 0.684 (p=4, n=4, 5%)

2) Grubbs's test (P=4, n=4)

Yi min = 294.33 Yi max = 298.65 Y = S1/p = 296.34

S = 2.240

Y - Yi min = 2.02

Yi max - Y = 2.31

lower = (Y - Yi min)/S = 0.901 < 1.481 (p=4, 5%)

upper = (Yi max - Y)/S = 1.030 < 1.481 (p=4, 5%)

3) Calculation of r and R

Mean; Y = S1 / p = 296.34

$S_r^2 = S3 / p$ = 2.159 S_r = 1.469

$S_L^2 = [(pS2-S1^2)/p(p-1)]-(S_r^2/n)$ = 4.476 S_L = 2.116

$S_R^2 = S_r^2 + S_L^2$ = 6.635 S_R = 2.576

$r = 2.8 \times S_r$ =	4.115
$R = 2.8 \times S_R$ =	7.212
$RSD_r = (S_r / mean) \times 100$ =	0.496
$RSD_R = (S_R / mean) \times 100$ =	0.869

Horwitz's value = 2 ^[1 - 0.5 x log (Y / 1000)] = 2.402

RSD_R < 2.402 (Horwitz's value)

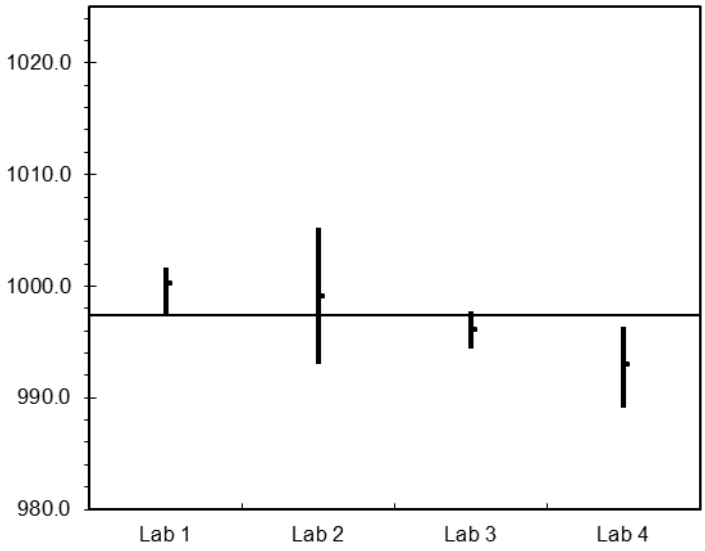

Figure 1 Cyenopyrafen Technical-1

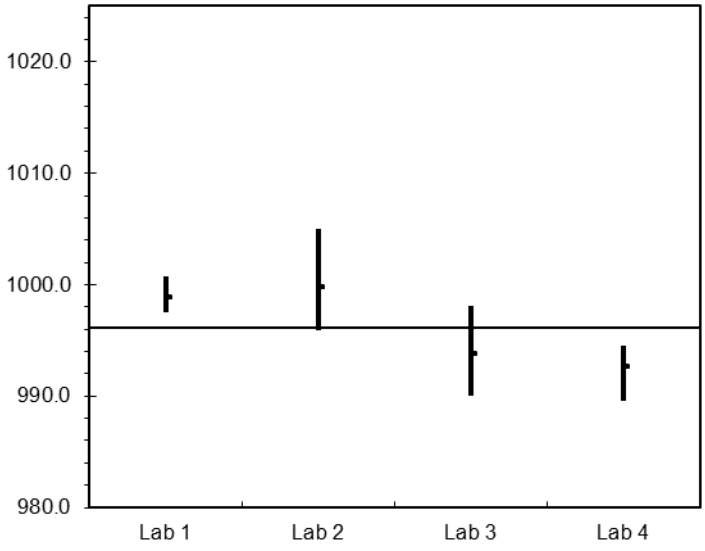

Figure 2 Cyenopyrafen Technical-2

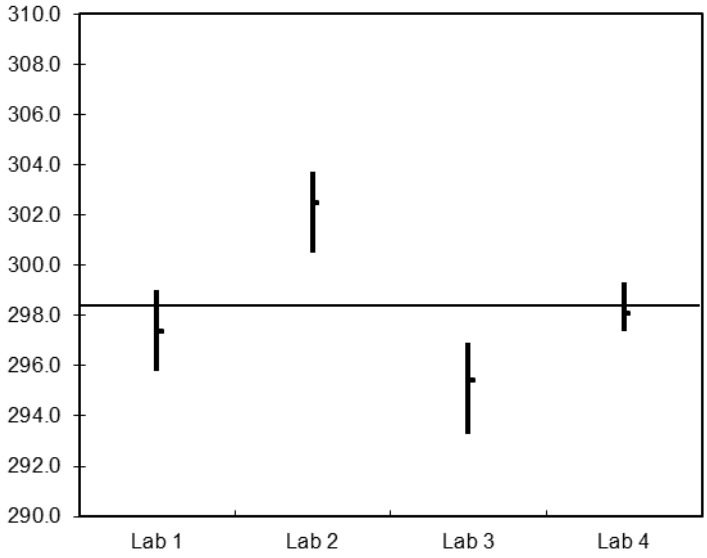

Figure 3 Cyenopyrafen Suspension Concentrate-1

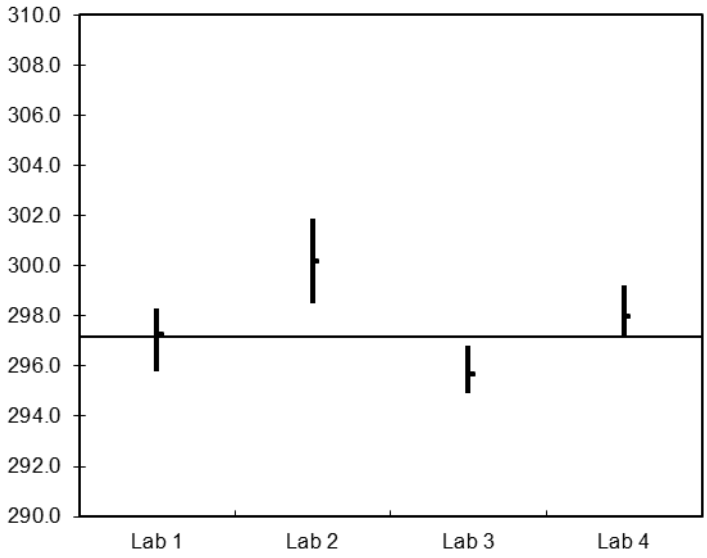

Figure 4 Cyenopyrafen Suspension Concentrate-2

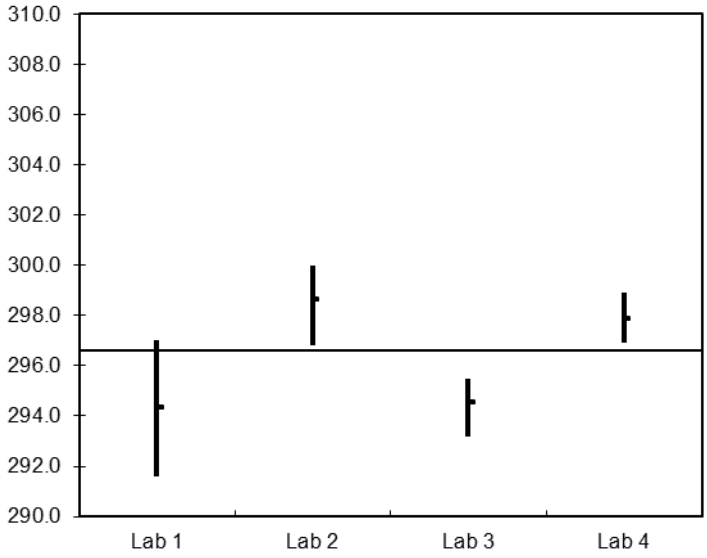

Figure 5 Cyenopyrafen Suspension Concentrate-3