Asia Pacific Laboratory Accreditation Cooperation

APLAC T021
Proficiency Testing Program of Alcoholic Beverage Testing

February 2006

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1. FOREWORD

This report summarises the results of APLAC T021 Proficiency Testing Program of Alcoholic Beverage Testing involving testing laboratories for the Asia Pacific Laboratory Accreditation Cooperation (APLAC). This program covered analysis Methanol and Sulfur Dioxide of Alcoholic Beverage samples.

The exercise was conducted by the CNLA/ TAF(Taiwan Accreditation Foundation). The aim of the program was to assess laboratories' ability to competently perform the tests examined.

2. FEATURES OF THE PROGRAM

a) APLAC, IAAC and EA members were invited to participate. There are in total 73 laboratory participants nominated by 27 accreditation bodies (ABs) in this program. A total of 21 laboratories did not send the samples due to the delivery problems. Three participating laboratories did not reply the result due to broken samples during delivery; hence the results from those laboratories were excluded from the analysis.

Economy	No. of Labs	Economy	No. of Labs
Argentina	1	Australia	4
Cuba	2	Ecuador	3
Guatemala	2	Hong Kong	1
India	4	Indonesia	4
Ireland	2	Italy	4
Japan	1	Mexico	2
Mongolia	4	New Zealand	1
France	4	Peru	2
Philippines	1	Chile	1
Singapore	1	Slovakia	4
Spain	4	Sweden	1
Taiwan	8	Tallinn Estonia	2
Trinidad and Tobago	2	Uruguay	2
Vietnam	4		

b) Participating laboratories were supplied two bottles of Alcohol Beverage samples labelled APT20A, and APT20B.

c) The following tests were performed on each sample in duplicate:
Methanol(mg/L)
Sulfur dioxide (mg/kg)

d) Prior to distribution the samples were analysed for homogeneity. The testing results showed that the samples were sufficiently homogeneous. Therefore any results later identified as outliers could not be attributed to any significant sample variability. (Appendix B)

e) Laboratories were requested to perform the tests according to their copy of the "Instructions to Participants" and to record their results on the accompanying "Results Sheet", both of which were distributed to participants with the sample. (Appendix C)

f) Each laboratory was randomly allocated a unique code number for the program to enable confidentiality of results. Reference to each laboratory in this report is made by its code number.

3. CONTENT OF APPENDICIES

APPENDIX A contains:

(i) The duplicate results reported by laboratories and the calculated average result for each test on each sample.

(ii) A table of robust statistics for each test - number of results, median, normalised IQR, robust CV, minimum, maximum and range.

(iii) Z-scores and z-score charts calculated for between laboratories and within laboratory for each test.

(iv) A Youden diagram for each test.

(v) Test methods and testing equipment reported for each lab.

APPENDIX B contains details of sample preparation and stability testing data.

APPENDIX C contains a copy of the “Instructions to participants” and the “Results Sheet”, as supplied to participants.

APPENDIX D contains details of statistical procedures, calculations and formulae.

4. STATISTICAL DESIGN OF THE PROGRAM

A split level statistical design was used in this program. The samples labelled APT20A, and APT20B were slightly different.

Robust statistical procedures were used to generate the z-scores and summary statistics for the sample - number of results, median, normalised interquartile range, minimum, maximum and range.

For each laboratory, the between-laboratories z-score was calculated for the sample pair. This was based on the (standardised) sum of the calculated mean of the duplicate results reported for each sample. The within laboratory z-score was based on the (standardised) difference between the mean of the duplicate results reported for each sample.

TABLE A - SUMMARY STATISTICS

Test	Summary Statistic	APLAC Sample A	APLAC Sample B
Methanol (mg/L)	No. of Results	44	42
	Median	99.585	108.468
	Normalized IQR	13.44	17.316
Sulfur dioxide (mg/Kg)	No. of Results	35	33
	Median	69.50	67.50
	Normalized IQR	7.59	8.21

5. OUTLIER RESULTS

In order to achieve the program's aim of assessing laboratories' testing performance, a robust statistical approach, which uses z-scores to assess participants performance has been utilised. The z-score is a measure of how far the result(s) is from the consensus value - a normalized value which gives a "score" to each result relative to the other results in the group. Therefore a z-score close to zero means that the result agrees well with those from other laboratories. An outlier will be any result(s) which has an absolute z-score value greater than three.

Appendix D given details on the calculation of z-scores and modes.

TABLE B
OUTLIER RESULTS
(Between-Laboratories and Within-Laboratory)

Test	Between - Laboratories Z-Score	Within - Laboratory Z-Score
Methanol (mg/L)	1, 4, 21, 27, 33, 34, 36, 39, 72	33, 34, 36, 72
Sulfur dioxide (mg/Kg)	12, 39, 41	N/A

There are in total 73 laboratory participants nominated by 27 accreditation bodies (ABs) in this program. A total of 21 laboratories did not send the samples due to the delivery problems. Three participating laboratories did not reply the result due to broken samples during delivery; out of the 154 results returned, the total of 16 results has been identified as extreme results (10.38 %).

The following parameters in Table C are used to calculate the z-score values.

TABLE C: Z-Score Values

Test	Standardised Sum		Standardised difference	
	Median	Norm IQR	Median	Norm IQR
Methanol (mg/L)	**146.49**	**17.65**	**5.58**	**5.19**
Sulfur dioxide (mg/Kg)	**97.56**	**9.92**	**2.12**	**2.68**

Refer to Appendix D for calculation of standardised sum and standardised difference.

6. TECHNICAL COMMENTS

General comments

From the summary statistics, these results agree well, especially considering the large number of countries and methods. Special cause errors have been marked as outliers on where they have occurred , and diagnostics are provided by z-scores for between-laboratories and within- laboratory variation（Youden plot main axis excursions）.

The results and causes are discussed generally in technical notes below.

It seems that one of the causes of within- laboratory variation was confused between A and B samples. It sounds that there are more examples than are pointed out below. It is likely that this confusion would occur less often if laboratories put all samples through their usual sample reception system. If not because of these reporting errors, analytical errors would have been small.

Correction of special causes will bring all results within the general agreement. By so doing, laboratories can use standard samples to help achieve and maintain the good level of analytical performance found in this APLAC program.

a) **Methanol**

Most of laboratories used methodology based on Gas Chromatography.

The robust CV of 13.5% and 15.9 % for the program indicate a good performance for this test. The median values of 99.58 mg/L and 108.46 mg/L are similar to pre-trial homogeneity test average value 95.52 mg/L and 103.75 mg/L.

Most of the outlier results（such as Lab Codes 1, 4, 21, 27, 33, 34,36, 38, 39 and 72）appear to be associated with systematic error or method bias （note：the outliers are mainly from between - laboratory measures, refer to z-score diagram & Youden diagram ）.

（1）There were many error factors（such as instrument analysis, operator precision, standard preparation, calculation and sample storage etc.）that probably resulted in the systematic error. Some of outlier results were resulted from the systematic error.

（2）Laboratories used different methods of test for methanol in alcoholic beverages such as Gas Chromatography, Spectrophotometry and Colorimetry etc.）. Some of outlier results were resulted from method bias .

These laboratories should recheck the recovery of control and reference standards used in their methanol method. Laboratories reporting outliers for within- laboratory Z-scores should recheck the method and operator precision.

b) **Sulfur dioxide**

Most of laboratories used methodology based on Alkaline Titration method（Rankine method）.

The robust CV of 10.9％ and 12.1％ for the program indicate a good performance for this test . The median value of 69.50mg/Kg and 67.50mg/Kg are different from pre-trial homogeneity test value 97.32 mg/Kg and 97.03 mg/Kg. Owing to test samples were delayed to send for one month, the content of Sulfur dioxide in alcoholic beverages was largely changed because of it easily evaporating to lose under test samples cold storage.

Most of the outlier results（such as Lab Codes 12, 17, 39, 41）appear to be associated with systematic error or method bias（note the outlier are mainly from between -laboratory measures，refer to Z-score diagram ＆ Youden diagram）.

（1）There were many error factors（such as aeration distillation, operator precision, titration, calculation and sample storage etc.）that probably resulted in the systematic error. Some of outlier results were resulted from the systematic error.

（2）Laboratories used different methods of test for Sulfur dioxide method in alcoholic beverages（such as Alkaline Titration method, Colorimetry and High Performance Ion Exclusion Chromatography etc.）. Some of outlier results were resulted from method bias .

These laboratories should recheck the recovery of control and reference standards used in their methanol method. Laboratories reporting outliers for within- laboratory Z-scores should recheck the method and operator precision.

c) As a general rule from the analytic results of Z-score, the related Laboratories with a Z-score outside the range ***-2～+2*** are suggested to check the factors of uncertainties of their measurement system; the related Laboratories with a Z-score outside the range ***-3～+3*** are encouraged to review the factors of uncertainties and even investigate “Quality Management” and “Technical Requirements” of their whole system.

APPENDIX A

Summary of Results

Item 1

Item	Test									
1	Methanol(mg/L)									
Lab Code	APT21A Result1 (mg/L)	APT21A Result2 (mg/L)	Average (mg/L)	APT21B Result1 (mg/L)	APT21B Result2 (mg/L)	Average (mg/L)	Between Laboratories Z-Score	Within Laboratory Z-Score	Expanded uncertainty	
									Sample A	Sample B
1	0.18	0.16	0.170	0.15	0.16	0.155	-8.29※	-1.08	N/A	N/A
2	94.24	88.36	91.300	112.02	112.43	112.225	-0.15	1.78	N/A	N/A
3	107.30	107.30	107.300	122.80	122.80	122.800	0.92	1.04	±31.6 %	±31.6 %
4	0.32	0.32	0.320	0.35	0.35	0.350	-8.28※	-1.07	N/A	N/A
5	100.76	97.49	99.125	99.99	99.06	99.525	-0.34	-1.02	±2.48 %	±2.48 %
6	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
7	99.73	100.17	99.950	108.06	108.01	108.035	0.03	0.03	±2.18 %	±1.90 %
8	82.51	81.90	82.205	89.56	90.61	90.085	-1.40	0.00	N/A	N/A
9	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
10	93.29	96.16	94.725	95.53	97.64	96.585	-0.64	-0.82	N/A	N/A
11	301.49	290.50	295.995	N/A	N/A	N/A	N/A	N/A	±6.68 %	±6.68 %
12	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
13	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
14	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
15	100.10	98.00	99.050	105.40	107.80	106.600	-0.06	-0.05	N/A	N/A
16	101.00	102.50	101.750	108.20	109.60	108.900	0.14	-0.10	N/A	N/A
17	94.00	95.00	94.500	98.00	101.00	99.500	-0.53	-0.39	±28 %	±29 %
18	85.43	88.59	87.010	95.71	94.13	94.920	-1.01	0.00	±2.37mg/L	±2.37mg/L
19	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
20	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
21	496.79	493.70	495.245	502.90	500.53	501.715	31.65※	-0.19	±17 %	±17 %
22	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
23	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
24	98.95	98.24	98.595	101.02	100.48	100.750	-0.31	-0.78	N/A	N/A
25	96.45	97.34	96.895	104.68	106.97	105.825	-0.18	0.14	N/A	N/A
26	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
27	294.92	300.76	297.840	325.11	321.63	323.370	16.59※	2.40	±8.45 %	±8.45 %
28	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
29	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
30	111.20	112.20	111.700	122.90	124.90	123.900	1.14	0.59	±20 %	±20 %
31	116.20	114.00	115.100	107.70	112.50	110.100	0.72	-1.76	N/A	N/A
32	96.52	97.10	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
33	229.85	249.21	239.530	216.55	223.13	219.840	10.11※	-3.76※	±33.5342 %	±30.7776 %

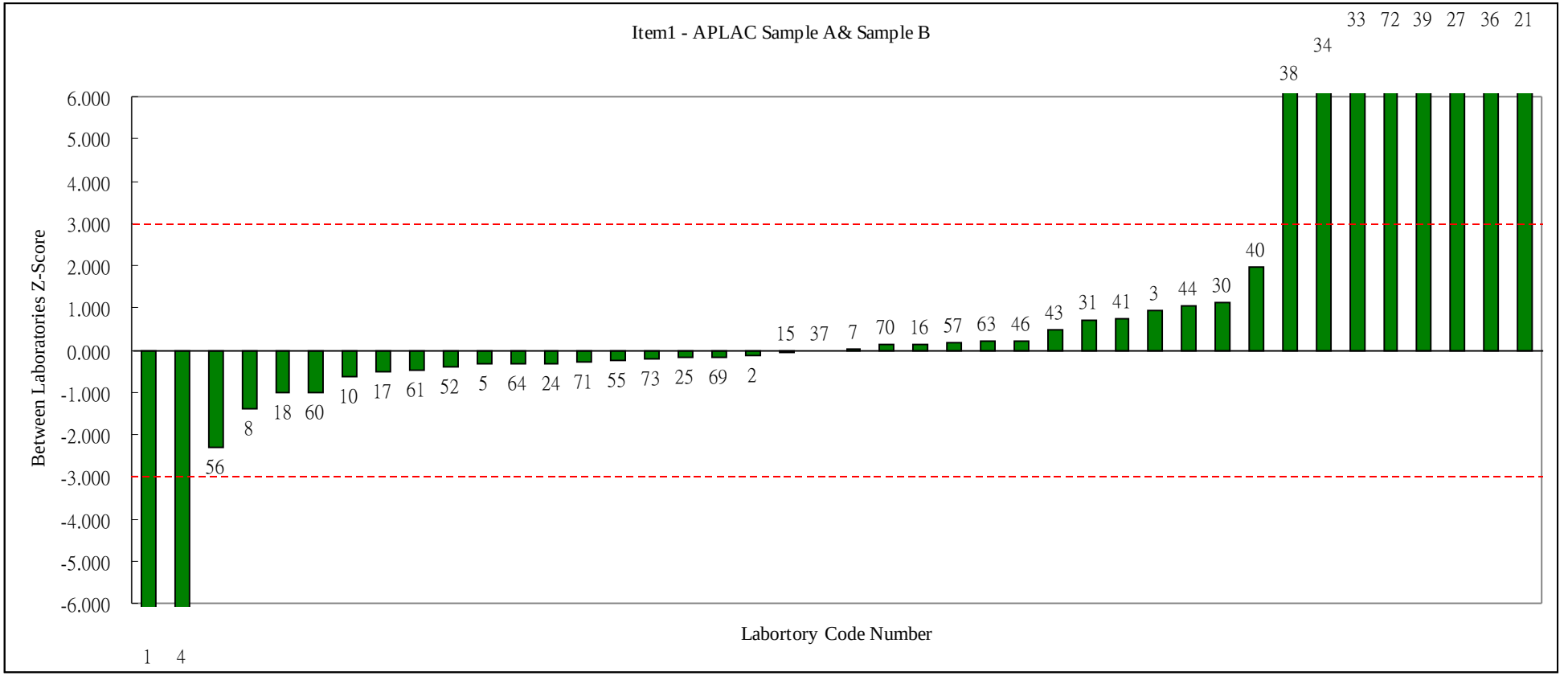
1	Methanol(mg/L)									
Lab Code	APT21A Result1 (mg/L)	APT21A Result2 (mg/L)	Average (mg/L)	APT21B Result1 (mg/L)	APT21B Result2 (mg/L)	Average (mg/L)	Between Laboratories Z-Score	Within Laboratory Z-Score	Expanded uncertainty	
									Sample A	Sample B
34	157.11	157.80	157.455	219.10	219.08	219.090	6.79※	7.32※	N/A	N/A
35	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
36	474.16	482.85	478.505	513.83	506.13	509.980	31.31※	3.21※	±6.69 %	±6.69 %
37	95.64	96.90	96.270	108.80	111.38	110.090	-0.03	0.81	N/A	N/A
38	173.00	173.00	173.000	187.30	187.30	187.300	6.14※	0.87	±5 %	±5 %
39	252.09	251.46	251.775	257.86	258.65	258.255	12.14※	-0.19	±1.87 %	±0.96 %
40	128.40	125.23	126.815	132.64	126.29	129.465	1.97	-0.71	N/A	N/A
41	107.49	106.47	106.980	119.04	119.18	119.110	0.76	0.58	±1.1845 %	±1.8769 %
42	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
43	106.20	108.20	107.200	110.80	112.00	111.400	0.46	-0.50	N/A	N/A
44	109.12	110.36	109.740	126.02	120.87	123.445	1.04	0.79	±18 %	±18 %
45	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
46	99.37	99.88	99.625	113.87	112.12	112.995	0.22	0.75	±23.1 %	±23.1 %
47	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
48	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
49	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
50	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
51	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
52	93.17	92.26	92.715	105.88	102.42	104.150	-0.41	0.48	±8.49 %	±9.29 %
53	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
54	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
55	97.82	96.60	97.210	103.70	104.25	103.975	-0.24	-0.15	±8.30 %	±8.30 %
56	75.23	71.96	73.595	74.62	76.71	75.665	-2.32	-0.79	±0.025 %	±0.025 %
57	93.69	105.48	99.585	106.85	116.21	111.530	0.16	0.55	N/A	N/A
58	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
59	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
60	87.03	87.60	87.315	97.74	91.87	94.805	-1.00	-0.06	±3.24 %	±0.82 %
61	101.74	92.51	97.125	100.64	95.56	98.100	-0.48	-0.94	N/A	N/A
62	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
63	103.30	99.10	101.200	111.80	110.95	111.375	0.22	0.31	±11 %	±11 %
64	99.00	99.80	99.400	99.20	100.10	99.650	-0.33	-1.04	±3 %	±3 %
65	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
66	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
67	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
68	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
69	96.20	96.70	96.450	106.20	106.70	106.450	-0.17	0.29	N/A	N/A

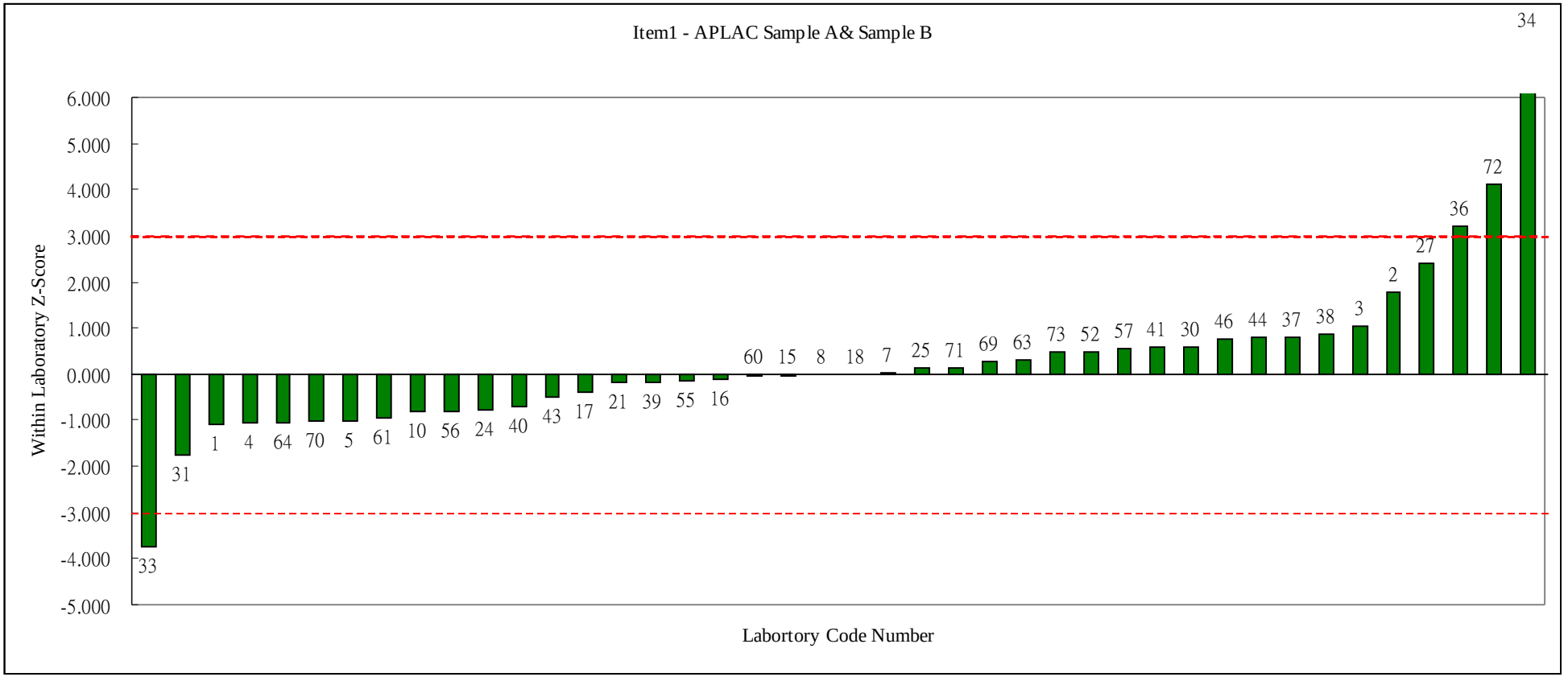
1	Methanol(mg/L)									
Lab Code	APT21A Result1 (mg/L)	APT21A Result2 (mg/L)	Average (mg/L)	APT21B Result1 (mg/L)	APT21B Result2 (mg/L)	Average (mg/L)	Between Laboratories Z-Score	Within Laboratory Z-Score	Expanded uncertainty	
									Sample A	Sample B
70	104.20	105.60	104.900	105.30	105.10	105.200	0.12	-1.04	N/A	N/A
71	95.41	95.57	95.490	104.25	104.67	104.460	-0.29	0.15	N/A	N/A
72	200.00	225.00	212.500	238.00	263.00	250.500	10.25※	4.10※	±17 %	±17 %
73	96.10	94.00	95.050	106.80	106.10	106.450	-0.23	0.48	N/A	N/A

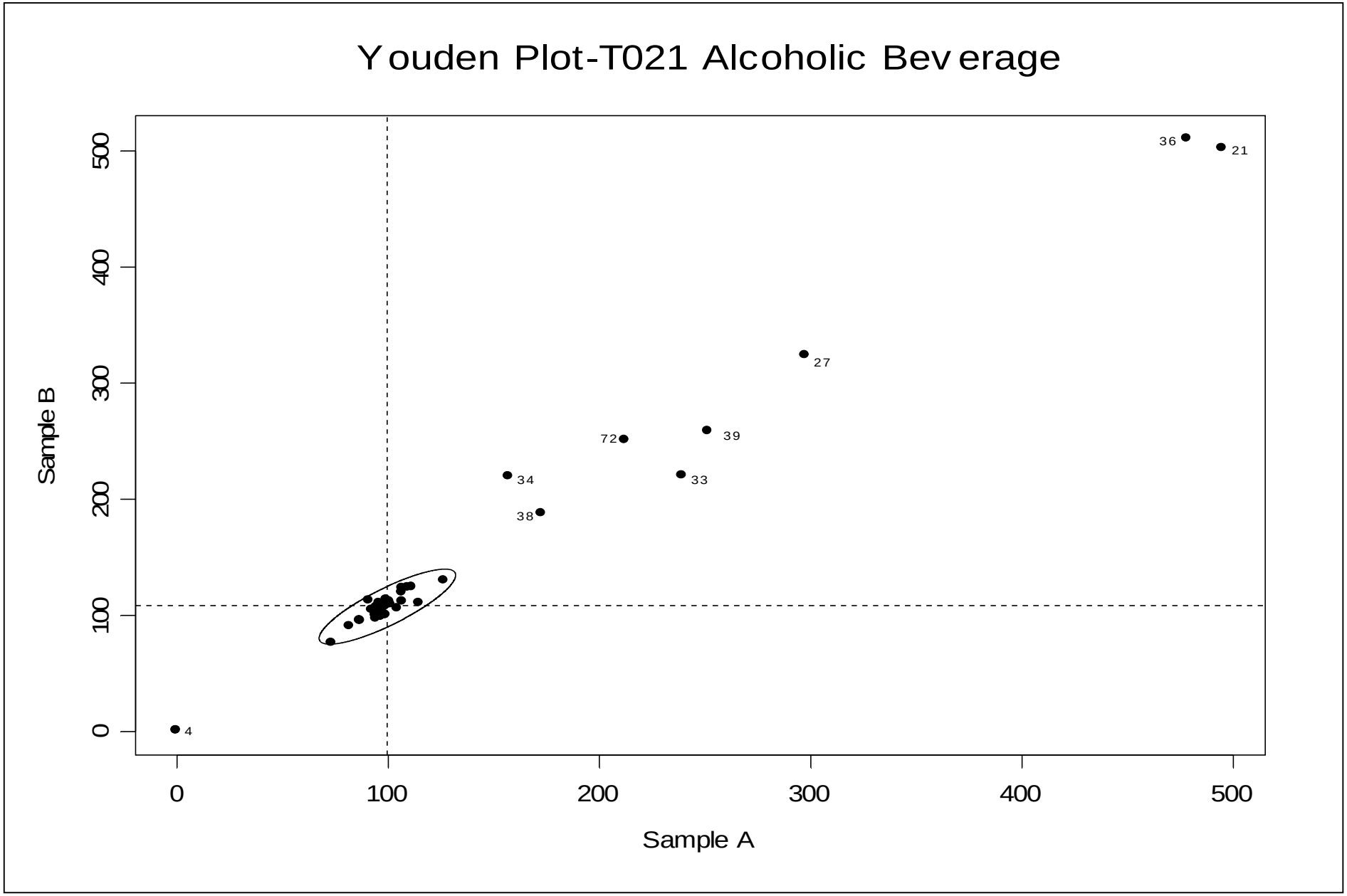
No. of result	43	42
Median	99.585	108.468
Normalized IQR	13.44	17.316
Robust CV(%)	13.496	15.964
Maximum	495.245	509.98
Minimum	0.17	0.155
Range	495.075	509.825

NOTE : ※ denotes an outlier (i.e. |z-score|>3)

Item 1 – APLAC Sample A & Sample B




Item1 - APLAC Sample A& Sample B
Within Laboratory Z-Score
6.000
5.000
4.000
3.000
2.000
1.000
0.000
-1.000
-2.000
-3.000
-4.000
-5.000
33 31 1 4 64 70 5 61 10 56 24 40 43 17 21 39 55 16 60 15 8 18 7 25 71 69 63 73 52 57 41 30 46 44 37 38 3 2 27 36 72 34
Labortory Code Number


Youden Plot-T021 Alcoholic Beverage
Sample B
Sample A
0
100
200
300
400
500
36
21
27
72
39
34
33
38
4

Item 2

Item	Test									
2	Sulfur dioxide (mg/kg)									
Lab Code	APT21A Result1 (mg/kg)	APT21A Result2 (mg/kg)	Average (mg/kg)	APT21B Result1 (mg/kg)	APT21B Result2 (mg/kg)	Average (mg/kg)	Between Laboratories Z-Score	Within Laboratory Z-Score	Expanded uncertainty	
									Sample A	Sample B
1	72.99	71.76	72.375	72.38	71.76	72.070	0.46	-0.71	N/A	N/A
2	80.00	73.00	76.500	83.00	76.00	79.500	1.29	-1.58	N/A	N/A
3	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
4	59.45	59.54	59.495	54.53	54.63	54.580	-1.70	0.51	N/A	N/A
5	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
6	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
7	72.47	72.37	72.420	65.47	65.71	65.590	0.00	1.01	±1.05 %	±0.66 %
8	67.24	65.89	66.565	61.76	60.22	60.990	-0.74	0.68	N/A	N/A
9	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
10	55.00	58.00	56.500	54.00	56.00	55.000	-1.89	-0.40	N/A	N/A
11	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
12	106.14	106.14	106.140	101.40	101.40	101.400	4.96※	0.46	±0.03 %	±0.03 %
13	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
14	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
15	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
16	77.00	76.00	76.500	72.00	71.00	71.500	0.72	0.53	N/A	N/A
17	49.00	52.00	50.500	53.00	56.00	54.500	-2.35	-1.84	±15 %	±16 %
18	57.25	56.67	56.960	54.86	53.05	53.955	-1.93	0.00	±1.21mg/kg	±1.21mg/kg
19	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
20	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
21	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
22	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
23	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
24	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
25	74.82	76.49	75.655	74.82	74.82	74.820	0.89	-0.57	N/A	N/A
26	58.66	58.66	58.660	54.14	54.14	54.140	-1.79	0.40	N/A	N/A
27	69.72	69.15	69.435	73.31	74.94	74.125	0.40	-2.03	±13.19 %	±13.19 %
28	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
29	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
30	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
31	73.10	65.90	69.500	63.80	63.80	63.800	-0.33	0.71	N/A	N/A
32	76.42	76.06	76.240	N/A	N/A	N/A	N/A	N/A	N/A	N/A
33	64.06	64.63	64.345	65.20	65.41	65.305	-0.59	-1.04	±1.1276 %	±1.1558 %

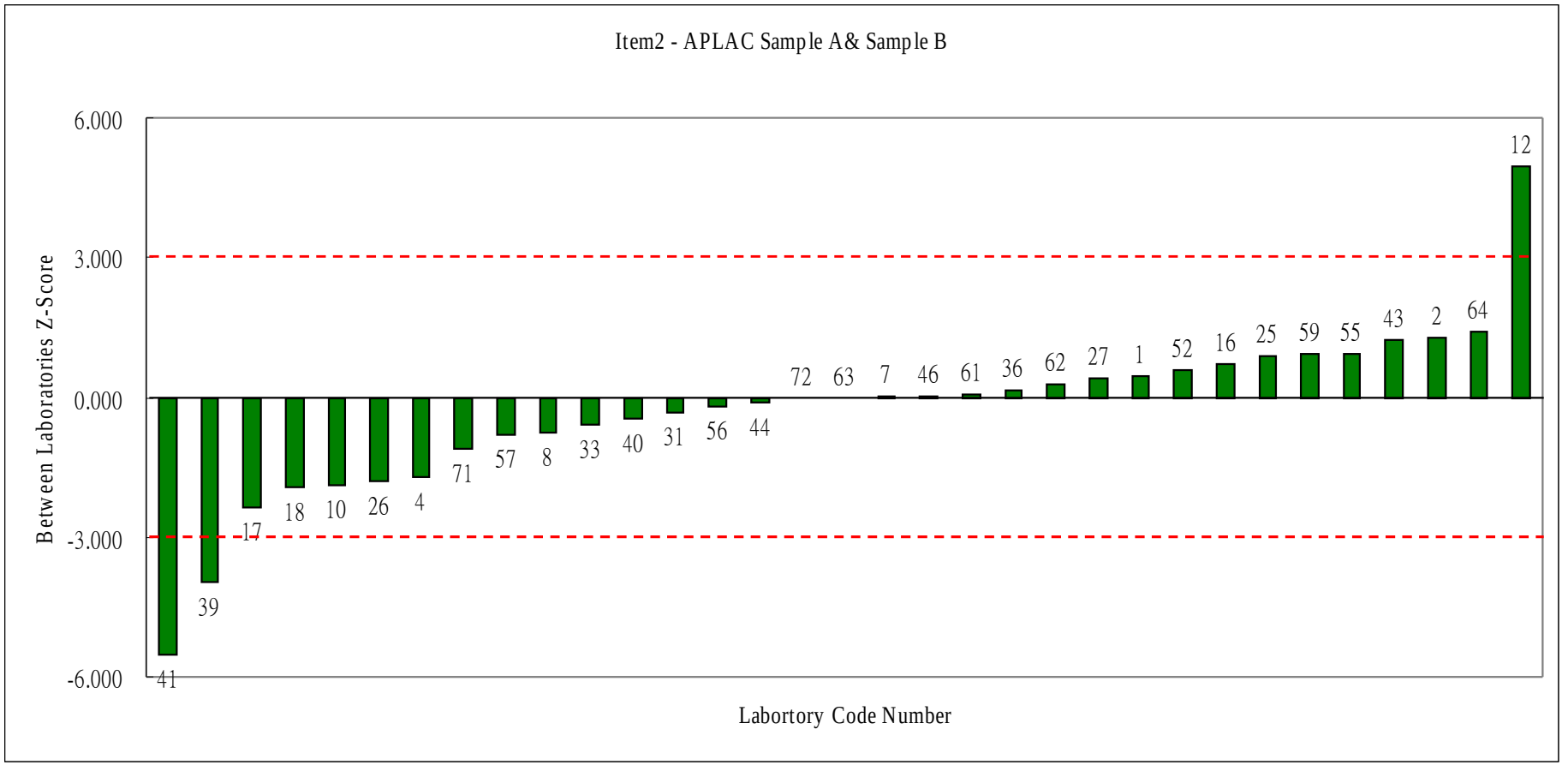
2	Sulfur dioxide (mg/kg)									
Lab Code	APT21A Result1 (mg/kg)	APT21A Result2 (mg/kg)	Average (mg/kg)	APT21B Result1 (mg/kg)	APT21B Result2 (mg/kg)	Average (mg/kg)	Between Laboratories Z-Score	Within Laboratory Z-Score	Expanded uncertainty Sample A	Expanded uncertainty Sample B
34	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
35	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
36	68.59	68.64	68.615	70.44	72.75	71.595	0.16	-1.58	±11.32 %	±11.32 %
37	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
38	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
39	40.92	39.62	40.270	42.20	41.54	41.870	-3.98※	-1.21	±0.88 %	±0.92 %
40	68.28	66.99	67.635	63.34	64.47	63.905	-0.46	0.19	N/A	N/A
41	30.38	30.25	30.315	30.25	30.38	30.315	-5.51※	-0.79	±0.71 %	±0.6343 %
42	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
43	80.00	83.00	81.500	74.00	74.00	74.000	1.25	1.19	N/A	N/A
44	74.93	73.63	74.280	60.00	64.50	62.250	-0.10	2.38	N/A	N/A
45	72.00	71.00	71.500	N/A	N/A	N/A	N/A	N/A	N/A	N/A
46	68.58	68.99	68.785	68.53	69.99	69.260	0.01	-0.92	N/A	N/A
47	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
48	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
49	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
50	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
51	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
52	76.01	75.03	75.520	71.94	68.86	70.400	0.57	0.56	±11	±11
53	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
54	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
55	77.90	78.42	78.160	72.44	72.97	72.705	0.92	0.65	±6.70 %	±6.70 %
56	71.06	69.82	70.440	65.18	64.56	64.870	-0.19	0.68	±2.16 %	±2.16 %
57	69.00	61.00	65.000	65.00	59.00	62.000	-0.78	0.00	N/A	N/A
58	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
59	76.38	75.02	75.700	74.67	75.38	75.025	0.91	-0.61	±0.22 %	±0.22 %
60	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
61	68.80	69.73	69.265	69.77	69.77	69.770	0.08	-0.92	N/A	N/A
62	72.14	72.51	72.325	69.41	69.41	69.410	0.27	-0.02	N/A	N/A
63	70.24	70.69	70.465	67.17	67.83	67.500	0.00	-0.01	±4.5 %	±4.5 %
64	80.26	81.92	81.090	77.57	76.16	76.865	1.43	0.32	±2.9 %	±4.6 %
65	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
66	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
67	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
68	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
69	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
70	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
71	65.80	65.60	65.700	56.30	56.90	56.600	-1.12	1.61	N/A	N/A

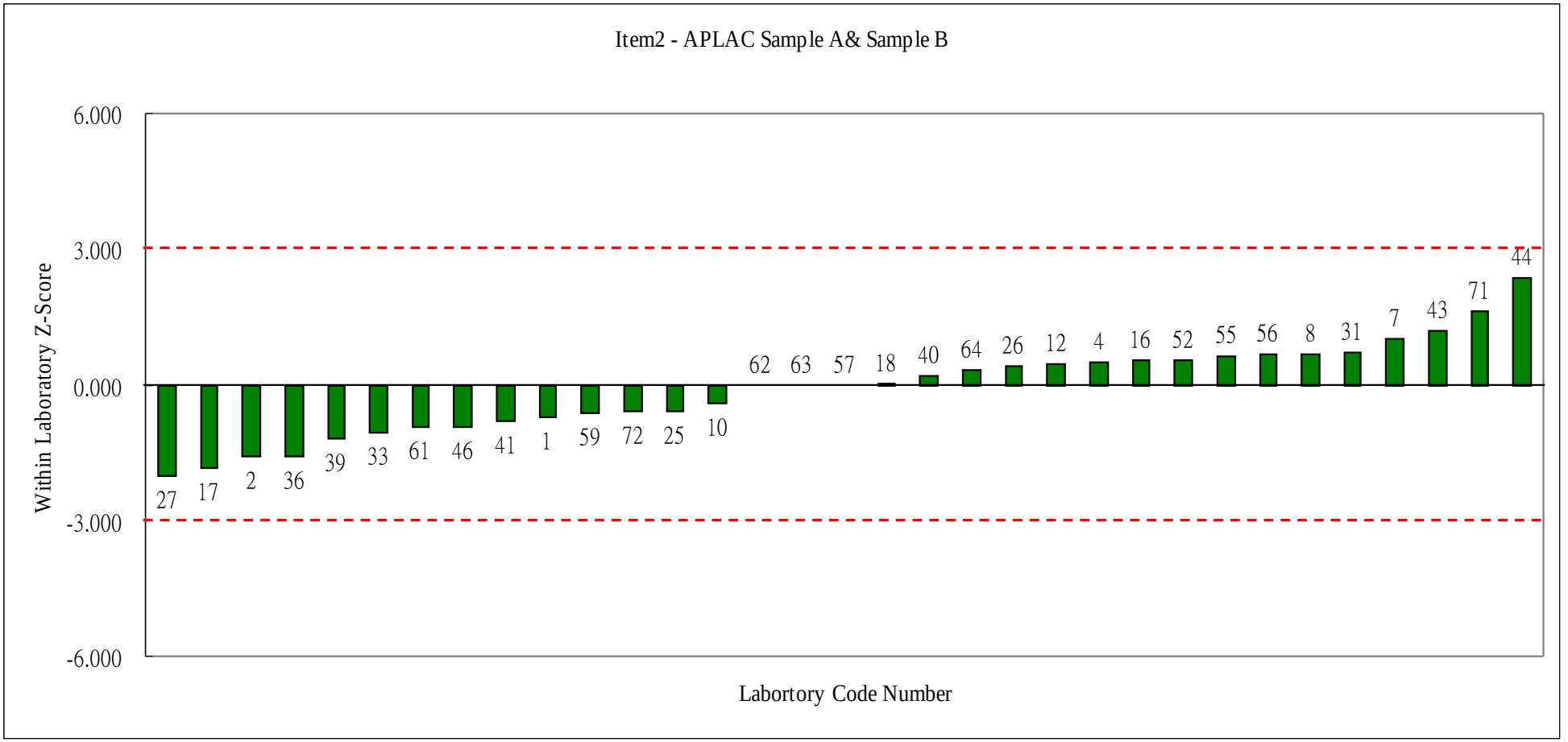
2	Sulfur dioxide (mg/kg)									
Lab Code	APT21A Result1 (mg/kg)	APT21A Result2 (mg/kg)	Average (mg/kg)	APT21B Result1 (mg/kg)	APT21B Result2 (mg/kg)	Average (mg/kg)	Between Laboratories Z-Score	Within Laboratory Z-Score	Expanded uncertainty Sample A	Expanded uncertainty Sample B
72	69.90	68.70	69.300	67.60	69.60	68.600	-0.01	-0.61	±8 %	±8 %
73	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

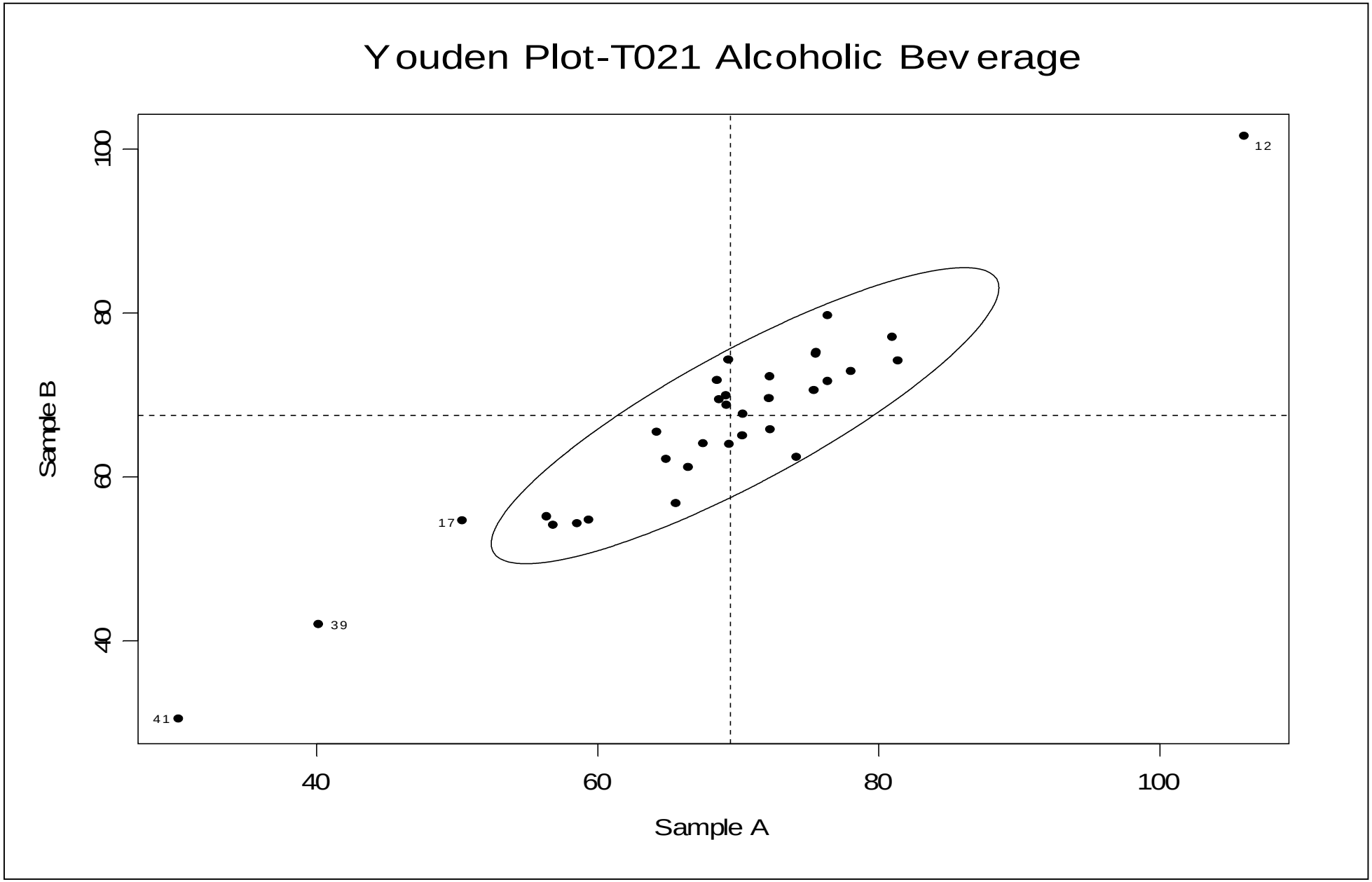
No. of result	35	33
Median	69.50	67.50
Normalized IQR	7.589	8.214
Robust CV(%)	10.92	12.168
Maximum	106.14	101.4
Minimum	30.315	30.315
Range	75.825	71.085

NOTE : ※ denotes an outlier (i.e. |z-score|>3)

Item 2 – APLAC Sample A & Sample B




Item2 - APLAC Sample A& Sample B
6.000
3.000
0.000
-3.000
-6.000
Within Laboratory Z-Score
27 17 2 36 39 33 61 46 41 1 59 72 25 10 62 63 57 18 40 64 26 12 4 16 52 55 56 8 31 7 43 71 44
Labortory Code Number


Youden Plot-T021 Alcoholic Beverage
Sample B
Sample A
100
80
60
40
40
60
80
100
12
17
39
41

Test methods and testing equipment

Item	Test	
1	Methanol(mg/L)	
Lab Code	Method	Technique
1	F14.2 in house diffect intection	Gas Chromatography
2	Internal Procedure	Gas Chromatography fid
3	MNS GOST R 51698:2004	HP GC 4890D
4	AOAC 972.11	Gas Chromatography
5	Method of Test for Alcoholic Beverages-Test of Methanol(GC)	Gas Chromatography
6	N/A	N/A
7	DOH Food Sanitation Regulation No. 0929214397(2003 7 23)	Gas Chromatography
8	AOAC 1997 Method 972.11	Gas Chromatography
9	N/A	N/A
10	Internal Procedure	Gas Chromatography
11	N/A	Gas Chromatography
12	N/A	N/A
13	N/A	N/A
14	N/A	N/A
15	DOH Food Sanitation Regulation No. 0929214397(2003 7 23)	Gas Chromatography
16	N/A	N/A
17	N/A	CPG
18	Gas Chromatography	Internal Standard

1	Methanol(mg/L)	
Lab Code	**Method**	**Technique**
19	N/A	N/A
20	N/A	N/A
21	MNS GOST R 51698:2004	GC 6850, FID 19091F-115, HP-FFAP
22	N/A	N/A
23	N/A	N/A
24	CRG1 0±V	N/A
25	Internal Procedure	Gas Chromatography / fid
26	Method Enclosed	Gas Chromatography
27	Headspace analysis	Gas Chromatography
28	N/A	N/A
29	N/A	N/A
30	MNS GOST R 51698:2004	GC-HP4890D
31	N/A	Gas Chromatography
32	N/A	Gas Chromatography
33	N/A	Gas Chromatography
34	AOAC 2000	GC-FID
35	N/A	N/A
36	Method of Test for Alcoholic Beverages-Test of Methanol(GC)	GC/FID(Gas Chromatography/flame ionigation detente)
37	N/A	GC
38	MNS GOST R 51698:2004	GC-FID Varian CP-3800
39	N/A	N/A
40	IN HOUSE LAB. METHOD	Gas Chromatography
41	N/A	Gas Chromatography
42	N/A	N/A

1	Methanol(mg/L)	
Lab Code	**Method**	**Technique**
43	Internal Procedure	Destilacion y Cromatografia de gases
44	AC163	Gas Chromatography
45	N/A	N/A
46	National Tax Administration Agency prescribed analysis method annotation	Gas Chromatography
47	N/A	N/A
48	N/A	N/A
49	N/A	N/A
50	N/A	N/A
51	N/A	N/A
52	Reg. CE/2728/2000/A11.3	Gas Chromatography
53	N/A	N/A
54	N/A	N/A
55	O.V-Rpsolution OENO 7012000	Gas Chromatography
56	SOP ORG.M.013/A	Gas Chromatography
57	Official Journal of the European Communities L272, Vol 33, 3 okt 1990	GC-FID
58	N/A	N/A
59	N/A	N/A
60	UNI 10629:June 1998	Gas Chromatography
61	CRU BDi202-RELOD	Gas Chromatography
62	N/A	N/A
63	SOP No. 5.40	Headspace Gas Chromatography
64	N/A	Gas Chromatography
65	N/A	N/A
66	N/A	N/A

1	Methanol(mg/L)	
Lab Code	**Method**	**Technique**
67	N/A	N/A
68	N/A	N/A
69	DOH Food Sanitation Regulation No. 0929214397(2003 7 23)	Gas Chromatography
70	Method of Test for Alcoholic Beverages-Test of Methanol(GC)	Gas Chromatography
71	DOH Food Sanitation Regulation No. 0929214397(2003 7 23)	Gas Chromatography
72	STN 56 0210-9:1986	Spectrophotometry
73	DOH Food Sanitation Regulation No. 0929214397(2003 7 23)	Gas Chromatography

2	Sulfur dioxide (mg/kg)	
Lab Code	**Method**	**Technique**
1	N/A	Titration
2	Internal Procedure	Autoanalizador FCSA
3	N/A	N/A
4	RANKIN METHOD	Distillation and Alkali titration
5	N/A	N/A
6	N/A	N/A
7	DOH Food Sanitation Regulation No. 0939320212(4.09)	Titration
8	CAC/RM5:1969	N/A
9	N/A	N/A
10	RECC 2676/90, anexo, capitulo 25 metodo 2.2	Titration
11	N/A	N/A
12	IS:7585/1995	Titration
13	N/A	N/A
14	N/A	N/A
15	N/A	N/A
16	N/A	N/A
17	Franfz-Paul	Titration
18	Distination	Titration
19	N/A	N/A

2	Sulfur dioxide (mg/kg)	
Lab Code	**Method**	**Technique**
20	N/A	N/A
21	N/A	N/A
22	N/A	N/A
23	N/A	N/A
24	N/A	N/A
25	RECC 2676/90, Anexo, punto 25, apartado 2.2	Titration
26	IS:7585/1995	Titration
27	MONIER WILLIAM	Titration
28	N/A	N/A
29	N/A	N/A
30	N/A	N/A
31	N/A	N/A
32	N/A	Titration
33	N/A	Titration
34	N/A	N/A
35	N/A	N/A
36	DOH Food Sanitation Regulation No. 0939320212(4.09)	Titration method
37	N/A	N/A
38	N/A	N/A
39	N/A	Tilrahion
40	MODIFIED MONIER-WILLIAMS METHOD	Tilrahion
41	N/A	Tilrahion
42	N/A	N/A
43	Internal Procedure	Titration valoracion con Iodo
44	AOAC 990.28	Titration

2	Sulfur dioxide (mg/kg)	
Lab Code	**Method**	**Technique**
45	N/A	N/A
46	Food additive analysis method in food, 2nd Edition (2000)	Titration
47	N/A	N/A
48	N/A	N/A
49	N/A	N/A
50	N/A	N/A
51	N/A	N/A
52	internal method	iodometric titration
53	N/A	N/A
54	N/A	N/A
55	N/A	Titration
56	STN 560246	Titration
57	Braun och Luebbe	Colorimete
58	N/A	N/A
59	Tanner Method	Titration
60	N/A	N/A
61	Brol BD12OL-RRVO	Distillation and titration
62	Tanner Method (Modified Monier-wiuiams iechnique)	Distillation and titration
63	STN 56 02 16	Titration
64	N/A	Titration
65	N/A	N/A
66	N/A	N/A
67	N/A	N/A
68	N/A	N/A
69	N/A	N/A

2	Sulfur dioxide (mg/kg)	
Lab Code	**Method**	**Technique**
70	N/A	N/A
71	DOH Food Sanitation Regulation No. 0939320212(2004 9 21)	alkaline titration
72	Modified method STN 560216	Titration
73	N/A	N/A

APPENDIX B

Preparation of the Samples

Homogeneity Testing

and
Stability Testing

PREPARATION OF THE SAMPLES

The test samples of methanol and Sulfur dioxide in alcoholic beverage were provided by Taiwan Tobacco & Liquor Corporation. The homogeneity of methanol was tested by the Chemistry testing laboratory of Department of Health（DOH）, Yulin city government, R.O.C. The homogeneity of Sulfur dioxide was tested by Bureau of Standards, Metrology and Inspection（BSMI）, Ministry of Economic Affairs, R.O.C.

HOMOGENEITY TESTING

To allow for a suitable and reliable inter-laboratory comparisons, homogeneity testing was conducted on randomly selected samples before the test samples were distributed to participants. The number of test samples selected for homogeneity testing and stability testing were based on the total number of expected participating laboratories. The homogeneity testing for methanol and Sulfur dioxide was conduced by DOH and BSMI, respectively. For each tests (sample A and sample B), there were 15 sample tested both for methanol and Sulfur dioxide.

For the samples to demonstrate having no significant variability and to be accepted as suitable for use in the program the calculated coefficient of variation (CV) was to be less than 2%. The homogeneity test results and summary statistics are reported on Page B2-B3.

The statistical analysis (CV%) of the results obtained indicated that no significant variability existed. Therefore it was concluded that any outlier results subsequently identified for all tests could not be attributed to sample variability.

STABILITY TESTING

Stability testing were carried out during 2005/5/20 ~ 2005/5/30. Due to delivery difficulties, sample receipt was delayed for participating laboratories. The first stability testing was carried out in the early of July which is the same period as participating laboratories commence the test. The second stability testing (only Sulfur dioxide) was carried out in October 2005.

The content of methanol was concluded to be stable during the period of homogeneity testing and testing by participating. The content of Sulfur dioxide goes unstable during the first stability test. In order to further understanding the content of Sulfur dioxide decrease with time, the second stability testing carried out in October 2005. As data shows, the decrease of sulphur dioxide may be due to evaporation problems of element characters in room temperature. The detail of stability test are reported on Page B4 – B6.

The homogeneity test results prior to dispatching the test samples to the participating laboratories.

Homogeneity Tests：

（A）Methanol test result

Test date	Sample A (mg/L)			Sample B (mg/L)		
	No.	Test	CV (%)	No.	Test 1	CV (%
2005/05/20 ~ 2005/05/24	A08	95.219	0.993	B08	104.720	0.831
	A17	94.970		B17	104.224	
	A32	94.094		B32	103.768	
	A41	93.935		B41	104.146	
	A56	93.692		B56	103.683	
	A65	93.929		B65	104.329	
	A80	94.173		B83	103.598	
	A89	92.409		B86	104.281	
	A104	92.634		B107	102.990	
	A113	92.358		B110	103.108	
	A128	92.332		B131	104.156	
	A137	93.029		B134	101.544	
	A152	93.583		B155	103.231	
	A161	92.619		B161	105.159	
	A163	93.872		B166	103.348	

（1）Test result of 15 Sample A（10% SampleA）：
Average ：95.523
CV% ：0.993
（2）Test result of 15 Sample B（10% SampleB）：
Average ：103.752
CV% ：0.831

（B）Sulfur dioxide test result

Test date	Sample A (mg/kg)				Sample B (mg/kg)			
	No.	t’	w	Result	No.	Test 1	w	Result
2005/05/23 ~ 2005/05/27	A075	97.344	2.9286	Uniform	B075	98.781		
	A100	96.220			B118	97.790		
	A136	97.730			B123	98.170		
	A088	98.392			B094	98.970		
	A129	98.488			B099	97.137		
	A153	98.826			B135	96.996		
	A114	97.499			B070	97.773		
	A131	97.798			B159	96.638		
	A165	96.956			B165	95.432		
	A035	96.944			B046	95.950		
	A051	97.015			B057	95.358		
	A066	96.870			B147	96.386		
	A026	95.964			B033	96.364		
	A011	96.792			B009	97.266		
	A019	96.954			B022	96.373		

（1）Test result of 15 Sample A（10% SampleA）：
Average ：97.319
CV% ：0.835
（2）Test result of 15 Sample B（10% SampleB）：
Average ：97.026
CV% ：1.145

Stability Tests：

（A）Methanol test result

Test date	Sample A (mg/L)			Sample B (mg/L)		
	No.	Test	CV (%)	No.	Test 1	CV (%)
2005/06/30 ~ 2005/07/01	A15	96.511	0.375	B08	105.893	0.393
	A39	96.127		B17	106.152	
	A63	95.509		B32	106.098	
	A87	96.125		B41	106.028	
	A106	96.146		B56	105.137	

（1）Test result of 5 Sample A（3％ SampleA）：
Average ：96.084
CV% ：0.375
（2）Test result of 5 Sample B（3％ SampleB）：
Average ：105.862
CV% ：0.393

（B1）Sulfur dioxide test result-1

Test date	Sample A (mg/L)			Sample B (mg/L)		
	No.	Test	CV (%)	No.	Test 1	CV (%)
2005/07/05 ~ 2005/07/06	A010	69.451	0.677	B003	68.121	0.706
	A069	70.123		B028	67.597	
	A090	69.125		B062	67.451	
	A091	70.219		B118	67.563	
	A141	69.994		B126	68.584	

（1）Test result of 5Sample A（3% Sample A）：
Average ：69.782
CV% ：0.677
（2）Test result of 5 Sample B（3% Sample B）：
Average ：67.863

CV% ：0.706

（B2）Sulfur dioxide test result-2

Test date	Sample A (mg/L)			Sample B (mg/L)		
	No.	Test	CV (%)	No.	Test 1	CV (%)
2005/10/4 ~ 2005/10/5	A-49	49.632	1.955	B-137	47.512	1.691
	A-123	50.804		B-79	47.973	
	A-85	50.973		B-133	47.824	
	A-86	51.196		B-146	48.247	
	A-111	49.975		B-140	46.453	
	A-92	50.288		B-164	48.308	
	A-109	50.625		B-167	45.922	

（1）Test result of 9 Sample A（6% Sample A）：

Average ：50.076

CV% ：0.677

（2）Test result of 9 Sample B（6% Sample B）：

Average ：47.446

CV% ：0.706

APPENDIX C

Instructions to Participants

Results Sheet

APLAC APT021 Proficiency Testing Program of Alcoholic Beverage Testing

INSTRUCTIONS TO PARTICIPATING LABORATORIES

To ensure that results from this program can be analyzed properly, participants are asked to adhere carefully to the following instructions.

1. SAMPLE

Two 350ml bags of samples labeled APT21A-__, APT21B-__, and the documents" Instructions To Participating Laboratories and Results Sheet" have been supplied to each laboratory. The Lab. Code is identified on the Result Sheets.

Upon receipt, unpack the artifacts and inspect them for any defects. Please contact your accreditation body if there is damage.

2. TESTS TO BE PERFORMED

Please ensure that the test is commence between 5th ~ 12th July 2005 and recorded on the Result Sheet.

Each sample should be testing both Methanol and Sulfur dioxide in duplicate to the reporting units and accuracy stated on the Result Sheet. Participants should use the routine test methods which accreditation is held.

3. DOCUMENTS TO BE SUBMITTED

Within one weeks of the completion of the tests, participating laboratories are required to send to their accreditation body:

No other documents are required. Laboratories should make a copy of all documents and worksheets for their own records and keep these on file for an adequate period of time (at least until a final report has been issued).

A final report will be issued at the end of the program with each laboratory only identified by a **confidential** code number.

4. CONFIDENTIALITY

For this program your laboratory has been allocated the code number shown on the results sheet. All reference to your laboratory in reports associated with this program will be with this code number, thus ensuring confidentiality of results.

5. GENERAL INFORMATION

For general queries, please contact your accreditation body.
Additional information may be obtained from:

Ms. Chan Yu-Ying
TAF/ Department of Laboratory Accreditation
FAX:+886-3-5714848ext203
TEL：+886-3-5726308
E-mail:yuyingchan@taftw.org.tw

APLAC APT021 Proficiency Testing Program of Alcoholic Beverage Testing

RESULTS SHEET

Laboratory Code:

Please complete this results sheet and return it to your national accreditation body and TAF/ Department of Laboratory Accreditation.

Testing Laboratory : _____ Date of test： _____
Test Sample ID : _____ (5th ~ 12th July 2005)

Summary of Test Results

Test	APT21A-__		APT21B-__		Method
	Result 1	Result2	Result1	Result2	
Methanol (mg/L)					
					Technique
Sulfur dioxide (mg/Kg)					
					Technique

REPORT ALL TEST TO 2DECIMAL PLACES
Note: Techniques may be Titration, gas chromatography….. etc.

Signature：_____ Date：_____

Measurement Uncertainty Budget

Items	Factors of Uncertainty x_i	Type A / Type B	Probability Distribution	Standard Uncertainty $u(x_i)$	Coverage Factor(κF
Combined Standard Uncertainty $u_c(Y)$ **:**					
Expanded Uncertainty (95 % confidence interval) $U_{exp}=\kappa=\kappa_c(y)$ **:**					

Note：Please participating laboratories provide test original data (curve diagrams) e-mail or fax to CNLA.

Signature：_____ Date：_____

INSTRUCTIONS – MEASUREMENT UNCERTAINTY
Part (1) Background information & justification for this change

ISO/IEC 17025 requires that, except under specified conditions, the uncertainty of measurement associated with the results of tests and measurements must be estimated.

What is uncertainty of measurement?
Uncertainty of measurement is defined as a "parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand" (the measurand is the particular quantity subject to measurement).

The result of a test or measurement is our best estimate of the true value of the measurand. The result is imperfect. The true value of the measurand is contained within a range of values about the measurement result and the "uncertainty of measurement" is an estimate of the magnitude of that range expressed at a given level of confidence (confidence interval). Uncertainty of measurement is usually given as a 95 % confidence interval and would normally be expressed in the appropriate SI units (ie. mm, °C, g/l, MPa etc).

For example, the result of a measurement might be 5.1 mg/l with an uncertainty of ±0.2 mg/l at a 95 % level of confidence. This means that there is an estimated 95 % probability that the true value is in the range 4.9 mg/l to 5.3 mg/l. The 95 % probability means that there is an estimated one in twenty chance that the true value is outside that range.

Uncertainty of measurement may also be expressed as a percentage where appropriate.

To assist laboratories to comply with the requirements of ISO/IEC 17025 for estimating uncertainty and to promote a uniform methodology in its estimation, information packages for APLAC PT testing program participants now include general guidance relating to estimating uncertainties for the specific testing involved, and final program reports will now include relevant worked examples. All program participants are required to report their estimates of uncertainty to their accreditation bodies along with their results unless the Technical Adviser to the program specifically waives any requirement to estimate uncertainties. The estimates of uncertainty provided by participants will be incorporated into the final program reports enabling direct comparison of uncertainty estimates across the program participants. The uncertainty estimates will not be used in the evaluation of the results on the primary samples.

How is uncertainty of measurement to be estimated?
APLAC expects that program participants' uncertainties of measurement would be estimated in accordance with the requirements of the respective member accreditation bodies. There are different approaches and methodologies available. Worked examples provided in APLAC PT program reports will generally be based on ISO GUM but will recognise other methodologies in accordance with 5.4.6.3 NOTE 3 in ISO 17025.

Estimates of uncertainty of measurement provided by program participants are required to be given at the 95 % level of confidence.

ISO GUM methodology
An estimate of uncertainty of measurement would usually be based on the combination of a number of influencing parameters (components of uncertainty) such as errors in reference values, instrument errors, repeatability, thermal effects, weighing errors, inhomogeneity etc. ISO GUM methodology requires that the influence of each component of uncertainty on the measurement result be quantified and expressed numerically as a standard deviation. These values are then combined according to the rules of the propagation of uncertainty to produce a combined standard deviation (combined standard uncertainty) and the combined standard uncertainty is multiplied by a coverage factor to produce an expanded uncertainty

at the required level of confidence. Detailed descriptions and information on the implementation of this methodology have been published by ISO[2] , UKAS[3] and Eurachem/CITAC[4] and made available over the internet[7].

Uncertainty of measurement is best estimated within the individual laboratory environment. All factors which will have a significant influence on the test or measurement result must be included in the estimation process. There must be suitable programs utilising reference standards, instruments and materials to ensure on-going and adequate quality control and repeatability and reproducibility of methods and equipment over time. In many instances, it will be possible to utilise quality control data in assessing uncertainty components such as precision. Where these data are not available, it may be necessary to carry out precision studies or to rely on published information about the method or portions of it until the laboratory can obtain its own estimates.

APLAC is aware of the general need for better estimates of uncertainty, and estimates that are obtained under similar conditions in all laboratories. PT programs are useful mechanisms for spreading awareness of uncertainty of measurement and the effects of different ways of estimating it. We anticipate that the information made available through PT programs will help focus discussions on uncertainty of measurement.
APLAC Technical Committees will interpret the information and report on current practices. They will also make recommendations for improving the collection of uncertainty data, the estimation of uncertainties and incorporating data and information on uncertainty of measurement into PT program reports. Therefore we anticipate an evolution in the mechanisms for collecting and reporting uncertainty data and associated information over the next few years.

Participation in APLAC PT programs should assist laboratories to develop appropriate estimates of uncertainty, help to guide accreditation bodies to adopting common and consistent approaches leading to enhanced understanding and international comparability of measurements among the member nations.

APLAC will consider the use of estimates of uncertainty of measurement in the evaluation of its PT testing program results after it is satisfied that participating laboratories are estimating uncertainties of measurement in an appropriate and consistent manner.

Here are a few important terms:

Standard uncertainty (*u(xi)*) is an input component of uncertainty *xi* expressed as a standard deviation. It should be expressed in the units of the influencing parameter, but may be expressed as a percentage where convenient.

Type A evaluation estimates of standard uncertainty are evaluated by applying statistical techniques to a series of repeatability or curve fitting data. For example, a standard uncertainty estimated from the repeatability of measurements on replicate samples is a Type A evaluation.

Type B evaluation estimates of standard uncertainty are based on assumed probability distributions, experience, laboratory records, or other information. For example, a standard uncertainty estimated using data provided on a calibration certificate is a Type B evaluation.

Sensitivity coefficient (*ci*) is the mathematical relationship between an influencing parameter and its effect on the result of a measurement. In many instances it is unity. That is, there is a one to one relationship between the value of the influence and its effect on the measurement result. For example, when weighing a sample of material, any uncertainty due to errors in the balance reading will have a one to one effect on the measurement result. On the other hand, if we are considering the influence of temperature on the length of a metal bar then the sensitivity coefficient is equal to the coefficient of linear

thermal expansion for the metal bar multiplied by the length of the bar. It is important to note that a sensitivity coefficient has units. It is also important to note that the calculation methodology used by Eurachem/CITAC4 incorporates sensitivity coefficients in a manner which does not require their specific evaluation.

Combined standard uncertainty (*uc(y)*) is the final estimate of uncertainty for the test or measurement result *y* expressed as a standard deviation. It is calculated by multiplying the standard uncertainty *u(xi)* for each input component *(xi)* with its respective sensitivity coefficient *ci* to produce *ciu(xi)* and then combining those values by taking the square root of the sum of their squares. Note that the products *ciu(xi)* must each be expressed in the same units as those required for expressing the combined estimate *uc(y).*

Expanded uncertainty (*U*) is the final result of our estimate of uncertainty expressed as a confidence interval. It is calculated by multiplying the combined standard uncertainty by a coverage factor to produce the desired level of confidence (usually 95 %).

Coverage factor (*k*) is a multiplier used to expand the combined standard uncertainty *uc(y)* to an interval that is estimated to contain the true value of the measurand at a given level of confidence ($U = k.uc(y)$). The coverage factor then represents the number of standard deviations in the expanded uncertainty and is determined according to the Student-t distribution. A coverage factor of 2 is commonly used to approximate the expanded uncertainty to the 95 % confidence level.

References

1. ISO-IEC 17025:1999. General requirements for the competence of testing and calibration laboratories. ISO, Geneva (1999)
2. Guide to the Expression of Uncertainty in Measurement. ISO, Geneva (1993)
3. UKAS LAB 12: The Expression of Uncertainty in Testing. UKAS, London(2000)
4. Eurachem / CITAC Guide QUAM:2000.P1. Quantifying Uncertainty in Analytical Measurement, 2nd Edition (2000)
5. ISO/DTS 21748:2002 Guide for the use of repeatability, reproducibility, and trueness estimates in measurement uncertainty estimation.
6. APLAC TC 005, Interpretation and Guidance on the Estimation of Uncertainty of Measurement in Testing
7. Websites: www.A2LA.org/ (for A2LA policies, links to guidance documents, including the UKAS Guide, and the Eurachem/CITAC Guide, at no cost) www.measurementuncertainty.org/ (Eurachem/CITAC Guide) www.fasor.com/iso25/ (general information, links, and discussion of ISO-IEC 17025)

APPENDIX D

Statistical Procedures, Calculations and Formulae

STATISTICAL PROCEDURES

For each statistically analysed test, the following information is given :

(a) a table of results and calculated z-scores;
(b) a list of summary statistics;
(c) ordered z-score charts; and
(d) a youden diagram

(a) Table of Results and Robust Z-Scores

These tables contain the results returned by each laboratory, and the z-scores calculated for each pair of results.

Please note that the results are presented in the table "as reported" by participants.
Outliers are identified in the table by a marker (※) next to the relevant z-scores

(b) Summary Statistics

The list of summary statistics appears at the bottom of the table of results and consists of:
(i) the number of results for that test/sample (*No. of Results*);
(ii) the median of laboratory's results - i.e. the middle value (*Median*);
(iii) the normalised interquartile range of the results (*Normalised IQR*) – the interquartile range times 0.7413;
(iv) the robust coefficient of variation, expressed as a percentage (*Robust CV*) - i.e. 100 × *Normalised IQR* ÷ *Median*;
(v) the minimum and maximum laboratory results; and
(vi) the range (*Maximum* - *Minimum*).

(c) Ordered Z-Score Charts

On these charts each laboratory's z-score is shown, in order of magnitude, and is marked with its code number. From these each laboratory can readily compare its performance relative to the other laboratories.

For sample pair A & B, the first chart in each section is of the between-laboratories z-scores for the sample pair and the second is of the within-laboratory z-scores (if applicable).

These charts contain solid lines at +3 and –3, so the outliers are clearly identifiable as the laboratories whose "bar" extends beyond these "cut off" lines. The y-axis has been limited to range from –5 to +5, so in some cases very large or small (negative) z-scores appear as extending beyond the limit of the chart.

(d) Youden Diagrams

Youden two-sample diagrams are presented to highlight laboratory systematic differences. They are based on a plot of each laboratory's pair of results, sample two versus sample one, represented by a black spot •.

These diagrams also feature an approximate 95 % confidence ellipse for the bivariate analysis of the results, and dashed lines which mark the median value for each of the samples.

All points which lie outside the ellipse are labelled with the laboratory's code number. Note however that these points may not correspond with those identified as outliers. This is because the outlier criterion (|z-score| > 3) has a confidence level of approximately 99 %, whereas the ellipse is an approximate 95 % confidence region.

So, the points outside the ellipse on the Youden diagram will roughly correspond to those with z-scores greater than 2 or less than –2. The laboratories which are outside the ellipse but have not been identified as extreme (those which have 2 < |z-score| < 3) are encouraged to investigate their results.

(i) laboratories with significant systematic error components (i.e. between-laboratories variation) will be outside the ellipse in either the upper right hand quadrant (as formed by the median lines) or the lower left hand quadrant, i.e. inordinately high or low results for both samples.

(ii) laboratories with random error components (i.e. within-laboratory variation) significantly greater than other participants will be outside the ellipse and (usually) in either the upper left or lower right quadrants, i.e. an inordinately high result for one sample and low for the other.

It is important to note however that Youden diagrams are an illustration of the data only, and are *not* used to assess the results (this is done by the z-scores).

STATISTICAL CALCULATIONS AND FORMULAE

Suppose we have pairs of results (for related samples) from a number of laboratories. Let *Ai* be the result for the first sample (A) from laboratory *i*. Similarly, *Bi* is the result from laboratory *i* for the second sample (B). The number of (pairs of) results is denoted by *N*.

The median is the middle value of the group, i.e. half of the results are higher than it and half are lower. It is calculated from the sorted values (from lowest to highest). If *N* is an odd number, the median is the singular central value. If *N* is even, it is the average of the two central values.

The interquartile range (*IQR*) is the difference between the lower and upper quartiles. The lower quartile (*Q1*) is the value *below* which a quarter of the results lie. Similarly, the upper quartile (*Q3*) is the value *above* which a quarter of the results lie. The quartiles are calculated analogously to the median and *IQR*=*Q3*-*Q1*. The "Normalised IQR" equals *IQR*x0.7413. The factor 0.7413 comes from the standard normal distribution, which has a mean of zero and a standard deviation equal to one. The width of the interquartile range of such a distribution is 1.34898 and 1/1.34898 = 0.7413.

Multiplying the *IQR* by this factor makes it comparable to a standard deviation. TheM"Robust CV" is a coefficient of variation and is equal to the normalised IQR divided by the median, expressed as a percentage (i.e. multiplied by 100). The minimum, maximum and range are the lowest value, the highest value and the difference between them (respectively).

Robust z-scores are calculated by replacing the mean and standard deviation in the "classical" z-score by the median and normalised IQR, respectively - i.e. the z-score for a result is the result minus the median (all) divided by the normalised IQR. As indicated above, the between-laboratories and within-laboratory z-scores are based on the (standardised) sum and difference of the pair of results.

Let *Si* be the standardised sum of laboratory's results. Also, *Di* is the standardised difference between the two results from laboratory *i*. Now

$$Si = \frac{(Ai + Bi)}{\sqrt{2}}$$

$$Di = \frac{(Ai - Bi)}{\sqrt{2}} \qquad \text{if } median(Ai) > median(Bi),$$

or

$$Di = \frac{(Bi - Ai)}{\sqrt{2}} \qquad \text{if } median(Ai) < median(Bi).$$

So, the between-laboratories z-score for laboratory *i* (denoted *ZBi*) is the robust z-score of its *Si* and their within-laboratory z-score (*ZWi*) is the robust z-score of its *Di* - i.e.

$$ZBi = \frac{Si - median(Si)}{IQR(Si) \times 0.7413}$$

and

$$ZWi = \frac{Di - median(Di)}{IQR(Di) \times 0.7413}$$