APLAC

Asia Pacific Laboratory Accreditation Cooperation

APLAC T056

Pesticide Residues in Rice Proficiency Testing Program

FINAL REPORT

China National Accreditation Service
for Conformity Assessment (CNAS)

November 2008

ACKNOWLEDGMENTS

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CNAS would like to appreciate Mr Cao Zhijun, the PT manager for conducting this program, also appreciate Mr Lin Weixuan, Mr Zheng Jiang, and Mr Dong Weifeng from Technical Centre of LNCIQ, and relevant experts for their arduous works on designing and coordinating this program, preparing samples and necessary documents, communicating with relevant parties, developing and implementing technical and statistical procedures, and issuing the interim and final reports.

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APLAC T056

Pesticide Residues in Rice Proficiency Testing Program

FINAL REPORT

1. Instruction

This report summarizes the results of APLAC Pesticide Residues in Rice Proficiency Testing Program T056.

This program was conducted in accordance with the interlaboratory testing scheme specified in *ISO/IEC Guide 43-1*, covered quantitative tests on **Fenvalerate** contents in rice powder samples. This program applies only to the use of interlaboratory comparisons of the purpose of proficiency testing. The aim of this program is to assess the performance of individual laboratories for specific tests. It does not include determining the effectiveness and precision of testing methods.

2. Main Relevant Parties

Asia Pacific Laboratory Accreditation Cooperation (APLAC) approved the program.

2.1 Organizing and Coordinating Bodies

APLAC T056 Program was organized by China National Accreditation Service for Conformity Assessment (CNAS) and coordinated by Technical Centre of Liaoning Entry-Exit Inspection and Quarantine Bureau of People's Republic of China.

2.2 Summary of Participants and Their Accreditation Situations

The members of APLAC, EA, IAAC and some other laboratory accreditation bodies were invited to nominate laboratories to participate in this program. A total of 53 laboratories from 23 economies were nominated.

8 laboratories could not report any results till the testing deadline, while 45 laboratories reported the testing results of fenvalerate contents in the three samples, in which 34 laboratories were accredited for testing fenvalerate contents by their accreditation bodies.

Each participating laboratory was endowed with an exclusive lab code. All references to the laboratories associated with this program are with these codes, respectively. The numbers of laboratories with respect to their accreditation bodies are listed in Table 1.

Table 1 Summary of Participants

Economy	Accreditation Body	Number of Labs
Argentina	Organismo Argentino de Acreditación (OAA)	2
Australia	National Association of Testing Authorities (NATA)	4
Brasil	General Accreditation Coordination – Cgcre/Inmetro	2
Canada	Standard Council Of Canada (SCC)	4
Chile	Instituto Nacional de Normalización (INN)	2
China	China National Accreditation Service for Conformity Assessment	4
Chinese Taipei	Taiwan Accreditation Foundation(TAF)	4
Czech Republic	Czech Accreditation Institute, o.p.s.	2
France	COFRAC	1
Chinese Hong Kong	Hong Kong Accreditation Service (HKAS)	2
Indonesia	National Accreditation Body of Indonesia (KAN)	4
Israel	Israel Accreditation (ISRAC)	3
Japan	The Japan Accreditation Board for Conformity Assessment (JAB)	1
New Zealand	International Accreditation New Zealand (IANZ)	3
Norway	Norwegian Accreditation (NA)	1
Philippines	Philippine Accreditation Office	4
Portugal	IPAC- Instituto Português de Acreditação, I.P.	2
Romania	RENAR-Romanian Accreditation Association	1
Singapore	Singapore Accreditation Council	2
Slovenia	Slovenian Accreditation	1
Sri Lanka	Sri Lanka Accreditation Board for Conformity Assessment	1
Trinidad and Tobago	Trinidad and Tobago Laboratory Accreditation Service	2
Viet Nam	Institute of Hygene and Public Health	1

3. Statistical Design

3.1 Agreement of Testing Methods

Fenvalerate is widely used as a pesticide in rice, tobacco, soybean, corn, fruit tree, vegetable and cotton to kill the pests. Unfortunately, fenvalerate is provided with middling toxicity, which is harmful to human health.

There are various methods for quantifying fenvalerate residues in plant products, however, there was no evidence on harmonization of these methods. Prior to this program, a series of experiments were carried out in our laboratory using some typical methods for rice powder. It indicated that extraction and purification efficiency are main factors leading bias to the testing results. Thus, an

operationally-defined testing method was suggested in the Instruction to Participants in this program.

3.2 Three Samples Employed

The accuracy of testing results may be different on samples with different residue levels. Consequently, discrepancy probably occurs for samples with different residue levels tested in different laboratories.

In this program, three samples with increasing contents of fenvalerate were employed, in which two levels were designed. The lower level was set at restriction level, the higher level was about 3.5 times the lower level. The accuracy of testing results at these different levels will be examined in this proficiency testing program.

Split-level design was used in this program, at the lower level, two samples with slightly different contents were employed. When the agreement of participants' results is well enough, the **laboratory repeatability** could be assessed.

3.3 Methods for Statistical Assessments

Robust statistical method was employed to assess the ability of participating laboratories to implement relevant tests of fenvalerate contents. Individual, within-lab and between-labs z-scores were intended to use as the assessments of the ability for an individual participating laboratory. Details are shown in Appendix D.

For each gross sample, the assigned value and the standard deviation for proficiency assessment were consensus values from participants. Statistical graphs, such as histograms and Youden plots were regarded as references to the overall effectiveness of this program.

3.4 Measurement Uncertainty

To ensure the **traceability**, the measurement uncertainty of the assigned values were evaluated and limited in sample preparation. It enables the assessments more reasonable.

4. Description of Samples

4.1 Preparation and Distribution

Each **gross sample** was prepared by adding designed amounts of fenvalerate (CAS Registering Number:51630-58-1 including four geometric isomers) in 30-60℃ petroleum ether to the blank rice powder, which had been crushed and ground to pass an 60-mesh sieve. Then, the petroleum ether was evaporated by vacuum distillation.

Respectively, each gross sample was divided and packed into light-resistant bags to make into testing samples.

The testing samples were randomly labeled and recorded. Testing samples packed with the Instructions for Participants (see Appendix E) were distributed directly to participating

laboratories as requested.

Note: *For the convenience of description in this report, these three gross samples are denoted as Gross Sample A, Gross Sample B and Gross Sample C, the testing samples prepared from each corresponding gross sample are denoted as Sample A, Sample B and Sample C, and the results obtained on these samples are denoted as Result A, Result B and Result C, respectively.*

4.2 Homogeneity and Stability

The samples randomly selected from each gross sample were determined for their homogeneity and stability. Details of sample homogeneity and stability check are described in Appendix C.

5. Testing Results and Assessments

5.1 Methods for Assessments

To assess performances of participants, individual z-score for each result was calculated, within-lab and between-labs z-scores for each pair of results (Result A and Result B) were derived based on the normalized difference and normalized sum of the paired results (also see Appendix D). As a general rule, according to *ISO/IEC GUIDE 43-1*, any absolute value of individual, within-lab or between-labs z-score falls in the range of 2 to 3 is regarded as a questionable result, while any absolute value of z-score exceeds 3 is regarded as an unsatisfactory result/pair of results.

The participants are encouraged to review, if any, the questionable or unsatisfactory results. It is suggested that the participants refer to the main technical aspects given in clause 6 of this report.

5.2 Statistics for Assessments

45 participating laboratories reported testing results of fenvalerate contents in samples A, B and C, the results are listed together with the testing methods in Appendix A. The robust mean, robust standard deviation and **standard uncertainty** for individual results A, B, C, normalized sum and normalized difference were estimated and listed in Table 2.

Table 2 Statistics for Assessments

Results	Robust Mean, mg/kg	Robust Standard Deviation, mg/kg	Standard Uncertainty of Assigned Value, mg/kg
Result A	0.51	0.17	0.04
Result B	0.54	0.16	0.03
Result C	1.86	0.52	0.11
Normalized Sum of Result A and B	0.73	0.22	0.05
Normalized Difference between Result A and B	0.02	0.05	0.01

A total of 14(31.1%) laboratories made questionable or unsatisfactory results, in which 7(15.6%) laboratories reported unsatisfactory results. The lab codes with questionable results are listed in Table 3.

Table 3 Laboratories Made Questionable or Unsatisfactory Results

z-scores	Questionable (2≤|z|<3)	Unsatisfactory (|z|≥3)
z-score of sample A (z_A)	T056-004, T056-038, T056-052	T056-003, T056-018, T056-033, T056-049, T056-051
z-score of sample B (z_B)	T056-047, T056-052	T056-003, T056-004, T056-018, T056-033, T056-038, T056-049, T056-051
z-score of sample C (z_C)	T056-033, T056-037, T056-038, T056-047, T056-052	T056-003, T056-004, T056-018, T056-049, T056-051
Between-labs z-score z_b(A&B)	T056-047, T056-050, T056-052	T056-003, T056-004, T056-018, T056-033, T056-038, T056-049, T056-051
Within-lab z-score z_W(A&B)	T056-003, T056-010, T056-033, T056-043, T056-049, T056-053	T056-018

6. Technical Commentary

In order to facilitate the participants to find the reasons of unsatisfactory results and improve their testing performance, main factors that influence the analytical results of fenvalerate contents are described as following

- Extracting method employed;
- Cleaning-up method employed;
- Correcting results by recovery;
- Testing conditions;
- Using and storage of reference materials;
- Storage conditions of samples.

In this program, nonpolar organic solvents or liquid-liquid extracting method was used by some participants to extract fenvalerate from the testing samples, it might lead to lower extraction efficiency and lower results. Extracting operation, such as oscillation, centrifugation and homogeneization, could cause loss of analytes if it is incomplete.

SPE methods were used by some participants for cleaning-up, however, unsuitable sort or volume of the elution solvents, or the unsuitable eluting rate may cause incomplete elution or loss of analyte. When inconsistent SPE columns or fussy cleaning-up steps were employed, the participant might receive large absolute within-lab z-score due to poor repeatability of the results. Some participants did not implement any cleaning-up steps, higer results were obtained due to interference.

Some participants used GC column with lower theoretical plates, some participants used improper chromatography columns or detectors, these may lead to inaccurate results.

According to some participants' feadback for the Interium Report of this program, the testing methods they used or the form of measurement uncertainty of testing results they reported were corrected in this final report.

APPENDIX A

Summary of Testing Results

The testing results on fenvalerate contents obtained from the participants with corresponding testing methods and the z-scores are listed in Table A.1.

In these tables, some abbreviations and symbols were used. The symbols z_A, z_B and z_C denote individual z-scores of result A, result B, result C, respectively. The symbols z_b and z_W denote between-labs z-scores and within-lab z-scores of paired results A and B, respectively. The symbol "#" indicates a z-score derived from a questionable result/pair of results, while "$" follows a z-score derived from an unsatisfactory result/pair of results. The abbreviations Norm. Sum and Norm. Diff. denote normalized sum and normalized difference of paired result A and B as described in Appendix D, respectively.

Table A.1 Testing Results with Their Assessments

LabCode	Result A (mg/ kg)	z_A	Result B (mg/ kg)	z_B	Result C (mg/ kg)	z_C	Norm. Sum (mg/ kg)	z_b	Norm. Diff. (mg/ kg)	z_W	Testing Method	LOD (mg/kg)
T056-001	0.46±0.14	-0.26	0.52±0.16	-0.11	1.6±0.5	-0.16	0.693	-0.19	0.042	0.46	GC-NPD	0.01
T056-002	0.49±0.10	-0.09	0.456±0.096	-0.50	1.79±0.38	-0.49	0.669	-0.30	-0.024	-0.87	GC-TOF-MS	0.05
T056-003	1.86±0.06	7.90$	1.74±0.05	7.45$	5.13±0.12	6.84$	2.546	8.17$	-0.085	-2.09#	GC-MS	0.05~0.11
T056-004	1.01±0.07	2.94#	1.13±0.08	3.67$	3.24±0.23	3.26$	1.513	3.51$	0.085	1.31	GC-ECD	0.02
T056-006	0.44±0.10	-0.38	0.52±0.10	-0.11	1.68±0.15	-0.16	0.679	-0.25	0.057	0.74	GC-ECD	0.01
T056-007	0.463±0.093	-0.25	0.469±0.094	-0.42	1.770±0.354	-0.47	0.659	-0.34	0.004	-0.31	GC-ECD	0.025
T056-008	0.40±0.01	-0.61	0.49±0.01	-0.29	1.70±0.05	-0.30	0.629	-0.47	0.064	0.89	GC-ECD	0.01
T056-010	0.4	-0.61	0.6	0.39	1.8	0.20	0.707	-0.12	0.141	2.45#	HPLC-PDA	0.01
T056-011	0.44±0.02	-0.38	0.43±0.02	-0.67	1.74±0.07	-0.49	0.615	-0.54	-0.007	-0.53	GC-ECD	0.01
T056-013	0.412±0.066	-0.54	0.323±0.052	-1.33	1.32±0.279	-1.37	0.520	-0.97	-0.063	-1.65	GC-ECD	0.01
T056-014	0.415±0.0167	-0.53	0.423±0.0152	-0.71	1.58±0.0295	-0.53	0.593	-0.64	0.006	-0.28	GC-ECD	0.0053
T056-015	0.453±1.32%	-0.30	0.496±1.11%	-0.26	1.905±2.59%	-0.23	0.671	-0.29	0.030	0.22	GC-MS	0.01
T056-016	0.3503±0.0581	-0.90	0.3882±0.0523	-0.92	1.5118±0.3207	-0.66	0.522	-0.96	0.027	0.15	GC-MS	0.036
T056-017	0.41±0.04	-0.56	0.55±0.06	0.08	1.61±0.16	0.03	0.679	-0.25	0.099	1.60	GC-ECD	0.01
T056-018	1.443±50%	5.47$	1.19±50%	4.05$	4.336±50%	4.77$	1.862	5.09$	-0.179	-3.98$	GC-TOF-MS	0.025
T056-019	0.287±30%	-1.27	0.364±30%	-1.07	1.143±30%	-1.03	0.460	-1.24	0.054	0.70	GC-MS	0.010
T056-020	0.410±0.070	-0.56	0.525±0.089	-0.08	2.230±0.38	-0.07	0.661	-0.33	0.081	1.24	GC-MS-MS	0.006

LabCode	Result A (mg/ kg)	z_A	Result B (mg/ kg)	z_B	Result C (mg/ kg)	z_C	Norm. Sum (mg/ kg)	z_b	Norm. Diff. (mg/ kg)	z_W	Testing Method	LOD (mg/kg)
T056-021	0.47	-0.21	0.49	-0.29	1.7	-0.30	0.679	-0.25	0.014	-0.11	LC-MS	0.1
T056-023	0.47±0.09	-0.21	0.53±0.11	-0.05	1.66±0.33	-0.05	0.707	-0.12	0.042	0.46	GC-MS/MS	0.01
T056-025	0.481±0.007	-0.14	0.506±0.005	-0.19	1.851±0.222	-0.22	0.698	-0.16	0.018	-0.04	GC-ECD	0.01
T056-026	0.439±0.102	-0.39	0.474±0.110	-0.39	1.736±0.403	-0.34	0.646	-0.40	0.025	0.11	GC-ECD/ GC-MS-MS	0.05
T056-027	0.534±0.060	0.17	0.514±0.058	-0.14	1.828±0.206	-0.20	0.741	0.03	-0.014	-0.67	GC-uECD-MS	0.01
T056-028	0.47±0.06	-0.21	0.52±0.06	-0.11	1.96±0.07	-0.13	0.700	-0.15	0.035	0.32	GC-ECD	0.01
T056-029	0.62±0.07	0.67	0.66±0.10	0.76	1.8±0.07	0.72	0.905	0.77	0.028	0.18	GC-MS	0.02
T056-030	0.50±15%	-0.03	0.52±15%	-0.11	1.60±15%	-0.11	0.721	-0.06	0.014	-0.11	GC-ECD	0.010
T056-031	0.436±0.10	-0.40	0.469±0.10	-0.42	1.77±0.45	-0.38	0.640	-0.43	0.023	0.08	GC-MS	0.01
T056-033	1.17±0.07	3.88$	1.03±0.06	3.05$	3.55±0.22	2.66#	1.556	3.70$	-0.099	-2.38#	GC-ECD	0.022
T056-034	0.456±0.296	-0.29	0.419±0.296	-0.73	1.693±0.296	-0.66	0.619	-0.52	-0.026	-0.92	GC-uECD	0.005
T056-035	0.587±0.223	0.48	0.575±0.219	0.23	2.509±0.953	0.09	0.822	0.39	-0.008	-0.56	GC-MS	0.040
T056-036	0.46	-0.26	0.50	-0.23	1.74	-0.22	0.679	-0.25	0.028	0.18	GC-ECD	0.05
T056-037	0.773±10%	1.56	0.754±10%	1.34	2.921±10%	2.02#	1.080	1.56	-0.013	-0.66	GC-ECD	0.020
T056-038	<0.005±0.00	-2.92#	0.031±0.01	-3.14$	0.662±0.07	-2.65#	0.025	-3.20$	0.018	-0.02	HPLC-UV	0.005
T056-039	0.50±4.40%	-0.03	0.52±4.40%	-0.11	1.82±4.40%	-0.11	0.721	-0.06	0.014	-0.11	GC-ECD	0.01
T056-041	0.475±0.022	-0.18	0.574±0.043	0.23	1.901±0.043	0.09	0.742	0.03	0.070	1.01	GC-ECD	0.005
T056-042	0.45±0.06	-0.32	0.53±0.07	-0.05	1.87±0.24	-0.01	0.693	-0.19	0.057	0.74	GC-uECD	0.003

LabCode	Result A (mg/ kg)	z_A	Result B (mg/ kg)	z_B	Result C (mg/ kg)	z_C	Norm. Sum (mg/ kg)	z_b	Norm. Diff. (mg/ kg)	z_W	Testing Method	LOD (mg/kg)
T056-043	0.71	1.19	0.59	0.33	1.22	0.10	0.919	0.83	-0.085	-2.09#	GC-ECD	0.01
T056-044	0.36±0.15	-0.85	0.36±0.15	-1.10	1.51±0.61	-1.22	0.509	-1.02	0.000	-0.39	GC-MS	<0.05
T056-046	0.68±0.12	1.02	0.70±0.12	1.01	1.97±0.24	1.26	0.976	1.09	0.014	-0.11	GC-MS	0.05
T056-047	0.838	1.94	0.917	2.35#	2.907	2.05#	1.241	2.29#	0.056	0.73	GC-MS	0.01
T056-048	0.52	0.09	0.48	-0.36	1.75	-0.31	0.707	-0.12	-0.028	-0.96	GC-MS	0.01
T056-049	1.58±20%	6.27$	1.46±20%	5.72$	4.51±20%	6.30$	2.150	6.38$	-0.085	-2.09#	GC-ECD	0.002
T056-050	0.269±0.0301	-1.38	0.2945±0.0301	-1.51	0.6005±0.0301	-2.29#	0.398	-1.52	0.018	-0.03	GC-ECD	0.001
T056-051	1.340±0.156	4.87$	1.455±0.056	5.69$	5.415±0.151	5.10$	1.976	5.60$	0.081	1.24	GC-ECD	0.084~0.234
T056-052	0.113±0.024	-2.29#	0.169±0.022	-2.28#	0.475±0.021	-2.41#	0.199	-2.41#	0.040	0.40	GC-ECD	0.005
T056-053	0.422±0.033	-0.49	0.600±0.029	0.39	1.900±0.078	0.22	0.723	-0.05	0.126	2.13#	GC-ECD	0.010

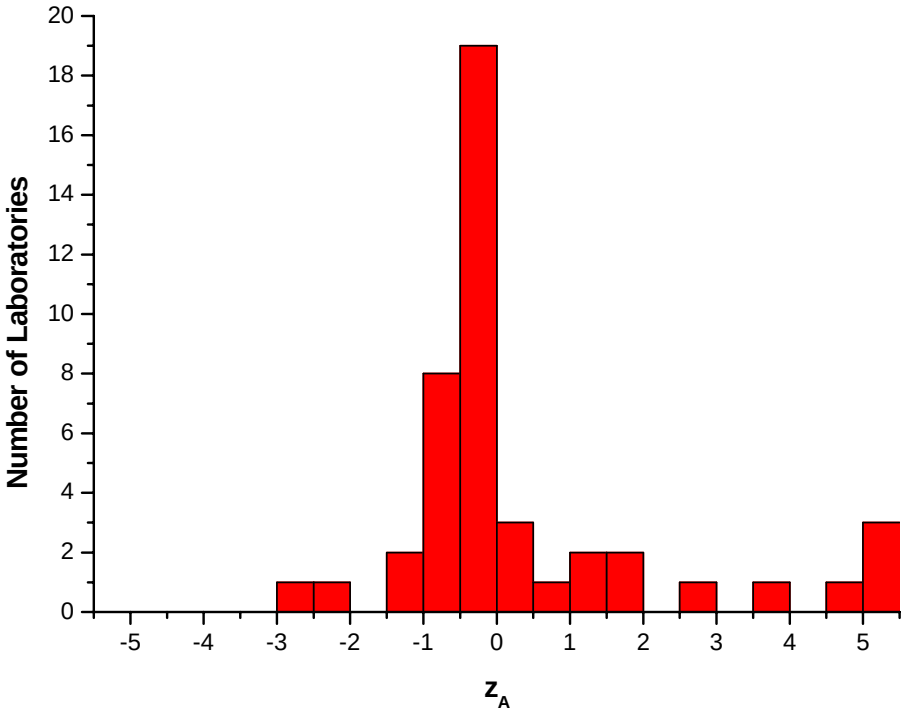
APPENDIX B

Graphical Display of Testing Results

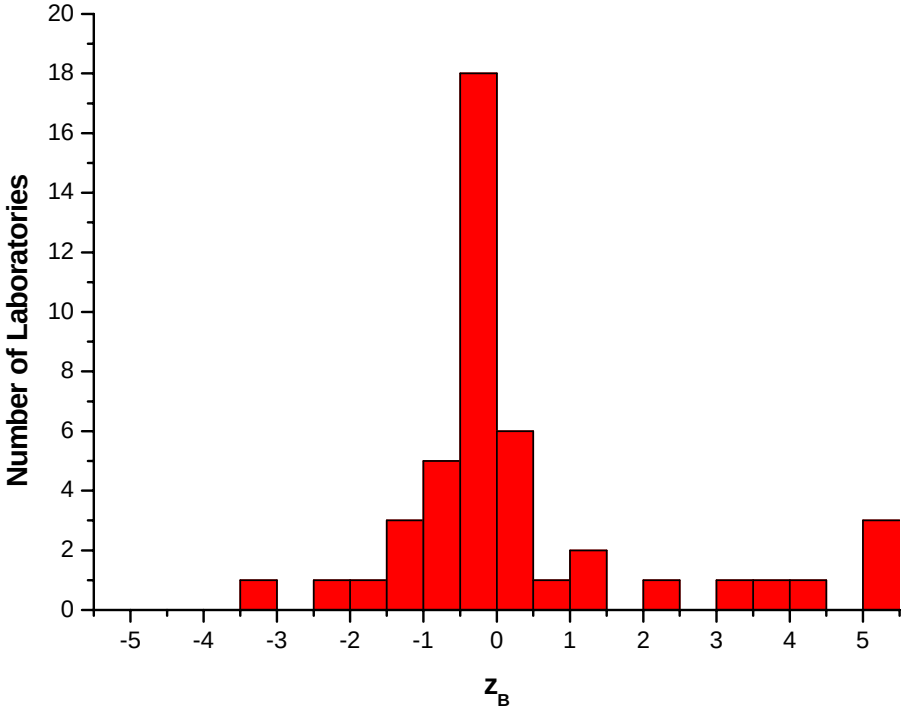
Here, graphs were made in order to give an open-and-shut display of testing results and their statistics.

Histograms of z-scores (B.1~B.5) show the distributions of testing results. Ordered z-score bar charts (B.6~B.10) are given in order to facilitate visual identification of the questionable and unsatisfactory results. Youden Plots of paired z-scores (B.11) distinctly reveal questionable and unsatisfactory results, points outside the ellipses indicate their well-separated from the rest of the data, where points far out along the major axis of the ellipses imply that the results are subject to bias or large variation, and those points far away from the major axis represent participants whose repeatability is poor. Generally, labs with large absolute between-labs z-scores should be outside the ellipse in quadrants 2 and 4, while labs with large absolute within-lab z-scores should be outside the ellipse in quadrants 1 and 3. Some points are too far away from the ellipses to be drawn on the Youden Plots, the corresponding lab codes are drawn together with arrows that indicate their orientations.

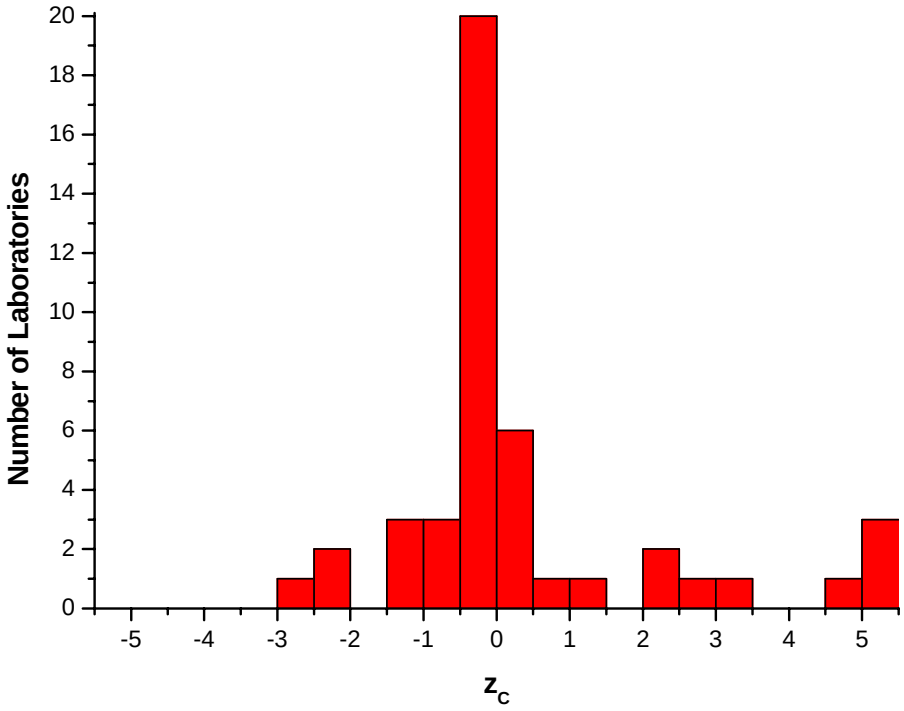
B.1 Distribution of Testing Results in Sample A



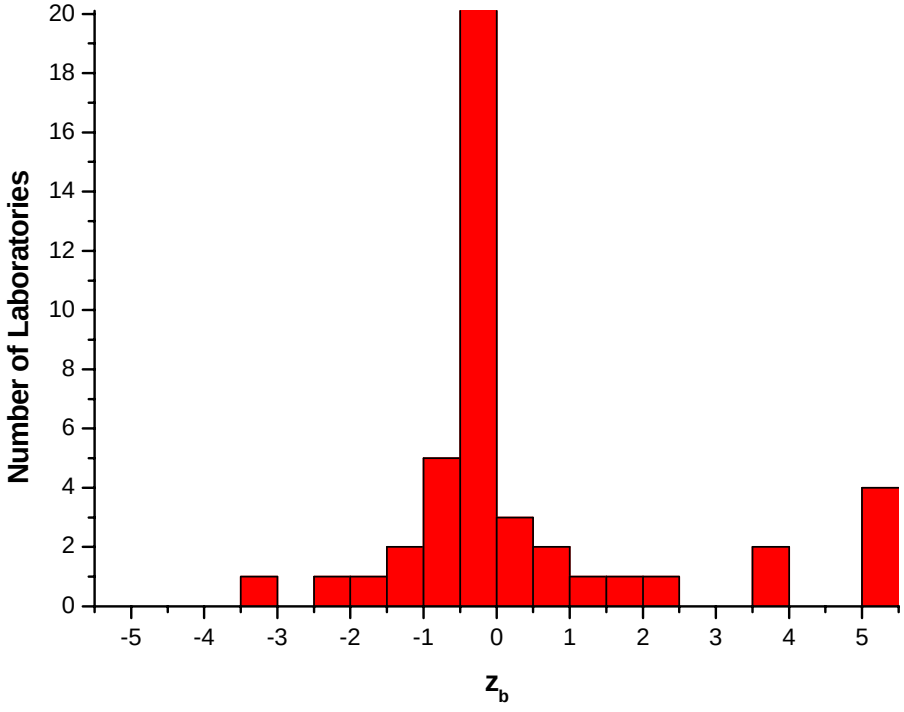
B.2 Distribution of Testing Results in Sample B



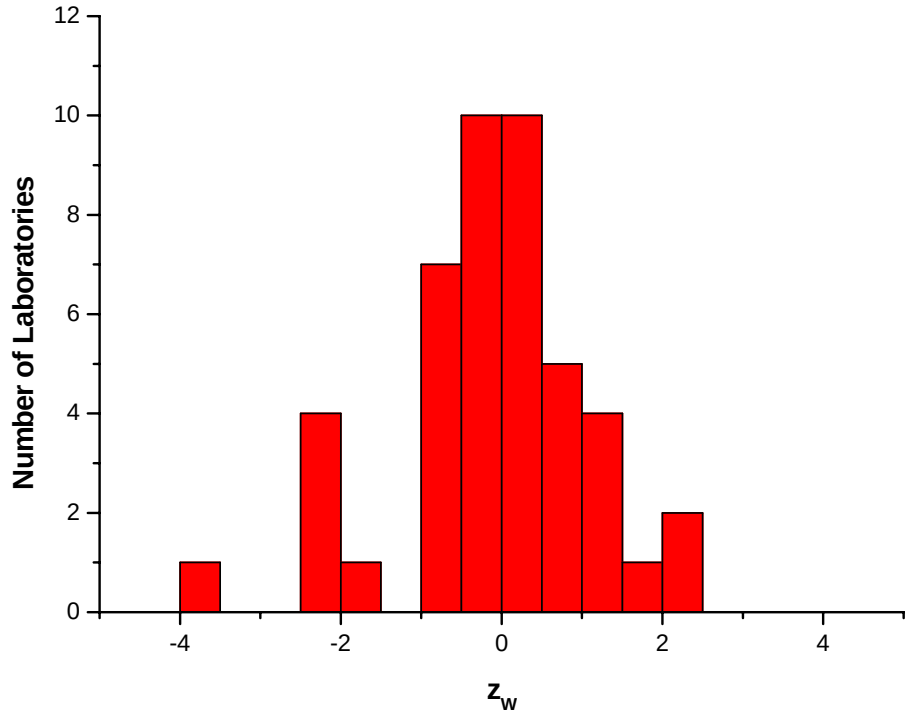
B.3 Distribution of Testing Results in Sample C



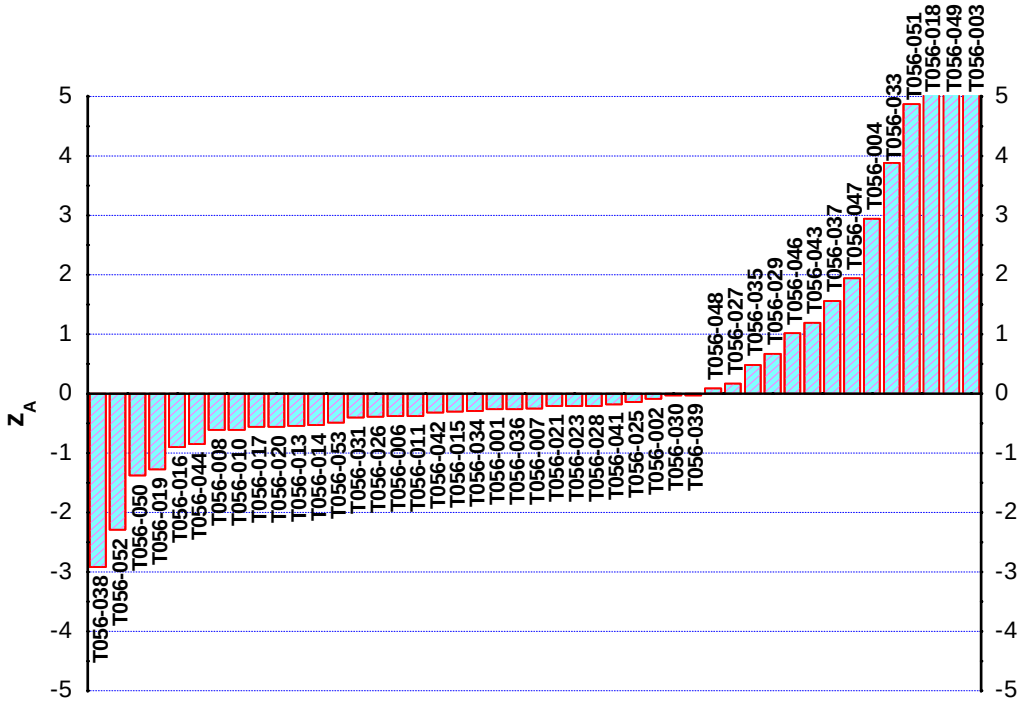
B.4 Distribution of Normalized Sum of Paired Results A and B



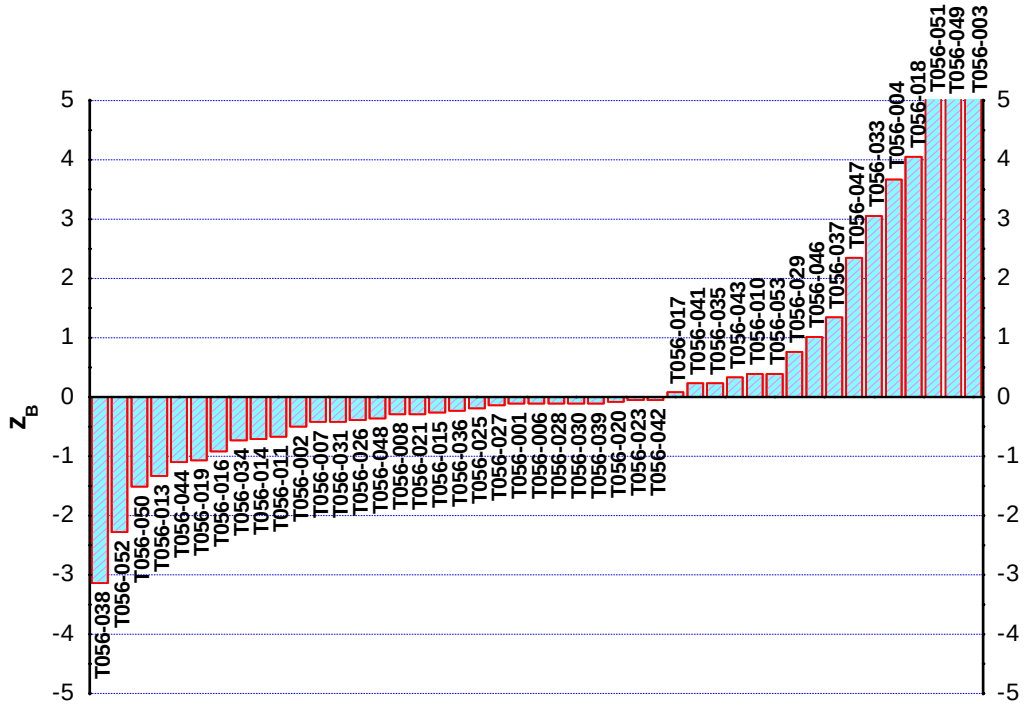
B.5 Distribution of Normalized Difference of Paired Results A and B



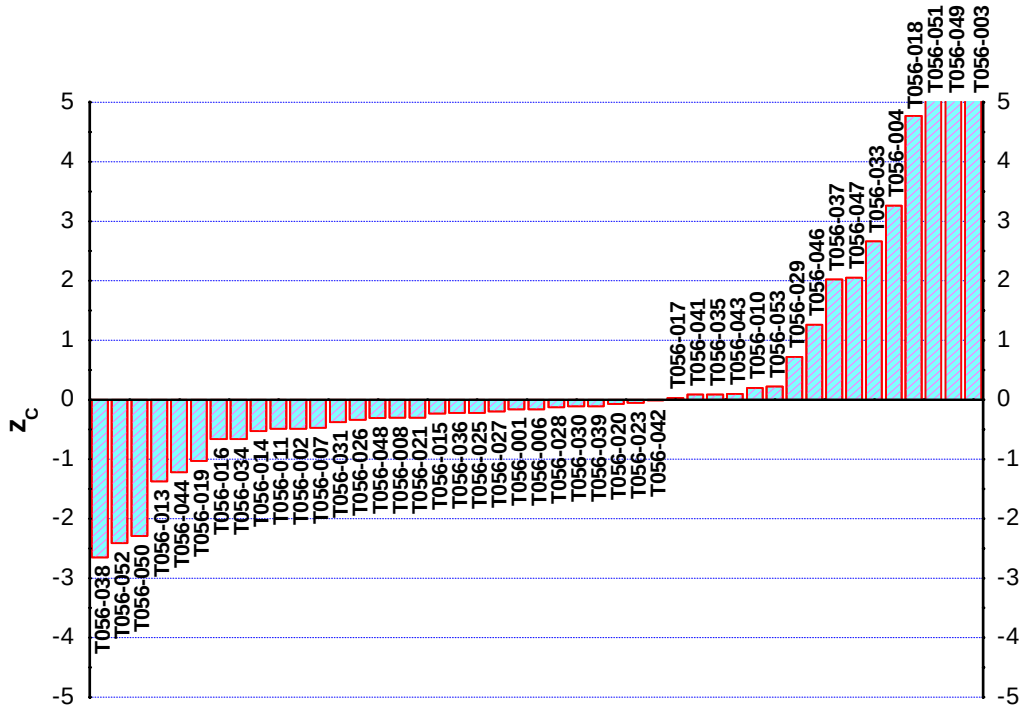
B.6 Ordered z-scores Bar Chart of Results A



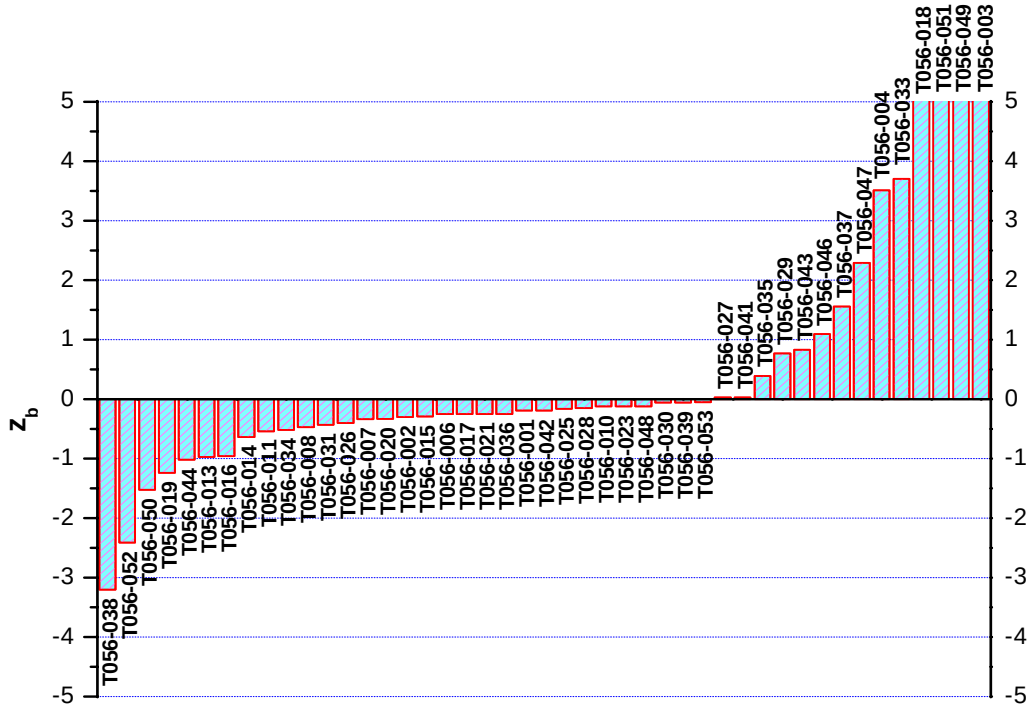
B.7 Ordered z-scores Bar Chart of Results B



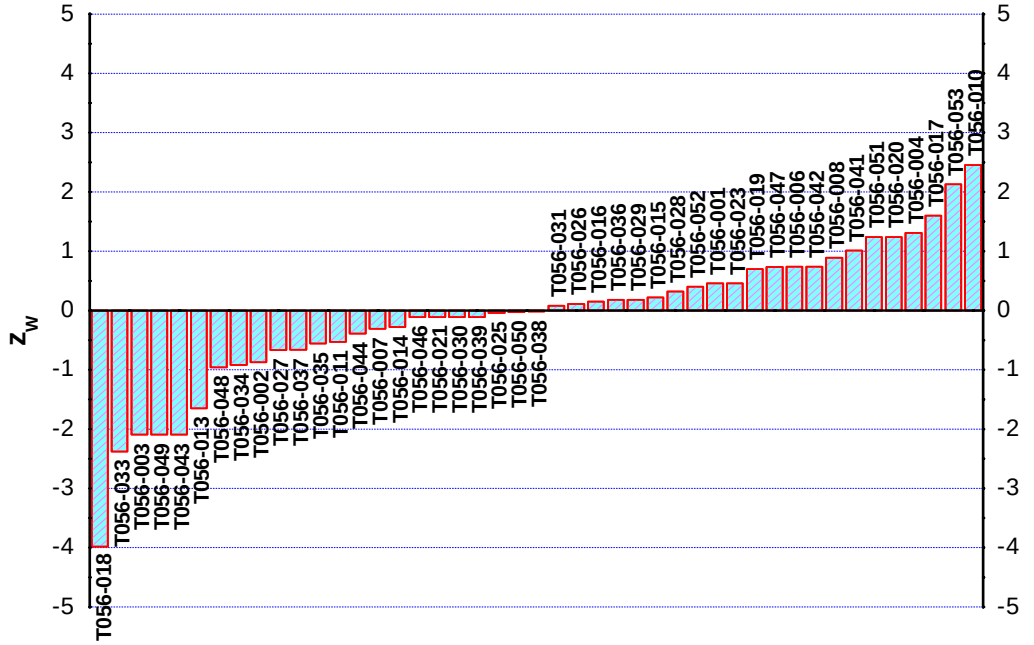
B.8 Ordered z-scores Bar Chart of Results C



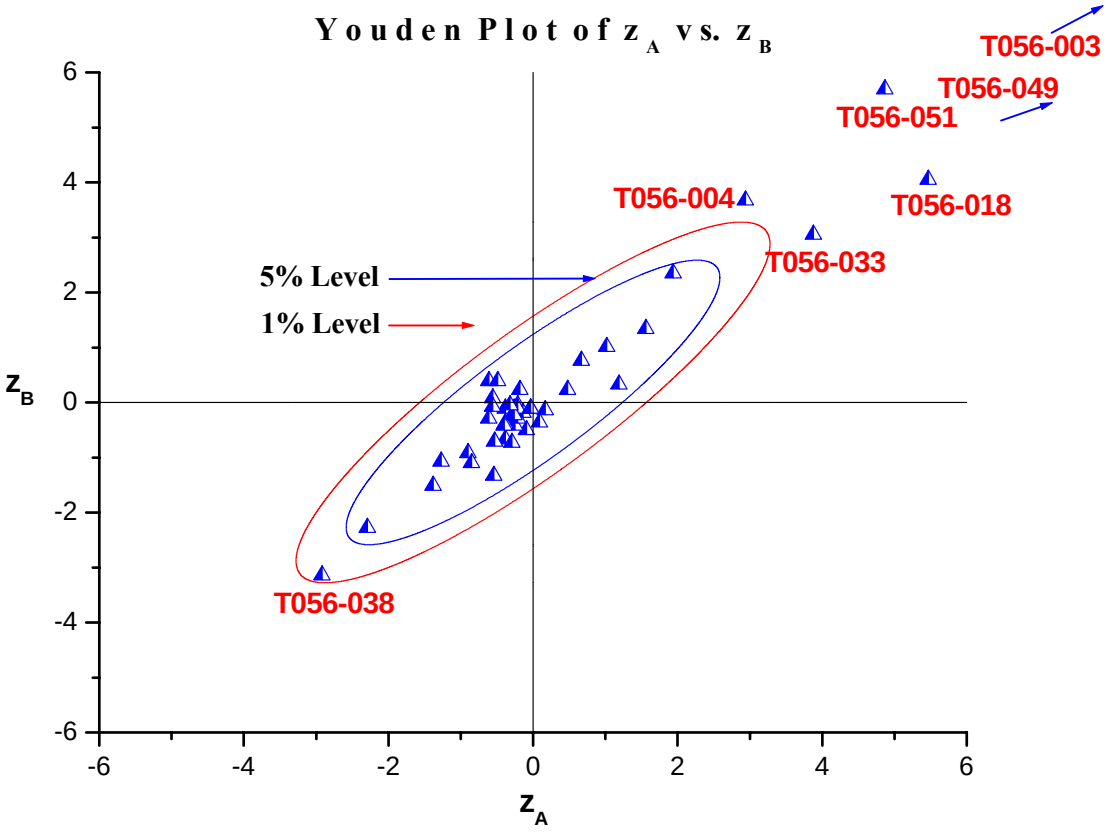
B.9 Ordered Between-labs z-scores Bar Chart of Paired Results A and B



B.10 Ordered Within-lab z-scores Bar Chart of Paired Results A and B



B.11 Youden Plot



APPENDIX C

Homogeneity and Stability Checks

C.1 Homogeneity Testing

For each gross sample, 15 samples were randomly selected and tested. Each sample was divided into two test portions, all test portions were tested in random order on the repeatability condition, that is to say, the testing was carried out during a short period by one person using the same testing method and apparatus in one laboratory. The results on each sample are listed in Table C.1~C.3.

The **between-samples standard deviations (s_s)** were calculated using the following formulae, where g is the number of samples used:

The **sample average** is $\bar{x}_t = (x_{t1} + x_{t2})/2$

The **between-test-portion range** is $w_t = | x_{t1} - x_{t2} |$

General average is $\bar{\bar{x}} = \sum \bar{x}_t / g$

The standard deviation of general average is $s_x = \sqrt{\sum (\bar{x}_t - \bar{\bar{x}})^2 / (g-1)}$

The within-sample standard deviation is $s_w = \sqrt{\sum w_t^2 / 2g}$

The between-samples standard deviation is $s_s = \sqrt{s_x^2 - s_w^2 / 2}$

Table C.1 Homogeneity Testing Results of Sample A

Sample	x_{t1}(mg/kg)	x_{t2}(mg/kg)	$\bar{x}_t$ (mg/kg)	w_t(mg/kg)	w_t^2, $(mg/kg)^2$
1	0.534	0.530	0.532	0.004	0.16×10^{-4}
2	0.530	0.551	0.541	0.021	4.41×10^{-4}
3	0.520	0.494	0.507	0.026	6.76×10^{-4}
4	0.505	0.534	0.520	0.029	8.41×10^{-4}
5	0.484	0.530	0.518	0.025	6.25×10^{-4}
6	0.543	0.530	0.537	0.013	1.69×10^{-4}
7	0.484	0.494	0.489	0.010	1.00×10^{-4}
8	0.568	0.551	0.560	0.017	2.89×10^{-4}
9	0.532	0.520	0.526	0.012	1.44×10^{-4}
10	0.488	0.474	0.481	0.014	1.96×10^{-4}
11	0.520	0.490	0.505	0.030	9.00×10^{-4}
12	0.530	0.520	0.525	0.010	1.00×10^{-4}
13	0.494	0.505	0.489	0.010	1.00×10^{-4}
14	0.463	0.474	0.469	0.011	1.21×10^{-4}
15	0.490	0.482	0.486	0.008	0.64×10^{-4}
$\bar{\bar{x}}$ =0.512mg/kg, Robust Mean=0.51mg/kg					
s_x =0.026mg/kg, s_w =0.013mg/kg, s_s=0.024mg/kg, Robust SD=0.17mg/kg,					
s_s/Robust SD=0.14<0.3					

Table C.2 Homogeneity Testing Results of Sample B

Sample	x_{t1}(mg/kg)	x_{t2}(mg/kg)	$\bar{x}_t$ (mg/kg)	w_t(mg/kg)	w_t^2, $(mg/kg)^2$
1	0.575	0.562	0.569	0.013	1.69×10^{-4}
2	0.530	0.545	0.538	0.015	2.25×10^{-4}
3	0.520	0.534	0.527	0.014	1.96×10^{-4}
4	0.534	0.545	0.540	0.011	1.21×10^{-4}
5	0.581	0.575	0.578	0.006	0.36×10^{-4}
6	0.562	0.545	0.554	0.017	2.89×10^{-4}
7	0.534	0.558	0.546	0.024	5.76×10^{-4}
8	0.568	0.562	0.565	0.006	0.36×10^{-4}
9	0.575	0.581	0.578	0.006	0.36×10^{-4}
10	0.566	0.545	0.556	0.021	4.41×10^{-4}
11	0.545	0.562	0.554	0.017	2.89×10^{-4}
12	0.505	0.520	0.513	0.015	2.25×10^{-4}
13	0.558	0.534	0.546	0.024	5.76×10^{-4}
14	0.562	0.545	0.554	0.017	2.89×10^{-4}
15	0.520	0.530	0.525	0.010	1.00×10^{-4}
$\bar{\bar{x}}$ =0.549mg/kg, Robust Mean=0.54mg/kg					
s_x =0.019mg/kg, s_w =0.011mg/kg, s_s=0.017mg/kg, Robust SD=0.16mg/kg,					
s_s/Robust SD=0.11<0.3					

Table C.3 Homogeneity Testing Results of Sample C

Sample	x_{t1}(mg/kg)	x_{t2}(mg/kg)	$\bar{x}_t$ (mg/kg)	w_t(mg/kg)	w_t^2, $(mg/kg)^2$
1	1.81	1.96	1.885	0.15	0.0225
2	1.95	1.88	1.915	0.07	0.0049
3	1.75	1.96	1.855	0.21	0.0441
4	1.81	2.06	1.935	0.25	0.0625
5	1.72	1.64	1.680	0.08	0.0064
6	1.68	1.72	1.700	0.04	0.0016
7	1.88	1.86	1.870	0.02	0.0004
8	1.76	1.82	1.790	0.06	0.0036
9	1.63	1.88	1.755	0.25	0.0625
10	2.06	2.02	2.040	0.04	0.0016
11	1.96	1.88	1.920	0.08	0.0064
12	2.06	2.02	2.040	0.04	0.0016
13	1.62	1.68	1.650	0.06	0.0036
14	2.06	1.93	1.995	0.13	0.0169
15	2.02	1.98	2.000	0.04	0.0016
$\bar{\bar{x}}$ =1.869mg/kg, Robust Mean=1.86mg/kg					
s_x =0.13g/kg, s_w =0.09mg/kg, s_s=0.11mg/kg, Robust SD=0.52mg/kg,					
s_s/Robust SD=0.22<0.3					

Comparing the between-samples standard deviation (s_s) with the corresponding standard deviation for proficiency assessment (Robust SD), all s_s are less than 0.3 Robust SD, it indicates that the variation between samples could be neglected in subsequently statistical analysis and proficiency assessments, in another word, the samples are homogenous enough.

C.2 Stability Testing

For Gross Sample A and C, 12 packaged testing samples were selected for stability testing, respectively. The samples were placed at room temperature (18~25 degrees C) for 2 days, then putted into an attemperator with a temperature of 40 degrees C for 7 days and placed at about 4 degrees C until stability testing finished, on the date 10, 30, 60 and 100 beginning from the day of homogeneity testing, every 3 samples per date were tested on the fenvalerate contents.

For all stability testing, the person, apparatus, testing method and laboratory were same as the homogeneity testing. The testing results of stability check are listed in Table C.4, every absolute differences from the general average of homogeneity tests were calculated using following formulae:

The sample average is $\bar{y}_t = (y_{t1} + y_{t2})/2$

General average is $\bar{\bar{y}} = \sum \bar{y}_t / g$

The difference between stability and homogeneity testing results is $|d| = |\bar{\bar{y}} - \bar{\bar{x}}|$

Comparing with the standard deviations for proficiency assessment (Robust SD) in this program, all maximal absolute differences between the stability testing results and the corresponding homogeneity testing results (|d|) for each sample are less than 0.3 Robust SD, it indicates that the

variation of samples could be neglected in subsequently statistical analysis and proficiency assessments.

As a conclusion, all samples are stable enough for the purposes of this program.

Table C.4 Stability Testing Results

Unit: mg/kg

Sample A						Sample C					
Day	y_{t1}	y_{t2}	$\bar{y}_t$	$\bar{\bar{y}}$	|d|	Day	y_{t1}	y_{t2}	$\bar{y}_t$	$\bar{\bar{y}}$	|d|
10	0.520	0.490	0.51	0.51	0.00	10	1.64	1.88	1.76	1.92	0.05
	0.484	0.505	0.49				2.06	2.02	2.04		
	0.543	0.530	0.54				1.95	1.98	1.97		
30	0.484	0.494	0.49	0.51	0.00	30	1.86	1.76	1.81	1.85	0.02
	0.520	0.535	0.53				1.76	1.81	1.79		
	0.505	0.520	0.51				1.88	2.02	1.95		
60	0.558	0.520	0.54	0.54	0.02	60	1.72	1.68	1.70	1.74	0.13
	0.534	0.558	0.55				1.72	1.76	1.74		
	0.530	0.520	0.53				1.81	1.76	1.79		
100	0.494	0.484	0.49	0.49	0.02	100	1.98	1.96	1.97	1.97	0.10
	0.463	0.474	0.47				1.95	1.93	1.94		
	0.505	0.534	0.52				1.96	2.06	2.01		
$\bar{\bar{x}}$ =0.51, Robust SD =0.17, max|d|/ Robust SD =0.14<0.3						$\bar{\bar{x}}$ =1.87, Robust SD =0.52, max|d|/ Robust SD =0.24<0.3					

APPENDIX D

Statistical Assessment Procedures

This appendix outlines the robust statistical assessment procedures used in this program.

D.1 Distribution of Testing Results

Since it was designed that all statistical assessments on participants' proficiency are based on the results obtained from participants, the assumption that the results follow a Normal distribution should be achieved. Shapiro-Wilk method was used to verify the normality of the distribution of results. A statistic W for this test was calculated as follows:

$$W = \left\{\sum \alpha_K \left[x_{n+1-K} - x_K\right]\right\}^2 / \sum_{K=1}^{n} \left(x_K - \bar{x}\right)^2 \qquad \text{(D.1)}$$

where, K in the subscript is equal to 1~n/2 when n is even, or 1~(n-1)/2 when n is odd, α_K is a factor related to n and K, $\bar{x}$ is the arithmetic mean of results x. When the statistic W is larger than the critical value W(n,P) that is related to n and the confidence probability P, the testing results are normally distributed. The factors α_K and W(n,P) can be found in related statistical tables. In this program, W values for Results A, B and C are 3.64, 3.38 and 3.32 respectively, the critical value W(n,P) is 0.945 when n=45 and P=95%, it indicates that the Results A, B and C follow normal distributions respectively.

Another method, kurtosis-deflection test method for normality test was used, the conclusion is consistent with that from Shapiro-Wilk method.

The histograms of z-scores for results in Appendix B.1~B.5 show approximate normal distribution as well, they were plotted by grouping and counting the numbers of z-scores with an interval of 0.5.

D.2 Summary Statistics

In most cases, robust statistics are not highly influenced by the extreme results comparing with the classical statistics. In this program, robust statistical method was used for evaluating the robust mean and standard deviation for proficiency assessment. The algorithm in this program is reproduced from ISO 5725-5 as follows:

Denote the p items of data, sorted into increasing order, by:

$x_1 , x_2 , \ldots , x_i , \ldots , x_p$

Denote the robust average and robust standard deviation of these data by x and s*.*

Calculate initial values for x and s* as:*

$x^* =$ median of x_i $(i = 1 , 2 , \ldots , p)$ (D.2)

$s^* = 1{,}483$ median of $|x_i - x^*|$ $(i = 1 , 2 , \ldots , p)$ (D.3)

Update the values of x and s* as follows. Calculate:*

$\varphi = 1{,}5\ s^*$ (D.4)

For each x_i (i = 1 , 2 , ... , p), calculate:

$$x_i* = \begin{cases} x*-\varphi & if \quad x_i < x*-\varphi \\ x*+\varphi & if \quad x_i > x*+\varphi \\ x* & if \quad otherwisw \end{cases} \tag{D.5}$$

Calculate the new values of x and s* from:*

$$x* = \sum x_i * / p \tag{D.6}$$

$$s* = 1.134\sqrt{\sum (x_i - x_i*)^2 /(p-1)} \tag{D.7}$$

where the summation is over i.

The robust estimates x and s* may be derived by an iterative calculation, i.e. by updating the values of x* and s* several times, until the process converges. Convergence may be assumed when there is no change from one iteration to the next in the third significant figure of the robust standard deviation and of the equivalent figure in the robust average. This is a simple method to program on a computer.*

In order to express the characteristics of population, standard uncertainty of robust mean was evaluated in this program by formula (D.8).

$$u(x*) = 1.23s* / \sqrt{p} \tag{D.8}$$

Details for evaluation of uncertainty refer to ISO GUM and related literatures on robust statistics.

D.3 Statistics for Assessment

A z-score is normalized value which gives a "score" to each result, relative to the other numbers in the group, a z-score value close to zero means that the result agrees well with those from the other laboratories. When robust summary statistics are used, it is a robust z-score which is calculated by formula (D.9).

$$z = \frac{x - x*}{s*} \tag{D.9}$$

For instance, a z-score for Result A is calculated by

$$z_A = \frac{x_A - x_A^*}{s_A^*}$$

According to statistical design in this program, split-level samples were used. Within-lab z-score (denoted as z_W) and between-labs z-scores (denoted as z_b) that are for evaluating both sources of variation -- the variability within a laboratory and the variability between laboratories were calculated by formulae (D.10) and (D.11).

$$z_W = \frac{Norm.Diff. - x^*(Norm.Diff.)}{s^*(Norm.Diff.)} \tag{D.10}$$

$$z_b = \frac{Norm.Sum - x^*(Norm.Sum)}{s^*(Norm.Sum)} \tag{D.11}$$

where, Norm. Diff. is normalized difference between paired results, which is calculated by $Norm.Diff. = (x_B - x_A)/\sqrt{2}$, while Norm. Sum is normalized sum of paired results, which is calculated by $Norm.Sum = (x_B + x_A)/\sqrt{2}$, in which x_B is the result obtained from the sample B with a higher robust mean, x_A is the result from the paired sample A with a lower robust mean.

D.4 Procedures for Drawing Youden Plots

Youden Plots for z-scores were constructed by plotting z-scores obtained from one gross sample against z-scores obtained from another gross sample, and by plotting confidence ellipses with two different confidence levels and straight lines marked the robust means of each gross sample in the same plots. The method for calculating the confidence ellipses is based on Jackson (Jackson, J. Edward, Quality control methods for two related variables, Industrial Quality Control, January, 1956.) and robust statistics are used. For convenience, only the calculating method for ellipses in Youden Plot for z_B against z_A is given in formula (D.12).

$$z_B = z_A \cdot \hat{\rho} \pm \sqrt{(1-\hat{\rho}^2)(T^2 - z_A^2)} \qquad \text{(D.12)}$$

where,

$\hat{\rho}$ is the estimation of correlation coefficient of the two sets of data, it can be calculated by formula (D.13).

$$\hat{\rho} = \frac{\sum (z_A - \bar{z}_A)^2 \sum (z_B - \bar{z}_B)^2}{\sum (z_A - \bar{z}_A)(z_B - \bar{z}_B)} \qquad \text{(D.13)}$$

T is related to projective range on the horizontal axis ($-T \le z_A \le T$) that can be derived from formula (D.14). When confidence level is given, for example, 5% or 1%, $F_{(1-\alpha),2,(n-1)}$, which is the tabulated $(1-\alpha)$-quartile of the F-distribution with 2 and (n-1) degrees of freedom can be obtained from related statistical tables.

$$T^2 = 2\frac{n-1}{n-2} F_{(1-\alpha),2,(n-1)} \qquad \text{(D.14)}$$

APPENDIX E

Models of Instructions, Forms and Interim Reports

In this appendix, models of Instructions to Participants, Receipt Form and Results Sheet are copied and attached. Due to confidential requests, the parts, which include participants' information, were deleted.

INSTRUCTIONS TO PARTICIPANTS

<LabName>:

Your laboratory has been nominated by the laboratory accreditation body in your economy, <AB's name>, to participate in the Asia Pacific Laboratory Accreditation Cooperation (APLAC) Pesticide Residues in Rice Proficiency Testing Program T056. In this program, each laboratory has a unique code number. Your laboratory's code number is <LabCode>. Considering the rules of protection of participants' confidentiality, the unique code number will represent your laboratory in the reports associated with this program.

Three samples have been sent to you in aseptic bags labeled as <Q_1>, <Q_2>,and <Q_3>. The weight of each sample is about 100 g. Enclosed with the samples are the following documents (total 13 pages):

- Instructions to Participants
- Receipt Form
- Results Sheet
- Testing Record Forms

To ensure that results from this program can be analyzed properly, you are asked to follow carefully to the instructions below.

♫ Samples were sent by mail at ambient temperature and you are requested to store them at 0-4℃ immediately upon arrival. Once the sample bags are opened, the tests must be performed immediately.

♫ You need to complete RECEIPT FORM **in English**, then **email or fax** this completed form to the coordinator **on the same day** as you receive the samples.

♫ These samples are for laboratory use only, we will take no obligation or charge arising from other purposes.

♫ Sample Description: All samples contain fenvalerate residue. The matrix is rice powder. The names and structures of this residue and its isomers were listed in Annex A of this file.

♫ Test method: You could analyze the samples using your preferably selected methods. It is recommended to use GC, GC-MS, HPLC, HPLC-MS methods; other suitable methods could also be used. Whatever method you selected, it should be recorded on the TESTING RECORD FORMS, and the limit of detection should be better than 0.01mg/kg.

♫ Testing requested: The samples are for quantifying the total content of fenvalerate in each sample. All samples must be analyzed and reported. It is recommended that each sample should be mixed, prior to test, thoroughly and respectively. It is suggested that the mass of each duplicated

test portion should be exceed 5g. Please record relevant information in TESTING RECORD FORMS in details, all you report will be benefit for analyzing testing results.

♫ Reporting results: For each sample, please report only one mean result of total amount of fenvalerate respectively on the RESULT SHEET. The test results shall be corrected by recovery. Measurement uncertainty shall be evaluated and reported referring to Annex B for each result. In this program, z-scores will be used as the main method for assessing the performance of participants. No influence will be with reporting uncertainty.

Please fill out all relevant information, then email or fax the RESULT SHEET to the coordinator of this program and your accreditation body **NO LATER THAN THE DEADLINE 20 March. 2008**. And the TESTING RECORD FORMS, relevant spectrums, your preferred form of Measurement Uncertainty Report and any supporting documents should be submitted to your accreditation body before the deadline. At the same time, email or mail all the documents to:

Coordinator

Mr. Zheng Jiang

Technology Center, Liaoning Entry-Exit Inspection & Quarantine Bureau of P. R. China

39, Renmin Road, Dalian, 116001, P.R. China

Phone/Fax: +86-0411-8258 3822/8258 3674

Email: PTC_China@126.com

Mr.Cao Zhijun

CNAS, The People's Republic of China

Annex A

(for Instruction to Participants)

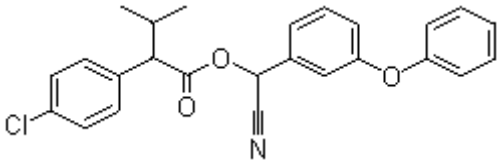
Structure of Pesticide to Be Analyzed

Fenvalerate:

CAS Registering Number: 51630-58-1

Molecular Formula: C25H22O3NCl, molecular weight: 419.91

Structure:



Note:

The pesticide includes four geometric isomers: RR, SS, RS and SR. The names and structures are as follows:

RR ((R-(R*,R*))-isomer): CAS Registering Number: 67614-33-9

name: Benzeneacetic acid, 4-chloro-a-(1-methylethyl)-(R)-cyano(3-phenoxyphenyl)methyl ester

SS ((S-(R*,S*))-isomer): CAS Registering Number: 67614-32-8

name: Benzeneacetic acid, 4-chloro-a-(1-methylethyl)-(S)-cyano(3-phenoxyphenyl)methyl ester,

RS ((R-(R*,S*))-isomer): CAS Registering Number: 66267-77-4

name: Benzeneacetic acid, 4-chloro-a-(1-methylethyl)-(R)-cyano(3-phenoxyphenyl)methyl ester,

SR ((S-(R*,R*))-isomer): CAS Registering Number: 66230-04-4

name: Benzeneacetic acid, 4-chloro-a-(1-methylethyl)-(S)-cyano(3-phenoxyphenyl)methyl ester.

Annex B

（for Instruction to Participants）

Instructions for Quantifying Measurement Uncertainty

Part 1 and Part 2 of this Annex are reproduced from APLAC PT002-2003.

Part 1 Background information & justification for this change

ISO/IEC 17025[1] 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 a 95% confidence interval and would normally be expressed in the appropriate SI units (ie. mm, ℃, g/l, Mpa etc).

For example, the result of a measurement might be 5.1 mg/l with an uncertainty of ±0.2mg/l at a 95% level of confidence. This means that there is an estimated 95% probability that the true value is in the range 4.9mg/l to 5.2mg/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 this 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 recognize 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 ISO2, UKAS3 and Eurachem/CITAC4 and made available over the internet7.

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 is satisfied that participating laboratories are estimating uncertainties of measurement in an appropriate and consistent manner.

References

1. ISO/IEC 17025:2005, General requirements for the competence of testing and calibration laboratories. ISO, Geneva(2005).
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 21748:2004, Guide for the use of repeatability, reproducibility, and trueness estimates in measurement uncertainty estimation.
6. APLAC – Policy, interpretation and guidance on the estimation of uncertainty of measurement in testing (Draft 5 September 2002)
7. Websites:
8. www.A2LA.org/ (for A2LA policies, links to guidance documents, including the UKAS Guide, and the Eurachem/CITAC Guide, at no cost)
9. www.measurementuncertainty.org/ (Eurachem/CITAC Guide)
10. www.fasor.com/iso25/ (general information, links, and discussion of ISO-IEC 17025)

Part 2 Evaluating participants' results

All APLAC PT program result sheets will provide a column on the PT results sheet to report an estimate of uncertainty of measurement for each reported measurement result. All estimates of uncertainty of measurement must be given as a 95% confidence interval (k≈2). The estimates would then appear in the final report, along with any relevant interpretations from experts. Detailed information on the estimation of the reported uncertainties must be provided to the relevant accreditation bodies for review and assessment.

The objective is to inform the participants so they can review and refine their own procedures and methodologies.

Program providers and technical advisers will include the reported uncertainty estimates either as summary data or directly with the submitted results.

APLAC PT testing programs will continue to use z-scores as the primary method for evaluating the relative performance of individual participant laboratories until such time as it is appropriate to incorporate quoted uncertainty estimates into the evaluation process and to assess performance using the En ratio method.

Part 3 Cases in this program

Considering the situation and needs available on evaluating uncertainty in this program, especially

some parameters could not be obtained from the participants, this part of Annex B outlines the information of these factors as follows.

Heterogeneity and Instability of the Samples The samples are stable during at least 40 days at ambient temperature in dark condition, the uncertainty caused by instability of the samples sent to you are far less than some main components of uncertainty such as the uncertainty caused by extraction and analysis processes. As well, the samples are homogeneous enough, the uncertainty of heterogeneity could be ignored. Another case is that the uncertainty of heterogeneity and instability may be included in other components when some special evaluation methods are used.

Precision The precision may vary depending on the testing methods, various approaches are available for estimating the repeatability and/or reproducibility. When Type A evaluation is employed for evaluating repeatability, special caution should be paid on testing processes due to limited masses of the samples.

Level of Confidence In this program, if the level of confidence other than 95% (or k=2) intends to be used, the estimates of uncertainty with relevant information, such as the actual level of confidence, degrees of freedom or coverage factor, shall be reported in your Measurement Uncertainty Report in a proper form listed in ISO GUM.

Annex C

（for Instruction to Participants）

A Commonly Used Method for Preparation and Storing up the Reference Materials and Their Solutions

Participating laboratory should pay attention to that fenvalerate is unstable in light. During handling and storage, it is suggested that suitable method should be used for keeping fenvalerate reference materials and their solutions away from light.

Annex D

（for Instruction to Participants）

Recommended Pretreatment Protocol

Each rice powder sample was directly extracted and purified, then the eluate could be analyzed by your preferable method.

Extraction Solution: petroleum ether(60-90℃ HPLC)

Procedures

- Weigh 10g of the rice powder.
- Add 25mL petroleum ether (60-90℃ HPLC) and mix with homogenizer for 2 min.
- Wash the homogenizer with 25mL petroleum ether (60-90℃) HPLC, collect all extracted solution.
- Centrifuge at 3000rpm for 5 min at room temperature.
- Vacuum distillate to dryness at 45℃.
- Add 1 mL petroleum ether(60-90℃ HPLC) to dissolve the residues thoroughly
- Purify eluate and use for analysis.

RECEIPT FORM

We are pleased to announce that in accordance with the distribution schedule of APLAC Pesticide Residues in Rice Proficiency Testing Program T056, we have dispatched the samples on 20 Jan. 2008 through TNT Express, along with Instructions to Participants, Receipt Form, Result Sheet and Testing Record Forms.

In order to monitor status of the samples, we kindly ask each participating laboratory on receipt of the samples to fill out this RECEIPT FORM and return a copy by **email or fax URGENTLY to**:

Mr. Zheng Jiang

Fax: +86-411-82583674

Email: PTC_China@126.com

Thank you in advance for your cooperation.

NAME OF LABORATORY: <LabName>

LAB CODE: <LabCode>

DATE SAMPLE RECEIVED:_____ SAMPLE AMOUNT:_____

The samples are labeled as follows: <Q_1>, <Q_2>, <Q_3>

Inspect the packaging. Was there any visible damage? ☐ **Yes** ☐ **No**

If yes, or any other problem is available, describe the problem below.

_____

_____

_____

_____

Signature: **Date:**

Results Sheet

Lab Code: <LabCode>

SAMPLE RECEIVED DATE: _____ **REPORT DATE:** _____ **SAMPLE PROCESSED DATE: From**_____**to**_____
Testing Method:_____

Sample	**Testing Result (mg/kg) of Fenvalerate With Measurement Uncertainty**	**Limit of Detection (mg/kg)**
<Q_1>		
<Q_2>		
<Q_3>		

Signature: **Date:**

Return this Results Sheet (including the Testing Record Form) by **no later than the deadline 20 March. 2008 (we will confirm it by local postmark) by fax or email, and then mail to:**

Mr. Zheng Jiang

Technology Center, Liaoning Entry-Exit Inspection & Quarantine Bureau of P. R. China

39, Renmin Road, Dalian 116001, P.R. China

Phone: +86-411-82583822

Fax: +86-411-82583674

Email: PTC_China@126.com

Testing Record Forms

Lab Code:<LabCode>

<table>
<tr><td colspan="3">Is the method used for the results submitted in your scope of accreditation?</td><td>☐ yes</td><td>☐ no</td></tr>
<tr><td rowspan="2">Reference:</td><td>☐ standard/ ☐ journal/ ☐ book</td><td>year</td><td>No./Vol /Edition</td><td>pages</td></tr>
<tr><td></td><td></td><td></td><td></td></tr>
<tr><td>Protocol for Quantification</td><td colspan="4">☐ External Standards ☐ Internal Standards
☐ Others (specify): _____</td></tr>
<tr><td>Reference Materials</td><td colspan="4">Names or Structures:

Supplier(s)： Purity：</td></tr>
<tr><td>Reagents and Materials</td><td colspan="4"></td></tr>
<tr><td>Extraction</td><td colspan="4">Extraction Method:

Instruments used:</td></tr>
<tr><td>Cleanup (if necessary)</td><td colspan="4">Cleanup Method:

Instruments used:</td></tr>
<tr><td>Concentration</td><td colspan="4">Concentration Method:

Instruments used:</td></tr>
<tr><td>Operating Condition</td><td colspan="4">Equipment Model：_____Detector:_____
Wavelength:_____Column (type and specification):_____
Mobile Phase:_____Flow Speed:_____ mL/min
Injection Volume：_____μL Column Temperature:_____ ℃</td></tr>
</table>

Testing Sample	Mass of Test Portions (in g) <Qxxx>: From_____to_____ <Qxxx>: From_____to_____ <Qxxx>: From_____to_____
Chromatogram	Chromatograms Attached: _____Pages The retention time of fenvalerate _____min
Calculating Formulae	
Additional Information	Method usually used for Extraction (including instruments used): **11** Solvent extraction **11** Immerging method **11** Shaking method **11** Homogenization **11** Soxhlet extraction **11** SFE **11** Other (specify):_____ Method usually used for Purification (including instruments used): **11** L-L partition **11** Column adsorption **11** SPE **11** GPC **11** SFE **11** Other (specify):_____ Method usually used for Concentration (including instruments used): **11** Speedy centrifugation **11** On-line concentration **11** Rotary evaporation **11** N_2 blowing instrument **11** natural evaporation **11** K.D concentration instrument **11** Other (specify):_____ 10 items most usually detected in your lab (including pesticide or veterinary drug residues): Do you usually use on-line analysis? **11** Yes **11** No Are the reference materials usually used in your lab certificated reference materials? **11** Yes **11** No Do you usually report the testing results with measurement uncertainty? **11** Yes **11** No Which method do you usually use in your determination? **11** Screening method **11** Detecting method **11** Confirming method (Extra sheet may be added if necessary)

Signature: Date:

Asia Pacific Laboratory Accreditation Cooperation

APLAC Pesticide Residues in Rice Proficiency Testing Program T056

INTERIM REPORT

Date of Issue : April 29, 2008

In this APLAC proficiency testing program, the total contents of Fenvalerate in rice powder samples were tested.

Three gross samples A, B and C were prepared and divided respectively to testing samples A, B and C, then every three testing samples A, B and C were distributed to the participating laboratories. There is a slightly lower total content of Fenvalerate in Sample A than that in Sample B, while Sample C bears a significant higher content than Samples A and Sample B.

The results for the tests on total content of Fenvalerate reported from the participating laboratories are listed in Table 1. Results reported on Sample A, B and C are listed in corresponding column Result A, Result B and Result C, respectively.

The statistics given in Table 2 were calculated by robust statistical methods based on the results listed in Table 1. The z-scores can be calculated by the following formulae. In Formula 1, Result is an individual Result A, Result B or Result C listed in Table 1, the normalized sum or normalized difference of a pair of results which can be calculated by Formula 2 and Formula 3, respectively. Paired results are the results on paired Sample A and Sample B.

Formula 1: z-score=(Result-Robust Mean)/ Robust Standard Deviation

Formula 2: Normalized Sum = (Result B + Result A)/$\sqrt{2}$

Formula 3: Normalized Difference = (Result B - Result A)/$\sqrt{2}$

As a general rule, any z-score outside the range of -2 to 2 indicates a questionable result/pair of results, while an outlier is any result/pair of results with a z-score outside the range of -3 to 3.

Please confirm this interim report NO LATER THAN MAY 18, 2008 with your lab's address, Lab Code No. in this program, email, phone and fax number, we will use them for sending the final report. Thanks for your cooperation.

If you have any question on any aspect of your test, or on this PT program, please feel free to contact the persons listed below.

PT Manager:

Mr. Cao Zhijun

CNAS, China

Web: www.cnas.org.cn

E-mail: caozj@cnas.org.cn

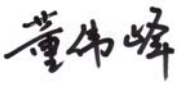
Coordinators:

Mr. Zheng Jiang

Fax: +86 411 82583674

Phone: +86 411 82583822

E-mail: PTC_China@126.com



Mr. Dong Weifeng

CNAS PROFICIENCY TESTING CNAS PT0005

Table 1 Reported Results of Total Contents of Fenvalerate

LabCode	Sample A	Result A (mg/kg)	Sample B	Result B (mg/kg)	Sample C	Result C (mg/kg)	Testing Method	LOD (mg/kg)
T056-001	Q098	0.46±0.14	Q003	0.52±0.16	Q051	1.6±0.5	GC-NPD	0.01
T056-002	Q100	0.49±0.10	Q006	0.456±0.096	Q052	1.79±0.38	GC-TOF-MS	0.05
T056-003	Q104	1.86±0.06	Q008	1.74±0.05	Q055	5.13±0.12	GC-MS	0.05~0.11
T056-004	Q107	1.01±0.07	Q011	1.13±0.08	Q058	3.24±0.23	GC-ECD	0.02
T056-006	Q113	0.44±0.10	Q017	0.52±0.10	Q063	1.68±0.15	GC-ECD	0.01
T056-007	Q116	0.463±0.093	Q020	0.469±0.094	Q064	1.770±0.354	GC-ECD	0.025
T056-008	Q120	0.40±0.01	Q024	0.49±0.01	Q067	1.70±0.05	GC-ECD	0.01
T056-010	Q126	0.4	Q027	0.6	Q077	1.8	GC-PDA	0.01
T056-011	Q127	0.44±0.02	Q033	0.43±0.02	Q080	1.74±0.07	GC-ECD	0.01
T056-013	Q135	0.412±0.066	Q039	0.323±0.052	Q087	1.32±0.279	GC-ECD	0.01
T056-014	Q136	0.415±0.0167	Q043	0.423±0.0152	Q090	1.58±0.0295	GC-ECD	0.0053
T056-015	Q140	0.453±1.32%	Q044	0.496±1.11%	Q092	1.905±2.59%	GC-MS	0.01
T056-016	Q094	0.3503±0.0581	Q047	0.3882±0.0523	Q142	1.5118±0.3207	GC-MS	0.036
T056-017	Q002	0.41±0.04	Q049	0.55±0.06	Q097	1.61±0.16	GC-ECD	0.01
T056-018	Q005	1.443±50%	Q053	1.19±50%	Q102	4.336±50%	GC-TOF-MS	0.025
T056-019	Q007	0.287±30%	Q057	0.364±30%	Q103	1.143±30%	GC-MS	0.010
T056-020	Q010	0.410±0.070	Q060	0.525±0.089	Q106	2.230±0.38	GC-MS-MS	0.006
T056-021	Q015	0.47	Q065	0.49	Q109	1.7	LC-MS	0.1
T056-023	Q021	0.47±0.09	Q070	0.53±0.11	Q117	1.66±0.33	HPLD	0.01
T056-025	Q025	0.481±0.007	Q075	0.506±0.005	Q121	1.851±0.222	GC-ECD	0.01
T056-026	Q029	0.439±0.102	Q078	0.474±0.110	Q124	1.736±0.403	GC-ECD/ GC-MS-MS	0.05
T056-027	Q032	0.534±0.060	Q079	0.514±0.058	Q129	1.828±0.206	GC-uECD-MS	0.01
T056-028	Q036	0.47±0.06	Q082	0.52±0.06	Q132	1.96±0.07	GC-ECD	0.01
T056-029	Q038	0.62±0.07	Q086	0.66±0.10	Q133	1.8±0.07	GC-MS	0.02
T056-030	Q040	0.50±15%	Q088	0.52±15%	Q138	1.60±15%	GC-ECD	0.010
T056-031	Q041	0.436±0.10	Q093	0.469±0.10	Q139	1.77±0.45	GC-MS	0.01
T056-033	Q050	1.17±0.07	Q099	1.03±0.06	Q001	3.55±0.22	GC-ECD	0.022
T056-034	Q054	0.456±0.296	Q101	0.419±0.296	Q004	1.693±0.296	GC-μ ECD	0.005
T056-035	Q056	0.587±0.223	Q105	0.575±0.219	Q009	2.509±0.953	GC-MS	0.040
T056-036	Q059	0.46	Q108	0.50	Q012	1.74	GC-ECD	0.05
T056-037	Q062	0.773(0.200±10%)	Q110	0.754(0.200±10%)	Q013	2.921(0.200±10%)	GC-ECD	0.020
T056-038	Q066	<0.005±0.00	Q112	0.031±0.01	Q014	0.662±0.07	HPLC-UV	0.005
T056-039	Q068	0.50±4.40%	Q115	0.52±4.40%	Q018	1.82±4.40%	GC-ECD	0.01
T056-041	Q073	0.475±0.022	Q122	0.574±0.043	Q028	1.901±0.043	GC-ECD	0.005
T056-042	Q076	0.45±0.06	Q125	0.53±0.07	Q030	1.87±0.24	GC-μ ECD	0.003
T056-043	Q081	0.71	Q128	0.59	Q031	1.22	GC-ECD	0.01
T056-044	Q083	0.36±0.15	Q148	0.36±0.15	Q034	1.51±0.61	GC-MS	<0.05
T056-046	Q089	0.68±0.12	Q137	0.70±0.12	Q042	1.97±0.24	GC-MS	0.05
T056-047	Q091	0.838	Q141	0.917	Q046	2.907	GC-MS	0.01
T056-048	Q095	0.52	Q144	0.48	Q048	1.75	GC-MS	0.01
T056-049	Q146	1.58±20%	Q145	1.46±20%	Q147	4.51±20%	GC-ECD	0.002
T056-050	Q151	0.269±0.0301	Q162	0.2945±0.0301	Q164	0.6005±0.0301	GC-ECD	0.001
T056-051	Q154	1.340±0.156	Q157	1.455±0.056	Q158	5.415±0.151	GC-ECD	0.084~0.234
T056-052	Q165	0.113±0.024	Q160	0.169±0.022	Q163	0.475±0.021	GC-ECD	0.005
T056-053	Q161	0.422±0.033	Q155	0.600±0.029	Q152	1.900±0.078	GC-ECD	0.010

Table 2 Statistics for the Test on Total Contents of Fenvalerate

	Total Number of Results	Robust Mean, mg/kg	Robust Standard Deviation, mg/kg
Result A	45	0.51±0.07, k=2	0.17
Result B	45	0.54±0.07, k=2	0.16
Result C	45	1.86±0.21, k=2	0.52
Normalized Sum of Result A and B	45	0.73±0.09, k=2	0.22
Normalized Difference between Result A and B	45	0.02±0.02, k=2	0.05