Asia-Pacific Economic Cooperation Proficiency Testing Programme (APEC PT)

(APEC Project CTI 21/2011T)

Essential and Toxic Elements in Seafood

Final Report – Using the Reference Values of APMP.QM-S5 as the Assigned Values for Performance Evaluation

Co-ordinated by

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Summary

1. The purposes of the APEC PT were (i) to assist participating laboratories in demonstrating competence on the measurement of the contents of the incurred analytes (iron, zinc, total arsenic and cadmium) at µg/g levels through testing of the proficiency test sample which is a dried shrimp powder by various analytical techniques; and (ii) to identify problems and opportunities for self-improvement. The mass fractions of the incurred analytes on a dry mass basis were used for comparability purposes.

2. A total of 18 laboratories from 10 economies registered for the programme. All 18 laboratories returned the results to the proficiency testing provider (Government Laboratory, Hong Kong) within the programme schedule.

3. The programme was conducted in parallel with the supplementary comparison - APMP.QM-S5 which was conducted under the auspices of the Asia-Pacific Metrology Programme using the same test material of dried shrimp powder. The reference values obtained from APMP.QM-S5, which had participation from national metrology institutes and designated institutes worldwide, were used as the assigned values for evaluating the performance of participants. Standard deviations for performance assessment were calculated using the Horwitz Equation. The z-scores were used to show the performance of participants with respect to the assigned values of the analytes of interest.

4. Participants' z-scores for the four analytes are summarized as follows:

z-Score	Number of Participants (Percentage)			
	Iron	**Zinc**	**Arsenic (total)**	**Cadmium**
$\|z\| \leq 2.0$	7 (50.0%)	13 (86.7%)	11 (68.8%)	14 (77.8%)
$2.0 < \|z\| < 3.0$	3 (21.4%)	1 (6.7%)	2 (12.5%)	1 (5.6%)
$\|z\| \geq 3.0$	4 (28.6%)	1 (6.7%)	3 (18.8%)	3 (16.7%)
Total:	14 (100%)	15 (100%)	16 (100%)	18 (100%)

5. Owing to the time constraint, the APEC Report on "Laboratory Capacity Building for the Determination of Toxic Contaminants in Seafood; APEC project CTI 21/2011T" was published in July 2012[9.1], with the "APEC PT - Essential and Toxic elements in Seafood: Final Report" that used the median values obtained from APMP.QM-S5 as the provisional assigned values for performance evaluation included as Annex C. Subsequently, at the Consultative Committee for Amount of Substance (CCQM) Inorganic Analysis Working Group (IAWG) Meeting held on 9-11 October 2012, the median values obtained from APMP.QM-S5 were approved to be the supplementary comparison reference values (SCRV), and the "Final report on APMP.QM-S5: Essential and toxic elements in seafood"

was published in the Key Comparison Database in February 2013[9.2]. As agreed at the beginning of the concerned APEC project that the SCRV of the comparison APMP.QM-S5 would be used for evaluation of the performance of the PT participants, this APEC PT Final Report is issued. There are no changes between the provisional assigned values used for performance evaluation and the SCRV, hence the z-scores as shown in Annex C of the APEC Report are the same as those data provided in this APEC PT Final Report. This Report gives a comprehensive overview of participants' results and detailed discussions on methods of analysis used by participants, and serves as a technical supplement to the published APEC Report when read in conjunction.

1. Introduction

1.1. Food tainted or contaminated with toxic elements is one of the major food safety issues in the Asia-Pacific region. Many APEC member economies have laboratories that carry out routine analyses of toxic and essential elements in food samples including seafood for regulatory compliance, nutritional studies and quality assurance purposes.

1.2. As part of its commitment to strengthening regional chemical metrology infrastructure, the Asia-Pacific Metrology Programme (APMP) has been organizing inter-comparisons for the purpose of establishing the technical basis for mutual recognition of measurement capabilities among national metrology institutes (NMIs)/designated institutes (DIs). To this end, a study on "Essential and Toxic Elements in Seafood" was organized by the APMP as a joint initiative of its Technical Committee for Amount of Substance (TCQM) and the Developing Economies' Committee (DEC). The study encompassed a supplementary comparison (APMP.QM-S5) and a proficiency testing programme (APMP PT 11-01) that was conducted in parallel using the same test material for examination. The main focus of the study was the determination of the essential elements (iron and zinc) and toxic elements (total arsenic and cadmium) in a dried shrimp material. Dried shrimps are usually prepared by drying of shrimps under the sun and are commonly used to impart a characteristic flavour to many Asian cuisines.

1.3 A project entitled "Laboratory Capacity Building for the Determination of Toxic Contaminants in Seafood (APEC Project CTI 21/2011T)" was carried out[9.1] with a view to developing laboratory capabilities of the food inspection laboratories in APEC member economies in respect of the measurement of contaminants (toxic elements) in seafood. The project followed on the issues identified through the APEC Project (CTI 20/2009T) "Strengthening Chemical Metrology Infrastructure for Member Economies". It also supported the objectives and work plans of the APEC Sub-committee on Standards and Conformance (SCSC) in the development of standards and conformance capacity within APEC economies as well as those of the APEC Food Safety Cooperation Forum (FSCF) and its Partnership Training Institute Network (PTIN). The project was undertaken with the direct oversight by APMP experts. APMP worked with its sister body in the Americas, the Inter-American Metrology System (SIM) to ensure appropriate traceability, quality and scientific credibility of outcomes for all participating APEC economies. The project consisted of the followings:

- Preparatory Workshop: The workshop (12-16 September, 5 days) involved hands-on laboratory training as well as training courses on estimation of measurement uncertainty and method validation. This was intended to enhance participants' understanding of good laboratory practice and ensure they know what would be expected of them in participating in a proficiency testing programme (APEC PT).

- APEC PT: The aim of the APEC PT (Scheme number: GL/2011/PT-2d) was to assess uptake from the preparatory workshop and evaluate the measurement capabilities of participating laboratories. The APEC PT was concurrently conducted in parallel with APMP.QM-S5 using the same test material of dried shrimp. The supplementary comparison reference values (SCRV) obtained from APMP.QM-S5 were used as the assigned values for evaluating the performance of participants in the APEC PT[9.2]. This would not only enhance the quality of the APEC PT but would also help build the measurement capability of the participants through a better linkage between the APMP NMIs/DIs and the food inspection laboratories from APEC member economies.

- Concluding Workshop: The workshop (18-20 June 2012, 3 days) could enable participants to share experience, identify further needs and develop action plans for improving laboratory practices and capabilities.

1.4. A total of 18 laboratories from 10 economies registered for the programme. All 18 laboratories returned the results to the proficiency testing provider within the scheduled timeline (TABLES I and II). Participants were confidentially assigned with unique laboratory codes (1 to 18) and the codes were used throughout the program.

2. Objectives

2.1. The present study was based on the analysis of the naturally incurred material of dried shrimp. The purposes of the study were (i) to assist participating laboratories in demonstrating competence on the measurement of the contents of the incurred analytes (iron, zinc, total arsenic and cadmium) at µg/g levels in dried shrimp powdered samples by various analytical techniques; and (ii) to identify problems and opportunities for self-improvement. The mass fractions of the incurred analytes on a dry mass basis were be used for comparability purposes.

2.2. Participants' results were processed in accordance with the statistical techniques outlined in ISO13528:2005[9.3] and in the International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories[9.4].

3. Proficiency test sample

3.1. Preparation of test material was performed in accordance with ISO/IEC 17043:2010[9.5].

3.2. About 13 kg of dried shrimps was purchased from the local market in Hong Kong. The dried shrimps were confirmed to contain quantities of incurred iron, zinc, arsenic and cadmium. The dried shrimps were rinsed with anhydrous methanol to remove dirt and foreign matter and air-dried in a Class 1000 cleanroom. The air-dried shrimps were blended in a high-speed blender (25000 revolutions per minute) to give small pieces, then de-fatted with n-hexane and air-dried in the cleanroom. The air-dried sample was further blended and ground to powder using the high-speed blender

(25000 revolutions per minute) to give powder. The powder was subject to a sieving process through 200 μm calibrated sieves. The sieved powder was thoroughly homogenized in a 3-dimensional mixer for 5 days. The powdered material was irradiated using a ^{137}Cs gamma source at a dose of about 10 kGy for disinfection. The irradiated material was packed into pre-cleaned and nitrogen-flushed amber glass bottles. About 300 bottles, each containing about 25 g of powdered sample, were prepared. Finally, each bottled sample was vacuum-sealed in a polypropylene bag and stored at room temperature (20 ± 5 °C) prior to distribution or use.

3.3. The homogeneity and stability studies of the test material were carried out in accordance with the procedures stipulated in APPENDIXES I and II. The results indicated the test material was considered to be sufficiently homogeneous and adequately stable for use in the proficiency testing programme.

3.4. Each registered participant was provided with one bottle containing about 25 g of dried shrimp powder, which was distributed by courier service in mid-September 2011. Relevant documents including "Study Protocol", "Sample Receipt Form" and "Result Proforma" were sent via emails (apecs5@govtlab.gov.hk) to the registered participants at the time of distribution of the proficiency test samples. Specimen copies of these documents are provided in APPENDIXES III to V. All of the four measurands and the range of values to be expected for the proficiency test sample are as follows:

Measurand	Mass fraction (expected range of values)
Iron	80-250 μg/g
Zinc	30-80 μg/g
Arsenic (total)	20-60 μg/g
Cadmium	0.05-1 μg/g

3.5. Upon receipt of the proficiency test samples, participants were requested to immediately check the physical conditions of the bottles and promptly acknowledge the proficiency testing provider by returning the "Sample Receipt Form" via e-mails (apecs5@govtlab.gov.hk). Replacement would be arranged if the proficiency test sample was identified to be not suitable for analysis. The proficiency testing provider did not receive any complaints in respect of loss/damage of samples.

4. Reporting and submission of results

4.1. Participants were required to report the mean value (μg/g) of at least 3 independent measurements of the analyte of interest on a dry mass basis using the test method of their choice.

4.2. Participants were requested to report analytical results to three significant figures.

4.3. Participants were advised to report the measurement uncertainty and the technical information about the methods of analysis.

4.4. All analytical results and the required information were reported in the "Result Proforma" provided.

5. Evaluation of performance of participants

5.1. Performance evaluation

5.1.1. Performance of the participants was assessed using the z-score, which is calculated as follows:

$$z = \frac{x_i - x}{\sigma}$$

where x_i = the reported result of the i^{th} participant
x = the assigned value*
σ = the standard deviation for proficiency assessment estimated from the Horwitz Equation
[$\sigma = 0.02c^{0.8495}$, where c is the assigned value of the analyte expressed as a dimensionless mass ratio (e.g. 1 µg/g = 1 ppm = 10^{-6})]

Note: *The median values of the analytes obtained from APMP.QM-S5 were used as the assigned values.

5.1.2. The z-Score is commonly interpreted as follows:

(a)	$\|z\| \leq 2.0$	Satisfactory
(b)	$2.0 < \|z\| < 3.0$	Questionable
(c)	$\|z\| \geq 3.0$	Unsatisfactory

5.1.3. Participants having $|z| \geq 3.0$ should thoroughly investigate their results. Participants having z-score(s) in the range $2.0 < |z| < 3.0$ are encouraged to review their results.

5.2. An interim report containing the participants' results and the corresponding z-scores was issued to participants on 14 June 2012. Participants were requested to check the correctness of their submitted results and to inform the proficiency testing provider of any mistakes found.

5.3. Owing to the time constraint, the APEC Report on "Laboratory Capacity Building for the Determination of Toxic Contaminants in Seafood; APEC project CTI 21/2011T"

was published in July 2012[9.1], with the "APEC PT - Essential and Toxic elements in Seafood: Final Report" that used the median values obtained from APMP.QM-S5 as the provisional assigned values for performance evaluation included as Annex C. At the Consultative Committee for Amount of Substance (CCQM) Inorganic Analysis Working Group (IAWG) Meeting held on 9-11 October 2012, the median values obtained from APMP.QM-S5 were approved to be the supplementary comparison reference values (SCRV), and the "Final report on APMP.QM-S5: Essential and toxic elements in seafood" was published on the Key Comparison Database in Feb 2013[9.2]. As agreed at the beginning of the concerned APEC project that the SCRV of the comparison APMP.QM-S5 would be used for evaluation of the performance of the PT participants, this APEC PT Final Report is issued. There are no changes between the provisional assigned values used for performance evaluation and the SCRV, hence, the z-scores as shown in Annex C of the APEC Report are the same as those data provided in this APEC PT Final Report. This Report gives a comprehensive overview of participants' results and detailed discussions on methods of analysis used by participants, and serves as a technical supplement to the published APEC Report when read in conjunction with the APEC Report.

6. Results and Discussions

6.1. Participants' results for Iron, Zinc, Arsenic (total) and Cadmium are given in TALBES III to VI and presented graphically in FIGURES I to IV.

6.2. Assigned values for evaluation of performance of participants

6.2.1. The assigned values were provided by the SCRV obtained from APMP.QM-S5. This was in line with the ISO/IEC 17043 recommendations on the determination of assigned values for proficiency testing schemes[9.5]. For APMP.QM-S5, a total of 18 institutes (NMIs/DIs) participated in the supplementary comparison. Most of the institutes used microwave acid digestion methods for sample dissolution. For instrumental determination, a variety of analytical techniques including inductively coupled plasma mass spectrometry (ICP-MS), isotope dilution inductively coupled plasma mass spectrometry (ID-ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), instrumental neutron activation analysis (INAA) and atomic absorption spectrometry (AAS) were employed by the participating institutes. The median values of the valid participants' results of APMP.QM-S5 with demonstrated metrological traceability for the four analytes were used to be the best estimate of SCRV. The expanded uncertainties of the SCRV were estimated using a coverage factor of 2 which gives a level of confidence of approximately 95%. (Note: The details of the metrological traceability and measurement uncertainty of each SCRV are provided in the reference given in Clause 9.2.) The SCRV and associated expanded uncertainties obtained from APMP.QM-S5 were used as the assigned values and expanded uncertainties of the assigned values respectively in this APEC PT Final Report.

6.2.2 Assigned values and expanded uncertainties of the assigned values are summarized as follows:

	Iron	Zinc	Arsenic (total)	Cadmium
Assigned value (μg/g)	183.5	60.0	44.7	0.224
Expanded uncertainty (μg/g)	4.3	1.1	1.2	0.011

6.3. Standard deviations for proficiency assessment estimated from the Horwitz equation are given as follows:

	Iron	Zinc	Arsenic (total)	Cadmium
Standard deviation for proficiency assessment in μg/g (percentage)	13.4 (7.3%)	5.2 (8.6%)	4.0 (9.0%)	0.045 (20%)

6.4. Overview of participants' results:

6.4.1. Participants' z-scores for Iron, Zinc, Arsenic (total) and Cadmium are given in TALBE VII and presented graphically in FIGURES V to VIII.

6.4.2. The number and percentage of z-scores in the satisfactory range ($|z| \leq 2.0$), questionable range ($2.0 < |z| < 3.0$) and unsatisfactory range ($|z| \geq 3.0$) are summarized as follow:

z-Score	Number of Participants (Percentage)			
	Iron	Zinc	Arsenic (total)	Cadmium
$\|z\| \leq 2.0$	7 (50.0%)	13 (86.7%)	11 (68.8%)	14 (77.8%)
$2.0 < \|z\| < 3.0$	3 (21.4%)	1 (6.7%)	2 (12.5%)	1 (5.6%)
$\|z\| \geq 3.0$	4 (28.6%)	1 (6.7%)	3 (18.8%)	3 (16.7%)
Total:	14 (100%)	15 (100%)	16 (100%)	18 (100%)

Most of the participants obtained satisfactory results related to the determination of zinc, arsenic (total) and cadmium. However, only 50% of participants obtained satisfactory results related to the determination of iron. Further improvement on the technical competence on the measurement of iron was necessary.

6.4.3 It is possible for the z-scores published in this report to differ slightly from the z-score that can be calculated using the equation given in Clause 5.1.1. These differences arise from the necessary rounding of the actual assigned values and standard deviations for proficiency assessment prior to their publication in TALBE VII.

6.5. Overview of methods of analysis used by participants

6.5.1. The technical information about the methods of analysis used by participants is given in TABLE VIII.

6.5.2. Digestion technique: Most of the participants used microwave-assisted digestion techniques for sample dissolution. A few number of participants employed dry ashing and wet digestion for sample dissolution. The number of participants using various digestion techniques is summarized as follows:

Digestion technique	**Iron**	**Zinc**	**Arsenic (total)**	**Cadmium**
Microwave digestion	11	11	12	12
Dry ashing	3	4	3	4
Wet digestion	0	0	0	1
Preparation of slurry for direct measurement	0	0	1	1

6.5.3. Digestion medium: Three digestion media, namely HNO_3, HNO_3/H_2O_2 and HNO_3/HCl, were commonly used by the participants for sample dissolution. The number of participants using various digestion media is summarized as follows:

Digestion medium	**Iron**	**Zinc**	**Arsenic (total)**	**Cadmium**
HNO_3	5	6	5	10
HNO_3/H_2O_2	5	5	6	6
HNO_3/HCl	3	3	2	2
HNO_3/HCl/H_2O_2	1	1	1	0
HNO_3/H_2O_2/Aqua regia	0	0	2	0

6.5.4 Matrix separation: Most of the participants did not carry out matrix separation. The number of participants carrying out matrix separation for analysis is summarized as follows:

Matrix separation	**Iron**	**Zinc**	**Arsenic (total)**	**Cadmium**
Matrix separation: Yes	3	3	3	3
Matrix separation: No	11	12	13	15

6.5.5 Quantification: Most of the participants employed external calibration for quantification. The number of participants employing various quantification methods is summarized as follows:

Quantification	**Iron**	**Zinc**	**Arsenic (total)**	**Cadmium**
External calibration	13	14	13	14
Internal calibration	1	1	2	3
Standard additions	0	0	1	1

6.5.6 Sources of calibration standards: The number of participants employing various calibration standards for analysis is summarized as follows:

Sources of calibration standards	**Iron**	**Zinc**	**Arsenic (total)**	**Cadmium**
Use of calibration standards not from national metrology institutes	12	13	13	15
Use of calibration standards from national metrology institutes	1	1	2	2
Information not provided	1	1	1	1

6.5.7 Use of internal standard(s): Most participants did not use internal standard(s) for analysis. The number of participants using internal standard(s) for analysis is summarized as follows:

Use of internal standard(s)	**Iron**	**Zinc**	**Arsenic (total)**	**Cadmium**
Use of internal standard(s)	2	2	4	3
No use of internal standard(s)	12	12	12	14
Information not provided	0	1	0	1

6.5.8. Analytical instrument(s): For analysis of Fe and Zn, most of the participants used Flame AAS and ICP-AES. For determination of As (total), participants employed ICP-AES, Hydride AAS and Graphite AAS as the major analytical instruments for measurement. For quantification of Cd, participants used Graphite AAS and ICP-MS as the major analytical instruments for measurement. The number of participants using various analytical instruments for analysis is summarized as follows:

Analytical instrument(s)	**Iron**	**Zinc**	**Arsenic (total)**	**Cadmium**
ICP-AES	6	6	5	2
Flame AAS	7	8	0	3
ICP-MS	1	1	2	4
Hydride AAS	0	0	5	0
Graphite AAS	0	0	4	9

6.5.9 Correction for recovery: Most of the participants did not carry out correction for recovery on their submitted results. The number of participants performing correction for recovery is summarized as follows:

Correction for recovery	**Iron**	**Zinc**	**Arsenic (total)**	**Cadmium**
Yes	1	1	1	2
No	13	14	15	16

6.5.10. Method accreditation: The number of participants using accredited/non-accredited analytical methods for analysis is summarized as follows:

Method accreditation	**Iron**	**Zinc**	**Arsenic (total)**	**Cadmium**
Use of accredited analytical methods for analysis	4	5	7	9
Use of non-accredited analytical methods for analysis	10	9	9	9

6.6 Measurement uncertainty

6.6.1. Although the measurement uncertainties reported by participants were not used in assessing the performance of participants, it was one of the important parameters that indicate the precision and accuracy of the analytical methods used by participants in accordance with the ISO/IEC 17025[9.6].

6.6.2. The number of participants reporting measurement uncertainty is given as follows:

	Iron	**Zinc**	**Arsenic (total)**	**Cadmium**
No. of participants reported measurement uncertainty	11	12	14	16
No. of participants did not report measurement uncertainty	3 (Lab Code: 3, 9 & 10)	3 (Lab Code: 3, 9 & 10)	2 (Lab Code: 9 & 10)	2 (Lab Code: 9 & 10)

7. Recommendations

7.1. For this APEC PT, less than 70% of participants obtained satisfactory results related to the determination of Iron and Arsenic (total). Training should be provided so as to improve laboratory competence on the measurement of such essential and toxic elements in food.

7.2. Further laboratory capacity building efforts in respect of estimation of uncertainty of measurement, which is one of the technical requirements under ISO/IEC 17025, are recommended. Though a Preparatory Workshop was organised under the concerned APEC Project for the participants, in which a training session on estimation of measurement uncertainty was included, some of the participants did show some difficulties in reporting the measurement uncertainties (either the measurement uncertainty was not reported or the reported measurement uncertainty was underestimated, e.g. reporting a relative expanded uncertainty of less than 1% for the concerned measurements).

8. Acknowledgements and Remarks

8.1. Contributions from all participants to this programme are gratefully noted. Special thanks are extended to APEC SCSC, APMP TCQM, APMP DEC and the Government Chemist of GLHK for their support to the programme.

8.2. If the participants have any queries about this report, please contact the coordinator of this proficiency testing programme as follows:

Government Laboratory
7/F., Homantin Government Offices, 88 Chung Hau Street, Kowloon, Hong Kong
Contact person: Dr. Yiu-chung YIP
E-mail: ycyip@govtlab.gov.hk.

8.3. Use of this report by participants shall only be allowed with the written permission of the coordinator of this proficiency testing programme.

9. References

9.1. C. Cherdchu, W.M. Sin, A. Samuel, L. Mackay. Laboratory Capacity Building for the Determination of Toxic Contaminants in Seafood, Publication number: APEC#212-CT-01.10, July 2012.

9.2. L. Valiente, J.W. Bennett, R.C. de Sena, B. Kotzeva, G. Massiff, J. Chao, J. Wang, R. Nasr, G. Labarraque, E. Kakoulidis, E. Lampi, W.M. Sin, C.S. Mok, S.K. Wong, Y.C. Yip, S.G. Aggarwal, P.K. Gupta, Y. Zhu, S.I. Miyashita, Y.H. Yim, O. Zakaria, J.V.L. Manzano, R. Shin, M. Horvat, C. Yafa. Final report on APMP.QM-S5: Essential and toxic elements in seafood, *Metrologia* , 2013, **50,** *Tech. Suppl.*, 08004.

9.3. International Standards Organization. ISO 13528:2005, Statistical methods for use in proficiency testing by interlaboratory comparisons, ISO, Geneva, Switzerland.

9.4. M. Thompson, S.L. Ellison, R. Wood. The International harmonized protocol for the proficiency testing of analytical chemistry laboratories (IUPAC technical report), *Pure Appl. Chem.*, 2006, **78**, 146-196.

9.5. International Standards Organization. ISO/IEC 17043:2010, Conformity assessment – General requirements for proficiency testing, ISO, Geneva, Switzerland.

9.6. International Standards Organization. ISO/IEC 17025:2005, Gerneral requirements for the competence of testing and calibration laboratories, ISO, Geneva, Switzerland.

9.7. International Standards Organization, ISO Guide 35: Reference materials – General and statistical principles for certification, Geneva, Switzerland, 2006.

TABLE I. APEC PT Programme Schedule

Schedule	Phase
8 July 2011	Call for Participation
20 August 2011	Deadline for registration
12-16 September 2011	Preparatory Workshop (5 days)
Mid-September 2011	Distribution of samples
20 February 2012	Deadline for submission of results
April 2012	Presentation of APMP.QM-S5 results at the CCQM IAWG Meeting
14 June 2012	Interim report for comments
18-20 June 2012	Concluding Workshop (3 days)
14 March 2013	Final report for comments

TABLE II. Geographical Distribution of Participants

No.	Economies	Participants enrolled	Returned results
1	Chile	1	1
2	Chinese Taipei	1	1
3	Malaysia	2	2
4	Mexico	4	4
5	Papua New Guinea	1	1
6	Peru	2	2
7	Philippines	1	1
8	Singapore	2	2
9	Thailand	2	2
10	Vietnam	2	2
	Total No.:	**18**	**18**

TABLE III. Participants' Results for Iron

Lab. Code	Mean Value (µg/g)	Combined standard uncertainty (µg/g)	Coverage factor k	Expanded uncertainty (µg/g)
1	122.278	0.016	2	0.031
2	167	4.3	2	8.6
3	179	---	---	---
4	143	5.00	2	10.0
5	153.923	14.882	2	29.764
6	207	---	2	11.1
7	---	---	---	---
8	178	8.03	2	16.1
9	194.855	---	---	---
10	204.110	---	---	---
11	---	---	---	---
12	145	6.10	2.26	13.8
13	185	11.6	2	23.2
14	127	4.13	2	8.26
15	131.175	14.1370	2	28.274
16	---	---	---	---
17	---	---	---	---
18	145	1.44	2	2.88

"---" Data or information was not provided.

TABLE IV. Participants' Results for Zinc

Lab. Code	Mean Value (µg/g)	Combined standard uncertainty (µg/g)	Coverage factor k	Expanded uncertainty (µg/g)
1	54.995	0.021	2	0.042
2	56.4	1.11	2	2.22
3	61.3	---	---	---
4	52.5	1.84	2	3.68
5	54.257	1.728	2	3.456
6	61.7	---	2	2.27
7	---	---	---	---
8	60.8	2.63	2	5.26
9	60.124	---	---	---
10	60.095	---	---	---
11	---	---	---	---
12	55.5	2.35	2.26	5.31
13	58.6	4.04	2	8.08
14	57.1	1.86	2	3.72
15	37.083	2.488	2	4.977
16	---	---	---	---
17	47.8	1.5	2	3
18	52.1	0.855	2	1.71

"---" Data or information was not provided.

TABLE V. Participants' Results for Arsenic (total)

Lab. Code	Mean Value (µg/g)	Combined standard uncertainty (µg/g)	Coverage factor k	Expanded uncertainty (µg/g)
1	34.842	0.121	2	0.241
2	43.5	0.5	2	1.0
3	46.8	0.067	2	0.134
4	38.9	1.36	2	2.72
5	50.073	2.794	2	5.588
6	22.0	---	2	1.69
7	38.479	0.07	2	0.14
8	44.2	1.86	2	3.73
9	37.404	---	---	---
10	40.642	---	---	---
11	46.1	1.9	2	3.8
12	51.1	0.913	2.26	2.06
13	53.5	2.90	2	5.80
14	---	---	---	---
15	25.841	2.253	2	4.506
16	---	---	---	---
17	26.8	1.3	2	2.7
18	39.2	1.57	2	3.14

"---" Data or information was not provided.

TABLE VI. Participants' Results for Cadmium

Lab. Code	Mean Value (µg/g)	Combined standard uncertainty (µg/g)	Coverage factor k	Expanded uncertainty (µg/g)
1	0.276	0.019	2	0.038
2	0.139	0.0025	2	0.005
3	0.056	0.000108	2	0.000217
4	0.121	0.00424	2	0.00848
5	0.368	0.063	2	0.126
6	0.242	---	2	0.013
7	0.751	0.08	2	0.16
8	0.231	0.010	2	0.021
9	0.185	---	---	---
10	0.176	---	---	---
11	0.243	0.010	2	0.020
12	0.233	0.00489	2.26	0.0111
13	0.218	0.009	2	0.018
14	0.304	1.99×10^{-3}	2	3.97×10^{-3}
15	0.250	0.0577	2	0.1155
16	0.232	0.001	2	0.002
17	0.29	0.02	2	0.033
18	0.202	0.003	2	0.006

"---" Data or information was not provided.

TABLE VII. Participants' z-Scores

Lab Code	z-Scores			
	Fe	Zn	As (total)	Cd
1	-4.57	-0.96	-2.44	1.16
2	-1.23	-0.69	-0.30	-1.90
3	-0.34	0.26	0.52	-3.74
4	-3.02	-1.44	-1.44	-2.30
5	-2.21	-1.10	1.33	3.21
6	1.75	0.34	-5.62	0.40
7	N/A	N/A	-1.54	11.74
8	-0.41	0.16	-0.12	0.15
9	0.85	0.03	-1.81	-0.87
10	1.54	0.03	-1.01	-1.07
11	N/A	N/A	0.35	0.42
12	-2.87	-0.86	1.59	0.20
13	0.11	-0.26	2.18	-0.14
14	-4.22	-0.55	N/A	1.78
15	-3.91	-4.42	-4.67	0.58
16	N/A	N/A	N/A	0.18
17	N/A	-2.35	-4.43	1.47
18	-2.87	-1.52	-1.36	-0.49

For $|z| \geq 3.0$, the result was underlined.
N/A: Not applicable

TABLE VIII. Technical Information - Methods of Analysis of Iron

Lab Code	Digestion technique	Digestion medium	Matrix separation	Quantification	Source(s) of Calibration standard(s)
1	Microwave-assisted digestion	HNO_3	Yes	External calibration	Iron (CENAM, México lote DMR-86c)
2	Microwave-assisted digestion	HNO_3/ HCl/ H_2O_2	No	External calibration	Mineral source
3	Microwave-assisted digestion	HNO_3/ H_2O_2	Yes	External calibration	Commercial standard from Perkin Elmer
4	Microwave-assisted digestion	HNO_3/ H_2O_2	No	External calibration	Merck Standard Solution
5	Microwave-assisted digestion	HNO_3/ H_2O_2	No	External calibration	---
6	Microwave-assisted digestion	HNO_3/ H_2O_2	Yes	External calibration	Merck
7	---	---	---	---	---
8	Microwave-assisted digestion	HNO_3/ H_2O_2	No	External calibration	ICP Multi Element Standard Solution XXI CertiPUR/Merck
9	Microwave-assisted digestion	HNO_3	No	External calibration	High Purity Standards Lot. 1100601
10	Microwave-assisted digestion	HNO_3	No	External calibration	High Purity Standards Lot. 1100601
11	---	---	---	---	---
12	Dry ashing	HNO_3/ HCl	No	External calibration	Inorganic Ventures
13	Microwave-assisted digestion	HNO_3	No	External calibration	Perkin-Elmer
14	Dry ashing	HNO_3/ HCl	No	External calibration	Fluka Fe Standard, 1000 µg/mL (diluted with 100 mL of conc. HCl + 850 mL MilliQ water); Exp Date, Dec.15, 2012
15	Dry ashing	Mixture HNO_3/ HCl	No	Internal calibration	ACR Elemental Standard
16	---	---	---	---	---
17	---	---	---	---	---
18	Microwave-assisted digestion	HNO_3	No	External calibration	Perkin Elmer

"---" Data or information was not provided.

TABLE VIII. Technical Information - Methods of Analysis of Iron (Cont'd)

Lab Code	Use of internal standard(s)	Analytical instrument(s)	Correction for recovery	Method accreditation	Additional information
1	No	ICP-AES	No	No	---
2	No	Flame AAS	No	No	---
3	No	ICP-AES	Yes: 96.95%	No	---
4	Yes: Yttrium	ICP-AES	No	Yes	---
5	No	Flame AAS	No	No	---
6	No	Flame AAS	No	Yes	---
7	---	---	---	---	---
8	No	ICP-AES	No	No	---
9	No	Flame AAS	No	No	This result is for the bottle 50
10	No	Flame AAS	No	No	This result is for the bottle 54
11	---	---	---	---	---
12	No	Flame AAS	No	Yes	---
13	No	ICP-MS	No	Yes	---
14	No	Flame AAS	No	No	Used DORM-3, Fish Protein Certified Reference Material for Trace Metals by National Research Council Canada as Quality Control Check; Exp Date: September 2016
15	Yes: Used as check standard only	ICP-AES	No	No	The preferred microwave digestion technique wasn't utilised here for the laboratory do not have any microwave digestor and a suitable water bath to facilitate this technique, thus dry ashing was used instead.
16	---	---	---	---	---
17	---	---	---	---	---
18	No	ICP-OES	No	No	---

"---" Data or information was not provided.

TABLE VIII. Technical Information - Methods of Analysis of Zinc

Lab Code	Digestion technique	Digestion medium	Matrix separation	Quantification	Source(s) of Calibration standard(s)
1	Microwave-assisted digestion	HNO_3	Yes	External calibration	Zinc (CENAM, México lote DMR-61e)
2	Microwave-assisted digestion	HNO_3/ HCl/ H_2O_2	No	External calibration	Mineral source
3	Microwave-assisted digestion	HNO_3/ H_2O_2	Yes	External calibration	Commercial standard from Perkin Elmer
4	Microwave-assisted digestion	HNO_3/ H_2O_2	No	External calibration	Merck Standard Solution
5	Microwave-assisted digestion	HNO_3/ H_2O_2	No	External calibration	---
6	Microwave-assisted	HNO_3/ H_2O_2	Yes	External calibration	Merck
7	---	---	---	---	---
8	Microwave-assisted digestion	HNO_3/ H_2O_2	No	External calibration	ICP Multi Element Standard Solution XXI CertiPUR/Merck
9	Microwave-assisted digestion	HNO_3	No	External calibration	High Purity Standards Lot. 1108909
10	Microwave-assisted digestion	HNO_3	No	External calibration	High Purity Standards Lot. 1108909
11	---	---	---	---	---
12	Dry ashing	HNO_3/ HCl	No	External calibration	Inorganic Ventures
13	Microwave-assisted digestion	HNO_3	No	External calibration	Perkin-Elmer
14	Dry ashing	HNO_3/ HCl	No	External calibration	Fluka Zn Standard, 1000µg/mL (diluted with 0.1M HNO_3); Exp Date, 15 December 2012
15	Dry ashing	Mixture HNO_3/ HCl	No	Internal calibration	ACR Elemental Standard
16	---	---	---	---	---
17	Dry ashing	HNO_3	No	External calibration	Merck HC090983; 1000 ± 2 mg/L
18	Microwave-assisted digestion	HNO_3	No	External calibration	Perkin Elmer

"---" Data or information was not provided.

TABLE VIII. Technical Information - Methods of Analysis of Zinc (Cont'd)

Lab Code	Use of internal standard(s)	Analytical instrument(s)	Correction for recovery	Method accreditation	Additional information
1	No	ICP-AES	No	No	---
2	No	Flame AAS	No	---	---
3	No	ICP-AES	Yes: 98.73%	No	---
4	Yes: Yttrium	ICP-AES	No	Yes	---
5	No	Flame AAS	No	No	---
6	No	Flame AAS	No	Yes	---
7	---	---	---	---	---
8	No	ICP-AES	No	No	---
9	No	Flame AAS	No	No	This result is for the bottle 50
10	No	Flame AAS	No	No	This result is for the bottle 54
11	---	---	---	---	---
12	No	Flame AAS	No	Yes	---
13	---	ICP-MS	No	Yes	---
14	No	Flame AAS	No	No	Used DORM-3, Fish Protein Certified Reference Material for Trace Metals by National Research Council Canada as Quality Control Check; Exp Date: September 2016
15	Yes: Used as check standard only	ICP-AES	No	No	The preferred microwave digestion technique wasn't utilised here for the laboratory do not have any Microwave digestor and a suitable water bath to facilitate this technique, thus dry ashing was used instead.
16	---	---	---	---	---
17	No	Flame AAS	No	Yes	---
18	No	ICP-OES	No	No	---

"---" Data or information was not provided.

TABLE VIII. Technical Information - Methods of Analysis of Arsenic (total)

Lab Code	Digestion technique	Digestion medium	Matrix separation	Quantification	Source(s) of Calibration standard(s)
1	Microwave-assisted digestion	HNO_3	Yes	External calibration	Arsenic (High Purity, lote 1021405)
2	Microwave-assisted digestion	HNO_3/ HCl/ H_2O_2	No	External calibration	Mineral source
3	Microwave-assisted digestion	HNO_3/ H_2O_2	Yes	External calibration	Commercial standard from Merck
4	Microwave-assisted digestion	HNO_3/ H_2O_2	No	External calibration	Merck Standard Solution
5	Microwave-assisted digestion	HNO_3/ H_2O_2	No	External calibration	---
6	Microwave-assisted	HNO_3/ H_2O_2	Yes	External calibration	Merck
7	Dry ashing	HNO_3	No	Internal calibration	DMR-312b CENAM Lot. CNM-MR-610-0051/2011 Exp. Date: 2012-10-20
8	Microwave-assisted digestion	HNO_3/ H_2O_2	No	External calibration	ICP Multi Element Standard Solution XXI CertiPUR/Merck
9	Microwave-assisted digestion	HNO_3/ H_2O_2/ Aqua regia	No	External calibration	High Purity Standards Lot. 1124927
10	Microwave-assisted digestion	HNO_3/ H_2O_2/ Aqua regia	No	External calibration	High Purity Standards Lot. 1124927
11	Preparation of slurry for direct measurement	HNO_3	No	Standard additions	SRM 3103a
12	Microwave-assisted digestion	HNO_3/ H_2O_2	No	External calibration	Inorganic Ventures
13	Microwave-assisted digestion	HNO_3	No	External calibration	Perkin-Elmer
14	---	---	---	---	---
15	Dry ashing	Mixture HNO_3/ HCl	No	Internal calibration	ACR Elemental Standard
16	---	---	---	---	---
17	Dry ashing	HNO_3/ HCl	No	External calibration	Merck HC088963; 1002 ± 5 mg/L
18	Microwave-assisted digestion	HNO_3	No	External calibration	Perkin Elmer

"---" Data or information was not provided.

TABLE VIII. Technical Information - Methods of Analysis of Arsenic (total) (Cont'd)

Lab Code	Use of internal standard(s)	Analytical instrument(s)	Correction for recovery	Method accreditation	Additional information
1	No	ICP-AES	No	No	---
2	No	Hydride generation AAS	No	No	---
3	No	ICP-AES	Yes: 98.94%	Yes	---
4	Yes: Yttrium	ICP-AES	No	Yes	---
5	No	ICP-OES	No	No	---
6	No	Hydride generation AAS	No	Yes	---
7	No	Hydride generation AAS	No	No	Reference: Pr EN 14546:2004:E European Standard. Foodstuffs - Determination of Trace Elements – Determination of Total Arsenic By Hydride Generation Atomic Absorption Spectrometry (HGAAS)
8	No	Graphite AAS	No	No	---
9	No	Graphite AAS	No	No	This result is for the bottle 50
10	No	Graphite AAS	No	No	This result is for the bottle 54
11	No	Graphite AAS	No	No	---
12	Yes: In115	ICP-MS	No	Yes	---
13	No	ICP-MS	No	Yes	---
14	---	---	---	---	The test for Total As was not carried out due to some technical difficulties in the operation of the equipment.
15	Yes: Used as check standard only	ICP-AES	No	No	1. The preferred microwave digestion technique wasn't utilised here for the laboratory do not have any microwave digestor and a suitable water bath to facilitate this technique, thus dry ashing was used instead. 2. We do not have an Hydride and our ICP-MS is still on its way therefore our end detection was done by ICP-AES.
16	---	---	---	---	---
17	Yes	Hydride generation AAS	No	Yes	---
18	No	Hydride generation AAS	No	Yes	---

"---" Data or information was not provided.

TABLE VIII. Technical Information - Methods of Analysis of Cadmium

Lab Code	Digestion technique	Digestion medium	Matrix separation	Quantification	Source(s) of Calibration standard(s)
1	Microwave-assisted digestion	HNO_3	Yes	External calibration	Cadmium (High Purity, lote 1005609)
2	Dry ashing	HNO_3/ HCl	No	External calibration	Mineral source
3	Microwave-assisted digestion	HNO_3/ H_2O_2	Yes	Internal calibration	Commercial standard from Perkin Elmer
4	Microwave-assisted digestion	HNO_3/ H_2O_2	No	External calibration	Perkin Elmer Standard Solution
5	Microwave-assisted digestion	HNO_3/ H_2O_2	No	External calibration	---
6	Microwave-assisted	HNO_3/ H_2O_2	Yes	External calibration	Merck
7	Microwave-assisted digestion	HNO_3	No	Internal calibration	NIST 3108 Lot. 060531 Exp. Date: 2014-05-31
8	Microwave-assisted digestion	HNO_3/ H_2O_2	No	External calibration	ICP Multi Element Standard Solution XXI CertiPUR/Merck
9	Microwave-assisted digestion	HNO_3	No	External calibration	High Purity Standards Lot. 1034341
10	Microwave-assisted digestion	HNO_3	No	External calibration	High Purity Standards Lot. 1034341
11	Preparation of slurry for direct measurement	HNO_3	No	Standard additions	SRM 3108
12	Microwave-assisted digestion	HNO_3/ H_2O_2	No	External calibration	Inorganic Ventures
13	Microwave-assisted digestion	HNO_3	No	External calibration	Perkin-Elmer
14	Dry ashing	HNO_3	No	External calibration	JT Baker Cd Standard, 1000µg/mL (Cd metal in 5% HNO_3); Exp Date: 31 July 2012
15	Dry ashing	Mixture of HNO_3/ HCl	No	Internal calibration	ACR Elemental Standard
16	Wet digestion	HNO_3	No	External calibration	Perkin Elmer
17	Dry Ashing	HNO_3	No	External calibration	Merck HC002003; 1000 ± 0.5 mg/L
18	Microwave-assisted digestion	HNO_3	No	External calibration	Perkin Elmer

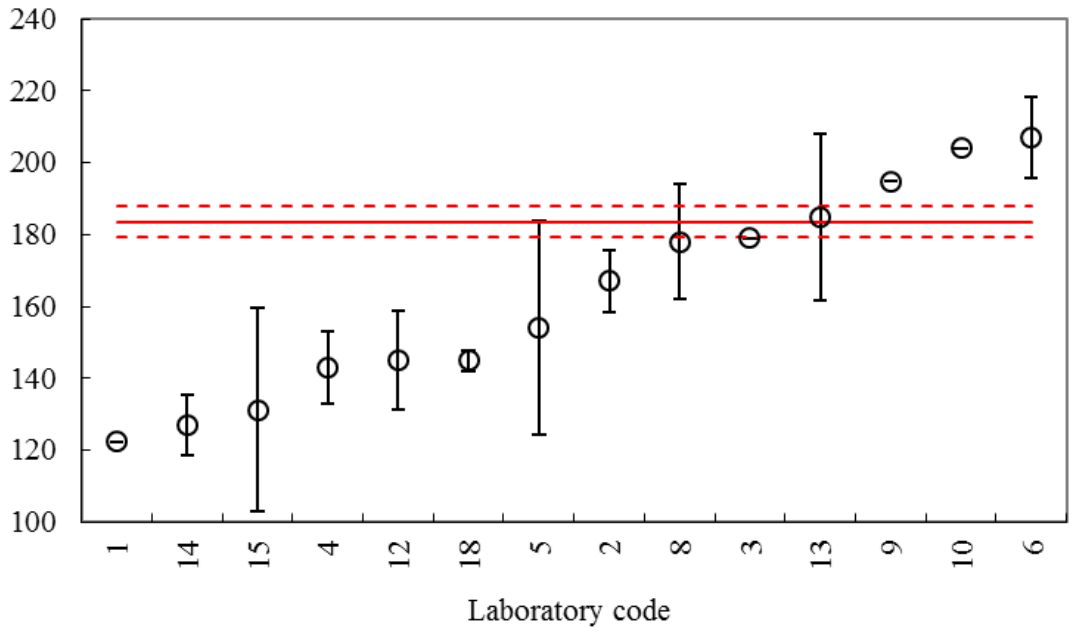
"---" Data or information was not provided.

TABLE VIII. Technical Information - Methods of Analysis of Cadmium (Cont'd)

Lab Code	Use of internal standard(s)	Analytical instrument(s)	Correction for recovery	Method accreditation	Additional information
1	---	ICP-AES	No	No	---
2	No	Flame AAS	No	No	---
3	Yes: Yttrium	ICP-MS	Yes: 100.15%	Yes	---
4	No	ICP-MS	No	Yes	---
5	No	Graphite AAS	No	No	---
6	No	Graphite furnace - AAS	No	Yes	---
7	No	Flame AAS	No	Yes	Reference: NOM-010-ZOO-1994 Modified
8	No	Graphite AAS	No	No	---
9	No	Graphite AAS	No	No	This result is for the bottle 50
10	No	Graphite AAS	No	No	This result is for the bottle 54
11	No	Graphite AAS	No	No	---
12	Yes: In115	ICP-MS	No	Yes	---
13	No	ICP-MS	No	Yes	---
14	No	Graphite AAS	No	No	Used DORM-3, Fish Protein Certified Reference Material for Trace Metals by National Research Council Canada as Quality Control Check; Exp Date: September 2016
15	Yes: Used as check standard only	ICP-AES	No	No	1. The preferred microwave digestion technique wasn't utilised here for the laboratory do not have any microwave digestor and a suitable water bath to facilitate this technique, thus dry ashing was used instead.
16	No	Graphite AAS	Yes: 85%	Yes	---
17	No	Flame AAS	No	Yes	---
18	No	Graphite AAS	No	Yes	---

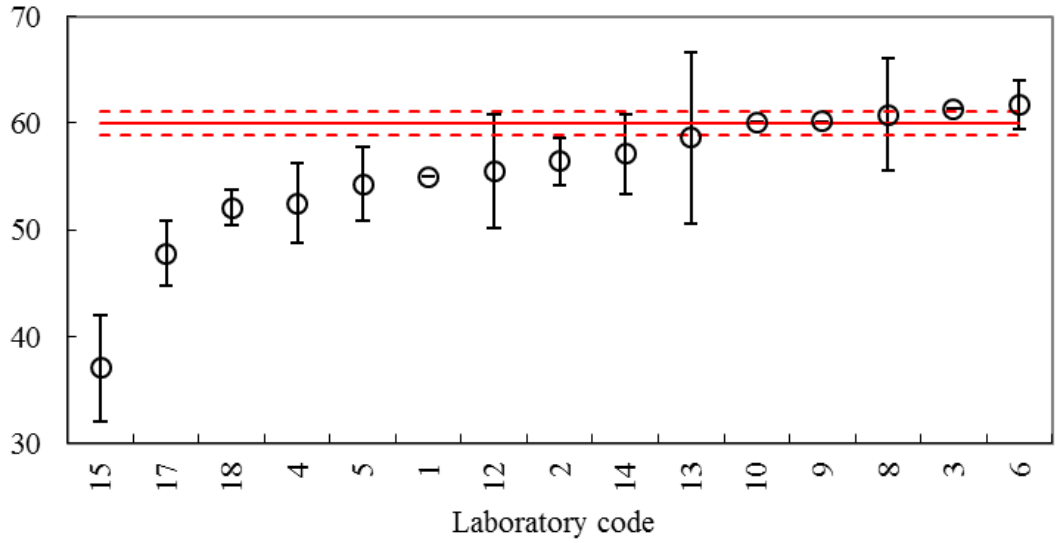
"---" Data or information was not provided.

FIGURE I. Participants' results (μg/g) for Iron (in ascending order)



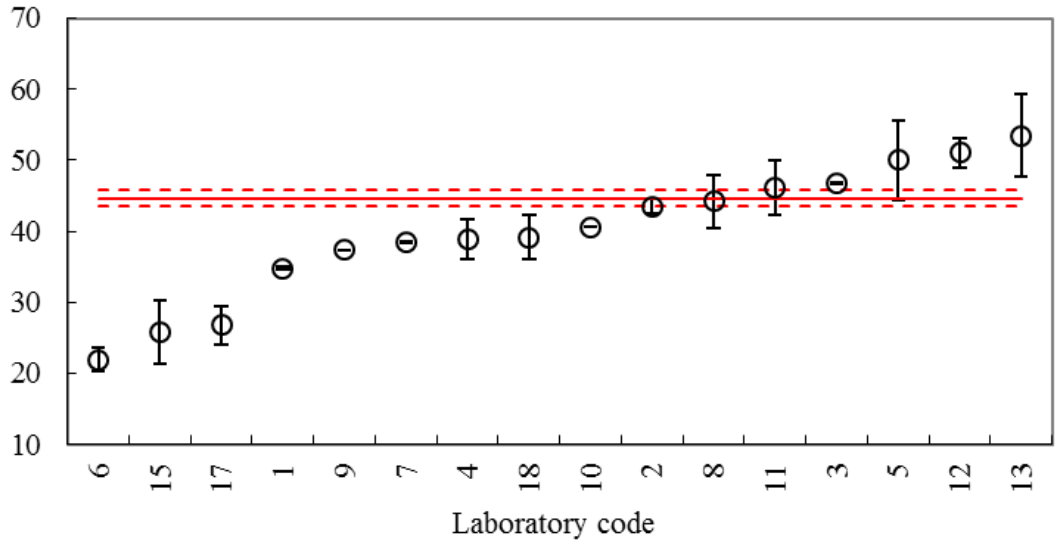
Note: Participants' results are displayed with error bars representing expanded uncertainties. The red solid horizontal line is the assigned value and the red dash lines show the expanded uncertainty of the assigned value.

FIGURE II. Participants' results (μg/g) for Zinc (in ascending order)



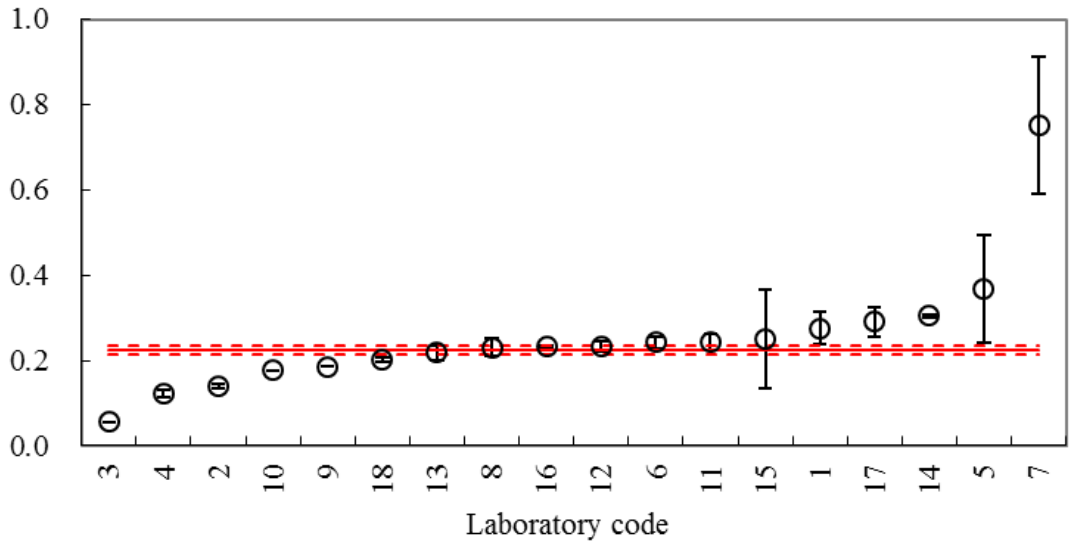
Note: Participants' results are displayed with error bars representing expanded uncertainties. The red solid horizontal line is the assigned value and the red dash lines show the expanded uncertainty of the assigned value.

FIGURE III. Participants' results (μg/g) for Arsenic (total) (in ascending order)



Note: Participants' results are displayed with error bars representing expanded uncertainties. The red solid horizontal line is the assigned value and the red dash lines show the expanded uncertainty of the assigned value.

FIGURE IV. Participants' results (μg/g) for Cadmium (in ascending order)



Note: Participants' results are displayed with error bars representing expanded uncertainties. The red solid horizontal line is the assigned value and the red dash lines show the expanded uncertainty of the assigned value.

FIGURE V. Participants' z-Scores for Iron

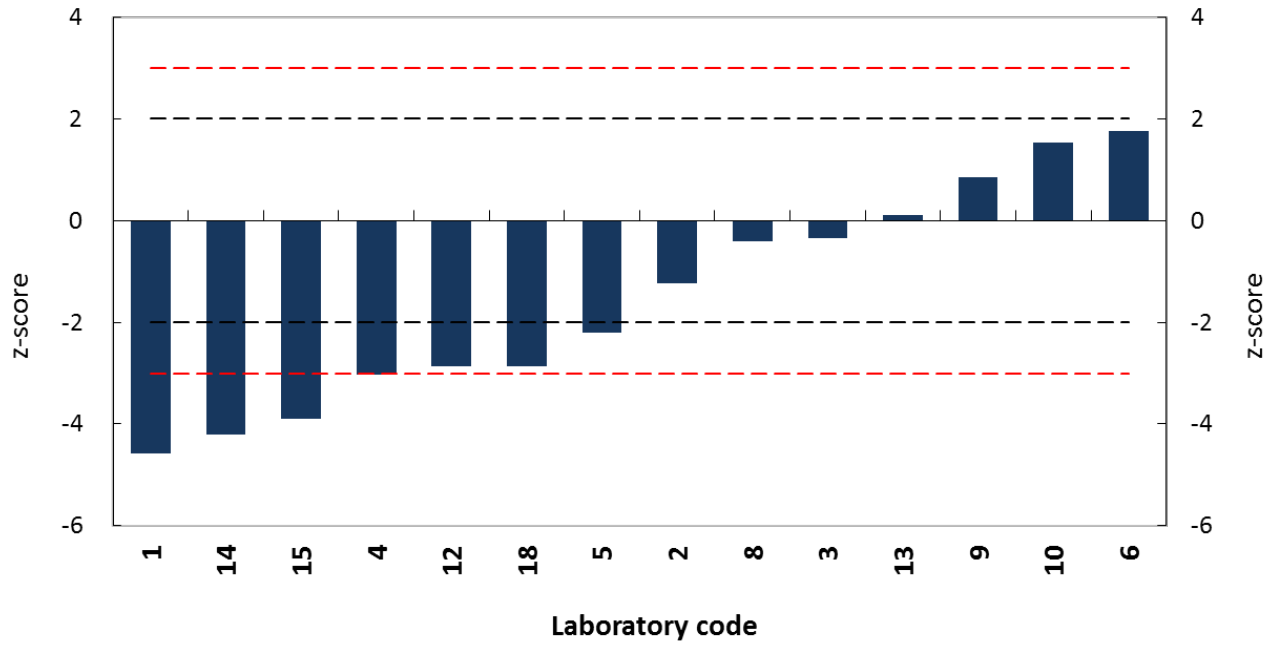


FIGURE VI. Participants' z-Scores for Zinc

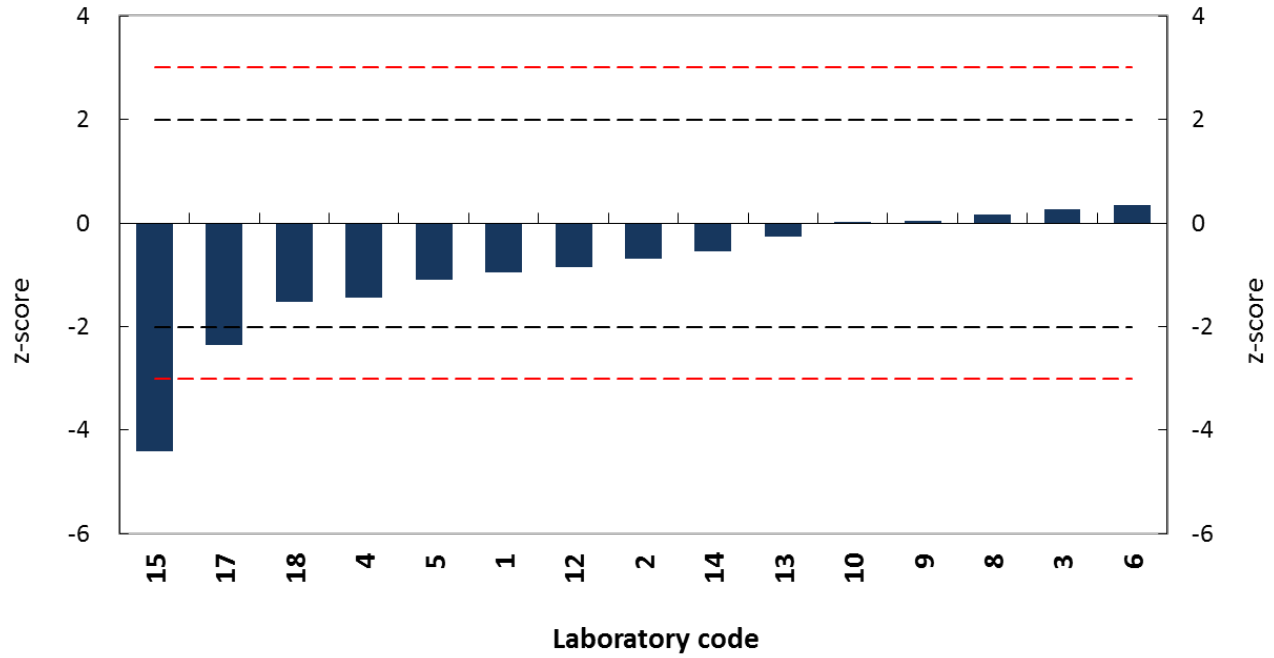


FIGURE VII. Participants' z-Scores for Arsenic (total)

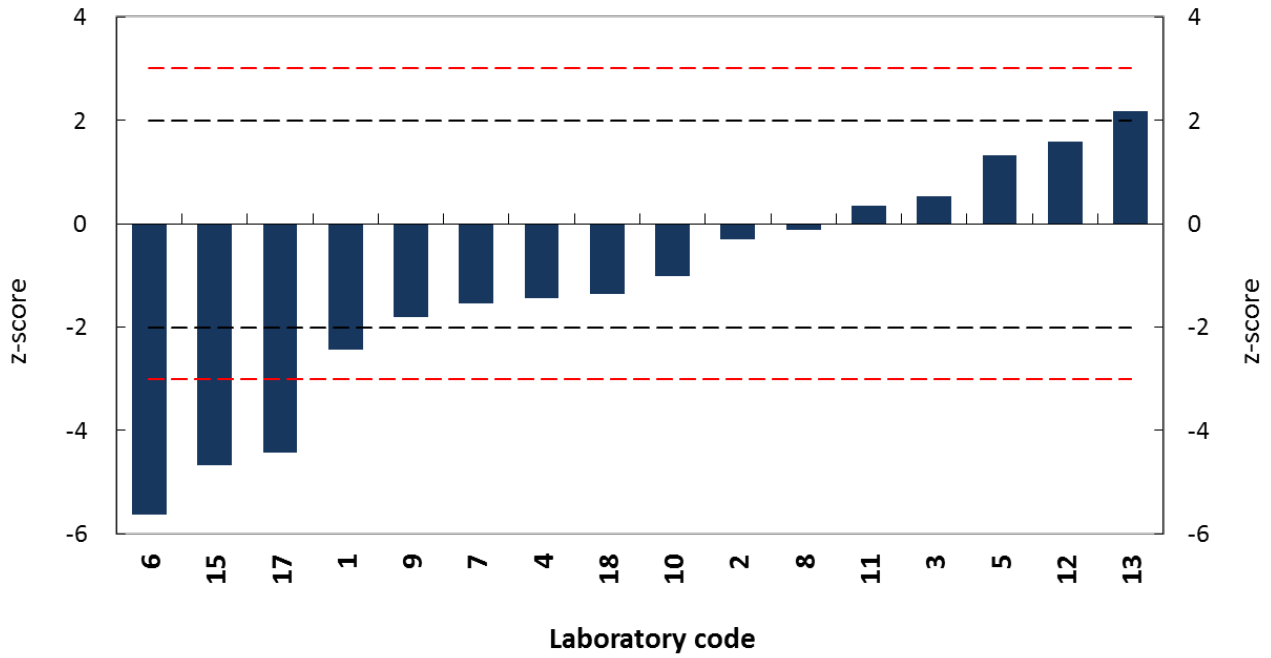
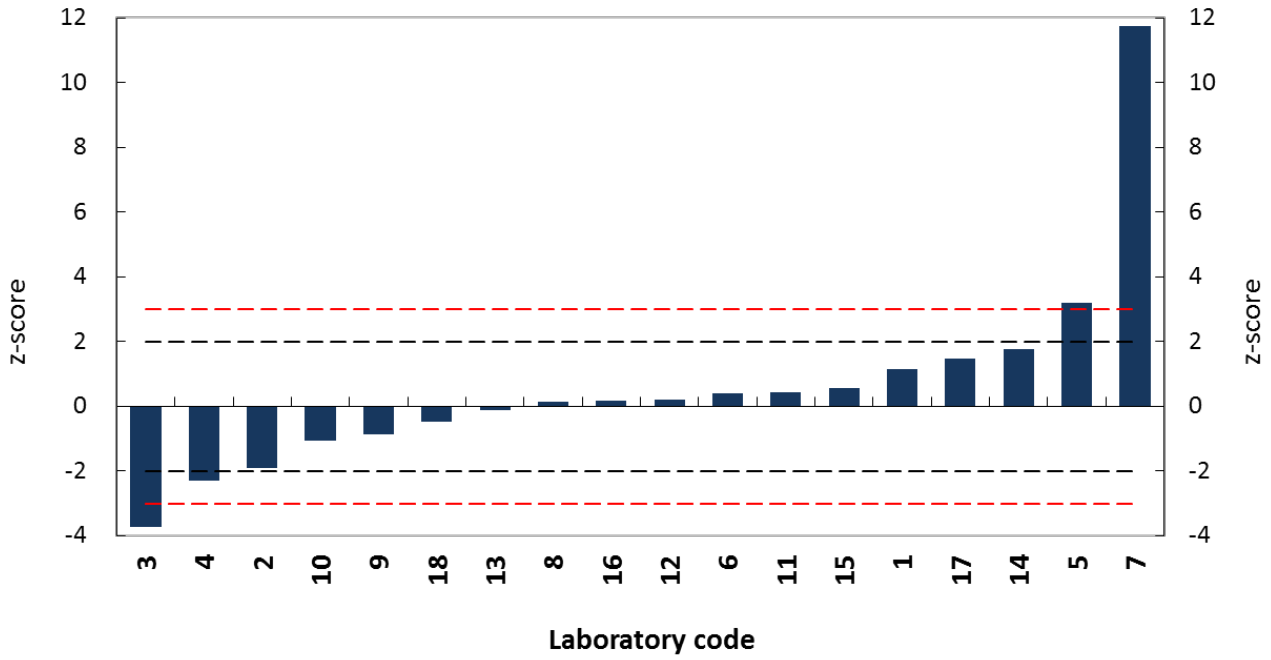


FIGURE VIII. Participants' z-Scores for Cadmium



APPENDIX I: Homogeneity Study

a. The homogeneity study was conducted after the test material bottled and irradiated. 10 bottles of the test material (conditioned at 20 ± 5 °C) were randomly selected from the prepared bottles of sample. Two test portions of 0.5 g were taken from each bottle for analysis.

b. The test portions were digested using microwave-assisted digestion. Following validated procedures, the digested samples and method blanks were analysed using standard additions with high resolution ICP-MS for the analysis of As, Cd and Zn, and using standard additions with ICP-AES for the analysis of Fe.

c. ANOVA technique was applied to assess the between bottle heterogeneity and the standard uncertainty originated from the between bottle heterogeneity was calculated using the equation given below in accordance with ISO Guide 35:2006[9.7].

$$u_{bb} = \sqrt{\frac{MS_{within}}{n}} \cdot \sqrt{\frac{2}{v_{MSwithin}}}$$

where
u_{bb} is the standard uncertainty due to between bottles heterogeneity;
MS_{within} is the mean square of within bottles variance;
$v_{MSwithin}$ is the degree of freedom of MS_{within};
n is the number of replicates.

d. The homogeneity study results are summarized in the following table.

Measurand	ANOVA test on heterogeneity		Relative standard uncertainty due to between bottle heterogeneity, u_{bb} (%)
	F-statistics	Critical value	
As	1.22	3.02	0.95
Cd	2.08	3.02	1.21
Fe	1.25	3.02	1.05
Zn	1.40	3.02	1.26

e. The homogeneity study results indicated that no significant heterogeneity was observed in the testing material. The test material was adequately homogeneous and was considered fit for the purpose of the APEC proficiency testing programme.

APPENDIX II: Stability Study

a. Long-term and short-term stability studies were conducted for the test material using the same analytical procedures for the homogeneity study. The long-term stability is associated with the behaviour of the test material under storage in participating laboratories while the short-term stability with any extra effects due to transport of the test material. The long-term stability was conducted at 20 ºC covering the period from the distribution of the test material to the deadline for submission of results. The short-term stability was conducted at 40 ºC and 50 ºC over a 4-week period (sampling points: 1 week, 2 weeks and 4 weeks).

b. The trend-analysis technique proposed by ISO Guide 35:2006[9.7] was applied to assess the stability of the test material at 20 ºC, 40 ºC and 50 ºC. The basic model for the stability study is expressed as the following equation.

$$Y = \beta_0 + \beta_1 X + \varepsilon$$

where β_0 and β_1 are the regression coefficients; and ε denotes the random error component.

c. With appropriate t-factor, β_1 can be tested for significance of deviation from zero. The results of the stability test at 20 ºC, 40 ºC and 50 ºC are summarized in the following table.

Measurand	p-value for significance test for β_1		
	20 ºC	40 ºC	50 ºC
As	0.267	0.583	0.931
Cd	0.173	0.649	0.640
Fe	0.142	0.378	0.570
Zn	0.668	0.569	0.173

d. As all p-values were greater than 0.05, it was concluded that the corresponding β_1 value was not significantly deviated from zero at 95% confidence level. In other words, no instability was observed for the test material at 20 ºC, 40 ºC and 50 ºC during the testing period. The test material was adequately stable and was considered fit for the purpose of the APEC proficiency testing programme.

e. To monitor the highest temperature that the test material would be exposed to during the transportation, temperature recording strips were sent along with the test material to the participants. According to the information provided by participants in the Sample Receipt Forms, the maximum temperatures that the test material experienced were all below 40 ºC.

APPENDIX III: Study Protocol

APEC Proficiency Testing Programme:
Essential and Toxic Elements in Seafood

Study Protocol

1. Introduction

Food contamination with toxic elements is one of the major food safety issues in the Asia-Pacific region. Most economies have laboratories that carry out routine analyses of toxic elements in seafood for regulatory compliance purposes. Examination of essential elements is performed for nutritional studies and quality assurance as well.

As part of its commitment to strengthening regional chemical metrology infrastructure, the Asia-Pacific Metrology Programme (APMP) has been organizing inter-comparisons for the purpose of establishing the technical basis for mutual recognition of measurement capabilities among national metrology institutes (NMIs)/designated institutes (DIs). To this end, a study on "Essential and Toxic Elements in Seafood" will be organized by the APMP as a joint initiative of its Technical Committee for Amount of Substance (TCQM) and the Developing Economies' Committee (DEC). The study encompasses a supplementary comparison (APMP.QM-S5) and a proficiency testing programme (APMP DEC PT) that will be conducted in parallel using the same test material for examination. The main focus of interest of the study is the determination of the essential elements (iron and zinc) and toxic elements (total arsenic and cadmium) in a dried shrimp material. Dried shrimps are prepared by drying of seawater shrimps under the sun and are commonly used to impart a characteristic flavour to many Asian cuisines.

With a view to increasing laboratory capacity building in the area of conformity assessment in the Asia-Pacific Economic Cooperation (APEC) region, a project entitled "Laboratory Capacity Building for the Determination of Toxic Contaminants in Seafood (APEC Project SCSC CTI 21 11T)" has been proposed. It aims to develop laboratory capabilities within the food inspection laboratories from APEC member economies in measurement, testing and inspection for contaminants (toxic elements) in seafood. The project follows on the issues identified through the APEC Project (CTI 20/2009T) "Strengthening Chemical Metrology Infrastructure for Member Economies". It also directly supports the objectives and work plans of the APEC Sub-committee on Standards and Conformance (SCSC) in the development of standards and conformance capacity within APEC economies as well as those of the APEC Food Safety Cooperation Forum (FSCF) and its Partnership Training Institute Network (PTIN). The project will be undertaken with the direct oversight by APMP experts. APMP will work with its sister body in the Americas, the Inter-American Metrology System (SIM) to ensure appropriate traceability, quality and scientific credibility of outcomes for all participating APEC economies. The project consists of:

APPENDIX III: Study Protocol (Cont'd)

- Preparatory Workshop: The workshop (5 days) will involve hands-on laboratory training as well as training courses on estimation of measurement uncertainty and method validation. This is intended to enhance participants' understanding of good laboratory practice and ensure they know what will be expected of them in participating in a proficiency testing programme (APEC PT).

- APEC PT: The aim of APEC PT is to assess uptake from the preparatory workshop and evaluate the measurement capabilities of participating laboratories. The APEC PT will concurrently be conducted in parallel with APMP.QM-S5 using the same test material of dried shrimp. The reference values obtained from APMP.QM-S5 will be used as the assigned values for evaluating the performance of participants in the APEC PT. This will not only enhance the quality of the APEC PT but will also help build the measurement capability of the participants through a better linkage between the APMP NMIs/DIs and the food inspection laboratories from APEC member economies.

- Concluding Workshop: The workshop (3 days) will enable participants to share experience, identify further needs and develop action plans for improving laboratory practices and capabilities.

2. Objectives

The present study is based on the analysis of the naturally incurred material of dried shrimp. The purposes of the study are (i) to assist participating laboratories in demonstrating competence on the measurement of the contents of the incurred analytes (iron, zinc, total arsenic and cadmium) at μg/g levels in the proficiency test sample containing the dried shrimp powder by various analytical techniques; and (ii) to identify problems and opportunities for self-improvement. Mass fractions of analytes on a dry mass basis will be used for comparability purposes.

3. Proficiency testing provider

The APEC PT is organized by the Government Laboratory, Hong Kong (GLHK) (Address: 7/F., Homantin Government Offices, 88 Chung Hau Street, Homantin, Kowloon, Hong Kong) in collaboration with APMP TCQM, APMP DEC and SIM. GLHK takes responsibility for all tasks in the development and operation of the proficiency testing programme, including preparation and distribution of proficiency test samples, data analysis and evaluation of results, preparation of interim and final reports, and communications with participants. Dr. Della W.M. Sin of GLHK is the co-ordinator of the proficiency testing programme.

4. Fee for participation

Free of charge.

APPENDIX III: Study Protocol (Cont'd)

5. Selection of participants

Through APMP, Asia Pacific Laboratory Accreditation Cooperation (APLAC), SIM, APEC SCSC and FSCF's contact networks, suitable laboratories will be identified for participation in the aforementioned project. Participation in the APEC proficiency testing programme is restricted to food inspection laboratories nominated by APEC member economies. It is anticipated that about 30 food inspection laboratories from APEC member economies will join the proficiency testing programme.

6. Proficiency test sample

About 13 kg of dried shrimps was purchased from the local market in Hong Kong. The dried shrimps were confirmed to contain quantities of incurred iron, zinc, arsenic and cadmium. The dried shrimps were rinsed with anhydrous methanol to remove dirt and foreign matter and air-dried in a Class 1000 cleanroom. The air-dried shrimps were blended and cut in a high-speed blender (25000 revolutions per minute) to give small pieces, which were then de-fatted with n-hexane and air-dried in the cleanroom. The air-dried sample was further blended and ground using the high-speed blender (25000 revolutions per minute) to give powder. The powder was subject to a sieving process through 200 μm calibrated sieves. The sieved powder was thoroughly homogenized in a 3-dimensional mixer for 5 days. The powdered material was irradiated using ^{137}Cs gamma source at a dose of about 10 kGy for disinfection. The irradiated material was packed into pre-cleaned and nitrogen-flushed amber glass bottles, each of about 25 g. About 300 bottles of sample were prepared. Finally, each bottled sample was vacuum-sealed in a polypropylene bag and stored at room temperature (20 ± 5°C) prior to distribution or use.

The homogeneity study will be performed. Not less than ten bottles (conditioned at 20 ± 5°C) will be taken randomly and analyzed in at least duplicate for determining the sample inhomogeneity. Also, the stability study will be conducted. Before the distribution of samples, not less than three bottles (conditioned at 40 ± 5°C or at an elevated temperature) will be taken randomly and analyzed in at least duplicate for monitoring the sample instability. After the deadline for submission of results, not less than three bottles (conditioned at 20 ± 5°C) will be taken randomly and analyzed in at least duplicate for monitoring the sample instability. Methods based on inductively coupled plasma atomic emission spectrometry/inductively coupled plasma mass spectrometry will be used in the homogeneity and stability studies. The minimum sample size taken for analysis should be about 0.5 g.

7. Instructions for participants

Participating laboratories will be provided with **ONE** bottle containing about **25 g** of dried shrimp powder.

The proficiency test sample should be stored under room temperature conditions (about 20 °C).

APPENDIX III: Study Protocol (Cont'd)

Participants should use the test method of their choice. The analysis should be conducted with a recommended sample size of at least 0.5 g. Participants are requested to perform at least three independent measurements on three separate portions of the sample and to determine the mass fractions of the analytes. All of the four measurands and the range of values to be expected for the proficiency test sample are given in Table 1.

Table 1

Measurand	Mass fraction (expected range of values)
Iron	80-250 μg/g
Zinc	30-80 μg/g
Arsenic (total)	20-60 μg/g
Cadmium	0.05-1 μg/g

Participants should also carry out the dry mass correction. For the determination of dry mass correction, a minimum of three separate portions (with a recommended sample size of about 1 g for each portion) of the sample should be taken and placed over anhydrous calcium sulphate (DRIERITE®) in a desiccator at room temperature for a minimum of 10 days until a constant mass is reached. Dry mass correction should be carried out at the same time as the test sample portions are to be analyzed.

For safety considerations, the proficiency test sample should be handled with care to avoid from inhaling the sample powder or contacting with eyes. Wash the suffered body areas with plenty of water and consult physicians when necessary.

For this proficiency testing programme, return of the untested portion of the proficiency test sample is not necessary.

8. Reporting and submission of results

Participants should complete the Result Proforma. The manners of reporting test results are as follows:

- For each analyte, the mean value of at least 3 independent measurements and its associated uncertainty (combined standard uncertainty at 1 sigma level) should be reported on a dry mass basis;
- Report the mass fractions of analytes in μg/g for iron, zinc, arsenic (total) and cadmium; and
- Participants should provide information about the methods of analysis.

Participants should be aware that any submitted results are considered final and accordingly such results and units should be thoroughly checked before submission. Participants should submit the Result Proforma electronically to the co-ordinator of the proficiency testing programme (E-mail: apecs5@govtlab.gov.hk) on or before the deadline 31 January 2012. Results submitted after the deadline will not be accepted. Participants are reminded that the ability to report results in the specified unit and within the given time scale are part of the proficiency test.

APPENDIX III: Study Protocol (Cont'd)

9. Measurement uncertainty

Measurement uncertainty is best estimated within the individual laboratory environment. An estimate of uncertainty of measurement is normally 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. As stipulated in ISO Guide to the Expression of Uncertainty in Measurement [1], the influence of each component of uncertainty on the measurement result should 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.

10. Evaluation of performance of participants

Performance of the participating laboratories is assessed using z-score, which is calculated as follows:

$$z = \frac{x_i - x}{\sigma}$$

where x_i = the reported result of the i^{th} participant
x = the assigned value*
σ = the standard deviation for proficiency assessment estimated from the Horwitz Equation

Note: * The assigned values will be provided by the reference values obtained from the APMP supplementary comparison (APMP.QM-S5).

z-Score is commonly interpreted as:

(i)	$\|z\| \leq 2$	Satisfactory
(ii)	$2 < \|z\| < 3$	Questionable
(iii)	$\|z\| \geq 3$	Unsatisfactory

Laboratories having a |z| score equal to or larger than 3 shall thoroughly investigate their results for the discrepancy and those having a z-score in the range $2 < |z| < 3$ are also encouraged to review their results.

11. Issue of reports

An interim report will be issued to participants for checking the correctness of results submitted. The draft final report will then be prepared and submitted to APEC SCSC for comments and approval. Upon approval, an electronic copy of the final report will be distributed to the participants.

The final report, part of the final report or its summary may be posted onto the websites of APEC and GLHK for public interest.

APPENDIX III: Study Protocol (Cont'd)

12. Confidentiality

The concerned parties (APMP TCQM, APMP DEC, APLAC, SIM, APEC SCSC and GLHK) strive to maintain strict confidentiality with respect to the composition of the proficiency test sample distributed and the performance of all participating laboratories. To preserve the confidentiality, participants receive reports giving all results for assessment but without identifying individual laboratories. The code number assigned to a participant in the proficiency testing programme is only made known to the contact person/authorized person of the participating laboratory.

The proficiency testing programme is conducted in the belief that participants will perform the analysis and report results with scientific rigour. Collusion and falsification of results are clearly against the spirit of the proficiency testing programme.

13. Proposed programme schedule

The proposed time schedule for the various phases of the proficiency testing programme (APEC PT) is as follows:

Proposed time schedule	Phase
19 July 2011	Call for participation
28 July 2011	Nomination of no more than 2 food inspection laboratories by each APEC member economy to participate in the APEC PT
20 August 2011	Deadline for registration
September 2011	Preparatory Workshop (5 days) (*Note: The details of the Preparatory Workshop will be announced later.*)
Mid-September 2011	Distribution of samples
31 January 2012	Deadline for submission of results
Mid-March 2012	Interim report for comments
May-June 2012	Draft final report for comments
May-June 2012	Concluding Workshop (3 days) (*Note: The details of the Concluding Workshop will be announced later.*)
End of June 2012	Issue of the final report

14. Contact

For enquiries, participants may wish to make contacts as follows:

The co-ordinator of the proficiency testing programme
E-mail: apecs5@govtlab.gov.hk

Dr. Della Wai-mei SIN, GLHK
E-mail: wmsin@govtlab.gov.hk
Tel.: +852 2762 3704

APPENDIX III: Study Protocol (Cont'd)

Dr. Chuen-shing MOK, GLHK
E-mail: csmok@govtlab.gov.hk
Tel.: +852 2762 3883

Dr. Yiu-chung YIP, GLHK
E-mail: ycyip@govtlab.gov.hk
Tel.: +852 2762 3853

Dr. Lindsey MACKAY
E-mail: Lindsey.Mackay@measurement.gov.au

Dr. Angela SAMUEL, NMIA
E-mail: Angela.Samuel@nmi.gov.au
Tel.: +61 2 8467 3580

Mr. José A. Dajes Castro, INDECOPI
E-mail: jdajes@indecopi.gob.pe
Tel.: +51 1 224 7800

15. References

1. International Standards Organization. ISO/IEC G98:1995, Guide to the Expression of Uncertainty in Measurement (GUM), ISO, Geneva, Switzerland.

APPENDIX IV: Sample Receipt Form

Sample Receipt Form

Institute/ Laboratory: _____

Postal address: _____

Contact person: _____ _____ _____

Title Given name Surname

E-mail: _____

Print name / Signature: _____

Date: _____

Confirmation of Package Contents

I hereby acknowledge the receipt of the sealed shipping box for the APEC proficiency testing programme. The box contains:

☐ One sample of dried shrimp powder with a bottle number _____.

☐ The sample is *Intact & Sealed / Broken / Missing** and should be *Suitable / Not Suitable** for analysis (* Please delete as appropriate).

☐ The temperature recording strip indicated that the maximum temperature experienced during the transport was:

☐ <29 °C ☐ ≥29 °C ☐ ≥33 °C ☐ ≥34 °C ☐ ≥37 °C ☐ ≥40 °C ☐ ≥42 °C

☐ The Material Safety Data Sheet for the sample.

Other comments: _____

Upon receipt of the sample, please complete this form and return it to the co-ordinator of the proficiency testing programme (E-mail: apecs5@govtlab.gov.hk).

APPENDIX V: Result Proforma

Result Proforma

Institute/ Laboratory: _____

Postal address: _____

Contact person: _____ _____ _____

Title Given name Surname

E-mail: _____

Print name / Signature: _____

Date: _____

1. Analytical results

Measurand	Mean value (μg/g)	Combined standard uncertainty (μg/g)	Coverage factor *k* (95% level of confidence)	Expanded uncertainty (μg/g)
Iron				
Zinc				
Arsenic (total)				
Cadmium				

Notes: (i) Report the analytical results and associated uncertainties in the unit μg/g; (ii) Report the analytical results on a dry mass basis; (iii) Report values to 3 significant figures; and (iv) If value determined is less than the limit of quantification (LOQ), please specify.

APPENDIX V: Result Proforma (Cont'd)

2. Methods of analysis

Measurand: Iron

1. *Digestion technique: Microwave-assisted digestion / Wet digestion / Dry ashing
Others (please specify): _____

2. *Digestion medium: HNO_3 / HCl / HF / H_2SO_4 / $HClO_4$ / H_2O_2 / *Aqua regia*
Others (please specify): _____

3. *Matrix separation: YES / NO

4. *Quantification: External calibration / Internal calibration / Standand additions
Isotope dilution mass spectormetry

5. Source(s) of calibration standard(s): _____

6. *Use of internal standard(s) YES (please specify): _____ / NO

7. *Analytical instrument(s): ICP-MS / ICP-AES / Flame AAS / Graphite AAS
Others (please specify): _____

8. *Correction for recovery YES (please specify recovery (%)): _____ / NO

9. *Method accreditation: YES / NO

10. Additional information: _____

* Please delete as appropriate

APPENDIX V: Result Proforma (Cont'd)

Measurand: Zinc

1. *Digestion technique:	Microwave-assisted digestion / Wet digestion / Dry ashing Others (please specify):
2. *Digestion medium:	HNO_3 / HCl / HF / H_2SO_4 / $HClO_4$ / H_2O_2 / *Aqua regia* Others (please specify):
3. *Matrix separation:	YES / NO
4. *Quantification:	External calibration / Internal calibration / Standand additions Isotope dilution mass spectormetry
5. Source(s) of calibration standard(s):	
6. *Use of internal standard(s)	YES (please specify): / NO
7. *Analytical instrument(s):	ICP-MS / ICP-AES / Flame AAS / Graphite AAS Others (please specify):
8. *Correction for recovery	YES (please specify recovery (%)): / NO
9. *Method accreditation:	YES / NO
10. Additional information:	

* Please delete as appropriate

APPENDIX V: Result Proforma (Cont'd)

Measurand: Arsenic (total)

1. *Digestion technique:	Microwave-assisted digestion / Wet digestion / Dry ashing Others (please specify):
2. *Digestion medium:	HNO_3 / HCl / HF / H_2SO_4 / $HClO_4$ / H_2O_2 / *Aqua regia* Others (please specify):
3. *Matrix separation:	YES / NO
4. *Quantification:	External calibration / Internal calibration / Standand additions Isotope dilution mass spectormetry
5. Source(s) of calibration standard(s):	
6. *Use of internal standard(s)	YES (please specify): / NO
7. *Analytical instrument(s):	ICP-MS / ICP-AES / Hydride generation AAS / Graphite AAS Others (please specify):
8. *Correction for recovery	YES (please specify recovery (%)): / NO
9. *Method accreditation:	YES / NO
10. Additional information:	

* Please delete as appropriate

APPENDIX V: Result Proforma (Cont'd)

Measurand: Cadmium

1. *Digestion technique:	Microwave-assisted digestion / Wet digestion / Dry ashing Others (please specify):
2. *Digestion medium:	HNO_3 / HCl / HF / H_2SO_4 / $HClO_4$ / H_2O_2 / *Aqua regia* Others (please specify):
3. *Matrix separation:	YES / NO
4. *Quantification:	External calibration / Internal calibration / Standand additions Isotope dilution mass spectormetry
5. Source(s) of calibration standard(s):	
6. *Use of internal standard(s)	YES (please specify): / NO
7. *Analytical instrument(s):	ICP-MS / ICP-AES / Flame AAS / Graphite AAS Others (please specify):
8. *Correction for recovery	YES (please specify recovery (%)): / NO
9. *Method accreditation:	YES / NO
10. Additional information:	

* Please delete as appropriate