Asia Pacific Laboratory Accreditation Cooperation Proficiency Testing Programme (APLAC T082)

Essential and Toxic Elements in Seafood

Proposal

Jointly coordinated by:

Government Laboratory Hong Kong (GLHK)

&

Hong Kong Accreditation Service (HKAS)

April 2011

Asia Pacific Laboratory Accreditation Cooperation Proficiency Testing Programme (APLAC T082): Essential and Toxic Elements in Seafood

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 quality assurance of food and for nutritional evaluation 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 the aim of enhancing the quality and traceability of measurements in various economies of the Asia-Pacific region through a better regional scientific infrastructure, APMP will also collaborate with the Asia Pacific Laboratory Accreditation Cooperation (APLAC). The same test material will be used in an APLAC PT (APLAC T082) that will be conducted in parallel with the APMP supplementary comparison (APMP.QM-S5).

The reference values obtained from the supplementary comparison (APMP.QM-S5), which in turn will have participation from NMIs/DIs worldwide, will be used as the assigned values for evaluating the performance of the participants in the APLAC PT. This will not only enhance the quality of the APLAC PT but will also help build the measurement capability of the participants through a better regional linkage between the NMIs/DIs of APMP and the accredited analytical laboratories in the Asia-Pacific region.

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. Organisers of the APLAC PT

The Government Laboratory Hong Kong (GLHK) (Address: 7/F., Homantin Government Offices, 88 Chung Hau Street, Homantin, Kowloon, Hong Kong) is the proficiency testing provider. 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. Y.C. Yip has been assigned as the co-ordinator of the proficiency testing programme.

Hong Kong Accreditation Service (HKAS) is the proposer. HKAS is responsible for proposing the proficiency testing programme for approval by the APLAC Proficiency Testing Committee, inviting participants, circulating the interim report, the draft final report and the final report to participants and acting as a contact point between APLAC, accreditation bodies/participating laboratories and GLHK.

4. Fee for participation

Free of charge.

5. Selection of participants

APLAC members as well as other non-APLAC accreditation bodies will be invited to participate in the programme. Invitations will be sent to all APLAC members and other accreditation bodies. Accreditation bodies will be asked to nominate laboratories for participation and indicate the accreditation status of the nominated laboratories for the test. The number of laboratories shall be preferably limited to 100. Therefore, a restriction on the number of participating laboratories from each accreditation body may need to be imposed. When the number of enrolments exceeds the limit, participants will

be selected on a first come first served basis. The organisers will, as far as possible, allow at least one laboratory to participate in this proficiency testing programme from each accreditation body.

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

Instructions for Accreditation Bodies and Participating Laboratories are given in Annexes A and B respectively. Sample Receipt Forms for Accreditation Bodies and Participating Laboratories are given in Annexes C and D respectively.

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

Participants should treat the proficiency test sample in the same manner as the majority of routinely tested samples. They are expected to use the test method of their choice, which should be consistent with their routine procedures.

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

The proficiency test sample should be mixed thoroughly before conducting the tests. 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 proficiency test sample is not necessary.

8. Reporting and submission of results

Participants should complete the Result Proforma (Annex E). 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: aplacs5@govtlab.gov.hk) on or before the deadline. 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. Under no circumstances, correction or adjustment of analytical data will be accepted after the issue of the interim report.

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 corresponding APMP supplementary comparison (APMP.QM-S5). This is in line with the ISO/IEC 17043 recommendations on the determination of assigned values for proficiency testing schemes.

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 and their respective accreditation bodies for checking the correctness of results submitted. The draft final report will then be prepared and submitted to APLAC PT Committee for comments and approval. Upon approval, an electronic copy of the final report will be distributed to the participants and their respective accreditation bodies.

12. Proposed programme schedule

The proposed time schedule for the various phases of the proficiency testing programme (APLAC T082) is as follows:

Proposed time schedule	Phase
8 July 2011	Call for Participation
20 August 2011	Deadline for registration
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
End of June 2012	Issue of the final report

13. Confidentiality

The concerned parties (APMP, APLAC, GLHK and HKAS) strive to maintain strict confidentiality with respect to 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 and/or the respective accreditation body.

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.

14. Contact

Participants may wish to contact the co-ordinator of the proficiency testing provider for any enquires (E-mail: aplacs5@govtlab.gov.hk).

If you have any query or comment on the proposal, please send it to Mr. W. W. Wong of HKAS at wwwong@itc.gov.hk.

15. References

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

Annex A

Instructions for Accreditation Bodies

1. Objectives

The APLAC proficiency testing programme "Essential and Toxic Elements in Seafood (APLAC T082)" is organized by the Government Laboratory Hong Kong (GLHK) in collaboration with Hong Kong Accreditation Service (HKAS) under the auspices of the Asia-Pacific Laboratory Accreditation Cooperation (APLAC). 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.

2. Analysis of the proficiency test sample

Accreditation bodies (AB) should receive the sealed shipping boxes containing the proficiency test samples and the instructions (softcopy) from the organizers. Upon receipt of the samples, please complete the Sample Receipt Form (Accreditation Bodies) and return it to the co-ordinator of the proficiency testing programme (E-mail: aplacs5@govtlab.gov.hk). Replacement will be arranged if the proficiency test samples are identified to be not suitable for analysis.

AB should distribute the proficiency test samples to the nominated laboratories as soon as possible. The proficiency test samples should be stored under room temperature conditions (about 20 °C) before distribution.

AB should request the nominated laboratories to carefully check the proficiency test samples upon receipt. Also, AB should ask the nominated laboratories to complete the Sample Receipt Form (Participating Laboratories) and return it to the co-ordinator of the proficiency testing programme (E-mail: aplacs5@govtlab.gov.hk).

3. Reporting and submission of results

AB shall remind the nominated laboratories to complete the Result Proforma and submit it electronically to the co-ordinator of the proficiency testing programme (E-mail: aplacs5@govtlab.gov.hk) on or before the deadline 31 January 2012. Under normal circumstances, results submitted after the deadline will not be accepted.

4. Contact

AB may wish to contact the co-ordinator of the proficiency testing programme for any enquires (E-mail: aplacs5@govtlab.gov.hk).

Annex B

Instructions for Participating Laboratories

1. Objectives

The APLAC proficiency testing programme "Essential and Toxic Elements in Seafood (APLAC T082)" is organized by the Government Laboratory Hong Kong (GLHK) in collaboration with Hong Kong Accreditation Service (HKAS) under the auspices of the Asia-Pacific Laboratory Accreditation Cooperation (APLAC). 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.

2. Analysis of the proficiency test sample

Participating laboratories will be provided with **ONE** bottle containing about **25 g** of dried shrimp powder. Upon receipt of the sample, please complete the Sample Receipt Form (Participating Laboratories) and return it to the co-ordinator of the proficiency testing programme (E-mail: aplacs5@govtlab.gov.hk). Replacement of a new bottle of sample will be arranged if the proficiency test sample is identified to be not suitable for analysis.

Participants should treat the proficiency test sample in the same manner as the majority of routinely tested samples. They are expected to use the test method of their choice, which should be consistent with their routine procedures.

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

The proficiency test sample should be mixed thoroughly before conducting the tests. 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 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

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 prevent inhaling the sample powder and getting into eyes. Wash the suffered body areas with plenty of water and consult physicians when necessary.

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

3. 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: aplacs5@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.

An electronic copy of the final report on the performance of participating laboratories would be distributed to the participants in June 2012. The report will reveal only the code number assigned to the designated participating laboratory and the identity of participants in this proficiency testing programme will be kept confidential.

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.

4. Contact

Participants may wish to contact the co-ordinator of the proficiency testing programme for any enquires (E-mail: aplacs5@govtlab.gov.hk).

Annex C

Sample Receipt Form
(Accreditation Bodies)

Accreditation Body: _____

Postal address: _____

Contact person: _____ _____ _____
Title Given name Surname

E-mail: _____

Print name / Signature: _____

Date: _____

Confirmation of Package Contents

I hereby acknowledge the receipt of _____ sealed shipping box(es) containing the proficiency test sample(s) for the APLAC proficiency testing programme (APLAC T082).

The sealed shipping box(es) is/are *Intact & Sealed / Broken / Missing** and should be *Suitable / Not Suitable** for analysis. (* Please delete as appropriate)

Other comments: _____

Upon receipt of the sample(s), please complete this form and return it to the co-ordinator of the proficiency testing programme (E-mail: aplacs5@govtlab.gov.hk).

Annex D

Sample Receipt Form
(Participating Laboratories)

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 APLAC proficiency testing programme (APLAC T082). The box contains:

☐ One sample of dried shrimp 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: aplacs5@govtlab.gov.hk).

Annex E

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.

Annex E

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

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

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

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