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

Trace Elements in Natural Water

Protocol

Coordinated by

Government Laboratory, Hong Kong (GLHK)

7/F., Homantin Government Offices

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Hong Kong, China

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APEC Proficiency Testing Scheme:
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1. Introduction

Water quality is a priority for all economies and underpins food security, agriculture, health, and trade facilitation – all ongoing priorities for Asia-Pacific Economic Cooperation (APEC). The "APEC Food Security Roadmap Towards 2030" was launched in 2021 to support inclusive, resilient and sustainable recovery of the APEC region. Goal 6 of the UN Sustainable Development Goals, availability and access to water, sanitation and hygiene (WASH) services is fundamental in maintaining public health and in the fight against COVID-19. The 2021 World Water Development Report on "Valuing Water" also identifies that a solid technical infrastructure is required to obtain good and reliable measurement data to make educated social, economic, and environmental decisions by all levels of governance. The need for traceable measurements supporting water quality policies has also been identified and supported under the European Water Framework.

With a view to help build laboratories capacities in the APEC region, a project entitled "Building laboratory capabilities to assure water quality in Asia Pacific Economies (APEC Project SCSC 01 2021)" was approved. Experts in chemical measurement from the Asia Pacific Metrology Programme (APMP) will work with colleagues from the Inter-American Metrology System (SIM) (APMP's counterpart in the Americas) to provide oversight and management of the project. Workshops will be organized for knowledge sharing with laboratory staff to measure parameters affecting water quality and sanitation. Experts from the Asia Pacific Accreditation Cooperation (APAC) will also provide advice and support to the project. By helping laboratories achieve comparability through internationally recognized measurement and accreditation frameworks, the project will increase the sustainability of benefits for all economies across the Asia Pacific region and beyond.

The participating measurement institutes/laboratories in this APEC PT scheme will be expected to measure parameters affecting water quality. The PT will help assess uptake of the knowledge and training from the Preparatory Workshop of the APEC Project and evaluate the measurement capabilities of participating institutes and laboratories. Metrologically traceable results will be used to benchmark the performance of participants. PT participants will also be invited to attend a Post-Measurement Workshop to share experience, identify further needs and develop action plans for improving laboratory practices and capabilities. Particular attention will be paid to the design and facilitation of the workshop to ensure that technical personnel involved in the actual measurements reflect on the learning outcomes from the project; identify needs for further support and skills development; and are able to implement their institute's action plans in their respective economies. The details of

the two workshops including registration, dates and venues will be announced separately.

2. Objectives

This PT scheme targets the analysis of four elements (antimony, arsenic, cadmium and lead) spiked in a natural water sample. The objectives of the scheme are (i) to assist participating laboratories in demonstrating competence on the measurement of the mass fractions of the analytes in the sample by various analytical techniques; and (ii) to identify problems and opportunities for further improvement. The mass fractions of the analytes reported on an as-received 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, China). GLHK takes responsibility for all tasks in the development and operation of the PT scheme, including preparation and distribution of PT samples, data analysis and evaluation of results, preparation of interim and final reports, and communications with participants.

4. Fee for participation

Participation in the PT scheme is free of charge.

Participants are responsible for responding to their local customs and couriers to ensure prompt receipt of the PT sample, which may not be replaced if there are damages after the participating laboratories have acknowledged receipt of the PT samples in good order.

5. Selection of participants

Eligible laboratories will be invited to participate in the PT scheme through the APEC Sub-Committee on Standards and Conformance (SCSC), APAC, APMP and SIM's contact networks. It is anticipated that about 100 water measurement laboratories mainly from APEC member economies will join the PT scheme.

6. Proficiency test sample

The source of the study material was commercially available natural mineral groundwater from Fanjing Mountain, World Natural Heritage, China. The study material was prepared by GLHK in middle September 2021. An acid-cleaned HDPE tank of 60 L capacity was filled with approximately 40 L of natural mineral water and concentrated nitric acid was added to adjust the acid volume fraction to approximately 2%. A preliminary ICP-MS analysis was performed to determine the levels of the elements of interest. The levels of As, Cd, Pb and Sb were gravimetrically adjusted by

additions of aliquots of known masses of single-element standard solutions. After thorough mixing with a mechanical stirrer for 2 h, an inductively coupled plasma mass spectrometry (ICP-MS) analysis was performed to confirm that the levels of the 4 elements of interest are within the target ranges. The sample solutions were packaged into pre-cleaned amber HDPE bottles of 250 mL capacity and sealed inside aluminized Mylar pouches. About 180 bottles of sample were prepared. Each bottle contains at least 200 mL of sample solution.

Randomly selected bottles were assessed for homogeneity. ANOVA at 95% level of confidence will be applied to assess the between-bottle homogeneity in accordance with ISO Guide 35:2017.

The short-term stability of the measurands over a period of 4 weeks at 60 °C was assessed using isochronous approach. Two randomly selected sample bottles were transferred from the storage condition at 4 °C to 60 °C on three occasions (2, 4 and 6 weeks) over the study period. Two subsamples were then taken from each bottle and analyzed by ICP-MS. Using the student's *t*-test on the slope of the linear regression at 95% level of confidence, no significant instability of the measurands was observed.

The long-term stability of the measurands in the comparison material at 4 °C will be assessed. The testing will be carried out before sample dispatch and continuously monitored until completion of the PT scheme using the classical approach. For each occasion of the stability testing, at least two bottles will be randomly selected, and two subsamples will be taken from each bottle. Student's *t*-test on the slope of the linear regression at 95% level of confidence will be used for the evaluation of instability of the measurands.

7. Instructions for participants

Each participant will receive one bottle of the sample containing at least 200 mL of sample. The samples will be distributed by courier to the participants (monitored by a temperature strip). Participants will be informed and provided with the tracking number after sample dispatch. Upon receipt, the samples should be stored at 4 °C. A Sample Receipt Form will be provided to the participating institutes for completion. The completed form should be sent to the organizer at the earliest convenience.

Samples should be shaken before use to account for any possible water condensation on the inner surfaces of the bottle. To avoid possible contamination, do not insert pipettes or other apparatus into the bottle. Samples should be treated at room temperature around 15 ºC to 25 ºC before use. To prevent evaporation loss, the bottle should be recapped tightly and returned to the aluminized plastic bag, which should be folded and sealed with sealing tape after use. Participants may check for any evaporation issues by weighing the bottle before and after taking sample aliquots between storage.

Participants may use any test method of their choice. The recommended minimum sample amount for analysis is 5 grams. The bottle contents should be well mixed by rotation and shaking prior to use. 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. The four measurands and the range of values expected are given in Table 1.

Table 1

Element	Expected mass fraction	Natural/Spiked	Description
Arsenic (As)	(0.1–30) µg/kg	Spiked	Toxic element
Cadmium (Cd)	(0.1–30) µg/kg	Spiked	Toxic element
Antimony (Sb)	(0.1–30) µg/kg	Spiked	Metalloid
Lead (Pb)	(0.1–30) µg/kg	Spiked	Toxic element

It is not necessary to return the untested portion of the PT sample to the organizer.

8. Reporting and submission of results

Participants should complete the Result Proforma (Annex A). The manner of reporting test results is 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;
- Report the mass fractions of analytes in μg/kg; and
- Participants should provide information about the methods of analysis.

Participants should be aware that any submitted results are considered final. Therefore, results and units of measurement should be thoroughly checked before submission. Participants should submit the Result Proforma electronically to the co-ordinator of the PT scheme (E-mail: apecpt2022@govtlab.gov.hk) on or before the end of September 2022. 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 PT.

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, 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:

$$z_i = \frac{x_i - x_{pt}}{\sigma_{pt}}$$

where x_i : the participant's result
x_{pt} : the assigned value
σ_{pt} : the standard deviation for proficiency assessment estimated from the Horwitz equation

Note: The reference values measured by NMIs/DIs with the support of CMC claims will be used as the assigned values. This is in accordance with the ISO/IEC 17043 and ISO 13528 recommendations on the determination of assigned values for proficiency testing schemes.

The 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.

For reference purpose, the performance of the participating laboratories will also be assessed using zeta-score (ζ), which is calculated as:

$$\zeta_i = \frac{x_i - x_{pt}}{\sqrt{u^2(x_i) + u^2(x_{pt})}}$$

where x_i = the participant's result
x_{pt} = the assigned value
$u(x_i)$ = the participant's estimate of the standard uncertainty of its result x_i
$u(x_{pt})$ = the standard uncertainty of the assigned value x_{pt}

ζ-score is interpreted in the same way as z-score using the critical values of 2.0 and 3.0. ζ-score may be used in conjunction with z-score, as an aid for improving the performance of laboratories. If participating laboratories obtain a |z| score that exceed 3.0, they may find it of value to examine their test procedure step by step and derive an uncertainty budget for that procedure. The uncertainty budget will identify the steps in the procedure where the largest uncertainties arise, so that the laboratories can see where to expend effort to achieve an improvement. If the |ζ| score also exceeds the critical value of 3.0, it implies that the uncertainty budget does not include all significant sources of uncertainty. The laboratories are encouraged to review their uncertainty budget.

11. Issuing of reports

An interim report will be issued to participants to check 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 participants.

The final report, part of the final report or its summary may be posted on the APEC website for public interest.

12. Confidentiality

The responsible parties will strive to maintain strict confidentiality with respect to the composition of the PT sample distributed and the performance of all participating laboratories. To preserve confidentiality, participants receive reports giving all results for assessment but without identifying individual laboratories. The code number assigned to a participant in the PT scheme is only made known to the contact person/authorized person of the participating laboratory.

The PT scheme is conducted on the understanding that participants will perform the analysis and report results with scientific rigour. Collusion and falsification of results are clearly against the spirit of the PT scheme.

13. Proposed schedule

The proposed schedule for the PT scheme (APEC PT) is as follows:

Proposed schedule	**Phase**
Late March 2022	Call for participation
23 April 2022	Deadline for registration
May – September 2022	Distribution of samples, measurements undertaken and results submitted
September – December 2022	Review of results /issue of interim PT report
April 2023	Issue of the final PT report

14. Intellectual Property

The PT organizer will provide APEC with information on the analytical methods used by the participants, results, etc in the Final PT Report, for which APEC will own the copyright. If you have any enquiries about this, please feel free to contact us.

15. Contact

Contact points for enquiries about the APEC Project are as follows:

General enquiries:
Dr. Angela SAMUEL
Project Overseer
Director, International Relations
National Measurement Institute, Department of Industry, Science, Energy and Resources, Australia.
E-mail: Angela.Samuel@measurement.gov.au

For technical enquiries, please contact the following co-ordinators of this PT scheme:

Dr. Della Wai-mei SIN, GLHK
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Tel.: +852 2762 3854

16. References

16.1 ISO/IEC 17000:2004, Conformity assessment – Vocabulary and general principles

16.2 ISO/IEC Guide 99:2007, International vocabulary of metrology – Basic and general concepts and associated terms (VIM)

16.3 ISO/IEC 17043:2010 “Conformity assessment – General requirements for proficiency testing”, 2010, Geneva, Switzerland.

16.4 ISO 13528:2015 “Statistical methods for use in proficiency testing by interlaboratory comparison”, 2015, Geneva, Switzerland.

16.5 ISO 17034:2016 “General requirements for the competence of reference material producers”, 2016, Geneva, Switzerland.

16.6 ISO Guide 35:2017 “Reference materials – Guidance for characterization and assessment of homogeneity and stability”, 2017, Geneva, Switzerland.

16.7 W. Horwitz. Evaluation of analytical methods used for regulations of food and drugs, Anal. Chem. 1982, 54:67A-76A.

16.8 The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories, Pure Appl. Chem. 2006, 78, 1, 145-196.

16.9 CODEX STAN 193-1995 “Codex General Standard for Contaminants and Toxins in Food and Feed”, 2016, CODEX Alimentarius.

16.10 ISO/IEC Guide 98-3:2008 “Uncertainty of measurement -- Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)”, 2008, Geneva, Switzerland.

16.11 Guidelines for drinking-water quality: fourth edition incorporating the first addendum, Geneva, World Health Organization; 2017. ISBN-13: 978-92-4-154995-0.

Annex A

Asia-Pacific Economic Cooperation

APEC Proficiency Testing Scheme

Trace Elements in Natural Water

Result Proforma

Institute/ Laboratory: _____

Contact person: _____ _____ _____

Title Given name Surname

E-mail: _____

Print name / Signature: _____

Date: _____

1. Analytical results

Analyte	Number of subsamples (n)	Mean value (µg/kg)	Combined standard uncertainty (µg/kg)	Coverage factor *k* (95% level of confidence)	Expanded uncertainty (µg/kg)
As					
Cd					
Sb					
Pb					

Notes: (i) Report the analytical results and associated uncertainty in µg/kg;

(ii) Report values with 3 significant figures.

Please complete this form and return it to the coordinator of the proficiency testing scheme (email: apecpt2022@govtlab.gov.hk) on or before ***30 September 2022****.*

Page 1 of 5

APEC Proficiency Testing Scheme

Trace Elements in Natural Water

2. Methods of analysis (As)

*Method accreditation:	Yes / No
Sample amount used for analysis:	_____
*Sample treatment	No treatment / Dilution / Wet digestion / Microwave-assisted digestion Others (please specify): _____
*Analytical Instrument(s):	ICP-MS / ICP-OES / Flame AAS / Others (please specify): _____
* Quantification technique:	External calibration / Internal calibration / Standard additions / Others (please specify): _____
Calibration standard:	_____
Internal standard (if any):	_____
Matrix CRM or QC sample (if any):	_____
Recovery of matrix CRM / QC (%):	_____
*Correction for recovery:	Yes / No

Additional information / Sources of MU / Any abnormal observations and problems encountered during analysis:

_____

_____

_____

* Please delete as appropriate

APEC Proficiency Testing Scheme
Trace Elements in Natural Water

3. Methods of analysis (Cd)

*Method accreditation:	Yes / No
Sample amount used for analysis:	_____
*Sample treatment	No treatment / Dilution / Wet digestion / Microwave-assisted digestion Others (please specify): _____
*Analytical Instrument(s):	ICP-MS / ICP-OES / Flame AAS / Others (please specify): _____
* Quantification technique:	External calibration / Internal calibration / Standard additions / IDMS / Others (please specify): _____
Calibration standard:	_____
Internal standard (if any):	_____
Matrix CRM or QC sample (if any):	_____
Recovery of matrix CRM / QC (%):	_____
*Correction for recovery:	Yes / No

Additional information / Sources of MU / Any abnormal observations and problems encountered during analysis:

_____

_____

_____

* Please delete as appropriate

APEC Proficiency Testing Scheme
Trace Elements in Natural Water

4. Methods of analysis (Sb)

*Method accreditation:	Yes / No
Sample amount used for analysis:	_____
*Sample treatment	No treatment / Dilution / Wet digestion / Microwave-assisted digestion Others (please specify): _____
*Analytical Instrument(s):	ICP-MS / ICP-OES / Flame AAS / Others (please specify): _____
* Quantification technique:	External calibration / Internal calibration / Standard additions / IDMS / Others (please specify): _____
Calibration standard:	_____
Internal standard (if any):	_____
Matrix CRM or QC sample (if any):	_____
Recovery of matrix CRM / QC (%):	_____
*Correction for recovery:	Yes / No

Additional information / Sources of MU / Any abnormal observations and problems encountered during analysis:

_____

_____

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* Please delete as appropriate

* Please delete as appropriate

5. Methods of analysis (Pb)

*Method accreditation:	Yes / No
Sample amount used for analysis:	
*Sample treatment	No treatment / Dilution / Wet digestion / Microwave-assisted digestion Others (please specify):
*Analytical Instrument(s):	ICP-MS / ICP-OES / Flame AAS / Others (please specify):
* Quantification technique:	External calibration / Internal calibration / Standard additions / IDMS / Others (please specify):
Calibration standard:	
Internal standard (if any):	
Matrix CRM or QC sample (if any):	
Recovery of matrix CRM / QC (%):	
*Correction for recovery:	Yes / No

Additional information / Sources of MU / Any abnormal observations and problems encountered during analysis:

* Please delete as appropriate

--- End --