



APMP-APLAC Joint Proficiency Testing Programme  
(APLAC T095)  
Determination of Elements (Calcium and Cadmium)  
in Drinking Water



## **APMP-APLAC Joint Proficiency Testing Programme (APLAC T095)**

### **Determination of Elements (Calcium and Cadmium) in Drinking Water**

Proposal

Coordinated by

National Metrology Institute of Japan (NMIJ)

&

Government Laboratory Hong Kong (GLHK)

August 2014



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## **APMP-APLAC Joint Proficiency Testing Programme**

### **Trace Elements in Drinking Water**

#### **1. Introduction**

The determination of trace elements in drinking water is a routine measurement by regulatory authorities and analytical laboratories. There is no single approach that is universally applicable as the nature and regulations for drinking water standards may vary among countries and regions. The proposed APMP-APLAC Joint Proficiency Testing Programme (APLAC T095) targets on the analysis of calcium and cadmium in a tap water sample. The proficiency test sample is prepared with reference to the maximum acceptable limit for cadmium i.e. 0.003 mg/L as listed in the World Health Organization's (WHO) Guidelines for Drinking Water Quality. The level of calcium in the proficiency test sample is similar to that of natural fresh water.

The reference values obtained from a CCQM key comparison (i.e. CCQM-K124 Trace Elements and Chromium Speciation in Drinking Water), which will have participation from national metrology institutes and designated institutes (NMIs/DIs) worldwide, will be used as the assigned values for evaluating the performance of the participants in this PT programme. This will not only enhance the quality of the PT programme but will also help build the measurement capabilities of the participants through a better regional linkage between the NMIs/DIs and the analytical laboratories in the Asia-Pacific region.

#### **2. Objectives**

The PT programme targets on the analysis of two elements (calcium and cadmium) in a tap water sample. The objectives of the programme are (i) to assist participating laboratories in demonstrating competence on the measurement of the mass fractions of the two analytes (mandatory measurand: calcium; optional measurand: cadmium) in the proficiency test 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. Organisers**

The PT programme is jointly coordinated by National Metrology Institute of Japan (NMIJ) (Address: 1-1-1 Umezono, Tsukuba, Ibaraki, 305-8563 Japan) and Government Laboratory of Hong Kong (GLHK) (Address: 7/F., Homantin Government Offices, 88 Chung Hau Street, Homantin, Kowloon, Hong Kong) according to the recommendation from the APMP-APLAC Joint PT Working Group which is established under the auspices of the Asia Pacific Metrology Programme (APMP) and the Asia Pacific Laboratory Accreditation Cooperation (APLAC). For this PT programme, NMIJ and



APMP-APLAC Joint Proficiency Testing Programme  
(APLAC T095)  
Determination of Elements (Calcium and Cadmium)  
in Drinking Water



GLHK take responsibility for preparation and distribution of proficiency test samples, provision of CCQM-K124 key comparison reference values for performance evaluation, and data analysis, preparation of interim and final reports, and communications with participants.

The proposal for this PT programme will be forwarded to the APMP-APLAC Joint PT Working Group for comments before submission to the APLAC PT Committee for approval.

#### **4. Fee for participation**

Free of charge.

#### **5. Selection of participants**

Due to the limited number of proficiency test samples available, the total number of participants for the proficiency testing programme will be restricted to about 85. Invitations will be sent to analytical laboratories nominated by the APMP Developing Economies' Committee (APMP DEC). The number of laboratories shall be preferably limited to 15. Invitations will be also sent to APLAC members who will be asked to nominate analytical laboratories under their respective accreditation bodies for participation. The number of laboratories shall be preferably limited to 70. Therefore, a restriction on the number of participating laboratories from each accreditation body may need to be imposed. When the number of enrolments exceeded the limit, participants will be selected on a first-come-first-served basis. The organisers will, as far as possible, allow at least one analytical laboratory to participate in this PT programme from each accreditation body.

#### **6. Preparation of proficiency test samples**

The tap water was collected in NMIJ (Tsukuba, Ibaraki, Japan) and filtered (pore size: 0.45  $\mu\text{m}$ ). Some elements standard solutions (As, Cd, Cr, Hg, Mn and Se) were spiked for elements with insufficient concentrations, and nitric acid and hydrochloric acid were added so that those final concentrations were adjusted to about 0.1 mol/L and 0.03 mol/L, respectively. The 150 L raw material was stirred using a magnetic stirrer for homogenisation in a 200 L polypropylene tank. After homogenisation, the water sample was filtered (pore size: 0.20  $\mu\text{m}$ ) and subdivided in polyethylene bottles (125 mL) by 100 mL each.

The homogeneity of the two analytes (calcium and cadmium) in the prepared sample bottles of water was performed. Ten randomly selected sample bottles of water conditioned at room temperature of 20 °C were analysed in duplicate by ICP-MS. ANOVA was applied to assess the between-bottle homogeneity. The test samples were found to be adequately homogeneous for the two analytes. The relative standard



APMP-APLAC Joint Proficiency Testing Programme  
(APLAC T095)  
Determination of Elements (Calcium and Cadmium)  
in Drinking Water



uncertainties due to between-bottle homogeneity for calcium and cadmium were found to be 0.43% and 0.19% respectively. Based on NMIJ's experience in producing River Water Certified Reference Materials, the stability of calcium and cadmium in this proficiency test sample of drinking water is expected to be satisfactory for the purpose of the present proficiency testing programme. As the stability study is still underway, NMIJ intends to report the results of stability study before distribution of samples.

### 7. Instructions for participants

Participating laboratories will be provided with **ONE** sample bottle containing about **100 mL** of water. Instructions for Participants are given in Annex A.

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

Participants should treat the proficiency test sample in the same manner as the majority of routinely tested samples. Participants should use the test method of their choice. Participants are requested to perform at least three independent measurements on three separate portions of the proficiency test sample and to determine the mass fractions of the analytes. The determination of calcium is mandatory to participants; whereas the analysis of cadmium is an optional one. The two 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)
Mandatory: Calcium	1 mg/kg to 20 mg/kg
Optional: Cadmium	0.5 µg/kg to 4 µg/kg

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

For this PT 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 (Annex B). The manners of reporting test results are as follows:

- For each analyte, the mean value of at least 3 independent measurements and the measurement uncertainty should be reported;
- Report the mass fraction of calcium in mg/kg;



APMP-APLAC Joint Proficiency Testing Programme  
(APLAC T095)  
Determination of Elements (Calcium and Cadmium)  
in Drinking Water



- Report the mass fraction of cadmium in  $\mu\text{g}/\text{kg}$ ; and
- Participants should provide information about 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 PT programme (E-mail: [aplact095@govtlab.gov.hk](mailto:aplact095@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.

### 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, etc. As stipulated in ISO Guide to the Expression of Uncertainty in Measurement [15.1], 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  $i^{\text{th}}$  participant  
 $x$  = the assigned value\*  
 $\sigma$  = 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 key comparison CCQM-K124.

z-Score is commonly interpreted as:

- (i)  $|z| \leq 2.0$  Satisfactory



APMP-APLAC Joint Proficiency Testing Programme  
(APLAC T095)  
Determination of Elements (Calcium and Cadmium)  
in Drinking Water



- (ii)  $2.0 < |z| < 3.0$  Questionable
- (iii)  $|z| \geq 3.0$  Unsatisfactory

Laboratories having a  $|z|$  score equal to or larger than 3.0 shall thoroughly investigate their results for the discrepancy and those having a z-score in the range  $2.0 < |z| < 3.0$  are also encouraged to review their results.

### 11. Issue of reports

An interim report will be issued to participants/accreditation bodies for checking the correctness of results submitted. The draft final report will then be prepared and submitted to the APMP-APLAC PT Working Group for comments before submission to the APLAC PT Committee for approval. Upon approval, an electronic copy of the final report will be distributed to the concerned participants/accreditation bodies.

Part of the final report or its summary may be posted onto the websites of APMP, APLAC, NMIJ and GLHK for public interest.

### 12. Confidentiality

The concerned stakeholders (APMP, APLAC, NMIJ and GLHK) strive to maintain strict confidentiality with respect to the composition of the proficiency test samples 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 PT programme is only made known to the contact person/authorized person of the participating laboratory and/or the respective accreditation body.

The PT 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 is as follows:

Proposed time schedule	Phase
August 2014	Call for participation
1 September 2014	Deadline for registration/nomination
September 2014	Distribution of samples
End of February 2015	Deadline for submission of results
May 2015	Interim report for comments
November 2015*	Final report for comments



APMP-APLAC Joint Proficiency Testing Programme  
(APLAC T095)  
Determination of Elements (Calcium and Cadmium)  
in Drinking Water



\* At the earliest. The date depends on the progress in CCQM-IAWG because the assigned values will be provided by the reference values obtained from the key comparison CCQM-K124.

#### 14. Contact

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

The co-ordinators of the PT programme

Dr. Akiharu HIOKI, NMIJ  
E-mail: [aki-hioki@aist.go.jp](mailto:aki-hioki@aist.go.jp)

Dr. Takayoshi KUROIWA, NMIJ  
E-mail: [t-kuroiwa@aist.go.jp](mailto:t-kuroiwa@aist.go.jp)

Dr. Yanbei ZHU, NMIJ  
E-mail: [yb-zhu@aist.go.jp](mailto:yb-zhu@aist.go.jp)

Dr. Wai-hong FUNG, GLHK  
E-mail: [whfung@govtlab.gov.hk](mailto:whfung@govtlab.gov.hk)  
Tel.: +852 2762 3862

Dr. Yiu-chung YIP, GLHK  
E-mail: [yicyip@govtlab.gov.hk](mailto:yicyip@govtlab.gov.hk)  
Tel.: +852 2762 3853

#### 15. References

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



APMP-APLAC Joint Proficiency Testing Programme  
(APLAC T095)  
Determination of Elements (Calcium and Cadmium)  
in Drinking Water



Annex A

**Instructions for Participants**

**1. Objectives**

The APMP-APLAC Joint Proficiency Testing Programme (APLAC T095) is jointly coordinated by National Metrology Institute of Japan (NMIJ) and Government Laboratory of Hong Kong (GLHK) according to the recommendation from the APMP-APLAC Joint PT Working Group, which is established under the auspices of the Asia Pacific Metrology Programme (APMP) and the Asia Pacific Laboratory Accreditation Cooperation (APLAC).

The programme targets on the analysis of two elements (calcium and cadmium) in a gravimetrically prepared water sample. The purposes of the study are (i) to assist participating laboratories in demonstrating competence on the measurement of the mass fractions of the two analytes (mandatory measurand: calcium; optional measurand: cadmium) in the proficiency test sample of water by various analytical techniques; and (ii) to identify problems and opportunities for self-improvement. The mass fractions of the analytes on an as-received basis will be used for comparability purposes.

**2. Analysis of the proficiency test sample**

Participating laboratories will be provided with **ONE** sample bottle containing about **100 mL** of water. Upon receipt of the sample, please complete the Sample Receipt Form and return it to the co-ordinator of the proficiency testing programme (E-mail: [aplact095@govtlab.gov.hk](mailto:aplact095@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.

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

Participants should treat the proficiency test sample in the same manner as the majority of routinely tested samples. Participants should use the test method of their choice. The proficiency test sample should be shaken thoroughly before conducting the tests. 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





APMP-APLAC Joint Proficiency Testing Programme  
(APLAC T095)  
Determination of Elements (Calcium and Cadmium)  
in Drinking Water



determination of calcium is mandatory to participants; whereas the analysis of cadmium is an optional one. The two 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)
Mandatory: Calcium	1 mg/kg to 20 mg/kg
Optional: Cadmium	0.5 µg/kg to 4 µg/kg

For safety considerations, the proficiency test sample should be handled with care to avoid from 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 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 the measurement uncertainty should be reported;
- Report the mass fraction of calcium in mg/kg;
- Report the mass fraction of cadmium in µg/kg; and
- Participants should provide information about 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: [aplact095@govtlab.gov.hk](mailto:aplact095@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.

Upon approval, an electronic copy of the final report on the performance of participating laboratories will be tentatively distributed to the participants in November 2015 at the earliest. 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.



APMP-APLAC Joint Proficiency Testing Programme  
(APLAC T095)  
Determination of Elements (Calcium and Cadmium)  
in Drinking Water



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: [aplact095@govtlab.gov.hk](mailto:aplact095@govtlab.gov.hk)).



APMP-APLAC Joint Proficiency Testing Programme  
(APLAC T095)  
Determination of Elements (Calcium and Cadmium)  
in Drinking Water



Annex B

**Result Proforma**

Institute/  
Laboratory: \_\_\_\_\_

Postal address: \_\_\_\_\_

Contact  
person: \_\_\_\_\_

Title	Given name	Surname
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E-mail: \_\_\_\_\_

Print name /  
Signature: \_\_\_\_\_

Date: \_\_\_\_\_

**1. Analytical results and measurement uncertainty**

Mandatory measurand	Mean value (mg/kg)	Combined standard uncertainty (mg/kg)	Coverage factor $k$ (95% level of confidence)	Expanded uncertainty (mg/kg)
Calcium				

Optional measurand	Mean value ( $\mu\text{g/kg}$ )	Combined standard uncertainty ( $\mu\text{g/kg}$ )	Coverage factor $k$ (95% level of confidence)	Expanded uncertainty ( $\mu\text{g/kg}$ )
Cadmium				

Notes: (i) Report the analytical results and associated uncertainties in the units specified; (ii) Report the analytical results on an as-received basis; (iii) Report values to 3 significant figures; and (iv) If value determined is less than the limit of quantification (LOQ), please specify.



APMP-APLAC Joint Proficiency Testing Programme  
(APLAC T095)  
Determination of Elements (Calcium and Cadmium)  
in Drinking Water



Annex B

**2. Methods of analysis**

**Mandatory measurand: Calcium**

1. \*Digestion technique: Microwave-assisted digestion / Wet digestion / Analysis after dilution  
Others (please specify): \_\_\_\_\_
2. \*Digestion medium: HNO<sub>3</sub> / HCl / HF / H<sub>2</sub>SO<sub>4</sub> / HClO<sub>4</sub> / H<sub>2</sub>O<sub>2</sub> / *Aqua regia*  
Others (please specify): \_\_\_\_\_
3. \*Matrix separation: YES / NO  
\_\_\_\_\_
4. \*Quantification: External calibration / Internal calibration / Standard additions / Isotope dilution mass spectrometry  
\_\_\_\_\_
5. Source(s) of calibration standard(s): Certified reference materials (please specify):  
Materials from commercial sources (please specify):  
\_\_\_\_\_
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



APMP-APLAC Joint Proficiency Testing Programme  
(APLAC T095)  
Determination of Elements (Calcium and Cadmium)  
in Drinking Water



**Optional measurand: Cadmium**

1. \*Digestion technique: Microwave-assisted digestion / Wet digestion / Analysis after dilution  
Others (please specify): \_\_\_\_\_
2. \*Digestion medium: HNO<sub>3</sub> / HCl / HF / H<sub>2</sub>SO<sub>4</sub> / HClO<sub>4</sub> / H<sub>2</sub>O<sub>2</sub> / *Aqua regia*  
Others (please specify): \_\_\_\_\_
3. \*Matrix separation: YES / NO  
\_\_\_\_\_
4. \*Quantification: External calibration / Internal calibration / Standard additions / Isotope dilution mass spectrometry  
\_\_\_\_\_
5. Source(s) of calibration standard(s): Certified reference materials (please specify):  
Materials from commercial sources (please specify): \_\_\_\_\_
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