



**KRISS** 한국표준과학연구원  
Korea Research Institute of Standards and Science

**APMP-APLAC Joint Proficiency Testing  
Programme (T093)  
Toxic Elements in Cabbage**



**Asia Pacific Metrology Program(APMP) -  
Asia Pacific Laboratory Accreditation  
Cooperation(APLAC)  
Joint Proficiency Testing Programme  
<APLAC PT T093>**

**Toxic Elements in Cabbage**

Jointly coordinated by:

Korea Research Institute of Standards and Science(KRISS)

&

Korea Laboratory Accreditation Scheme(KOLAS)

July 2014



**KRISS** 한국표준과학연구원  
Korea Research Institute of Standards and Sciences

## APMP-APLAC Joint Proficiency Testing Programme (T093)

### Toxic Elements in Cabbage



# APMP-APLAC Joint Proficiency Testing Programme: Toxic Elements in Cabbage

## 1. Introduction

Kimchi cabbage, a type of cabbage and a main ingredient of Kimchi, a fermented Asian dish, is widely cultivated and the most popular Brassica vegetable in the Asia-Pacific region. It is a good source of nutrients but it is prone to be contaminated with toxic elements such as lead and cadmium from fertilizer, contaminated agricultural soil and water. Many countries set food safety regulations limiting the amount of toxic elements in agricultural products. With increasing international trade of food and agricultural products, traceable measurements of hazardous elements in agricultural products have become one of the essential requirements for ensuring food safety.

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, the Asia-Pacific Metrology Programme (APMP) and the Asia Pacific Laboratory Accreditation Cooperation (APLAC) agreed to strengthen bilateral cooperation and established the APMP-APLAC Joint Proficiency Testing Working Group (PTWG) in November 2013. As an initiative of the joint proficiency testing (PT) programme Korea Research Institute of Standards and Sciences (KRISS), a member of APMP, proposed a PT scheme jointly with Korea Laboratory Accreditation Scheme (KOLAS), a member of APLAC, for the determination of toxic elements (cadmium and lead) in freeze dried kimchi cabbage. The purpose of this study is to demonstrate the capability of participating laboratories in measuring toxic elements in the test sample of dried kimchi cabbage. A domestic PT round for National Agricultural Products Quality Management Service (NAQS) in Korea will be conducted in parallel with the APMP-APLAC joint PT.

Reference values provided by KRISS for cadmium and lead in the test sample will be used as the assigned values for evaluating measurement results of participants. The relevant Calibration and Measurement Capabilities (CMCs) of KRISS are registered in the Key Comparison Data Base (KCDB) of the Comité International des Poids et Mesures (CIPM, International Committee for Weights and Measures) Mutual Recognition Arrangement (MRA). The use of reference values traceable to the International System of Units (SI, *Système international d'unités*) provided by NMIs with appropriate CMCs as PT reference values at this and forthcoming APMP-APLAC Joint PTs will allow the rigorous evaluation of the accuracy of participants' results. It will enhance the quality of the PT programme and 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



**KRISS** 한국표준과학연구원  
Korea Research Institute of Standards and Science

## APMP-APLAC Joint Proficiency Testing Programme (T093)

### Toxic Elements in Cabbage



The aim of this study is to demonstrate the capability of participating laboratories in measuring the amount of lead and cadmium at mg/kg levels in the test sample of kimchi cabbage by various analytical techniques.

### 3. Organisers of the joint PT Programme

KRISS(Address: 267 Gajeong-Ro, Yuseong-Gu, Daejeon 305-340, Republic of Korea) is the National Metrology Institute (NMI) of Korea. KRISS 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.

KOLAS(Address: 93, Isu-ro, Maengdong-myeon, Eumseong-gun, Chungcheongbuk-do, 369-811, Republic of Korea) is the governmental accreditation body of Korea. KOLAS is responsible for proposing the proficiency testing programme, inviting participants, circulating the interim report, the draft final report and the final report to participants and acting as a contact point between participating accreditation bodies/participants and KRISS.

### 4. Fee for participation

Free of charge.

### 5. Call for participation

APLAC members as well as non-APLAC members will be invited to participate in the programme. Invitations will be sent to all APLAC members and other accreditation bodies. Participating accreditation bodies will be asked to nominate laboratories to participate and indicate the accreditation status of the nominated laboratories for the test. The number of laboratories shall be limited to 100 due to the limitation of the test sample prepared in KRISS(participants for the parallel NAQS PT round will not be included in this number). APLAC members are invited to nominate up to a maximum of 3 laboratories and non-APLAC members are invited to nominate up to a maximum of 2 laboratories. When enrolment exceeds the limit, the number of participating laboratories from each accreditation body will be limited upon discussion with APLAC.

### 6. Test sample



**KRISS** 한국표준과학연구원  
Korea Research Institute of Standards and Science

## APMP-APLAC Joint Proficiency Testing Programme (T093)

### Toxic Elements in Cabbage



Approximately 210kg of kimchi cabbage cultivated in greenhouses was purchased from a local farm in Korea. The outer leaves of cabbage were peeled off and the cabbage top was removed and then it was sliced. Sliced cabbage was rinsed 4 times with tap water to remove dirt and foreign particles. Thoroughly washed cabbages were soaked in distilled water and sieved to remove excess water. The washed cabbages were frozen for 2 hours and then dried for 90 hours using a freeze dryer(PVRFD 100R, Ilshin Lab, Korea) with capacity of 100kg. The weight loss due to freeze-drying was about 95%. Freeze-dried kimchi cabbages were ground using a laboratory mill(Pulvurissette 14; Fritsch, Idar-Oberstein, Germany) with a 0.5mm sieve ring. The speed of rotor was 12000rpm. Dried cabbage powders were sieved using a vibrating sifter(V/Sifter-141, Daega, Korea) to collect powder with limited range of particle size, 50 $\mu$ m~250 $\mu$ m. Appropriate amounts of lead and cadmium solutions were added into the prepared cabbage powder to make it into a paste form, and then mixed in a Teflon-coated mixing bowl for 4 hours. The mixed cabbage paste was re-freeze-dried in freeze-dryer and re-sieved. It was further homogenized with a V-blender(Daega Powder, Korea) for over 10 hours and then bottled into pre-cleaned 60mL amber bottles in 10g per unit. The sample bottles were sealed and then sterilized by irradiation of  $^{60}\text{Co}$  gamma rays at a dose of about 25kGy. Sample bottles were stored at room temperature prior to distribution or use.

The homogeneity study of the proficiency test sample was carried out using Isotope dilution Inductively Coupled Plasma Mass Spectrometry(ID-ICP/MS) analysis after microwave digestion of subsamples. Twelve bottles were taken with even interval following the bottling order from the sample batch. One subsample from each bottle with a minimum sampling size of 0.5g was analysed. The relative standard deviations of Cd and Pb contents due to between-sample in homogeneity were less than 0.13 % and 0.60 %, respectively, which are satisfactory for the present proficiency testing.

The contents of non-volatile elements for food materials in a dried powder form sterilized with gamma ray irradiation are generally known to be stable more than 5 years at room temperature. The stability assessment on the previous batch of cabbage CRM also demonstrated excellent stability of non-volatile elements in dried food materials. Therefore, the stability of the proficiency test sample is expected to be satisfactory for the purpose of present proficiency testing based on the previous stability studies of KRISS.

#### 7. Reporting and submission of results

Participants should complete the Result Report(Annex C). The guideline of reporting results is as followings:

- For each analyte, the mean value of at least three independent measurements and its associated expanded uncertainty with 95 % level of confidence should be reported on a dry mass basis;



**KRISS** 한국표준과학연구원  
Korea Research Institute of Standards and Science

## APMP-APLAC Joint Proficiency Testing Programme (T093)

### Toxic Elements in Cabbage



- Report the mass fractions of analytes in mg/kg for cadmium and lead; and
- Participants should provide information on 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 Report electronically to the coordinator of the proficiency testing programme (E-mail: [aplacpt.inorg@kriss.re.kr](mailto:aplacpt.inorg@kriss.re.kr)) 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.

#### 8. Measurement uncertainty

Measurement uncertainty is best estimated within the individual laboratory environment. An estimate of measurement uncertainty is normally based on the combination of a number of influencing parameters (components of uncertainty). As stipulated in ISO Guide to the Expression of Uncertainty in Measurement [1], the uncertainty of each individual parameter should be quantified and expressed numerically as a standard uncertainty. These values are then combined according to the rules of the propagation of uncertainty and the combined standard uncertainty is multiplied by a coverage factor to produce an expanded uncertainty at the 95 % level of confidence.

#### 9. Evaluation of performance of participants

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

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

- where
- $x_i$  = the reported result of individual participant
  - $x$  = the assigned value\*
  - $\sigma$  = the standard deviation for proficiency assessment estimated from the Horwitz Equation

\* Note: The reference values determined by KRISS will be used as the assigned values. This is in accordance with the ISO/IEC 17043 recommendations on the determination of assigned values for proficiency testing schemes.

*z*-Score is commonly interpreted as:



**KRISS** 한국표준과학연구원  
Korea Research Institute of Standards and Science

## APMP-APLAC Joint Proficiency Testing Programme (T093)

### Toxic Elements in Cabbage



- |       |               |                |
|-------|---------------|----------------|
| (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.

#### 10. 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 be then prepared and submitted to APMP-APLAC PTWG for comments and approval. Upon approval, an electronic copy of the final report will be distributed to the participants and their respective accreditation bodies.

#### 11. Proposed program schedule

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

Time schedule	Phase
14 July 2014	Call for participation
24 July 2014	Deadline for registration
31 July 2014	Distribution of samples
5 September 2014	Deadline for submission of results
14 November 2014	Issue of the interim report
28 February 2015	Issue of the final report

#### 12. Confidentiality

The concerned parties (APMP, APLAC, KOLAS and KRISS) strive to maintain strict confidentiality of the characteristic properties 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 will be provided only to the contact person/authorized person of the participating laboratory and/or the respective accreditation body.



**KRIS** 한국표준과학연구원  
Korea Research Institute of Standards and Science

## APMP-APLAC Joint Proficiency Testing Programme (T093) Toxic Elements in Cabbage



### 13. Contact

For more information on the proficiency testing programme, please contact the coordinator by e-mail (E-mail: [aplacpt.inorg@kriss.re.kr](mailto:aplacpt.inorg@kriss.re.kr)).

If you have any query or comment, please send it to the following contact points:

Dr. Yong-Hyeon Yim or Dr. Sook Heun Kim, [aplacpt.inorg@kriss.re.kr](mailto:aplacpt.inorg@kriss.re.kr)

Mr. Kyunghee Lee, [kolas1@korea.kr](mailto:kolas1@korea.kr)

### 14. References

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



**KRIS** 한국표준과학연구원  
Korea Research Institute of Standards and Science

## APMP-APLAC Joint Proficiency Testing Programme (T093)

### Toxic Elements in Cabbage



#### Annex A

### Instructions for Participants

#### 1. Analysis of the proficiency test sample

##### (1) Sample information

- Participating laboratories will be provided with **TWO** bottles containing about **10g** of dried kimchi cabbage powder. The analyte contents in each bottle should be considered equivalent after dry-mass correction within the level of the between-sample homogeneity. The date of dispatching of samples will be informed to participants. Participants are required to confirm the receipt of the samples(including the serial number of the sample, date of receipt, any damages found in the sample package) by e-mail([aplacpt.inorg@kriss.re.kr](mailto:aplacpt.inorg@kriss.re.kr)) using the sample receipt form attached in Annex B. If any damage on the sample is observed on arrival, please contact us immediately.
- Analytes and their approximate mass fractions are given as follows.

Element	Mass fraction (expected range of values )
Cadmium(Cd)	0.5-10mg/kg
Lead(Pb)	0.5-10 mg/kg

- Homogeneity: ID-ICP/MS analysis of one subsample taken from each of 12 bottles was carried out. The relative standard deviations of the results obtained from 12 bottles were 0.13 % and 0.60 % for Cd and Pb, respectively, which are satisfactory for the present proficiency testing.

##### (2) Sample storage

- The proficiency test sample should be kept sealed in its original bottle and stored under room temperature conditions.
- Opening of the sample bottle should be carefully planned to avoid contamination and deterioration of the sample.
- For safety considerations, the proficiency test sample should be handled with care to prevent inhaling the sample powder and getting into eyes. In the case of accidental exposure to sample, wash the exposed areas with plenty of water and consult physicians when necessary.
- For this proficiency testing programme, it is not required to return remaining sample.





## APMP-APLAC Joint Proficiency Testing Programme (T093)

### Toxic Elements in Cabbage



#### (3) Guidelines for sample preparation and dry-mass correction

- Sample preparation for analysis:
  - Sample handling in a laboratory with well-controlled humidity and temperature is recommended. Any kind of contamination should be avoided.
  - Sampling for the analysis should be carried out at the same time as sampling for the dry-mass correction.
  - Digest the kimchi cabbage powder material completely, if the method used requires digestion.
  - The proficiency test sample should be mixed thoroughly before taking an aliquot of sample from a bottle.
  - The analysis should be conducted with a recommended sample size of at least 0.5g.
  - Participants are recommended to perform at least triplicate measurements and report the mean and associated measurement uncertainty for each analyte as specified in the Result Report. Participants should estimate the measurement uncertainty using their own practice.
- Dry-mass correction:
  - Participants should also carry out the dry mass correction.
  - Sampling for the dry mass correction should be carried out at the same time as the sampling for analysis.
  - At least three separate portions from a sample bottle (with a recommended sample size of about 0.5g for each portion) should be taken as dry mass correction samples and placed over  $P_2O_5$  in a desiccator at room temperature for 7 days (168 hours).
  - Calculate the moisture content from the mass change observed in the three aliquots and use it for dry-mass correction.

#### (4) Measurement method

- Participants are expected to use the test method of their choice, which should be consistent with their routine procedures. If the laboratory is accredited, it is recommended to use the method listed in the scope of its accreditation.



**KRIS** 한국표준과학연구원  
Korea Research Institute of Standards and Science

## APMP-APLAC Joint Proficiency Testing Programme (T093)

### Toxic Elements in Cabbage



## 2. Reporting and submission of results

Participants should complete the Result Report(Annex C). The manners of reporting test results are as follows:

- For each analyte, the mean value of at least three independent measurements and its associated expanded uncertainty with 95% level of confidence should be reported on a dry mass basis;
- Report the mass fractions of analytes in mg/kg for cadmium and lead; and
- Participants should provide information about the method 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 Report electronically to the coordinator of the proficiency testing programme(E-mail: [aplacpt.inorg@kriss.re.kr](mailto:aplacpt.inorg@kriss.re.kr)) 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.

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.

## 3. Contact

Participants may wish to contact the coordinator of the proficiency testing programme for any enquires (E-mail:[aplacpt.inorg@kriss.re.kr](mailto:aplacpt.inorg@kriss.re.kr)):

Dr.SookHeun Kim  
Senior Research Scientist  
Center for Inorganic Analysis  
Division of Metrology for Quality of Life  
Korea Research Institute of Standards and Science (KRIS)  
267 Gajeong-Ro, Yuseong-Gu, Daejeon 305-340, Republic of Korea  
Tel: +82-42-868-5756  
Fax: +82-42-868-5801



**KRISS** 한국표준과학연구원  
Korea Research Institute of Standards and Science

# APMP-APLAC Joint Proficiency Testing Programme (T093)

## Toxic Elements in Cabbage



Annex B

**Sample Receipt Form  
(Participating Laboratories)**

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

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

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

Title	Given name	Surname

E-mail: \_\_\_\_\_

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

Date of Receipt: \_\_\_\_\_

### Confirmation of Package Content

Please choose the state of the sample:  intact  
 broken  
 others: \_\_\_\_\_

Please write the serial numbers of the sample bottle: \_\_\_\_\_, \_\_\_\_\_

Please complete this form and return it to Dr.SookHeun Kim, KRISS(E-mail: [aplacpt.inorg@kriss.re.kr](mailto:aplacpt.inorg@kriss.re.kr)) by email immediately after receipt of the sample.



**KRIS** 한국표준과학연구원  
Korea Research Institute of Standards and Science

# APMP-APLAC Joint Proficiency Testing Programme (T093)

## Toxic Elements in Cabbage



Annex C

### Result Report

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

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

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

Title	Given name	Surname
_____	_____	_____

E-mail: \_\_\_\_\_

Laboratory accreditation: YES (based on ISO 17025/ ISO 9000 series/ GLP/ under the law of your economy(please specify)) /NO \_\_\_\_\_

If yes, please specify the name of accreditation body.

### 1. Analytical results

1) Mass fractions of Cd and Pb in kimchi cabbage

Analyte	Analytical result (mg/kg)	Combined standard uncertainty (mg/kg)	Coverage factor <i>k</i> (95% level of confidence)	Expanded uncertainty (mg/kg)
Cadmium (Cd)				
Lead (Pb)				

Notes: (i) Report the analytical results and associated uncertainties in the unit mg/kg; (ii) Report the analytical results on a dry mass basis.



## APMP-APLAC Joint Proficiency Testing Programme (T093)

### Toxic Elements in Cabbage



#### 2) Results from individual aliquot (dry-mass corrected)

Aliquot number	Cd (mg/kg)	Pb (mg/kg)
1		
2		
3		
4		
Average		
Standard deviation		
Standard deviation of the mean		

Please insert more lines for more determinations.

#### 3) Dry-mass Correction

Moisture content (% in mass): \_\_\_\_\_

Correction factor: \_\_\_\_\_

## 2. Methods of analysis

### 1) Analyte: Cadmium

a) Sample size used for analysis: \_\_\_\_\_

g

Microwave-assisted digestion / Wet digestion / Dry ashing

b) Digestion technique: Others (please specify): \_\_\_\_\_

c) 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): \_\_\_\_\_

d) Matrix separation: YES / NO \_\_\_\_\_

e) Calibration method: External calibration / Internal calibration / Standard additions / Isotope dilution mass spectrometry \_\_\_\_\_

f) Source(s) of calibration standard(s): \_\_\_\_\_



**KRIS** 한국표준과학연구원  
Korea Research Institute of Standards and Science

## APMP-APLAC Joint Proficiency Testing Programme (T093)

### Toxic Elements in Cabbage



- g) Use of internal standard(s): YES (please specify): \_\_\_\_\_ / NO
- h) Analytical instrument(s): ICP-MS / ICP-AES / Flame AAS / Graphite AAS  
Others (please specify): \_\_\_\_\_
- i) Correction for recovery: YES (please specify recovery (%)): \_\_\_\_\_ / NO
- j) Method validation: YES(please specify): \_\_\_\_\_ / NO
- k) Additional information: \_\_\_\_\_
- 2) Analyte: Lead**
- a) Sample size used for analysis: \_\_\_\_\_ g
- b) Digestion technique: Microwave-assisted digestion / Wet digestion / Dry ashing  
Others (please specify): \_\_\_\_\_
- c) 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): \_\_\_\_\_
- d) Matrix separation: YES / NO
- e) Calibration method: External calibration / Internal calibration / Standard additions / Isotope dilution mass spectrometry
- f) Source(s) of calibration standard(s): \_\_\_\_\_
- g) Use of internal standard(s): YES (please specify): \_\_\_\_\_ / NO



**KRIS** 한국표준과학연구원  
Korea Research Institute of Standards and Science

## APMP-APLAC Joint Proficiency Testing Programme (T093)

### Toxic Elements in Cabbage



- h) Analytical instrument(s): ICP-MS / ICP-AES / Flame AAS / Graphite AAS  
Others (please specify): \_\_\_\_\_
- i) Correction for recovery: YES (please specify recovery (%)): \_\_\_\_\_ / NO \_\_\_\_\_
- j) Method validation: YES(please specify): \_\_\_\_\_ / NO \_\_\_\_\_
- k) Additional information: \_\_\_\_\_

Print name/ Signature of responsible person:

Date:     /     /  
      dd mm yyyy