Trends in Analytical Chemistry 85 (2016) 98–106

Contents lists available at ScienceDirect

Trends in Analytical Chemistry

journal homepage: www.elsevier.com/locate/trac

Asia-Pacific Metrology Program (APMP) and Asia-Pacific Laboratory Accreditation Cooperation (APLAC) joint proficiency testing with metrological reference values for hazardous elements in cabbage

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ARTICLE INFO

Keywords:
Proficiency testing (PT)
Certified reference value
Reference material
Cabbage
Element
APMP
APLAC

ABSTRACT

The Asia Pacific Metrology Program (APMP) and Asia Pacific Laboratory Accreditation Cooperation (APLAC) joint proficiency testing (PT) program was established to improve the ability of quantitative analysis and enhance the quality of the PT program through a better regional linkage between the national metrology institutes (NMIs) and the accreditation bodies (ABs) in the Asia-Pacific region. The first APMP-APLAC joint PT was carried out to quantify hazardous elements Cd and Pb in kimchi cabbage powder, where a candidate certified reference material (CRM) was used as the PT material. A total of 83 laboratories from 37 countries registered, of which 73 laboratories submitted their results. Certified reference values (RVs) provided by Korea Research Institute of Standards and Science (KRISS) were used to evaluate the *z*-scores (*z*) of participants' results. This program confirms significant importance of the use of metrologically traceable RVs as PT assigned values for rigorous evaluation and reliable assessment.

Contents

1. Introduction

Participation in proficiency testing (PT) is an essential part of a quality management system to evaluate and monitor the performance of individual laboratories for specific tests or measurements [1–3]. Participation in PT schemes allows laboratories to assess the reliability of their data. The PT programs are also useful for enhancing the measurement quality of participating laboratories [4]. Accreditation bodies (ABs) thus require laboratories to participate in PT programs for all types of measurements undertaken in that laboratory for ISO/IEC 17025 accreditation [5].

Asia Pacific Laboratory Accreditation Corporation (APLAC) is a cooperation of accreditation bodies in the Asia Pacific region that accredit laboratories, inspection bodies and reference material producers [6]. APLAC is also recognized by the International Laboratory Accreditation Cooperation. Most signatories of the APLAC Mutual Recognition Arrangement (MRA) are also members of International Laboratory Accreditation Cooperation (ILAC). One of the APLAC's primary objectives is to organize PTs and related activities in the region. To achieve such an important role, the APLAC PT Committee was founded in 1994. The responsibilities of the PT Committee are to oversee all works in relation to the conduct of APLAC measurement audits and PT programs. Since its first PT program in 1994, APLAC has organized more than 100 PT programs [7,8]. APLAC recognized that the variations of results from PT participants were significantly large and there could be possible biases with PT

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http://dx.doi.org/10.1016/j.trac.2016.09.004
0165-9936/

consensus values (means or medians of the PT results), especially in the fields of chemical analysis. This tendency is currently well known and there are many requirements for the use of metrologically traceable reference values as PT assigned values [9–21].

Joint PT programs have been organized through collaboration between APLAC and the Asia Pacific Metrology Program (APMP) since 2014 to support APLAC PTs by providing metrologically traceable reference values. APMP is a regional metrology organization recognized by the International Committee for Weights and Measures (CIPM) for the purpose of worldwide mutual recognition of measurement standards and of calibration and measurement certificates. APLAC PT T093 was the first joint PT program performed in 2014 and 2015. It was co-coordinated by the Korea Research Institute of Standards and Science (KRISS), a member of APMP, and the Korea Laboratory Accreditation Scheme (KOLAS), a member of APLAC. The main objective of the program is to assist participating laboratories in demonstrating competence in quantitative analysis, as well as enhancing the quality and traceability of measurements through a regional scientific infrastructure. Laboratories testing food for toxic elements were compared to identify measurement capabilities for safety and quality in the food trade. Toxic elements in food were selected because they are one of the most important concerns in food safety, and comparable measurements have become one of the essential requirements for ensuring food safety with increasing international trade of food and agricultural products.

KRISS, the national metrology institute (NMI) of Korea, carried out APLAC PT T093 by providing test materials with certified reference values (RVs) for use as assigned reference values for the PT. The relevant Calibration and Measurement Capabilities (CMCs) of KRISS are published in the Key Comparison Data Base (KCDB) under the CIPM MRA. Using certified RVs that are traceable to the International System of Units (SI) as assigned RVs for PT allows for rigorous evaluation of accuracy. The study reports operations and results of this program.

2. Testing material and instructions for participants

The test material was kimchi cabbage powder fortified with cadmium and lead. The preparation and certification of the test material followed the regular procedures maintained by KRISS for the production of CRMs. Approximately 210 kg of kimchi cabbage cultivated in greenhouses was purchased from a local farm in Korea. The outer leaves were peeled off, the roots were removed, and the cabbages were sliced. The sliced pieces were rinsed 4 times with tap water to remove dirt and foreign particles. The 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 in a freeze-dryer (PVRFD 100R, Ilshin Lab, Korea). The weight loss due to freeze-drying was about 95%.

The freeze-dried cabbage pieces were pulverized using a laboratory mill (Pulvurisette 14; Fritsch, Idar-Oberstein, Germany) with a titanium blade and a 0.5-mm titanium sieve ring. Cabbage powders were sieved using a vibrating sifter (V/Sifter-141, Daega, Korea) to collect particles in the range of 50 to 250 μm. Appropriate amounts of lead and cadmium solutions were added to the prepared cabbage powder to make a paste, which was mixed in a Teflon-coated mixing bowl for 4 hours. The mixed cabbage paste was processed again with another cycle of freeze-drying, pulverization, and sieving. The paste was further homogenized with a V-blender (Daega Powder, Korea) for over 10 hours and then bottled in pre-cleaned 60 mL amber bottles with 10 g per unit. The sample bottles were sealed and sterilized by irradiation with ^{60}Co gamma rays at a dose of about 25 kGy. The sample bottles were stored at room temperature prior to distribution or use.

The homogeneity study of the testing materials was carried out at KRISS using double isotope dilution inductively coupled plasma mass spectrometry (ID-ICP/MS) after microwave (MW) digestion of the subsamples. ID-ICP/MS was also used for the certification of the material. Twelve bottles were selected systematically at regular intervals, including the first and last bottles of the sample batch, and one aliquot from each bottle was subsampled for homogeneity testing and certification. The relative standard deviations of cadmium and lead contents were less than 0.13% and 0.60%, respectively, which are satisfactory for this PT according to ISO 13528:2005 [3]. The homogeneity test results were combined into the uncertainties of the certified values. Each participant received two bottles of sample and was asked to determine the mass fractions (in mg/kg) of cadmium and lead on a dry mass basis. Participants were given a fixed protocol for dry mass correction which is described in the section 3 of this paper. Participants were also asked to report details about the analysis methods, such as the analytical instruments, digestion technique, the use of internal standard, correction for recovery, accreditation for the test, and method validation.

3. Assigned values for the study

The PT protocol indicates that participants' results will be evaluated by comparing them with the reference values that were certified by KRISS using double ID-ICP/MS to determine the reference values and their associated uncertainties. Double ID-ICP/MS is widely used for certification of trace elements in CRMs by many NMIs for highly accurate and SI-traceable determination of elemental contents in complex matrices. It is one of a few methods recognized by the *Comité Consultatif pour la Quantité de Matière* (CCQM) as a metrologically higher-order method and a potential primary method in chemical metrology [22].

Approximate levels of Cd and Pb in kimchi cabbage were measured using ICP/MS with external calibration prior to ID-ICP/MS. The results provide a means to design optimal sampling, to validate the digestion conditions for complete dissolution of the material, and to identify potential biases in isotope ratios from spectral interferences. Preliminary ID-ICP/MS was performed with two subsamples taken from one sample bottle, and the results were used to design the ID for an exact matching approach in double ID-ICP/MS. Kim et al. provide a detailed description of the general certification process and uncertainty evaluation applied by KRISS [23].

For representative sampling and ID-ICP/MS analysis from the batch of cabbage powder, 12 bottles were systematically selected. A subsample of about 0.5 g was taken from each selected bottle and accurately weighed in a pre-cleaned Teflon digestion vessel. A spike solution of the corresponding enriched isotope was prepared for each element to be analyzed. The isotopes ^{111}Cd (US Services) and ^{206}Pb (NIST SRM 991) were used as internal standards. Preliminary analysis was done to prepare a working solution of a spike isotope so that the isotope ratios of a subsample when blended with the spike isotope (sample blend) were close to 0.25 and 1.0 for ^{110}Cd/^{111}Cd and ^{208}Pb/^{206}Pb, respectively. At least three procedure blanks were also prepared using pre-cleaned Teflon digestion vessels by adding known amounts of diluted spike solutions (typically 1:100) of ^{111}Cd or ^{206}Pb and treating them with the same procedure used for cabbage powder samples. Subsamples not spiked with enriched isotopes were also prepared to measure the natural isotope ratios in the cabbage and to check for potential isobaric interferences in the ICP/MS analysis.

Four calibration blends were prepared by adding the spike isotope to an appropriately diluted primary standard of the element to be analyzed. For exact matching one-point calibration, the calibration blends were prepared so that their isotopic ratios and ICP/MS responses were almost the same as those of the sample blends. The moisture content of the cabbage sample was obtained for dry-mass correction of the analytical samples. Three 0.5-g subsamples were taken from each selected bottle in parallel with the samples for ID-ICP/MS and placed over P_2O_5 in a desiccator at room