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DEVELOPMENT OF PROFICIENCY TESTING SCHEME FOR MEASUREMENTS OF TOXIC AND ESSENTIAL ELEMENTS IN RICE AS AN AGRICULTURAL PRODUCT

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Abstract: A proficiency testing scheme for inorganic analysis and its application to agricultural products are presented and discussed to show how Korea Research Institute of Standards and Science (KRISS), the National Metrology Institute of Korea, has provided reliability and traceability of measurements in safety and quality of food through the reference materials. With collaboration between KRISS and the National Agricultural Products Quality Management Service (NAQS), the proficiency testing scheme was developed based on ISO/IEC 17043 for international harmonization. The material, which was prepared by KRISS based on ISO/IEC Guide 34 and 35, was rice powder and the mass fractions of toxic and essential elements were assigned by isotope dilution mass spectrometry. From the converted z-scores, the performances of participants for cadmium and copper measurements were assessed and adequate to the fitness-for-purpose.

Keywords: Proficiency testing, Chemical metrology, Reference material, Isotope dilution mass spectrometry, Elements, Rice

1. INTRODUCTION

Rice is a dominant source of food, especially, in Asian countries. Therefore, accurate and reliable measurements of toxic and essential elements in rice play a key role for food–safety. In order to achieve these purposes, metrological infrastructures providing traceability to SI and method validation should be established. Based on these fundamentals, appropriate programs for quality assurance and performance monitoring procedures such as proficiency testing have been recommended to ensure that a laboratory has produced reliable data consistently. Proficiency testing has been used to assess laboratory performances usually by analyzing the test materials which are distributed to the participants without the assigned values of the measurands, so called 'blind' sample. Then the reported results are processed statistically to z-scores and interpreted as performances of the participants[1]. However, when the improper assigned value is determined and used for proficiency testing, it is possible that biased results can be obtained but not to be recognized it leading to failure for checking whether participants have produced reliable data. For elemental analysis in agricultural products, relevant proficiency testing programs frequently exhibit unexpected biases.

According to ISO/IEC 17043[2], known values and certified reference values are on top of the list which describes the procedures to determine the assigned values in order of small expected uncertainties. Therefore, National Metrology Institutes (NMIs) are able to contribute to develop and improve proficiency testing schemes with various aspects. For example, as certified reference material (CRM) producers[3,4], CRMs can be provided as test materials for proficiency testing with the assigned values which will be released as certifies values after carrying out relevant proficiency testing. In addition, NMIs can provide robust metrological fundamentals such as traceability to SI for the assigned values to achieve international harmonization for the proficiency testing. Korea Research Institute of Standards and Science (KRISS) has also contributed to the improvement of proficiency testing as activities to encourage dissemination of measurement standards in the fields of foods and environments for both domestic and Asia regions. In this article, based on the collaboration between KRISS and the National Agricultural Products Quality Management Service (NAQS) which is in governmental sector related to managing agricultural products in Korea, the development procedures of a proficiency testing for the analysis of cadmium and copper in rice powder were presented from preparation of rice test material to the evaluation of results of participants.

2. PROFICIENCY TESTING SCHEME

Each participant received two bottles of rice test material containing approximately 30 g in each bottle. Mass fraction of cadmium and copper in test material as representatives of toxic and essential elements in agricultural product, respectively, were required to report as measurands for this proficiency testing by a given date. Participants were asked to report results based on dry mass corrected by protocol in instruction - weight loss under a P_2O_5 desiccator for 1 week. Analytical methods for participants to analyze the test material were recommended to use the appropriate methods for their routine work, and not to adopt special methods for the proficiency testing.

The rice test material was carefully selected and prepared in well controlled environment by KRISS. With instruction, it was announced that assigned values would be used for the purpose of calculating scores which is intended to assess participants' laboratory performance in this proficiency testing. Hence, assigned values and uncertainties of mass fractions of cadmium and copper were determined before distribution including characterization such as homogeneity and stability, and were not disclosed until the deadline. Isotope dilution inductively coupled plasma mass spectrometry (ID-ICP/MS) was applied for assigning the values and evaluating the homogeneity. Based on the experiences about stability of similar matrix CRM for elemental analysis, test materials were stored and distributed at room temperature. As soon as receiving all reports from participants, the submitted results were converted statistically into z-scores using fitness-for-purpose based standard deviation for proficiency assessment. It should be noticed before carrying out proficiency testing which the deviation would be used for the testing and, here, it was selected to be the larger one between the standard deviation among participants and the standard deviation estimated by Horwitz equation. When the results among participants would be in good agreement with one another and simply the standard deviation of them would be used to assess the proficiency, it is possible to underestimate some participants showing relatively worse results even though good performance. After interpretation of z-scores of participants, performance report was made and provided to each participant.

2. PRODUCTION OF REFERENCE MATERIALS

The material for the proficiency testing must have homogeneity and stability implying all participating laboratories receive nearly "the same" material. To ensure these features, the material was carefully selected and prepared in well controlled environment. The candidate reference material, rice powder, was prepared based on the procedures for production of freeze-dried powder CRM maintained in KRISS, which were described in previous papers [5]. In brief, about 50 kg of rice obtained from a local market was washed, freeze-dried, and pulverized. Considering homogeneity, particles of the powder with range of 50-250 μm were only selected by sieving and, then, homogenized by mixing with V-blender. The collected rice powder was subdivided into 60 mL wide-bore amber bottles with 30 g per unit and sealed with Teflon coated caps in clean draft. In order to improve stability, the bottles were sterilized by irradiation of γ-ray of around 25 kGy in other facility. The sterilized bottles were stored at room temperature prior to distribution to the laboratories which participated the proficiency testing.

Table 1 ID-ICP/MS results of Cd and Cu in rice.

Element	Assigned value (mg/kg)	Expanded uncertainty (mg/kg)	Coverage factor (k)[1]
Cd	0.3592	0.0067	1.97
Cu	2.615	0.049	2.306

[1] 95 % confidence level

3. ASSINGED VALUES OF REFERENCE MATERIALS

The certified values of KRISS using ID-ICP/MS method were used as the assigned values. Ten bottle of the rice test material including the first and the last bottles from 1190 bottles were sampled randomly with minimum sampling size of 0.5 g for measurement of both Cu and Cd. For dry mass correction, three subsamples of 0.5 g from each bottle in parallel with sampling for ICP/MS analysis were taken and placed in a P_2O_5 desiccator for 1 week. Then, the dried weights of subsamples were measured. These drying procedures were repeated several weeks until the weights of subsamples were reached to a constant. Finally, the loss of weight was used for the correction.

For isotope dilution, ^{111}Cd and ^{65}Cu enriched isotope dilution solution, respectively, were spiked into samples and standards to make isotope dilution blended solutions with appropriate isotope abundance ratios which were determined by considering the propagation of uncertainty in ratio measurements. Then, the spiked samples in Teflon vessels were digested with concentrated nitric acid of 9 mL and 30 % H_2O_2 of 1 mL in microwave digestion system (ETHOS PLUS, Milestone, USA) where the procedure took 10 min at 200 °C after increasing temperature from room temperature to 200 °C for 10 min. The digested spiked samples were transferred into LDPE bottles and diluted with water - called as "sample blend solutions".

Inductively coupled plasma mass spectrometric (ICP/MS) measurements were carried out using a Thermo Element2 magnetic sector type ICP-MS system (Thermo Fisher Scientific, German). For cadmium measurements, at low resolution mode, the isotope abundance ratios of ^{110}Cd and ^{111}Cd of sample blend solutions were compared to those of the calibration blend solutions which were the spiked standard solution by the same enriched isotope solution. For copper measurements, the ratios of ^{63}Cu and ^{65}Cu were measured at the medium resolution ($R > 4000$) of ICP-MS to avoid interferences. From the results of isotope abundance ratio measurements with masses of sample, spike, and standard to be used, the assigned values of mass

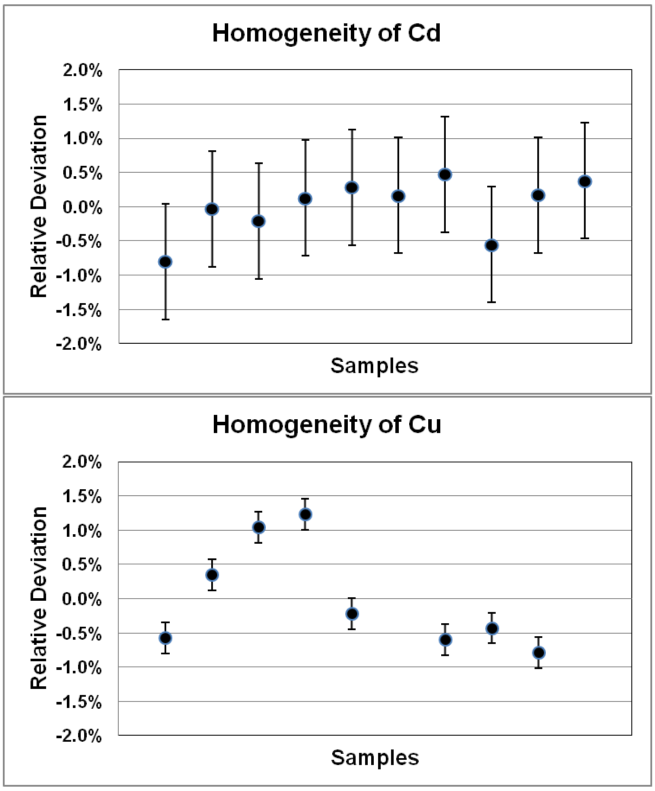

Figure 1 Homogeneities of Cd and Cu in rice test materials.

fractions of Cd and Cu in rice test material were calculated and the measurement uncertainties were estimated following the GUM[7]. The results were listed in Table 1.

The standard deviation of the results among selected bottles obtained by ID-ICP/MS was used to evaluate the homogeneity of rice test materials for each element. As shown in Fig. 1, the relative standard deviation between bottles was 0.41 % for cadmium and 0.78 % for copper. Since the standard deviation included the measurement uncertainty, the homogeneity was estimated to be less than the standard deviation.

4. RESULTS AND DISCUSSION

Summary of the results of this proficiency testing are given in Table 2 anonymously by using laboratory codes. Total 15 laboratories were participated in this proficiency testing for both of cadmium and copper. The median, mean, and standard deviation were calculated from the reported results of participants, statistically. The means of participants are 2.6 % lower for cadmium and 2.0 % higher for copper than the corresponding assigned values, respectively. In addition, relative standard deviations of participants show relatively high values of 5.4 % and 10.6 % for cadmium and copper, respectively. Then, all reported results were converted into z-scores according to the following equation[1,2,6]:

$$z = \frac{x - X}{\sigma_{PT}} \qquad (1)$$

where x is the submitted result of each participant, X is the assigned value of KRISS, and σ_{PT} is the fitness-for-purpose based standard deviation for this proficiency testing. σ_{PT} was determined to be the larger one between the standard deviation of participants' results, σ_L, and the standard deviation estimated by Horwitz equation, σ_H. For cadmium, σ_H of 0.067 mg/kg was larger than σ_L of 0.019 mg/kg and selected as σ_{PT}. For copper, σ_H of 0.362 mg/kg was used as σ_{PT}. The calculated z-scores for cadmium and copper were graphically presented in Figure 2. For both cadmium and copper, all of the particpants' z-scores are within ±2 which are designated satisfactory. It means that the qualities of the analytical data routinely produced by the participants are likely to be adequate for their intended purposes. Also, the relative differences of participants' results from the assigned values by KRISS were less than 3 % which imply that it is difficult to find scientific or technical apparent reasons although there might be bias. For copper, the standard deviation among participants was 10.6 % which is higher than cadmium of 5.4 %. Considering the higher concentration of copper, it is interesting result. To improve the performance of copper measurements, method validation should be carried out careful enough to avoid interferences to copper such as $^{23}Na^{40}Ar$ (mass to charge ratio = 53) before their routine procedures for copper measurements in participants' laboratories. In addition, it is well recognized that the biases are mainly due to the improper method

Table 2 Summary of results of the proficiency testing.

	Cd	Cu
No. of participants	15	15
Median of participants' results (mg/kg)	0.358	2.644
Mean of participants' results (mg/kg)	0.350	2.667
Standard deviation of participants' results (σ_L, mg/kg)	0.019	0.282
Relative standard deviation of participants' results (%)	5.4 %	10.6 %
Standard deviation estimated from Horwitz equation (σ_H, mg/kg)	0.067	0.362
Assigned value of KRISS (mg/kg)	0.3592 ± 0.0067	2.615 ± 0.049
Difference of participants' results from assigned value by KRISS (mg/kg)	0.009	0.052
Relative difference (%)	2.6 %	2.0 %

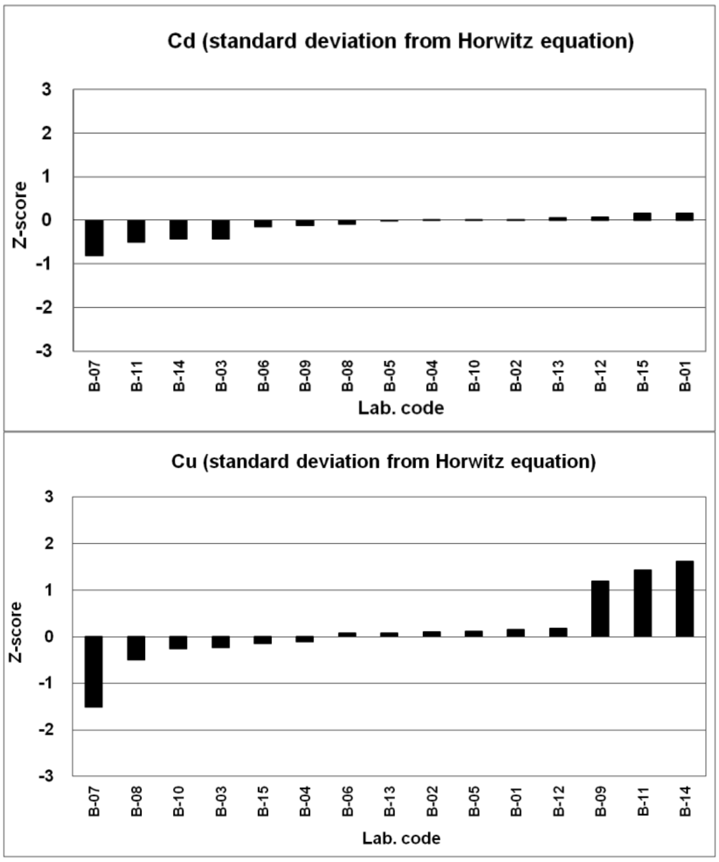

Figure 2 Results of proficiency testing for the analysis of cadmium and copper in rice powder. The Z-scores were calculated using standard deviation from Horwitz equation.

validation including insufficient acid digestion or recoveries in case there are elements such as silicone in some rice samples.

5. CONCLUSION

A proficiency testing scheme for inorganic analysis in agricultural products was demonstrated by measurements of cadmium and copper in rice powder based on collaboration between KRISS and NAQS. The rice test materials were prepared carefully to ensure homogeneity by KRISS. The certified values of KRISS using ID-ICP/MS method were used as the assigned values for both cadmium and copper. From the converted z-scores, the performances of participants for cadmium and copper measurements were assessed against the fitness-for-purpose. Most of participants' z-scores are within ±2 implying that the measurement results of cadmium and copper in grain samples such as rice routinely produced by the participants are likely to be adequate for their intended purposes. The assigned values by higher-order measurement method provided by an NMI are very helpful to assure the performance of analytical laboratories participated in this proficiency testing.

6. REFERENCES

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