P73: ESTABLISHMENT OF TRACEABILITY OF CHEMICAL MEASUREMENTS FOR TRACE METALS IN DRINKING WATER OF LOCAL LABORATORIES IN THE PHILIPPINES

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Abstract – Reference Material (RM) also used as Proficiency Test (PT) materials were developed for trace metals including lead, cadmium, copper and iron in drinking water where 28 to 31 local laboratories participated in the PT scheme. The PT material was characterized for homogeneity and stability. Reference values were determined using double isotope dilution Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). The PT was organized by the Industrial Technology Development Institute (ITDI) in the Philippines in accordance with ISO/IEC 17043:2010.

Keywords: Drinking water, Proficiency Test, Reference Material, Trace Metals

1. INTRODUCTION

The quality of drinking water is essential to sustain life. Millions of people are exposed to dangerous levels of contaminants in their drinking water, giving rise to a range of health implications [1]. Trace metals in drinking water such as Lead (Pb), Cadmium (Cd), Copper (Cu), and Iron (Fe) are monitored by regulatory bodies of several countries. Maximum allowable limits are indicated in the guidelines formulated by the World Health Organization for managing the risks that may compromise the safety of drinking water [2]. These guidelines were used as reference in the establishment of the Philippine National Standards for Drinking Water [3]. Thus, to ensure safety of consumers, a reliable and accurate result is important in conducting analytical measurements.

In this study, reference material for trace metals in drinking water was prepared and characterized. Using the reference material, ITDI designed a PT scheme for the analysis of trace metals near the concentration levels set by the Philippine National Standards for Drinking Water in accordance with ISO/IEC 17043:2010 [4]. The PT was intended to assess the capabilities of local testing laboratories for low concentration analysis of metals. Moreover, this enables the laboratories to evaluate the accuracy of their test results based on their own established test methods and improve their measurements in the analysis of trace metals in drinking water.

2. EXPERIMENTAL

2.1 Reference Material Preparation

About twenty five (25) liters of mixed metals solution was prepared from NIST 3128 (Pb), NIST 3108 (Cd), NIST 3126a (Fe) and KRISS 105-02-CU2 (Cu). Standard solutions were individually weighed and diluted with 5% nitric acid to a final weight of 25 kgs. Homogenization was done by mechanical shaking for thirty (30) minutes. The homogenized solution was transferred into low density polyethylene (LDPE) bottles, capped, sealed, labeled and stored in sealed plastic packs. A total of ninety five (95) bottles were produced, each containing approximately 130 mL solution. Bottled samples were stored in the refrigerator at 4°C.

2.2 Homogeneity and Stability Study

Ten (10) RMs were analyzed in duplicate for Pb, Cd, Cu and Fe after systematic random sampling. Stability study was carried out in accordance with ISO Guide 35 [5]. Two different temperatures, 4°C and 30°C, were applied for transport and storage using the classical approach with an exposure period of 2, 3 and 6 months. Two (2) sample bottles from each exposure were obtained and analyzed for Pb, Cd, Cu and Fe (5 replicates each).

2.3 Reference Values of RM

Metrologically traceable reference values were provided by the National Measurement Institute of Australia (NMIA), instead of consensus values that is commonly used by commercial PT providers. The quantification method was by Inductively Coupled Plasma (ICP) - Double-Isotope Dilution Mass Spectrometry (d-IDMS) using NIST SRMs 3128 (Pb), 3108 (Cd), 3114 (Cu) and 3126a (Fe) as primary calibration materials. The standard deviation for proficiency assessment and reference value used for z-score calculation are shown in Table 1.

Table 1. Reference values, expanded uncertainties, and SD for PT

Measurand	Reference Value, mg/L	Expanded Uncertainty, mg/L (95% CL, k=2)	SD for PT, mg/L
Pb	0.04313	0.00028	0.01107
Cd	0.03102	0.00031	0.00837
Cu	0.8301	0.0054	0.13656
Fe	1.2639	0.0073	0.19518

2.4 PT Scheme Implementation

Each laboratory received one (1) bottle of the PT sample and was asked to report one (1) value for the mass fraction (mg/kg) of Pb, Cd, Fe, and Cu with measurement uncertainty using their own analytical procedures. Laboratory codes were assigned to participants and reports were issued with these codes for confidentiality.

2.5 Evaluation of PT Performance

The results from participants were evaluated according to ISO 13528 using z-scores [6]. The laboratory performance statistic was calculated using formula (1):

$$z = \frac{x - X}{\sigma} \quad (1)$$

where z is the z-score, x is the laboratory result, X is the reference value, and σ is the standard deviation for proficiency assessment. Z-scores are interpreted as i) Satisfactory (S), $|z| \leq 2.0$; ii) Questionable (Q), $2.0 < |z| < 3.0$; iii) Unsatisfactory (U), $|z| \geq 3.0$.

The value of the standard deviation from proficiency testing was derived from a general model for the reproducibility of the measurement method. Equation 2, from Horwitz general model [7], was used to compute for the Standard Deviation (SD) for PT.

$$\sigma_R = 0.02c^{0.8495} \quad (2)$$

3. RESULTS AND DISCUSSION

3.1 Homogeneity and Stability Testing

The RM developed was concluded to be homogeneous for all the metals based on IUPAC criteria for sufficient homogeneity [8] and ISO 13528 criteria for adequate homogeneity [6] as shown in Table 2. Cochran's test for outliers was also conducted.

Table 2. Homogeneity Test results for Pb, Cd, Cu, and Fe.

Test Parameter	Test for	Results
Cochran	Outliers	passed
s_{an}/σ_p	Analytical Precision	passed
s_{sam}	Adequate Homogeneity	passed
s^2_{sam}	Sufficient Homogeneity	passed

Stability was evaluated by trend analysis using Student's t-test for significance of slope at 95% confidence level and n-2 degrees of freedom [4]. The sample was found to be stable until the 6th month period from preparation date for both 4°C and 30°C.

3.2 Results of PT Round

Thirty four (34) local laboratories registered and received samples. Of these laboratories, two (2) did not return their results and one (1) submitted a late result for Pb analysis which was not evaluated. Majority of the laboratories obtained satisfactory performance as shown in Table 3.

Out of the 117 calculated z-scores, 101 (86%) were satisfactory, 2 (2%) were questionable. From Table 3, only 78.6% of the participants obtained "S" z-scores for Pb while the highest percentage was for Fe analysis (90.3%). Nineteen (19) laboratories have satisfactory scores for all 4 measurands.

Table 3. Number and percentage of laboratories with satisfactory scores (|z|≤2)

Measurand	Total No. Of Participants	No. Of Laboratories with satisfactory scores (%)
Pb	28	22 (78.6%)
Cd	29	25 (86.2%)
Cu	29	26 (89.7%)
Fe	31	28 (90.3%)
TOTAL	117	101 (86%)

Analytical difficulty was revealed for Pb analysis. However, laboratories that obtained "U" scores may need to review their laboratory calculations, methods and quality control practices, specifically for those with unusually high z-scores and those that have reported using validated methods with ISO/IEC 17025 accreditation for these measurements.

Laboratories were asked to report the expanded measurement uncertainties of their results as shown in Figures 1 to 4. Eighty nine (89%) of the laboratories reported results with an expanded measurement uncertainty, thus demonstrating compliance to ISO/IEC 17025 requirement [9].

The participants used a range of analytical techniques as shown in Figure 5 which include Flame-Atomic Absorption Spectrophotometry (F-AAS), Graphite Furnace-AAS (GF-AAS),

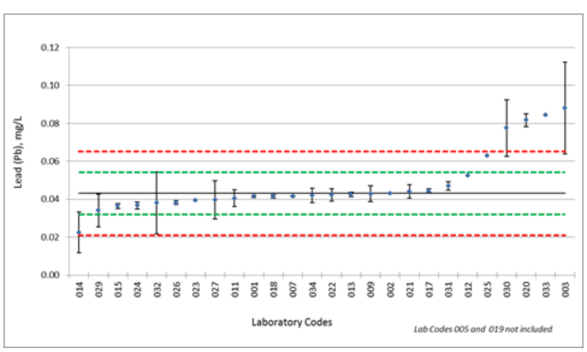

Figure 1. Participants' results reported for Lead. The dotted lines in green and red corresponds to ±1σ and ±2σ, respectively, and error bars represent the measurement uncertainty and arrows.

Figure 2. Participants' results reported for Cadmium. The dotted lines in green and red corresponds to ±1σ and ±2σ, respectively, and error bars represent the measurement uncertainty and arrows.

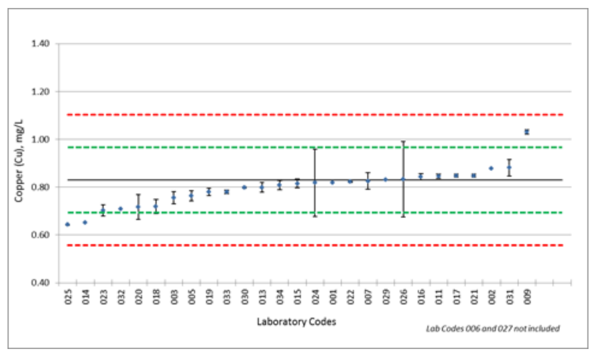

Figure 3. Participants' results reported for Copper. The dotted lines in green and red corresponds to ±1σ and ±2σ, respectively, and error bars represent the measurement uncertainty and arrows.

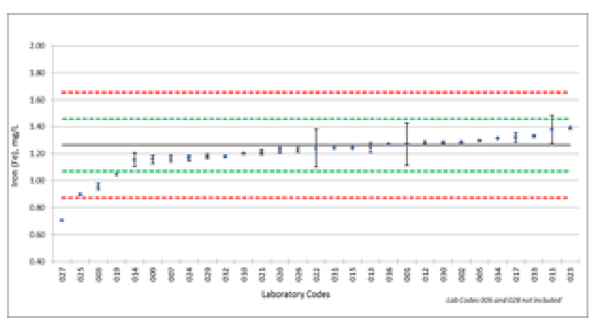

Figure 4. Participants' results reported for Iron. The dotted lines in green and red corresponds to ±1σ and ±2σ, respectively, and error bars represent the measurement uncertainty and arrows.

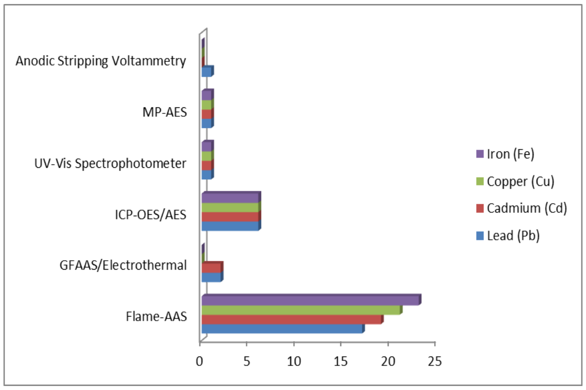

Figure 5. Analytical techniques used for lead, cadmium, copper and iron.

Inductively Coupled Plasma-Optical Emission Spectrophotometry (ICP-OES), Ultraviolet-Visible (UV-Vis) Spectrophotometry, Microwave Plasma-Atomic Emission Spectrophotometry (MP-AES) and Anodic Stripping Voltammetry (for Pb analysis). The F-AAS is the most widely used technique among the participating laboratories.

4. CONCLUSION

The RM for trace metals in drinking water was sufficiently homogenous and stable. The metrological approach to PT Round was emphasized where the assigned value to the RM used as PT material was determined from a well-defined measurement method traceable to the International System (SI) of units. To realize this, high accuracy mass spectrometry with double isotope dilution was used to provide the reference value. In the PT round, majority of the participants achieved satisfactory results which showed the traceability of laboratories' results with the reference value and good interlaboratory comparability.

ACKNOWLEDGMENT

The Standards and Testing Division (STD) of the Industrial Technology Development Institute (ITDI) gratefully acknowledges the funding support from the Department of Science and Technology (DOST) and the Philippine Council for Industry, Energy and Emerging Technology Research and Development (PCIEERD) as the monitoring agency.

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