

Evaluation of performance of chemical laboratories for sulfite mass fraction determination in Philippine export products by proficiency testing

Pauline Ann M. Quiton, Aaron C. Dacuya, Johnester D. Maniego, Angelo Bryan M. Lazo, Christian D. Laurio, Clarissa J. Gatchalian, Elyson Keith P. Encarnacion, Cyril C. Ramil, Alleni T. Junsay and Benilda S. Ebarvia

Department of Science and Technology, Industrial Technology Development Institute (DOST-ITDI), National Metrology Laboratory of the Philippines (NML), Taguig City, Philippines, mic@itdi.dost.gov.ph

Abstract – This study assesses the analytical performance of Philippine chemical laboratories in determining sulfite levels in dried mango and desiccated coconut, two major export products. The accuracy-based proficiency testing (PT) schemes, organized by the National Metrology Laboratory of the Philippines, aimed to ensure accurate sulfite measurement for food safety and market acceptance. Participants' performance was evaluated against assigned values obtained using liquid chromatography-isotope dilution mass spectrometry (LC-IDMS). Results showed that 40% (2 of 5) of laboratories achieved satisfactory performance in the dried mango PT, while 75% (3 of 4) succeeded in the desiccated coconut PT. Participation in these PT schemes enabled laboratories to assess and improve their technical capabilities, ensuring more accurate sulfite determination in Philippine export products and supporting food safety and trade compliance.

I. INTRODUCTION

Sulfites are commonly used as preservatives in food processing due to their antimicrobial and antioxidant properties [1]. They are particularly prevalent in dried fruits and coconut-based products such as dried mango and desiccated coconut—two major Philippine export commodities [2], [3]. However, excessive intake of sulfites can cause adverse reactions in sensitive individuals, including asthma attacks and allergic reactions, prompting regulatory agencies to impose strict limits on sulfite residues in food [4].

To ensure compliance with these international regulatory requirements, it is essential that chemical laboratories involved in food testing demonstrate reliable analytical performance. Proficiency testing (PT) provides

an objective means of evaluating laboratory competence by comparing results across a group of participants using standardized test materials [5]. Such assessments are essential for maintaining the integrity of food safety systems, ensuring consumer protection, and supporting market access for export products.

To evaluate and enhance the capability of testing laboratories to measure sulfite in Philippine export products, the Metrology in Chemistry (MiC) Section of the National Metrology Laboratory (NMLPhil), a technical service division under the Industrial Technology Development Institute (ITDI) of the Department of Science and Technology (DOST) organized the PT schemes 12-2019-PTILC(MiC2)-0013: Sulfite in Dried Mango (PT-0013) and 10-2022-PTILC(MiC)-0017: Sulfite in Desiccated Coconut (PT-0017). These PT schemes concluded in 2020 and 2023, respectively.

II. MATERIALS AND METHODS

A. Proficiency testing items

The proficiency testing items (Fig. 1) used for the PT schemes PT-0013 and PT-0017 were Philippine Reference Material (PRM) 0501 Sulfite in Dried Mango (Batch no. 05010718) and PRM 0502 Sulfite in Desiccated Coconut (Batch no. 05021018), respectively. These are reference materials (RMs) produced by NMLPhil.

Commercially available dried mango and desiccated coconut from the same batches were purchased from a local supermarket to produce PRM 0501 and PRM 0502, respectively. The overview of the preparation of proficiency testing items is shown in Fig. 2. PRM 0501 and PRM 0502 were prepared as a slurry material and powdered material, respectively. Both were spiked with



Fig. 1. Proficiency testing items PRM 0501 Sulfite in Dried Mango (a) and PRM 0502 Sulfite in Desiccated Coconut (b)

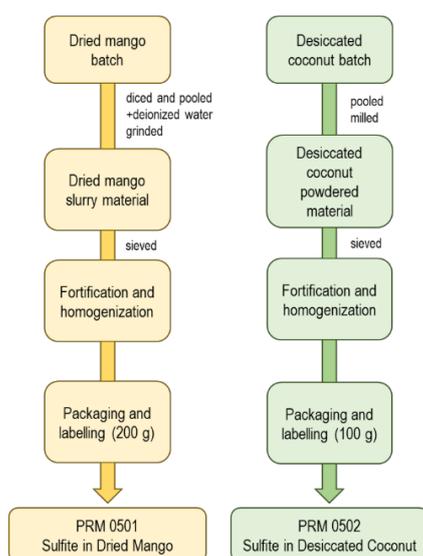


Fig. 2. Preparation of proficiency testing items

sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$), homogenized, and packed in individual aluminum foil pouches. The PT items were stored at $-35\text{ }^\circ\text{C}$ prior to testing and dispatch to participants.

B. Homogeneity and stability of proficiency testing items

The assessment of homogeneity and stability, and characterization of the PT items followed the requirements based on ISO Guide 35:2017 [6], the standard during the production. Homogeneity and stability tests were conducted using a validated Optimized Monier-Williams distillation method with gravimetric sample preparation technique for the target matrices.

For homogeneity testing, eleven (11) units were selected from each batch through stratified random sampling and analyzed in triplicate. Visual inspection showed no bottling trend on both PT items. Measurement results were statistically evaluated and passed the following criteria: (a) test for outliers by Cochran's test, (b) test for bottling trend by regression analysis, and (c) test for homogeneity by

one-way analysis of variance (ANOVA). The calculated relative uncertainty due to inhomogeneity (u_{homo}) for PRM 0501 and PRM 0502 are 0.70 % and 0.86 %, respectively.

Short-term stability testing was performed to assess suitable transportation duration and environmental conditions. The study followed the isochronous approach at two test temperatures, $-20\text{ }^\circ\text{C}$ and $4\text{ }^\circ\text{C}$, and a control temperature of $-35\text{ }^\circ\text{C}$. Trend analysis by linear regression indicated no significant instability at both test temperatures for 3 weeks. Test temperature at $40\text{ }^\circ\text{C}$ was also evaluated, however degradation of sulfite content was observed. Thus, the PT items were shipped to participants packaged with dry ice to ensure its stability.

Assessment of long-term stability followed the classical approach. Randomly selected units of the PT items were stored at $-20\text{ }^\circ\text{C}$ and were analyzed at a defined period. Regression analysis showed no significant change in the sulfite mass fraction in both PT items at $-20\text{ }^\circ\text{C}$ within a 12-month period. The calculated relative uncertainty due to long-term stability (u_{lt}) for PRM 0501 and PRM 0501 are 4.28 % and 3.16 %, respectively.

C. Assigned value and standard deviation for proficiency assessment

The assigned value of sulfite expressed as sulfur dioxide (SO_2) is a reference value (X) provided by NMLPhil as summarized in Table 1. The reference values were determined by averaging six measurements, obtained from two subsamples taken from each of three units of the respective PT item batch. The characterization was performed using Liquid Chromatography-Isotope Dilution Mass Spectrometry (LC-IDMS) with a gravimetric sample preparation technique. Sodium sulfite (Na_2SO_3) was used as the calibration standard, and isotopically enriched sodium sulfite ($\text{Na}_2^{34}\text{SO}_3$) served as the internal standard; both were sourced from Sigma-Aldrich.

Table 1. Assigned value (X), expanded uncertainty (U) and standard deviation for proficiency assessment (σ_{pt})

PT scheme	Mass fraction of sulfite (as SO_2), mg/kg		σ_{pt} , mg/kg
	X	U	
PT-0013	931	94	53
PT-0017	180.8	12.8	13.2

The uncertainty (U) of the assigned value is an expanded uncertainty at approximately 95 % confidence level ($k=2$) calculated according to Equation 1, based on ISO Guide 35:2017. The combined standard uncertainty (u_X) was calculated according to Equation 2 by combining the uncertainty sources, including characterization (u_{char}), inhomogeneity (u_{homo}) and long-term storage (u_{lt}). In both PT schemes, uncertainty from potential degradation due to transport (u_{tm}) was assumed to be negligible since the

transport conditions of the PT items were selected so that the effects were negligible.

$$U = k \times u_X \quad (1)$$

$$u_X = \sqrt{u_{\text{char}}^2 + u_{\text{homo}}^2 + u_{\text{its}}^2} \quad (2)$$

The standard deviation for proficiency assessment (σ_{pt}) was derived from a general model for chemical applications, the Horwitz equation (σ_{R}) [7]:

$$\sigma_{\text{pt}} = \sigma_{\text{R}} = 0.02c^{0.8495} \quad (3)$$

where c is the unitless mass fraction of the measurand. The Horwitz function is acknowledged as a fitness-for-purpose criterion for the analysis of food and drugs [8] and have been used as σ_{pt} in PT schemes [9]–[11].

D. Operation of the PT

The PT schemes were organized based on the requirements of ISO/IEC 17043:2010 [5], the standard version during the PT operation. The PT schemes were designed as shown in Fig. 3, wherein NMLPhil, as the PT provider, simultaneously dispatched the PT items to all participants. For confidentiality purposes, laboratory codes were assigned to participating laboratories, which were different for each PT scheme.

Each participant was provided one (1) unit of PT item and was instructed to store the PT item at -20 ± 5 °C. The participating laboratories were asked to use the test method and equipment of their choice and to perform at least three independent measurements. The PT item is equilibrated to room temperature prior to analysis. Participants were given 30 days to conduct the analysis and were requested to report the results with their associated uncertainties and information on their procedures used.

E. Evaluation of performance of participants

Statistical evaluation of the results is based on ISO 13528:2015 [7]. The participants' performance for both PT schemes was assessed using the z' -score (z') calculated according to the following equation:

$$z' = \frac{x - X}{\sqrt{\sigma_{\text{pt}}^2 + u_X^2}} \quad (4)$$

The z' -score was used because the combined standard uncertainty (u_X) of the reference value is greater than $0.3\sigma_{\text{pt}}$. The z' -scores were interpreted in accordance with ISO 17043:2010 [5], where $|z'| \leq 2.0$ indicates "satisfactory" performance, requiring no action. A $2.0 < |z'| < 3.0$ indicates "questionable" performance and triggers a warning signal, while $|z'| \geq 3.0$ indicates "unsatisfactory" performance and prompts an action signal.

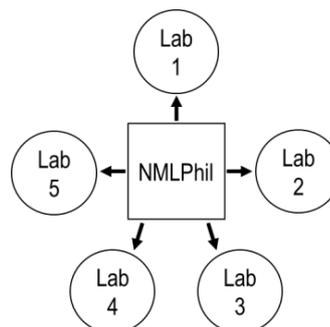


Fig. 3. Implementation of PT scheme

III. RESULTS AND DISCUSSION

A. Participants' reported results and methods used

For PT-0013, 5 participants submitted results to the PT provider ranging from 374 to 885 mg/kg. Fig. 4 shows that only 40 % or 2 out of 5 participating laboratories obtained a satisfactory z' -score for the analysis of sulfite (as SO_2) in dried mango matrix. The mean and relative standard deviation of results from the participants with satisfactory performance are 853 mg/kg and 5.4 %, respectively. These participants with satisfactory performance used the AOAC Official Method 990.28 Optimized Monier-Williams Method [12] based on acid-base titration. The other 3 laboratories employed iodometric titration methods in which resulted in 1 questionable and 2 unsatisfactory performances.

For PT-0017, 4 laboratories participated and reported results ranging from 110.4 to 176 mg/kg. Based on Fig. 5, 75% or 3 out of 4 participating laboratories obtained satisfactory performance for the analysis of sulfite in desiccated coconut matrix. The mean and relative standard deviation of results from the participants with satisfactory performance are 169 mg/kg and 5.3 %, respectively. Similarly, with the PT on dried mango, the AOAC 990.28 method was used by the laboratories with satisfactory performance. The remaining laboratory that obtained unsatisfactory performance used an iodometric titration method reported by J.D. Ponting & G. Johnsons [13].

Negative z' -scores were observed in the analysis of sulfite (as SO_2) in dried mango and desiccated coconut against the assigned value obtained from the LC-IDMS method. Determination of sulfite in food matrices requires complete hydrolysis with a highly concentrated strong acid to release bound sulfites. As such, incomplete distillation may result in low recovery of sulfite in food samples. Low recovery may also result from improper handling and storage of the PT item, potentially causing sample degradation. In such cases, sulfite may oxidize to sulfate, which is not detectable by sulfite titration methods.

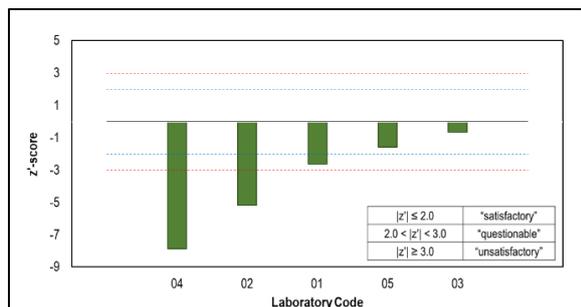


Fig. 4. Participants z' -score for 12-2019-PTILC(MiC2)-0013: Sulfite in Dried Mango

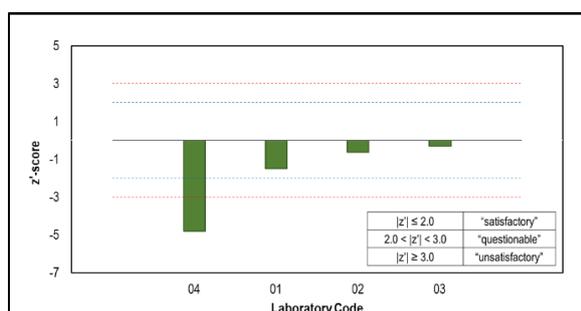


Fig. 5. Participants z' -score for 10-2022-PTILC(MiC)-0017: Sulfite in Desiccated Coconut

All satisfactory performances were observed for those who used the AOAC 990.28, whereas laboratories that used the iodometric titration method gave a more underestimated result. These laboratories are encouraged to conduct root cause analysis for attaining a questionable or unsatisfactory z' -score and assess the factors that may have contributed to the deviation. Method validation or verification was also recommended to establish the fitness for purpose of their existing methods. The importance of quality control measures was also demonstrated in these PT schemes, as PT-0013 Lab 03 and 05, as well as PT-0017 Lab 03, conducted recovery analyses and achieved satisfactory performance.

IV. CONCLUSIONS

NMLPhil organized the PT schemes for sulfite mass fraction determination in Philippine export products—dried mango and desiccated coconut. The reference values were assigned using a higher-order method, LC-IDMS with gravimetric sample preparation. The PT for sulfite in dried mango served as the initial assessment of local testing capability for sulfite analysis, revealing varying performance outcomes. However, this was improved in the PT for sulfite in desiccated coconut, where most participants achieved satisfactory performance.

Participation in these PT schemes provided local laboratories with an effective means of assessing their technical capabilities and enhancing their measurement

methods, thus supporting the accurate determination of sulfite levels in Philippine export products.

Acknowledgements

The authors gratefully acknowledge the Department of Science and Technology (DOST) and the Philippine Council for Industry, Energy, and Emerging Technology Research and Development (DOST-PCIEERD) for their funding support of this research through the project “Chemical Metrology for Toxic elements in food and water,” under the Metrology Program “Enhancement of the Competence and Capabilities of the National Metrology Laboratory of the Philippines.”

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