



First Indonesian proficiency testing using reference value from isotope dilution mass spectrometry method for benzoic acid, methyl paraben, and *n*-butyl paraben in sweet soy sauce

Nurhani Aryana¹ · Dillani Putri Ramadhaningtyas¹ · Dyah Styarini² · Yosi Aristiawan²

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Abstract

Research Center for Chemistry-Indonesian Institute of Sciences (RCChem-LIPI) has successfully organized proficiency testing (PT) for the determination of benzoic acid, methyl paraben, and *n*-butyl paraben in sweet soy sauce. This is the first PT in Indonesia that uses reference values derived from a primary method gas chromatography–isotope dilution mass spectrometry method. Twenty participants from four economies registered in this PT. This paper presents the procedures in the preparation of the PT samples, the homogeneity and stability checks, as well as in the determination of the assigned values. The test samples were a candidate certified reference material prepared in accordance with ISO 17034 and ISO Guide 35. The performance evaluation of participants' results was conducted in accordance with ISO 13528 by using the PROLab™ software. This paper also discusses the approaches taken in the calculation of the performance's scores which were set according to the criterion required in homogeneity check, stability check, and limit of uncertainty.

Keywords Benzoic acid · GC-IDMS · Methyl paraben · *n*-Butyl paraben · Proficiency testing · Sweet soy sauce

Introduction

Soy sauce, one of the oldest condiments in the world, is extensively used in Indonesian cuisine. The Indonesian soy sauce is dark and sweet, obtained from the fermentation process of soybean (*Glycine max* L.) and by adding sugar or brown sugar, with or without caramelization process, with or without the addition of other materials, with the basic characteristics of total sugars not less than 40 % [1]. Different from the traditional soy sauce that was made only from soybean, water, and salt, currently, some chemicals are added to the soy sauce material to reduce the fermentation time and enhance the taste and color. Food additives with antimicrobial, antioxidant, and buffer properties were

also added as preservatives to prevent from spoilage thereby allowing the product to be stored for a longer time.

Benzoic acid and parabens were commonly used as preservatives in some food products, including soy sauce. Benzoic acid in the form of its sodium salt constitutes one of the most common chemical food preservatives. Sodium benzoate is a common preservative in acid or acidified foods such as fruit juices, and syrups [2]. Yeasts are inhibited by benzoate to a greater extent than molds and bacteria [3]. Parabens are popular preservatives due to their stability, high water solubility, broad-spectrum antimicrobial activity, and low allergenicity [4].

Though the addition of these preservatives is allowed, their use is monitored under strict standards since they can potentially cause harm when consumed above the permitted limits. According to the Regulation of the Head of Agency of Drug and Food Control, the Republic of Indonesia Number 36 Year 2013 [5] concerning the maximum limit of use of food additive preservatives, the maximum mass fraction of benzoic acid and methyl paraben that is allowed in the fermented soy sauce is 1000 mg/kg and 600 mg/kg, respectively. In 1974, the Joint FAO/WHO Expert Committee on Food Additives proposed an acceptable daily intake (ADI) for the sum of the three parabens, methyl paraben, ethyl

✉ Nurhani Aryana
nurh020@lipi.go.id

¹ Research Center for Chemistry, Indonesian Institute of Sciences, Building 452, Kawasan Puspiptek, Serpong, Tangerang Selatan, Indonesia

² National Standardization Agency of Indonesia, Building 420, Kawasan Puspiptek, Serpong, Tangerang Selatan, Indonesia

paraben, and propyl paraben, at 0 mg/kg/day–10 mg/kg/day [4, 6, 7]. As a result of the regulations and the side effects of consuming preservatives, the analysis of food additives is an important issue in the food industry and regulatory authorities [8–10].

Proficiency testing (PT) is one of the key elements in the implementation of an appropriate quality assurance program and performance monitoring procedure for chemical analysis laboratories [11–15]. In Indonesia, several PT programs on preservatives in food samples have been conducted by other PT providers. The assigned value for these PTs is often derived from the consensus value of the participants' result. However, the use of consensus values to determine the assigned value of a PT program presents critical disadvantages [2]. In this PT, the Research Center for Chemistry-Indonesian Institute of Sciences (RCChem-LIPI) provided sweet soy sauce candidate certified reference material (PKM16) as a test sample. The assigned values of the target preservatives were assessed by characterization using gas chromatography-isotope dilution mass spectrometry (GC-IDMS) method, a primary method. The aim of this PT is to evaluate participants' capability on the measurement of benzoic acid, methyl paraben, and *n*-butyl paraben in sweet soy sauce.

Experimental

Preparation of the test samples

The preparation of the test samples was undertaken by RCChem-LIPI in accordance with ISO 17034 [16] and ISO Guide 35 [17]. Commercially available sweet soy sauce was chosen as the raw material and was known to contain the preservative sodium benzoate as stated in its label. Pre-analysis by using a high-performance liquid chromatography–diode array detector (HPLC–DAD) has confirmed that the raw material only contained the target parameter sodium benzoate and did not contain any quantity of methyl paraben and *n*-butyl paraben. These two analytes were spiked into the raw material by using the pure standard of methyl paraben (HRM 1003A, with mass fraction 999.5 mg/g $\pm$ 3.2 mg/g, HSA Singapore) and *n*-butyl paraben (HRM 1004A, with mass fraction 999.2 mg/g $\pm$ 3.3 mg/g, HSA Singapore). The spiked solutions were prepared by dissolving the pure standards of approximately 360 mg of methyl paraben and approximately 450 mg of *n*-butyl paraben in separate vials by methanol. The spiked solutions were poured into 500 ml of sweet soy sauce raw material placed in a mixer. The first homogenization process was conducted for 1 h. The homogenization process was repeated for the addition of every 500 ml of unspiked samples into the spiked samples until reaching the final volume of 3 L. The final spiked samples were bottled into 50-ml amber glass

bottles that were sealed with screw caps (30 ml each), resulting in a total of 103 bottles. The candidate test samples were subsequently labeled as PKM16 and stored at room temperature.

Homogeneity and stability checks of the test samples

The homogeneity and stability checks of the test samples were undertaken by RCChem-LIPI in accordance with ISO 13528 [18]. The test samples were checked for homogeneity and stability in transportation conditions before being distributed to the participants and also checked for stability in storage condition during the analysis period. For homogeneity check, ten bottles were selected from the bulk by random stratified order. From each bottle, two subsamples with a sample size of approximately 2 g were taken and analyzed under repeatability conditions. A solid-phase extraction (SPE) technique was used for the sample preparation. The analysis was conducted by using a validated method employing HPLC–DAD. In summary, approximately 2 g of the sweet soy sauce sample was diluted five times with ultrapure water in a centrifuge tube. The mixture was mixed by using a vortex for 1 min and followed by centrifugation for 10 min at 2500 rpm. For the extraction procedure, an SPE Bond Elut C18 cartridge (Agilent, CA, USA) was conditioned with 4 ml of methanol and 3 ml of ultrapure water. Approximately 1 ml of the aliquot was weighted and loaded on the cartridge under gravity. The clean-up process was followed immediately by flowing 4 ml of 10 % methanol solution (in 1 % phosphoric acid), and the analyte was subsequently eluted with 3 ml of methanol. The collected methanol phase was filtered by using a 0.45 μ m PTFE syringe filter and ready to be injected into the HPLC–DAD instrument. The criterion for the homogeneity check is shown in Eq. (1),

$$s_s \leq 0.3\sigma_{pt} \quad (1)$$

where s_s is an estimation of the between-sample standard deviation and σ_{pt} is the standard deviation for proficiency assessment.

Both stability checks were carried out by using isochronous design over a period of four weeks with four points of observation (one sample each week). The stability check for transportation condition was performed at 40 °C before the distribution of the test samples and conducted by using the same measurement method as the homogeneity test. Meanwhile, the stability check during the analysis period was performed at room temperature (25 °C) and analyzed after the deadline of results submission by using the same method as the homogeneity check. The reference temperature is 4 °C. The criterion for the stability check for both the conditions is shown in Eq. (2),

$$|\bar{y}_1 - \bar{y}_2| \leq 0.3\sigma_{pt} \quad (2)$$

where $\bar{y}_1$ is the average of the homogeneity check results and $\bar{y}_2$ is the average of the stability check results of each condition.

Analysis by participants

This PT round was announced in February 2016 to the testing laboratory and food manufacturers and subscribed by 20 participants from four economies: Indonesia, Myanmar, India, and Thailand. The test samples were distributed on June 2, 2016, in conjunction with the technical meeting. For the laboratories that did not attend the technical meeting, the test samples were dispatched by an express mail. Each participant received one bottle of test sample together with the relevant documents, such as a sample receipt form, technical instructions, and a result report form. Participants were requested to determine the mass fraction of the test parameters (in mg/kg) by using a routine method applied in each participant's laboratory. The participants were asked to report the measurement results in three significant figures, in the provided result report form in an Excel spreadsheet. They were also asked to report the technical information of their methods such as the extraction and clean-up procedure, operating condition of the instrument, and internal standard used if any. The deadline of the test results submission was set to July 15, 2016.

Determination of the assigned values, standard uncertainties, and standard deviation for proficiency assessment

The assigned value (x_{pt}) of each test parameter was determined by the GC-IDMS method by using isotopes of benzoic acid (chemical formula $^*C_6H_5COOH$, CLM 1813-0.5), methyl paraben (chemical formula $^*C_6C_2H_8O_3$, CLM 8249-1.2), and *n*-butyl paraben (chemical formula $HO^*C_6H_4CO_2-(CH_2)_3CH_3$, CLM 8285-1.2) from Cambridge Isotope Laboratories (MA, USA). For the sample blend preparation, in summary, a certain amount of sweet soy sauce sample (2 g) was accurately weighed in a centrifuge tube. Approximately 10 ml of ultrapure water was subsequently added into the vial containing the sample, and the final mass of the solution was recorded. Following this, 1 ml aliquot of the diluted sample was weighted and added by an appropriate quantity of the isotopes. The mass ratio of the natives to isotope compounds in the mix solution was maintained as close to unity as possible. The sample blend solution was stored in the refrigerator overnight to reach equilibrium before further analysis. The next steps were the extraction procedure and GCMS analysis by using the procedures that have been described elsewhere [19]. For the calibration blend, the working standard of the native solutions and working standard of isotope solutions with a specific concentration were

mixed to represent the ratio of the compounds in the sample blend. The measurement was taken based on an exact matching approach by using a single-point calibration method. Two calibration standards at the 1:1 ratio were measured. Detection was performed using the selective ion monitoring (SIM) mode at m/z as shown in Table 1.

The method was validated by using a matrix CRM of preservatives in soy sauce (HRM 1005A, with the assigned values of $871.1 \text{ mg/kg} \pm 21.6 \text{ mg/kg}$ for benzoic acid, $237.6 \text{ mg/kg} \pm 13.5 \text{ mg/kg}$ for methyl paraben, and $93.7 \text{ mg/kg} \pm 6.0 \text{ mg/kg}$ for *n*-butyl paraben, HSA Singapore). The trueness of the method was estimated by means of recovery experiments in the analysis of the matrix CRM ($n=8$) analyzing the target product ions in two different days. The percent recoveries for quantifying ion of benzoic acid, methyl paraben, and *n*-butyl paraben were 95.35 %, 98.42 %, and 91.03 %, respectively. The precision of the method was determined in terms of relative standard deviation from the recovery experiments. The RSD mean values were 6.05 %, 4.49 %, and 4.17 %, respectively, for benzoic acid, methyl paraben, and *n*-butyl paraben.

For the determination of the assigned values, ten bottles were selected from the bulk and two subsamples from each bottle were analyzed. The mass fraction of each analyte in the test sample was calculated from the isotope ratio of the sample blends, calibration blend, sample, spike, and primary standards. The mean of all the bottles was assigned as the certified value of each analyte. The combined standard uncertainties were calculated by using the bottom-up approach with a sensitivity coefficient ($\delta y/\delta x$) method [20]. The overall combined standard uncertainty was estimated by combining all the measurement equation factors (including method precision) and additional factors (such as interference and method recovery). The combined standard uncertainty was subsequently used as the standard uncertainty due to characterization (u_{char}).

The standard uncertainty due to differences between the test samples (u_{hom}) was calculated according to the ISO Guide 35 [17] by using an analysis of variance (ANOVA) two-factor without replication approach calculated as Eq. (3):

Table 1 Optimized quantifier and qualifier ions for analyzing the preservatives by GC-IDMS

Compounds	Quantifying ion	Qualifying ion
Benzoic acid	105	122 and 77
Methyl paraben	121	152 and 93
<i>n</i> -Butyl paraben	121	138 and 93
$^{13}C_6$ benzoic acid	111	128 and 83
$^{13}C_6$ methyl paraben	127	158 and 99
$^{13}C_6$ <i>n</i> -butyl paraben	127	144 and 99

$$u_{\text{hom}} = \sqrt{\frac{MS_{\text{between}} - MS_{\text{within}}}{n_0}} \quad (3)$$

where MS_{between} is the mean square of between-bottle variation derived from the ANOVA table, MS_{within} is the mean square of within-bottle variation derived from the ANOVA table, and n_0 is the number of replications.

In the distribution of the test samples to the participants, the condition was maintained close to room temperature, so the standard uncertainty due to transportation condition was assumed to be 0. Therefore, only the standard uncertainty due to instability during the analysis period contributes to the calculation of the standard uncertainty of the assigned value and is defined as u_{stab} . The standard uncertainty was evaluated by using ANOVA for linear regression. The estimation of uncertainty is calculated by using Eq. (4):

$$u_{\text{stab}} = \sqrt{\Delta^2 + u_{\Delta}^2} \quad (4)$$

where Δ is the expected change during the analysis period (gradient in 4 weeks) and u_{Δ} is the standard uncertainty of the expected change during the analysis period (gradient standard error in 4 weeks).

The standard uncertainty of the assigned value for each test parameter was then calculated with Eq. (5):

$$u(x_{\text{pt}}) = \sqrt{u_{\text{char}}^2 + u_{\text{hom}}^2 + u_{\text{stab}}^2} \quad (5)$$

where $u_{(x_{\text{pt}})}$ denotes the standard uncertainty of the assigned value, u_{char} denotes the standard uncertainty due to characterization, u_{hom} denotes the standard uncertainty due to differences between test samples, and u_{stab} denotes the standard uncertainty due to instability during the analysis period.

For the performance evaluation, the standard deviation for proficiency assessment (σ_{pt}) was derived from the Horwitz equation [Eq. (6)] for all test parameters.

$$\sigma_{\text{pt}} = 0.02c^{0.8495} \quad (6)$$

The robust mean (x^*) and robust standard deviation of the participants' results (s^*) were also calculated by using Algorithm A as described in ISO 13528 [18] and presented as informational values. The standard uncertainty of the robust mean of the participants' results ($u(x^*)$) was calculated by using Eq. (7):

$$u(x^*) = 1.25 \times \frac{s^*}{\sqrt{p}} \quad (7)$$

where p is the number of participants.

Criterion in the calculation of participants' performance

The performance statistics was calculated in accordance with ISO/IEC 17043 [21] and ISO 13528 [18] by using a software analytical quality assurance for interlaboratory studies PRO-Lab™ Plus. Prior to selecting the criterion for performance evaluation, the standard uncertainty of the assigned value was compared to σ_{pt} . If the criterion in Eq. (8) is met, the standard uncertainty of the assigned value can be considered to be negligible and need not be included in the interpretation of the results of the round of proficiency testing [18]; therefore, the laboratory performances will be assessed by using z-score as shown in Eq. (9).

$$u(x_{\text{pt}}) < 0.3\sigma_{\text{pt}} \quad (8)$$

If the criterion in Eq. (8) is not met, the standard uncertainty of the assigned value should be included in the interpretation of the results of the proficiency testing and the laboratory performances will be assessed by using z' -score as shown in Eq. (10),

$$z_i = \frac{(x_i - x_{\text{pt}})}{\sigma_{\text{pt}}} \quad (9)$$

$$z'_i = \frac{x_i - x_{\text{pt}}}{\sqrt{\sigma_{\text{pt}}^2 + u^2(x_{\text{pt}})}} \quad (10)$$

where x_i is the submitted participants' result.

Results and discussion

Homogeneity and stability check results

The results of the homogeneity check are summarized in Table 2. The heterogeneity standard deviations (s_s) were

Table 2 Summary of homogeneity check results of the test samples

Test parameter (mass fraction)	Benzoic acid	Methyl paraben	<i>n</i> -Butyl paraben
Unit	mg/kg	mg/kg	mg/kg
s_s	3	1	0.2
s_r	9	1	2.2
$0.3\sigma_{\text{pt}}$	9	3	2.0
Ratio of s_r/σ_{pt}	0.3	0.1	0.3
$s_r/\sigma_{\text{pt}} < 0.5$	OK	OK	OK
ISO 13528:2015 test for adequate homogeneity	OK	OK	OK

3 mg/kg, 1 mg/kg, and 0.2 mg/kg, respectively, for benzoic acid, methyl paraben, and *n*-butyl paraben. The ratio between the repeatability standard deviations (s_r) and σ_{pt} for all the parameters is less than 0.5. The test samples met the assessment criterion in Eq. (1) and hence can be considered as sufficiently homogeneous and suitable for the proficiency testing. The results of the stability checks are summarized in Table 3. For the stability check during the analysis period, the assessment criterion was met by all of the test parameters. For the transportation stability, benzoic acid and methyl paraben met the assessment criterion. Meanwhile, *n*-butyl paraben did not meet the assessment criterion; therefore, according to ISO 13528, the standard uncertainty of the assigned value was included in the interpretation of the results of the proficiency testing, and the laboratory performances were assessed by using z' -score.

The assigned values, standard uncertainties, and standard deviation for proficiency assessment

The assigned values and standard uncertainties of all the test parameters are summarized in Table 4. As indicated in Table 4, the standard uncertainties of the assigned values of all the test parameters did not meet the criterion as shown in Eq. (8); therefore, the laboratory performances were assessed by using z' -score.

Analytical methods and results of the participants

All of the participants returned their results before the deadline. There were 20 laboratories submitted the results for

benzoic acid, 16 laboratories submitted the results for methyl paraben, and 13 laboratories submitted the results for *n*-butyl paraben. The participants' results for each test parameter together with its associated uncertainties are shown in Fig. 1. Five sample preparation techniques were used by the participants—solid-phase extraction (SPE), liquid–liquid extraction (LLE), solid–liquid extraction (SLE), vortex, and others. Most of the participants used liquid chromatography with an ultraviolet detector (LC-UV) which employs a reversed-phase chromatography column such as C18 and ODS-3. Furthermore, some participants did not specify the method adopted and merely reported it as 'other.' None of the laboratories used any internal standard. The recovery values were reported in the range of 60 %–106.2 %; furthermore, only one participant corrected the result with the recovery factor.

The robust mean and robust standard deviation of the participants' results are summarized in Table 5. The difference between the robust mean (x^*) and the assigned value, x_{diff} , of each test parameter was calculated by using Eq. (11), and the standard uncertainty of the difference was estimated as Eq. (12)

$$x_{diff} = |x^* - x_{pt}| \quad (11)$$

$$u_{diff} = \sqrt{u^2(x^*) + u^2(x_{pt})} \quad (12)$$

The results of x_{diff} and u_{diff} of each test parameter are shown in Table 5. The x_{diff} for all the test parameters are less than twice its associated u_{diff} ; therefore, based on ISO 13528,

Table 3 Summary of stability check results of the test samples

Test parameter (mass fraction)	Benzoic acid	Methyl paraben	<i>n</i> -Butyl paraben
Unit	mg/kg	mg/kg	mg/kg
$0.3\sigma_{pt}$	9	3	2.0
$ \bar{y}_1 - \bar{y}_2 $ for storage stability at 25 °C	4	1	0.9
ISO 13528:2015 test for adequate stability	Stable	Stable	Stable
$ \bar{y}_1 - \bar{y}_2 $ for transportation stability at 40 °C	2	1	2.1
ISO 13528:2015 test for adequate stability	Stable	Stable	Not stable

Table 4 Summary of the assigned value and the associated standard uncertainty

Test parameter	Benzoic acid	Methyl paraben	<i>n</i> -Butyl paraben
Assigned value, x_{pt} (mg/kg)	467	111	79.8
u_{char} (mg/kg)	10	3	2.3
u_{hom} (mg/kg)	6	1	0.8
u_{stab} (mg/kg)	0	0	0.0
Standard uncertainty, $u(x_{pt})$ (mg/kg)	12	4	2.4
Coverage factor (k)	2	2	2
Expanded uncertainty, $U(x_{pt})$ (mg/kg)	24	7	4.8
σ_{pt} (mg/kg)	30	9	6.6

Fig. 1 Participants' results together with their associated uncertainties and the analytical method used in the determination of **a** benzoic acid; **b** methyl paraben; and **c** n-butyl paraben

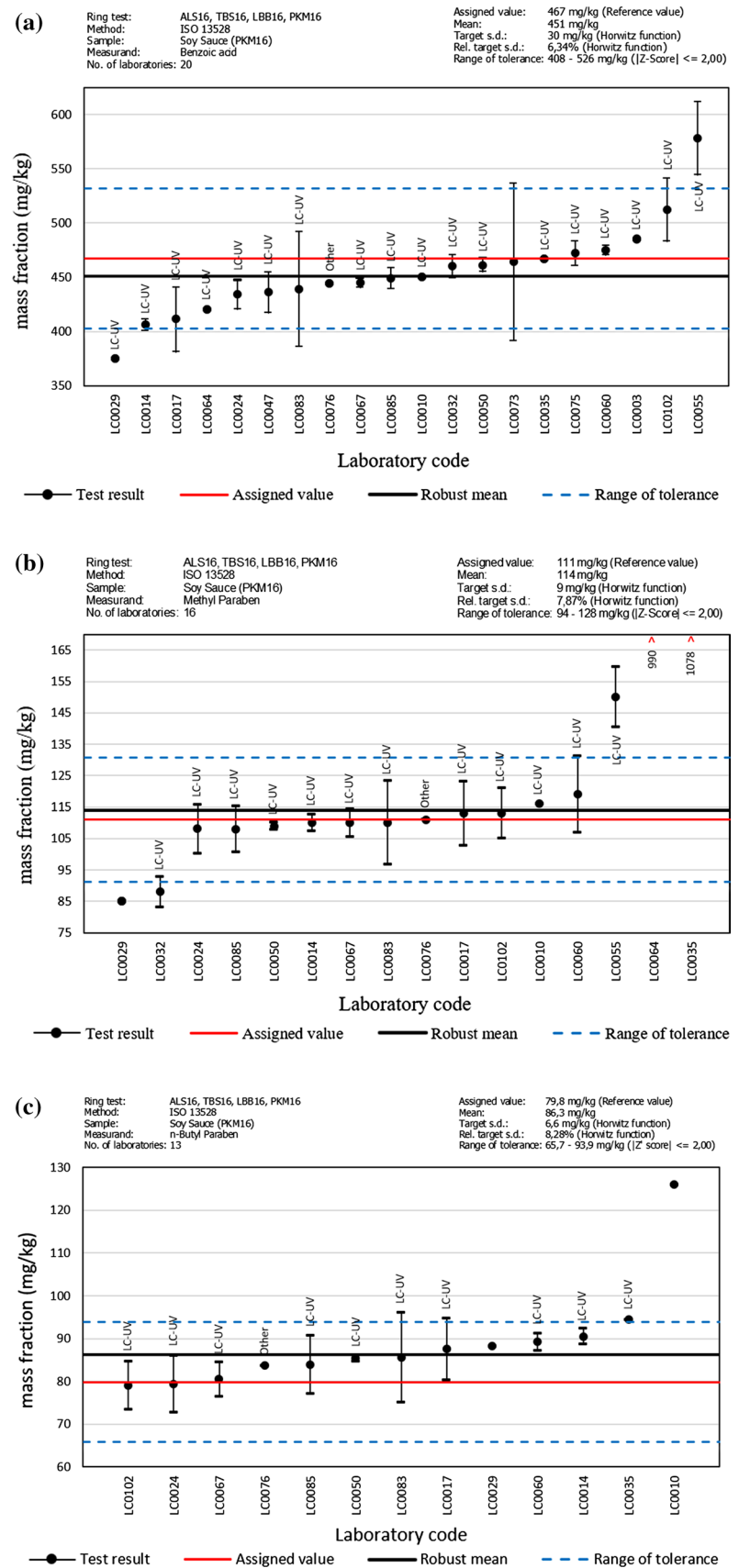


Table 5 Summary of participants' results

	Benzoic acid	Methyl paraben	<i>n</i> -Butyl paraben
No. of results submitted	20	16	13
Robust mean of participants' results (x^*) (mg/kg)	451	114	86.3
Robust standard deviation of participants' results (s^*) (mg/kg)	32	18	5.9
Standard uncertainty of the robust mean ($u(x^*)$) (mg/kg)	9	6	2.0
x_{diff} (mg/kg)	16	3	6.5
u_{diff} (mg/kg)	15	7	3.2

Table 6 Summary of performance of participants' results

Performance of participants	Number of Participants (%)		
	Benzoic acid	Methyl paraben	<i>n</i> -Butyl paraben
Satisfactory	18 (90 %)	11 (69 %)	11 (85 %)
Questionable	1 (5 %)	2 (12 %)	1 (8 %)
Unsatisfactory	1 (5 %)	3 (19 %)	1 (8 %)
Total	20	16	13

no action is recommended since the bias in the methods is understood.

Evaluation of participants' performance

The performance of the participants in terms of z' -score for benzoic acid, methyl paraben, and *n*-butyl paraben is summarized in Table 6. Participants' performance was ranked into three categories based on ISO/IEC 17043 [21] as follows:

- (1) $|z'| \leq 2.00$ is considered to be satisfactory,
- (2) $2.00 < |z'| < 3.00$ is considered to be questionable, and
- (3) $|z'| \geq 3.00$ is considered to be unsatisfactory.

Ten participants reported the measurement results for all the test parameters and achieved satisfactory results. Few participants received questionable and unsatisfactory results. In this case, the trueness and precision of the method have to be evaluated for improving the analytical method's performance. The distribution of the participants' performance for each test parameter is shown in Fig. 2.

When the z -scores were assessed by the robust mean and robust standard deviation of participants' results, the percentage of laboratories that show satisfactory results increased from 69 % and 85 % to 88 % and 92 % for methyl paraben and *n*-butyl paraben, respectively. For benzoic acid, one unsatisfactory result (LC0029) became a questionable result. For methyl paraben, two questionable results (LC0029 and LC0032) became satisfactory results. For *n*-butyl paraben, one questionable result (LC0035) became a satisfactory result.

This change might be due to the 3 %, 3 %, and 8 % difference between the robust mean of the participants' results and the assigned value for benzoic acid, methyl paraben, and *n*-butyl paraben, respectively.

The performance evaluation was also done by the zeta-score to evaluate participants' ability to have results that were close to the assigned values within their claimed uncertainty. The zeta-scores (ζ) are calculated as Eq. (13):

$$\zeta_i = \frac{(x_i - x_{\text{pt}})}{\sqrt{u^2(x_i) + u^2(x_{\text{pt}})}} \quad (13)$$

Interpretation of the zeta-scores can be in a similar manner as the z' -scores, where in terms of absolute value, scores ≤ 2 are considered satisfactory, scores between 2 and 3 are questionable, and scores ≥ 3 are unsatisfactory.

With the zeta-scores evaluation, four satisfactory (LC0017, LC0024, LC0047, and LC102) became questionable, and one satisfactory (LC0064) and one questionable (LC0014) became unsatisfactory for benzoic acid. For methyl paraben, two questionable results (LC0029 and LC0032) became unsatisfactory. For *n*-butyl paraben, three satisfactory results (LC0014, LC0029, and LC0060) became unsatisfactory, one satisfactory (LC0050) became questionable, and one questionable result (LC0035) became unsatisfactory. The change in the evaluation results for these laboratories may be caused by their underestimated measurement uncertainty since $u(x_i)$ are smaller than $u(x_{\text{pt}})$. The laboratory carrying out the analysis by a routine method is likely to have bigger measurement uncertainty $u(x_i)$ than the standard uncertainty of the assigned value $u(x_{\text{pt}})$, that is, derived by IDMS method [22].

Conclusions

The first proficiency testing for the determination of benzoic acid, methyl paraben, and *n*-butyl paraben in sweet soy sauce by using reference values derived from gas chromatography–isotope dilution mass spectrometry (GC-IDMS) method was successfully initiated. Twenty participants submitted the results for the measurement of benzoic acid,

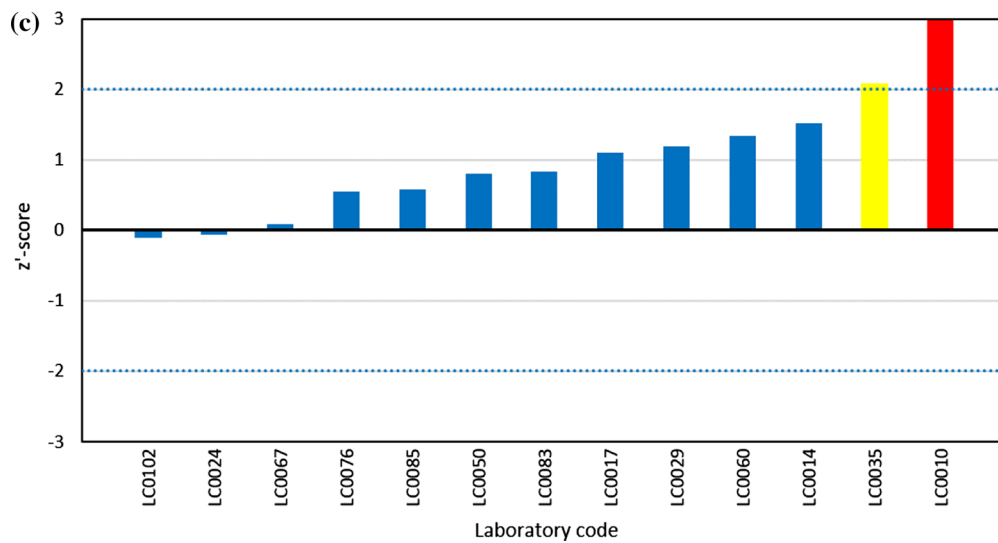
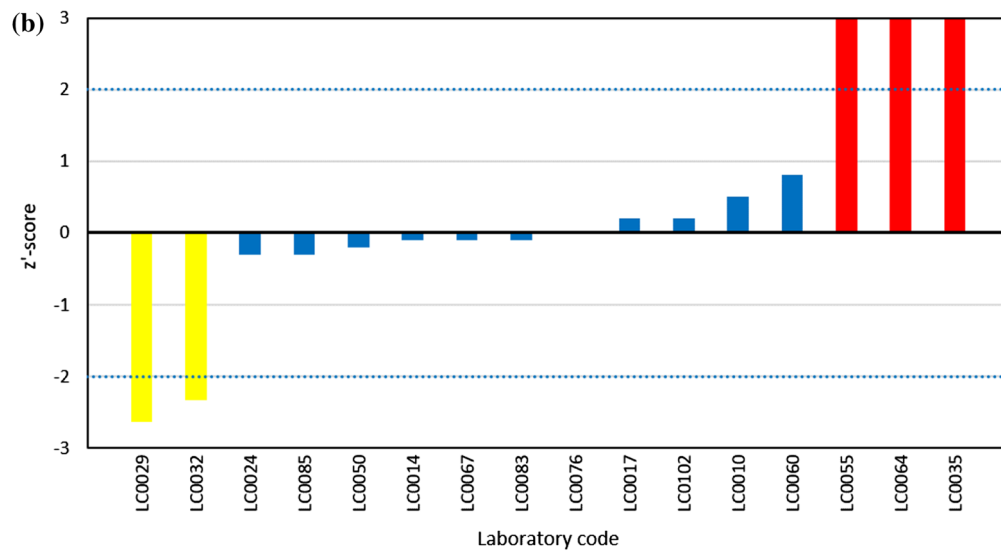
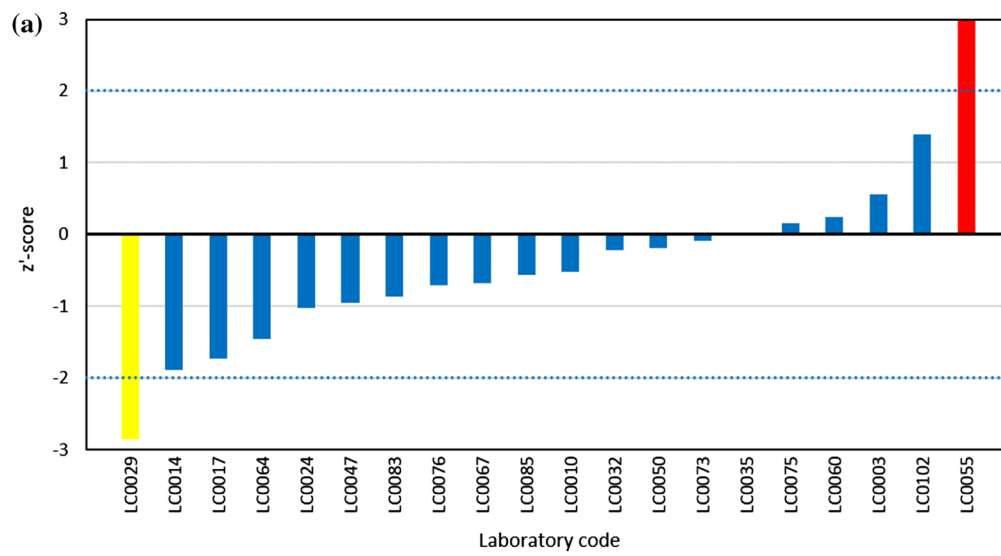


Fig. 2 Distribution of **a** z' -score of benzoic acid; **b** z' -score of methyl paraben; and **c** z' -score of *n*-butyl paraben. The blue dotted lines indicate the range of tolerance where $|z'| \leq 2.00$, the blue bars indicate satisfactory results, the yellow bars indicate questionable results, and the red bars indicate unsatisfactory results

methyl paraben, and *n*-butyl paraben in sweet soy sauce. Statistical data evaluation was done in accordance with ISO 13528 by using the PROLab™ software. Based on the criterion required in the homogeneity check, stability check, and limit of uncertainty, the performance evaluation of the participants' results was carried out by using the z' -score for benzoic acid, methyl paraben, and *n*-butyl paraben. In summary, approximately 90 %, 69 %, and 85 % of the participants achieved satisfactory results in the PT for the determination of benzoic acid, methyl paraben, and *n*-butyl paraben in sweet soy sauce, respectively. The percentage of laboratories showing satisfactory results increased to 88 % and 92 % for methyl paraben and *n*-butyl paraben, respectively, when the z -scores were assessed by the robust mean and robust standard deviation of participants' results. By the zeta-scores evaluation, the percentage of laboratories that have satisfactory results are 60 %, 69 %, and 54 %, respectively, for benzoic acid, methyl paraben, and *n*-butyl paraben. The change in the evaluation results for these laboratories may be caused by their underestimated measurement uncertainty. The present study explicitly demonstrates the significant importance of using metrologically traceable reference values as the PT assigned values in achieving a reliable assessment, especially when the PT has a limited number of participants.

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