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Technical Report

Borax buffer solution for pH measurement: Homogeneity and stability studies and its application in the proficiency testing program

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Abstract

This paper describes the preparation of borax buffer solution and its application as proficiency testing (PT) test samples in a PT scheme. The test samples were made gravimetrically from 0.01 M sodium tetraborate decahydrate and pH of the test samples were measured by using a differential potentiometric cell. Homogeneity and stability of test samples were evaluated in accordance to ISO13528:2015. The results obtained revealed that test samples met the PT requirement criteria in terms of stability and homogeneity. The prepared PT test samples were used in the 2016 PT scheme. From the results received from 50 participants, it was found that about 44 % of participants achieved satisfactory results, 38 % achieved unsatisfactory results, while the remaining participants (about 18 %) showed a questionable result.

Keywords

Sodium tetraborate decahydrate; pH measurements; Proficiency testing scheme; ISO 17043; ISO 17025

Introduction

Metrology in Chemistry Laboratory of Indonesian Institute of Sciences (MiC Lab-LIPI) is an accredited Proficiency Testing (PT) provider in Indonesia having responsibility for all tasks in the PT scheme development and operation within the Institute. Based on ISO 17043:2010, the PT scheme is to design and operate for one or more rounds in a specific area of testing, measurement, calibration or inspection [1]. The PT is widely known as a tool to evaluate the performance of participant's laboratories for accreditation process purposes [2]. For the participant, in particular, there are some benefits in joining the PT, including to confirm the competence of the participant,

to identify the possible problem related to testing or measurement, to compare methods and procedures used, to improve performance and to boost confidence to conduct a specific measurement, to educate staff, and to assure the quality of the test result as required by ISO 17025:2008 [3-5].

The PT program at the MiC Lab-LIPI has been conducted since 2013. This is in the MiC Lab-LIPI's annual agenda to disseminate the PT test samples together with the reference standard solution, to different testing laboratories in Indonesia. The PT program covers various commodities and parameters including metals in drinking water, wastewater, fish flour and rice flour, pesticide in tea, food additive in soy sauce, and buffer solution. All these PT samples were prepared and measured by MiC Lab-LIPI.

pH measurement is also one of the parameter in the PT program of MiC Lab-LIPI because the pH measurement is very common and widely used in quantitative measurements in the field of chemical analysis [6]. In addition, the data obtained from pH measurement is widely used as the basis for making environmental-related decisions and for the evaluation of product quality in industries [7]. In 2013, the range of pH measurement was between acid and neutral (pH 4.00-7.00). For the acid pH, 70 % of participants achieved satisfactory result, while 80 % participants got satisfactory result for measuring the neutral pH. In 2014-2015, the range of the pH measurement was between pH 1.00-5.00 (acid pH). In 2014, 54 % of participants got satisfactory result and it was increased up to 91 % in 2015 [8].

In 2016, MiC Lab-LIPI provided a PT item in the range of pH alkaline to assess the performance of participant laboratories. The PT samples were borax buffer solution and it was distributed to registered participant laboratories. However, before distribution, two specified tests have to be conducted including homogeneity and stability testing in order to meet the criteria of the PT samples with the purpose to reduce the bias of the measurement result [1,9].

In this paper, preparation of the borax buffer solution for pH measurement including its homogeneity and stability evaluation, as well as its application as samples in the PT scheme are presented and the results are discussed.

Experimental

Materials

All chemicals were of the analytical grade and used as received without any further purification. Platinum tetrachloride (PtCl_4) anhydrous (57.5 % Pt), Lead (II) acetate (99.5 % purity), nitric acid (HNO_3 , 65 % purity) and hydrochloric acid (HCl, 37 % purity) were purchased from Merck, Germany. Hydrogen (H_2) gas (99.9 % purity) was purchased from SII Gas Indonesia. Sodium tetraborate decahydrate (99.6 % purity) was purchased from Wako, Japan, while SRM[®] 187e was purchased from NIST, USA. Demineralized water ($0.05 \mu\text{S cm}^{-1}$) was produced from a Thermo Scientific Barnstead Smart2 pure water purification system and used in all experiment runs.

Equipment

Equipment used were the analytical balance with accuracy 1 mg (PR5003 DualRange, Mettler Toledo Switzerland) and Flowmeter (ADM1000, Agilent). A set of differential potentiometric cell systems include a digital multimeter 0.01 mV (34461A, Agilent Technologies Sdn Bhd, Malaysia), digital thermometer (MKT50, Anton Paar GmbH, Germany), water bath 0.1°C (Thomas T- N22D, Japan), chiller (Thomas TRL-117NF, Japan), Baucke Cell, chamber, and Pt electrode. A magnetic

stirrer (Cimarec 2, Barnstead Thermolyne Corp. USA), Direct Current (DC) power supply 0.01 A (Ad-8723D, China), stopwatch, HDPE bottles 25 L and 250 mL, clean glassware and clean spatula.

Preparation of PT samples

The PT samples were prepared gravimetrically from sodium tetraborate decahydrate 0.01 M. This gravimetric preparation could eliminate the need to weigh exactly the predetermined mass of solid samples. 3.83 g of sodium tetraborate decahydrate was transferred into a clean and dry beaker glass (1 L) then diluted using fresh demineralized water until the total weight obtained was 1002.85 g. The solution containing sodium tetraborate decahydrate was shaken thoroughly using magnetic stirrer until the solid was totally dissolved. The procedure was repeated as much as 19 times. After that, the solution was transferred to HDPE bottle 25 L. After homogenization process in one night, the solution was transferred into smaller and clean HDPE bottle 250 mL. The volume of sample has been estimated enough for the participant laboratories to conduct duplicate measurement and their quality control. The label of the bottle was code by LBB16-XXX (LBB is code for borax buffer solution, 16 is code for the year 2016 and XXX was a number of the bottle). Each bottle containing borax buffer solution was packaged and sealed using a plastic seal.

Preparation of standard solution

The standard solution was made from SRM[®] 187e. The similar procedure was applied for preparing the standard solution as described above. Shortly, 3.83 g of SRM[®] 187e was transferred into a clean and dry beaker glass (1 L), diluted using fresh demineralized water and stirred thoroughly. The prepared standard solution was placed into a beaker glass and was tightly covered to avoid against CO₂ contamination.

Preparation of Pt electrode

A Pt electrode was used for the pH measurement by the secondary method using differential potentiometric cell. In order to achieve sufficiently small bias of potentials value and to avoid possible interference during the pH measurement, the Pt electrode was firstly cleaned by removing impurities on the electrode surface using hot *aqua regia* solution [10,11]. After that, the Pt electrode was rinsed with demineralized water. The cleaned Pt electrode was then platinized by an electrolytic method using DC power supply and solution containing a mixture of platinum tetrachloride (PtCl₄), lead (II) acetate and hydrochloric acid (HCl). The platinization process was conducted under the current of 0.25 A for 2.5 minutes. Under these conditions, the Pt electrode having a potential bias below 3 μV could be achieved [10].

pH measurement

The pH values of all PT samples were measured using differential potentiometric cell, called Baucke cell. The Baucke cell was firstly introduced in 1994 [6]. A schematic diagram of the differential potentiometric cell system used in this measurement is shown in Figure 1. The shape of the cell is like U-shaped cell that is separated by a sintered glass disk in the middle, so it also called a two-half cell. In this two-half cell system, one cell contains the standard solution (SRM[®] 187e) and platinized Pt electrode. Another cell contains the PT sample of borax buffer solution and platinized Pt electrode. The potential difference between the standard solution and PT sample solution were assigned as ΔE . After that, the hydrogen (H₂) gas was fed into each cell under the flow rate of 500 ml/h [10]. It should be noticed that H₂ gas was pre-humidified before entering the Baucke cell by passing H₂ into two chambers containing borax buffer solution [6]. Both, cell and the cell chamber

were placed into the water by keeping its temperature at 25 °C using chilled circulation system. The platinized Pt electrodes were then connected to a digital multimeter. Under stable condition (1 hour is required to stabilize the potential), ΔE was observed and recorded every 10 minutes. The pH value of PT sample (borax buffer solution sample) was calculated using eq. (1).

$$pH_s = pH_p - (\Delta E F / RT \ln 10) \tag{1}$$

where pH_s is a pH value of PT sample, pH_p is pH value of standard solution, ΔE is potential difference between the standard solution and PT sample (V), F is Faraday constant (96485.332 C mol⁻¹), R is the universal gas constant (8.3144621 J K⁻¹ mol⁻¹), and T is temperature of measurement (K).

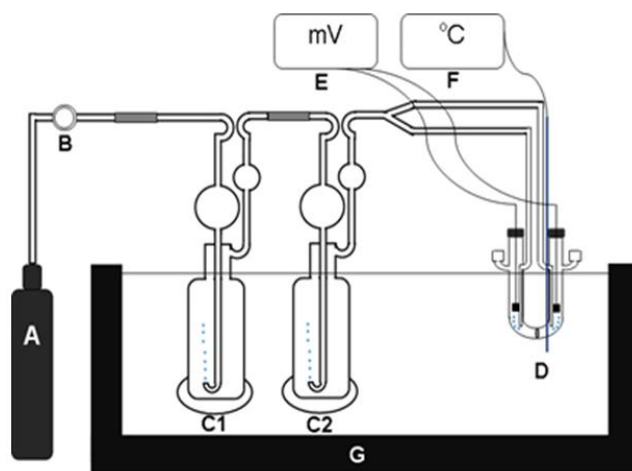


Figure 1. A schematic diagram of differential potentiometric cell system: **A** - H₂ gas, **B** - flowmeter, **C1** and **C2** - chambers containing borax buffer solution, **D** - Baucke cell and the platinized Pt electrodes, **E** - digital multimeter, **F** - digital thermometer, **G** - chilled circulation system

Homogeneity testing

All the PT samples were evaluated for their homogeneity before distributing to the participants. The homogeneity test was conducted in accordance to Annex B of ISO 13528:2015 and the results were statistically evaluated by F-test using one-way analysis of variance (ANOVA). Ten bottles of the prepared PT sample were selected by stratified random sampling and were measured in duplicate using differential potentiometric cell under repeatable condition. Based on the Annex B of ISO 13528:2015, the calculation was conducted as follows:

Define the sample averages (\bar{x}_t)

$$\bar{x}_t = \frac{x_{t,1} + x_{t,2}}{2} \tag{2}$$

where $x_{t,i}$ represents the proficiency test item ($t = 1, 2, \dots, g$), and the between test portion ranges (w_t)

$$w_t = |x_{t,1} - x_{t,2}| \tag{3}$$

Calculate the general average (\bar{x})

$$\bar{x} = \frac{1}{g} \sum_{t=1}^g \bar{x}_t \tag{4}$$

estimate the standard deviation of sample averages (s_x)

$$s_x = \sqrt{\frac{\sum_{t=1}^g (\bar{x}_t - \bar{x})^2}{g-1}} \quad (5)$$

and the within sample standard deviation (s_x):

$$s_w = \sqrt{\frac{\sum_{t=1}^g w_t^2}{2g}} \quad (6)$$

Finally estimate the between sample standard deviation (S_s) as:

$$s_s = \sqrt{s_x^2 - \frac{s_w^2}{2}} \quad (7)$$

The estimated value of s_s^2 becomes negative when s_s is relatively smaller than s_w . This can be expected when PT samples are highly homogeneous [12].

Stability testing

Two different types of stability testing were performed *i.e.*, one is stability monitoring to simulate the transport condition where the samples were stored at 40 °C for 4 weeks and another is stability monitoring during the PT scheme. The stability testing was performed according to the Annex B of ISO 13528:2015. Two bottles of the PT sample were selected for stability monitoring at 40 °C and then the PT samples were measured consecutively after 2, 3, and 4 weeks. Another three bottles of PT sample were selected randomly for stability monitoring during the PT scheme in conjunction with the due date of participants reports submission. The pH measurement for the stability monitoring was conducted by duplicate by using differential potentiometric cell. The PT samples are considered to be adequately stable if:

$$|\bar{y}_1 - \bar{y}_2| \leq 0.3\sigma_{pt} \quad (8)$$

where \bar{y}_1 is the average pH value of the homogeneity check, \bar{y}_2 is the pH value from stability check and σ_{pt} the standard deviation of PT. In this PT scheme, the value of σ_{pt} was set 0.03 according to IUPAC recommendation as a maximum measurement uncertainty for the glass electrode method with two-point calibrations (bracketing procedure)[13]. Based on MiC Lab-LIPI's experience in organizing previous 2 rounds of pH measurement scheme by applying such σ_{pt} value, it was found that the value 0.03 can fit for this purpose and can be used as the performance evaluation criteria for pH measurement.

Application

The prepared borax buffer solution was used as the PT samples. These PT samples were found homogenous and stable at high temperature for 1 month and they were distributed on the PT scheme during a scheduled technical meeting. For some laboratories who can not join the technical meeting, the samples were dispatched by a courier. Each participant received one bottle containing about 250 mL of tetraborate buffer solution (LBB16). Each bottle of LBB16 has a specific number, example No. LBB16-001. Each laboratory received one bottle with a different number.

Results and discussion

The borax buffer solution is a very common and widely used as a pH standard solution for the calibration of the glass electrode. The borax buffer solution has long time storage characteristic until 2 years under closed bottle [14]. In addition, the borax buffer solution could be used directly and

stored at room temperature for long period without decomposition [15]. Before used as the PT sample, the borax buffer solution was evaluated for its homogeneity and stability in order to assure that all PT participants can receive the same PT sample with sufficiently homogeneous and stable properties; thus all PT results can be compared [1, 12].

Homogeneity testing

Homogeneity is defined as a material condition having uniform in term of its structure or composition-related specified properties [16]. The homogeneity assessment of PT samples was conducted before distribution to the PT participants [1,17], with the primary aim to verify that all units of the PT samples can be considered identical when a batch of certification is envisaged [18].

Homogeneity of borax buffer solution was checked by measuring the pH values of 10 bottles taken by random sampling and using the differential potentiometric cell. The results of duplicate analysis are listed in Table 1. It can be seen from data in Table 1, that the general average of pH value for 10 PT samples is 9.186. This value was put as the assigned value for the PT scheme 2016 and denoted as \bar{y}_1 in the stability monitoring using Eq. (8).

Table 1. pH values of 10 selected bottles with borax buffer solution

No. of Bottle	pH	
	Measurement 1	Measurement 2
1	9.188	9.185
13	9.192	9.185
25	9.187	9.185
37	9.187	9.187
49	9.187	9.184
61	9.189	9.185
73	9.185	9.184
85	9.187	9.184
97	9.185	9.186
109	9.184	9.187
General average of pH value (\bar{x})		9.186

After getting the pH values from 10 measurements, the homogeneity testing was statistically evaluated by the *F*-test using one-way analysis of variance (ANOVA) and the results are tabulated in Table 2. As can be seen from Table 2, the value of *F* is smaller than *F*_{critical} (*F* < *F*_{critical}), meaning that the homogeneity of PT samples is found insignificant. Insignificance in homogeneity indicates that no significant difference exists between PT samples (different bottles) and within the PT sample (the same bottle). Therefore, the PT samples were found homogenous.

Table 2. ANOVA results of homogeneity testing of PT samples

Source of variation	SS ^a	df ^b	MS ^c	F ^d	P-value ^e	F _{crit}
Between Groups	2.745E-05	9	3.05E-06	0.616162	0.760518	3.020383
Within groups	4.95E-05	10	4.95E-06			
Total	7.695E-05	19				

^athe sums of squares, ^bthe associated degrees of freedom, ^cthe mean squares, ^d*F* test indicated that the result of the homogeneity is insignificant if *F* < *F*_{crit}, with the critical value of *F* for α = 5 %, and ^egives the level for which the observed *F* = *F*_{crit} [19].

In addition to ANOVA evaluation, the homogeneity of PT samples was evaluated by using another statistical analysis (eq. 7) according to the Annex B of ISO 13528:2015 and the results are shown in Table 3. It can be seen in Table 3, that the estimated value of s_s^2 is found negative, showing that s_s value is relatively smaller than s_w . This finding indicates that PT samples were highly homogeneous. This result agrees with the ANOVA evaluation.

Table 3. Result of homogeneity testing of PT samples according to Annex B of ISO 13528:2015

No. of Bottle	pH		\bar{x}_t	w_t	$w_t^2 \times 10^{-6}$	\bar{x}	$(\bar{x}_t - \bar{x})^2 \times 10^{-7}$	$s_x \times 10^{-3}$	$s_w \times 10^{-3}$	$s_s^2 \times 10^{-6}$
	Meas. 1	Meas. 2								
1	9.188	9.185	9.187	0.003	9.0		1.22			
13	9.192	9.185	9.189	0.007	49.0		55.2			
25	9.187	9.185	9.186	0.002	4.0		0.225			
37	9.187	9.187	9.187	0.000	0.0		7.22			
49	9.187	9.184	9.186	0.003	9.0		4.23			
61	9.189	9.185	9.187	0.004	1.6	9.186	7.22	1.13	2.31	-1.39
73	9.185	9.184	9.185	0.001	1.0		27.2			
85	9.187	9.184	9.186	0.003	9.0		4.23			
97	9.185	9.186	9.186	0.001	1.0		4.23			
109	9.184	9.187	9.186	0.003	9.0		4.23			

Stability testing

Stability testing is another criterion for obtaining good and suitable PT samples. The stability defines the ability of a reference material, when kept under a certain conditions, to preserve a pointed property value within specified limits and period of time [16]. There are two types of stability tests for PT samples. Firstly, stability testing at elevated temperature was performed to elucidate whether any degradation is occurred during transport. This testing is usually conducted within a short time period, typically not longer than 4 weeks. In this case, the stability was monitored for sample transportation purposes and it was checked for samples stored for 4 weeks at 40 °C. From data presented in Table 4, it can be seen that PT samples of borax buffer solution have fulfilled the criteria of stability testing according to ISO 13528:2015 and eq. (8). It means that the PT item of borax buffer solution is stable at 40 °C for 4 weeks.

Table 4. Stability monitoring data for PT sample at 40°C

Week	pH			$ \bar{y}_1 - \bar{y}_2 $, where $\bar{y}_1 = 9.186$	Criteria ISO 13528:2015 $ \bar{y}_1 - \bar{y}_2 \leq 0.3\sigma_{pt}$ Where $\sigma_{pt} = 0.03$, so: $ \bar{y}_1 - \bar{y}_2 \leq 0.9$
	Measurement 1	Measurement 2	Average (\bar{y}_2)		
2	9.186	9.185	9.186	0	OK
3	9.183	9.186	9.185	0.001	OK
4	9.181	9.181	9.181	0.005	OK

Secondly, the stability testing of PT samples was conducted during the PT scheme. It is a time period in which the PT participants should perform their analyses in order to assure that the pH value of PT sample will not change during the measurement at the participant’s laboratory. The criteria for the stability monitoring were already discussed above together with eq. (8), while the results are tabulated in Table 5. From Table 5, it can be observed that PT samples met the stability

testing criteria according to ISO 13528:2015, indicating that PT samples were stable during the PT scheme.

Table 5. Data for the stability monitoring of the 2016 PT sample

No. of Bottle	pH			$ \bar{y}_1 - \bar{y}_2 $, where $\bar{y}_1 = 9.186$	Criteria ISO 13528:2015 $ \bar{y}_1 - \bar{y}_2 \leq 0.3\sigma_{pt}$ Where $\sigma_{pt} = 0.03$, so: $ \bar{y}_1 - \bar{y}_2 \leq 0.9$
	Measurement 1	Measurement 2	Average (\bar{y}_2)		
38	9.181	9.179	9.180	0.006	OK
64	9.182	9.179	9.181	0.005	OK
115	9.179	9.179	9.179	0.007	OK

Application

The PT program for the pH measurement was successfully conducted. After the PT samples met the criteria for homogeneity and stability monitoring for transportation, the PT samples were distributed to each participant by dispatching using a courier in the same day. The participants were asked for checking the physical conditions of the PT sample. The MiC Lab-LIPI as the PT provider assured that the samples were received in good conditions. Participants were requested to conduct the pH measurement for the given PT sample by using their routine method. One month is given time for the participants to conduct their measurements and to report their results. There were 50 laboratories who participated in the PT scheme. All PT results were statistically assessed through the statistical evaluation. The performance score was typically derived by comparing the difference between the values of participants and assigned value together with standard deviation [12].

The assigned value of PT sample was determined by the differential potentiometric cell at 25 °C, using a secondary method of pH measurement. The pH measurement was traceable to SRM® 187e and the assigned value of this scheme was obtained from the average of pH value that was 9.186. All submitted data from the participants were then analysed by using the software analytical-quality-assurance for interlaboratory studies, PROLAB Plus. In order to avoid wrong data input, all data were imported automatically by using the RingDat.exe application as a part of the reporting procedure used in Prolab software. The performance of the participant laboratory was assessed by comparing the submitted results against assigned value using the z-score method. The z-score (z_i) of each participant result was calculated using eq. (9).

$$z_i = (x_i - x_{pt}) / \sigma_{pt} \tag{9}$$

In eq. (9), x_i is the submitted result by individual participant, x_{pt} is the assigned value of the test material, σ_{pt} is the standard deviation for proficiency assessment (the value of this scheme was 0.03). The interpretation of z-score is as follows:

- a) A result that gives $|z\text{-score}| \leq 2.00$ is considered to be satisfactory, given by symbol “OK”.
- b) A result that gives $2.00 < |z\text{-score}| < 3.00$ is considered to be questionable, given by symbol “\$”.
- c) A result that gives $|z\text{-score}| \geq 3.00$ is considered to be unsatisfactory, given by symbol “\$\$”.

The z-score results for 50 participants presented in Figure 2 can be summarized as follows: 22 laboratories (44 %) achieved the satisfactory result, 19 laboratories (38 %) reported the unsatisfactory result, while 9 laboratories (18 %) predicated the questionable result. Taking this z-score result into consideration, one can notice that pH measurements conducted in some participant laboratories are still needed to be improved. In addition, investigation regarding the possible mistake sources are essential to be performed.

Ring Test: ALS16, TBS16, LBB16, PKM16
 Method: ISO 13528
 Sample: Tetraborate Buffer (LBB16)
 Measurand: pH
 No. of Laboratories: 50

Assigned value: 9.186 (Reference value)
 Mean: 9.134
 Target s.d.: 0.03 (Reference value)
 Rel. target s.d.: 0.33% (Reference value)
 Range of tolerance: 9.126 – 9.246 ($|Z\text{-Score}| \leq 2.00$)

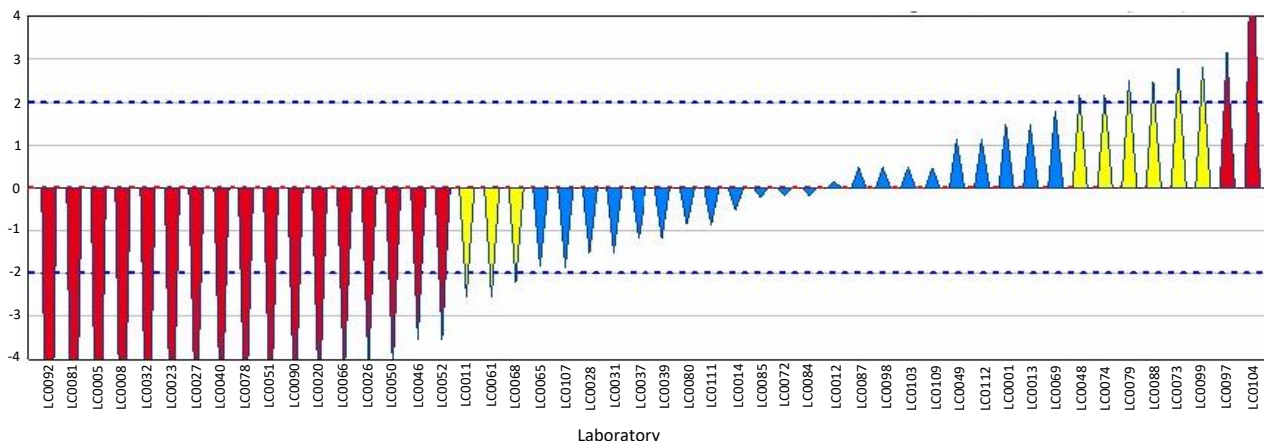


Figure 2. Plot of z-score of participants results of pH measurement

Conclusions

The prepared PT samples (borax buffer solution) have fulfilled the criteria for homogeneity and stability according to ISO 13528:2015. The homogenous and stable PT samples were distributed to the participant laboratories for the PT 2016 program. The results of evaluation regarding to each participant's laboratory performance showed that 44 % of participant laboratories achieve the satisfactory result, 38 % of participant laboratories achieve the unsatisfactory result and 18 % of participant laboratories achieve the questionable result. These results imply that pH measurements conducted in these laboratories are still needed to be improved. It is also required to investigate the possible source of mistakes.

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