

Development of metrology for pH measurement in Thailand

Bunthoon Laongsri · Cheerapa Boonyakong ·
Nongluck Tangpaisarnkul · Chainarong Cherdchu

Received: 2 June 2006 / Accepted: 20 September 2006
© Springer-Verlag 2006

Abstract It has not been long that metrology is well accepted as an important part in analytical chemistry since it helps the chemists to receive the best measurement and accurate results with traceability. The National Institute of Metrology Thailand (NIMT), which is a public agency under the supervision of the Ministry of Science and Technology, not only focuses on physical standards but also provides and maintains standards in chemical field. pH measurement is one of the most widely used in the laboratories including industries and medical area in Thailand. The chemical laboratory starts working on the project with the objective of disseminating an accurate result in routine pH measurement. In 2002, the laboratory provided a service in calibration of pH meter and organized the first local interlaboratory comparison program (NIMT-C-ILC-1: pH buffer) in pH measurement. There were three buffer solution samples in the range of acid, neutral, and base. A total of 44 laboratories participated in this program. The NIMT chemical laboratory also participated in the proficiency testing program that was conducted by PSB Corporation Testing Group in Singapore. In 2003, NIMT started research in preparation of secondary buffers by using highly accurate pH meters with glass electrode systems. The laboratory produced three secondary buffers, which were pH 4.01, 6.86, and 9.18 with uncertainty 0.020 pH at 25°C. The competence of the laboratory was shown by the measurement results of the pilot study (APMP.QM-P06), which was organized by the APMP electrochemical analysis working group (EAWG/TCQM)

in 2005. The title of this study was “pH determination of two phosphate buffers by Harned cell method and glass electrode method”. NIMT aims to achieve for establishment of the primary method for pH measurement in the near future.

Keywords pH measurement · Interlaboratory · Buffer · pH

Introduction

The determination of pH is one of the most common processes in chemical measurements. The major use of pH in industry is process control. Controlling pH helps ensure product quality, reduces corrosion in plant equipment, and protects the environment by helping wastewater dischargers meet regulatory limits. Many national metrology institutes try to disseminate the accurate pH measurement results in order to achieve the metrological quality.

By notional definition, pH is defined as the relative activity of hydrogen ions in solution [1]:

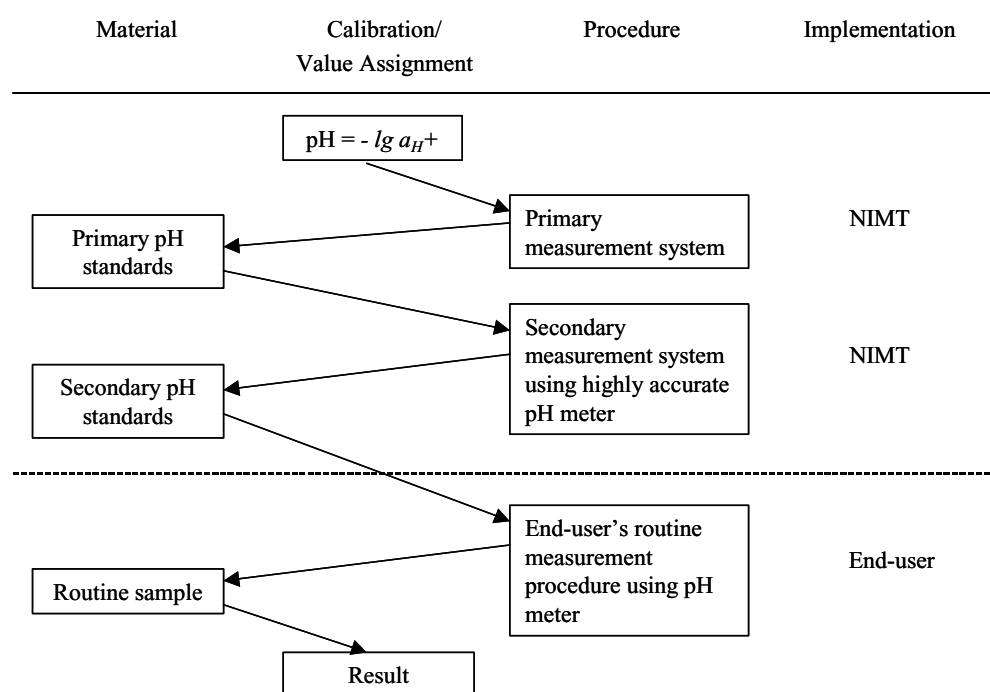
$$\text{pH} = -\lg a_{\text{H}^+} = -\lg (m_{\text{H}} \gamma_{\text{H}} / m^0) \quad (1)$$

where a_{H^+} is the relative activity and γ_{H} is the molal activity coefficient of the hydrogen ion H^+ at the molality m_{H} , and m^0 is the standard molality. The primary measurement procedure for pH is based on the measurement of the potential difference between a platinum hydrogen electrode and a silver/silver chloride reference electrode of an electrochemical cell filled with a selected buffer solution, often called the Harned cell and now recommended by IUPAC.

Presented at – ‘BERM-10’ – April 2006, Charleston, SC, USA

B. Laongsri (✉) · C. Boonyakong · N. Tangpaisarnkul ·
C. Cherdchu

Chemical Laboratory, National Institute of Metrology Thailand,
3/4-5 Moo 3, Klong 5, Klongluang, Pathumthani, 12120 Thailand
e-mail: bunthoon@nimt.or.th

Fig. 1 Calibration hierarchy in pH measurement

The need for traceable pH measurements increases for quality assurance in laboratories [2]. The National Institute of Metrology Thailand (NIMT) begins approaching to the traceability of pH measurement within the Thai metrological infrastructure as shown in Fig. 1.

Method for pH measurement development in Thailand

During 2001–2002, the National Institute of Metrology Thailand (NIMT) provided a service of pH meter calibration and organized local interlaboratory comparison program (NIMT–C-ILC-1: pH buffer) [3] in pH measurement. Distribution of the samples commenced in September 2001 and the final report was completed in May 2002. A total of 44 laboratories, which were from both governmental and private sectors, participated in this program. For confidentiality, each participating laboratory was assigned a laboratory code number that was used in the report. Each laboratory was supplied with three buffer solution samples of approximately 50 mL, the protocol for NIMT-C-ILC-1, and the measurement results sheet. The sample details are shown as follows:

Participating laboratories were asked to measure the samples according to their laboratory's own procedure or the procedure that is briefly shown in protocol based on ASTM D1293-95 [4]. They reported their test results, the details of pH meters and electrodes used, standard buffers and environmental conditions in the measurement results sheet. The results were evaluated and reported as abso-

lute differences according to the ISO/IEC Guide 43-1: 1996 [5], i.e.,

$$\frac{|x - X|}{X} \times 100 \quad (2)$$

where, x , the participant's result; X , the assigned value.

The assigned value with uncertainty for each buffer solution is the mean value of the measurements carried out by NIMT chemical metrology department. NIMT B001, NIMT B002 and NIMT B003 have a pH value of 4.008, 6.877, and 9.182 with expanded uncertainty ($k = 2$) of $\text{pH} = 0.010$. Typical results are presented in Table 2 and Figs. 2–4.

The laboratory also participated in a proficiency-testing program on pH measurement that was organized by PSB Corporation Testing Group. The primary aim of the program is to promote quality in pH measurement. The program was divided into two rounds and commenced in July 2002 and in January 2003. A total of ten laboratories participated in the program. Participating laboratories were supplied with two samples of which the pH ranges were between 3.00 and 8.00. NIMT chemical laboratory's results were satisfied well in both rounds [6, 7].

Table 1 Sample identification of NIMT-C-ILC-1

Sample identification	Type
NIMT B001	pH buffer (acidic range)
NIMT B002	pH buffer (neutral range)
NIMT B003	pH buffer (basic range)

Table 2 Summary of results

Sample	Statistical parameters	Before removing extreme results	After removing extreme results
NIMT B001	Number of labs	44	38
	Mean	3.978	4.000
	Standard deviation	0.146	0.046
	Minimum	3.570	3.840
	Maximum	4.460	4.100
	Range	0.890	0.260
NIMT B002	Number of labs	44	41
	Mean	6.893	6.879
	Standard deviation	0.099	0.032
	Minimum	6.760	6.800
	Maximum	7.470	6.940
	Range	0.710	0.140
NIMT B003	Number of labs	44	36
	Mean	9.139	9.159
	Standard deviation	0.173	0.085
	Minimum	8.560	8.970
	Maximum	9.680	9.300
	Range	1.120	0.330

In 2003, NIMT started research into preparation of secondary buffers by using a highly accurate pH meter with a glass electrode system, which is shown in Fig. 5.

According to IUPAC recommendations 2002, this method cannot be considered as a primary method for measuring pH. The buffers, whose pH value is assigned by comparison with primary buffers, called secondary buffers. The cell reaction involves a glass electrode and silver-silver chloride reference electrode comparing with two standard buffers. The electrochemical cell of pH glass electrode, which is in the form of single probes or combination electrodes, is shown below.

reference electrode $[\text{KCl}(c \geq 3.5 \text{ mol dm}^{-3}) \parallel \text{solution} [\text{pH}(S)$
or $\text{pH}(X)] \mid \text{glass electrode}$ (3)

where, $\text{pH}(S)$, standard buffers; $\text{pH}(X)$, prepared sample

An NIMT glass electrode was calibrated by two-point calibration or bracketing procedure using two standard buffers come from National Institute of Standards and Technology (NIST) with pH values $\text{pH}(S_1)$ and $\text{pH}(S_2)$. The pH value of prepared sample is obtained from Eq. (4).

$$\text{pH}(X) = \text{pH}(S_1) - [E_V(X) - E_V(S_1)]/k' \quad (4)$$

and the practical slope factor k' is given by

$$k' = [E_V(S_1) - E_V(S_2)]/[\text{pH}(S_2) - \text{pH}(S_1)] \quad (5)$$

where, $E_V(X)$, is the measured potential difference of prepared sample; $E_V(S_1)$, is the measured potential difference of standard buffer 1; $E_V(S_2)$, is the measured potential difference of standard buffer 2.

The laboratory produced three secondary pH standards that were pH 4.01, 6.86, and 9.18 with expanded uncertainty

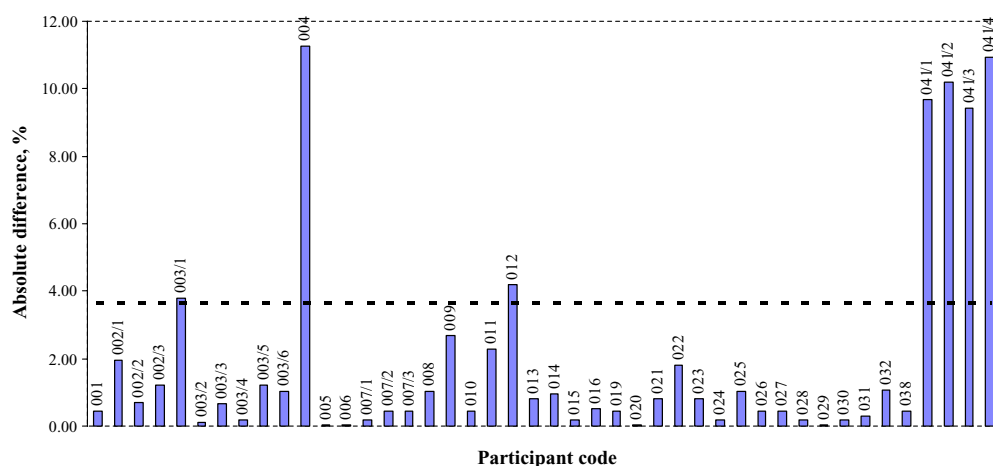
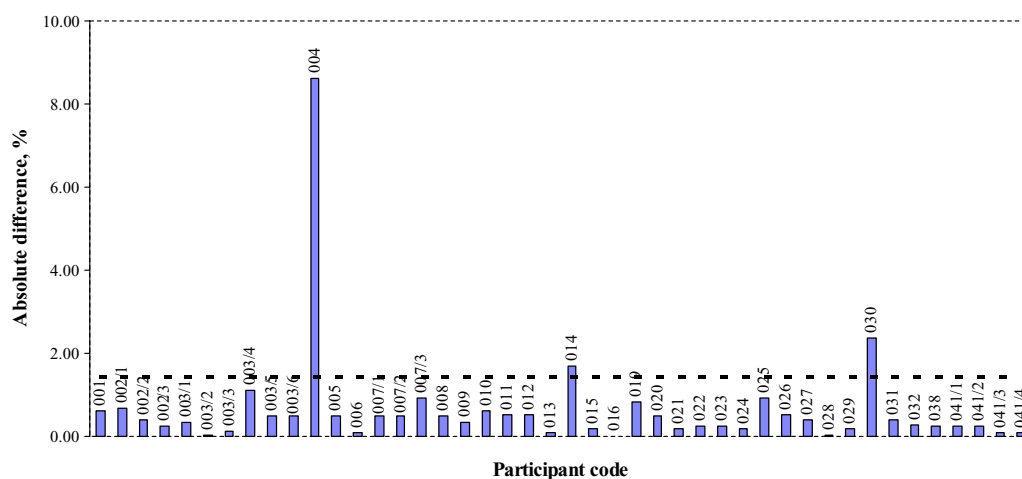
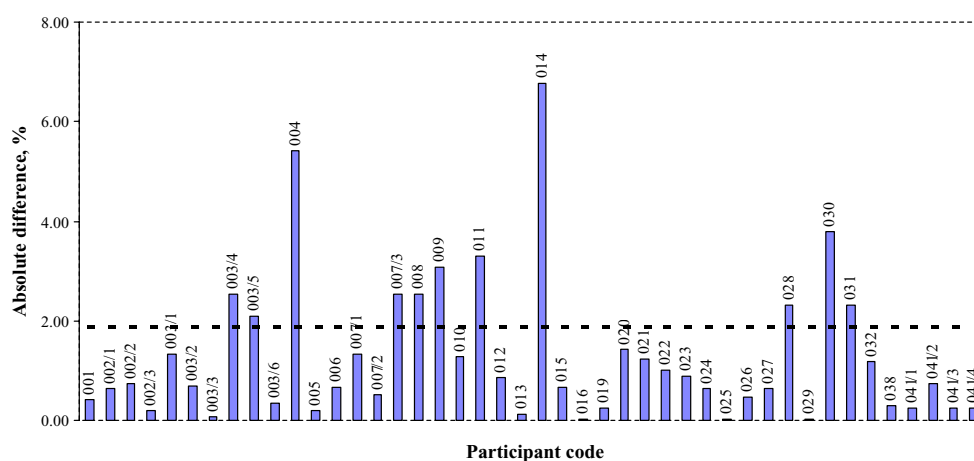
Fig. 2 pH difference from assigned value (NIMT B001)

Fig. 3 pH difference from assigned value (NIMT B002)**Fig. 4** pH difference from assigned value (NIMT B003)**Fig. 5** Highly accurate pH meter

($k = 2$) $pH = 0.02$ at 25°C as outlined in more detail in the Appendix. The standard operating procedure for preparation of NIMT pH standard was performed following the National Bureau of Standards (NBS) Special Publication 260-53 [8]. Some details of these standards are shown in Table 3.

Table 3 NIMT secondary pH standards prepared by glass electrode system

Part no.	Description	pH value	Expanded uncertainty ($k = 2$)
NIMT 0001/01	Phthalate pH standard	4.01	0.02
NIMT 0001/02	Phosphate pH standard	6.86	0.02
NIMT 0001/03	Tetraborate pH standard	9.18	0.02

Figure 6 shows the stability test of secondary pH standards. The mean pH values were measured by using a highly accurate pH meter system and the tests were carried out for 6 months. The standard deviations of pH value for phthalate buffer, phosphate buffer and tetraborate buffer are 0.00347, 0.00492, and 0.00585, respectively. The expanded uncertainties, U ($k = 2$) for each pH measurement are calculated following both IUPAC recommendations and the “Guide to the expression of uncertainty in measurement” (GUM) [1, 9, 10]. The uncertainty values are reported in the error bars and the process of uncertainty estimation is explained in the Appendix.

During 2004-05, NTMT participated in regional interlaboratory comparison in pH measurement, which is the first study in Asia Pacific Metrology Program (APMP). This

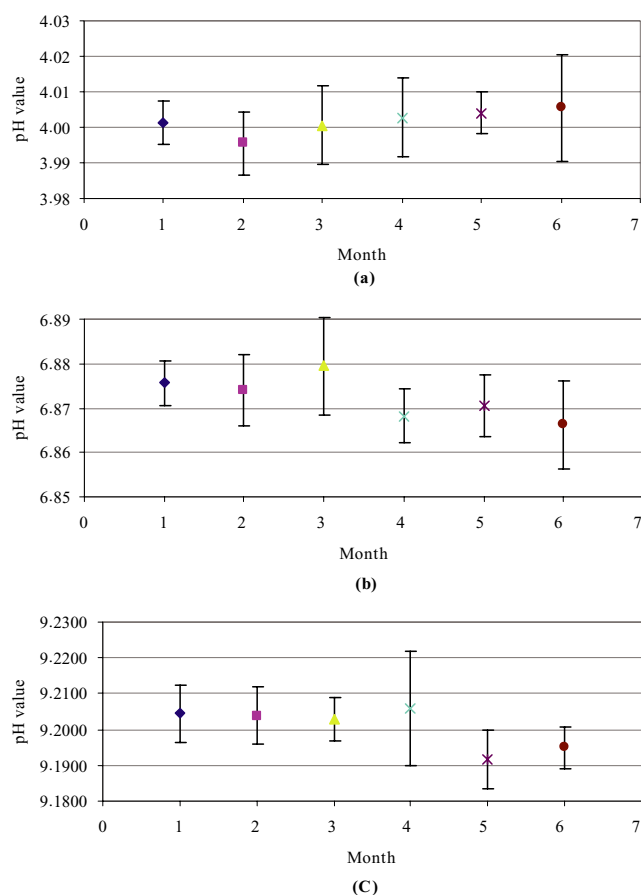


Fig. 6 Stability test of secondary pH standards (the results are reported with expanded uncertainty, $k = 2$): (a) Phthalate buffer, (b) Phosphate buffer, (c) Tetraborate buffer

study, APMP.QM-P06, was organized by the APMP electrochemical analysis working group (EAWG/TCQM) and was piloted by the National Metrology Institute of Japan (NMIJ) [11]. The title was “pH determination of two phosphate buffers by Harned cell method and/or glass electrode method”. The purpose of this comparison was to assess the degree of equivalence of national standard measurement procedures for the determination of the pH values. Two phosphate buffer samples, both containing potassium dihydrogen phosphate (KH_2PO_4) and disodium hydrogen phosphate (Na_2HPO_4) in different molalities were chosen as transfer standards. There is one known sample that is $0.025 \text{ mol} \cdot \text{kg}^{-1}$ of KH_2PO_4 mixed with $0.025 \text{ mol} \cdot \text{kg}^{-1}$ of Na_2HPO_4 and one unknown sample. NIMT chemical laboratory only measured the pH value by using glass electrode method and Fig. 7 shows the degree of equivalence of the measurement results at 25°C .

In early 2006, NIMT also participated in APMP QM. P-09. This pilot study was focused on the determination of phthalate buffer by using the Harned cell method and/or glass electrode method.

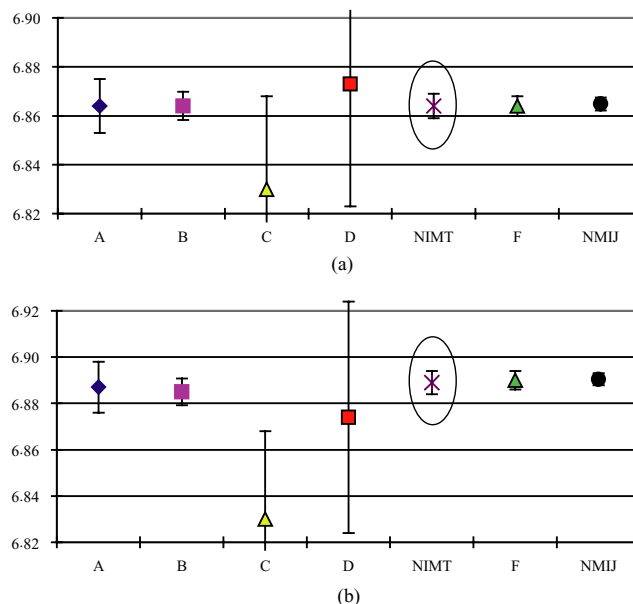


Fig. 7 Results of pH measurement with expanded uncertainties, $k = 2$ at 25°C : a Sample 1; b Sample 2 (unknown)

Conclusions

The NIMT chemical laboratory is in the beginning stage of metrological approach in pH measurement. For the mutual recognition agreement, it is necessary to demonstrate the competence of the laboratory by participating both regional and global interlaboratory comparison. The development of a primary method is a very important task to approach metrology in pH. In the next 1–2 years, NIMT is certain to complete and to establish a traceability chain for pH measurement within Thailand.

Acknowledgements The authors are very grateful to Flt. Lt. Bunjob Suktat, former deputy director of NIMT, who approved the first local interlaboratory comparison (NIMT–C-ILC-1: pH buffer) in pH measurement.

Appendix

Estimation of pH measurement uncertainty

Below is an example of the estimation of the measurement uncertainty for prepared secondary pH standards by using a highly accurate pH meter. The procedure follows a two-point calibration (bracketing procedure) referred to as pH glass electrode. The equipment and pH standards of this system are listed below:

- Highly accurate pH meter (resolution 0.0001 pH and 0.01 mV)

- Sample flow system
- Combined pH glass electrode
- Water bath
- Data control
- NIST's pH standards (Phthalate, Phosphate, Tetraborate)

Example

The equation to calculate the pH value of phthalate buffer is shown by (A.1).

$$\text{pH}(X) = \text{pH}(S_1) - \frac{(E_V(X) - E_V(S_1))}{k'} \quad (\text{A.1})$$

The practical slope factor k' is given by (A.2).

$$k' = \frac{E_V(S_2) - E_V(S_1)}{\text{pH}(S_1) - \text{pH}(S_2)} \quad (\text{A.2})$$

where $\text{pH}(S_1)$, standard pH1; $\text{pH}(S_2)$, standard pH2; $\text{pH}(X)$, prepared buffer; $E_V(X)$, the measured potential difference of prepared buffer; $E_V(S_1)$, the measured potential difference of standard pH1; $E_V(S_2)$, the measured potential difference of standard pH2

Description and quantification of the uncertainty components

The standard uncertainties of $\text{pH}(S_1)$ and $\text{pH}(S_2)$ are associated with the standard pH1 and pH2. In this case, pH1 is 4.01, pH2 is 6.86, and the expanded uncertainty, U , is given in the certificate. The standard uncertainties of $\text{pH}(S_1)$ and $\text{pH}(S_2)$ are expressed as follows:

$$u(\text{pH}(S_1)) = \frac{U(\text{pH}(S_1))}{2} = \frac{0.005}{2} = 0.0025$$

$$u(\text{pH}(S_2)) = \frac{U(\text{pH}(S_2))}{2} = \frac{0.005}{2} = 0.0025$$

The standard uncertainties $u(E_V(S_1))$ and $u(E_V(S_2))$ include contributions from the effect below

- The resolution of the meter (res): rectangular distributions are assumed.
- The liquid junction potential (lj): It is recommended for calibration should be stated for every type of pH electrodes by the producer.
- Repeatability (rep): the calibration cycle is repeated N times the uncertainty due to the repeatability, $u(rep)$, can

be estimated by (A.3)

$$u(rep) = \sqrt{\frac{\sum_{i=1}^N (E_V(S_1)_i - \bar{E}(S_1))^2 + \sum_{i=1}^N (E_V(S_2)_i - \bar{E}(S_2))^2}{2(N-1)}}, \quad i = 1, \dots, N \quad (\text{A.3})$$

where; $\bar{E}(S_1)$, is the mean pH value of measured potential difference of standard pH1; $\bar{E}(S_2)$, is the mean pH value of measured potential difference of standard pH2.

The combined standard uncertainty of $u(E_V(S_1))$ and $u(E_V(S_2))$ is shown in (A.4)

$$\begin{aligned} u(E(S)) &= \sqrt{u(E_{lj})^2 + u(E_{res})^2 + u(rep)^2} \\ u(E_V(S_1)) &= 0.003 \\ u(E_V(S_2)) &= 0.003 \end{aligned} \quad (\text{A.4})$$

The standard uncertainty of measured potential in the sample $u(E_V(X))$ includes the repeated measurement for K times as shown in (A.5)

$$u(rep) = \sqrt{\frac{\sum_{k=1}^K (E_V(X)_k - \bar{E}(X))^2}{(K-1)}}, \quad k = 1, \dots, K \quad (\text{A.5})$$

where, $\bar{E}_V(X)$, is the mean pH value of measured potential difference of prepared buffer.

The combined standard uncertainty of $u(E_V(X))$ is given in (A.6)

$$\begin{aligned} u(E_V(X)) &= \sqrt{u(E_{lj})^2 + u(E_{res})^2 + u(rep, X)^2} \\ u(E_V(X)) &= 0.413 \end{aligned} \quad (\text{A.6})$$

The combined standard uncertainty of phthalate buffer, $u_c(\text{pH}(X))$, is equal to the positive square root of the combined variance computed from the standard uncertainties of all components as described above multiplied by the sensitivity coefficient c_i associated with it. For the sensitivity coefficient, Eqs. (A.1) and (A.2) are arranged to be calculated as in (A.7).

$$\begin{aligned} \text{pH}(X) &= \text{pH}(S_1) + (\text{pH}(S_1) \\ &\quad - \text{pH}(S_2)) \cdot \frac{(E_V(X) - E_V(S_1))}{(E_V(S_2) - E_V(S_1))} \end{aligned} \quad (\text{A.7})$$

Sensitivity coefficients of phthalate buffer are

$$\frac{\partial \text{pH}(X)}{\partial \text{pH}(S_1)} = 1 - \frac{(E_V(X) - E_V(S_1))}{(E_V(S_2) - E_V(S_1))} = -0.006$$

$$\frac{\partial \text{pH}(X)}{\partial \text{pH}(S_2)} = \frac{(E_V(X) - E_V(S_1))}{(E_V(S_2) - E_V(S_1))} = 1.006$$

$$\begin{aligned} \frac{\partial \text{pH}(X)}{\partial E_V(S_1)} &= \frac{-(\text{pH}(S_2) - \text{pH}(S_1))}{(E_V(S_2) - E_V(S_1))} + (\text{pH}(S_2) \\ &\quad - \text{pH}(S_1)) \cdot \frac{(E_V(X) - E_V(S_1))}{(E_V(S_2) - E_V(S_1))^2} - 0.0001 \end{aligned}$$

$$\begin{aligned} \frac{\partial \text{pH}(X)}{\partial E_V(S_2)} &= -(\text{pH}(S_2) - \text{pH}(S_1)) \cdot \frac{(E_V(X) - E_V(S_1))}{(E_V(S_2) - E_V(S_1))^2} \\ &= 0.0172 \end{aligned}$$

$$\frac{\partial \text{pH}(X)}{\partial E_V(X)} = \frac{(\text{pH}(S_2) - \text{pH}(S_1))}{(E_V(S_2) - E_V(S_1))} = -0.0171$$

The combined standard uncertainty of phthalate buffer, $u_c(\text{pH}(X))$, is given in (A.8).

$$\begin{aligned} u_c^2(\text{pH}(X)) &= \left[\left(\frac{\partial \text{pH}(X)}{\partial \text{pH}(S_1)} \right)^2 \cdot (u(\text{pH}(S_1)))^2 \right] \\ &\quad + \left[\left(\frac{\partial \text{pH}(X)}{\partial \text{pH}(S_2)} \right)^2 \cdot (u(\text{pH}(S_2)))^2 \right] \\ &\quad + \left[\left(\frac{\partial \text{pH}(X)}{\partial E_V(S_1)} \right)^2 \cdot (u(E_V(S_1)))^2 \right] \\ &\quad + \left[\left(\frac{\partial \text{pH}(X)}{\partial E_V(S_2)} \right)^2 \cdot (u(E_V(S_2)))^2 \right] \\ &\quad + \left[\left(\frac{\partial \text{pH}(X)}{\partial E_V(X)} \right)^2 \cdot (u(E_V(X)))^2 \right] \end{aligned}$$

$$u_c(\text{pH}(X)) = 0.0075 \quad (\text{A.8})$$

The expanded uncertainty is based on a combined standard uncertainty multiplied by a coverage factor $k = 2$, providing a level of confidence of approximately 95%.

$$U(\text{pH}(X)) = k \cdot u_c(\text{pH}(X)) = 2 \cdot u_c(\text{pH}(X)) = 0.015$$

At NIMT, an electrode calibration with two-point calibration procedure is used and the reported uncertainty is quoted as the target expanded uncertainty $\text{pH} = 0.02$. This is because the laboratory also used the other standard pHs with difference uncertainty. The uncertainties of standard pHs contribute to the strong influence on the expanded uncertainty $U(\text{pH}(X))$.

References

1. Buck RP, Rondinini S, Baucke FGK, Camoes MF, Covington AK, Milton MJT, Mussini T, Naumann R, Brett CMA, Pratt KW, Spitzer P, Wilson GS (2002) *Pure Appl Chem* 74:2169–2200
2. Spitzer P (2001) *Accred Qual Assur* 6:55–60
3. Department of Chemical Metrology, National Institute of Metrology (Thailand), Report of interlaboratory comparison (2002) NIMT-C-ILC-1: pH BUFFER
4. American Society for Testing and Materials (1995) ASTM D 1293:1995 Standard Test Method for pH of water
5. International Organization for Standardization (1997) ISO Guide 43–1:1996 International Standard, Proficiency testing by interlaboratory comparison – Part 1: Development and operation of proficiency testing schemes
6. PSB Corporation, Report of proficiency testing programme on pH measurement (2002) Round 1
7. PSB Corporation, Report of proficiency testing programme on pH measurement (2003) Round 2
8. Richard A, Durst, Standard Reference Materials: Standardization of pH Measurements (1988) National Bureau of Standards Special Publication 260-53
9. Leito I, Strauss L, Koort E, Pihl V (2002) *Accred Qual Assur* 7:242–249
10. International Organization for Standardization (1993) Guide to the expression of uncertainty in measurement. BIPM IEC IFCC ISO IUPAC IUPAP OIML, ISO, Geneva, Switzerland
11. Nakamura S, Mei-Fung Kong, Siu-Kay Wong, Shikakume K, Hanaoka Y, Maksimov I, Oohata M, Subedi S, Shailesh KJ, Chua-suwan A, Laongsri B, Chinh NT (2005) Report of APMP-QM-P06