CCQM WG on Electrochemical Analysis and Classical Chemical Methods

CCQM-K99.1 - pH measurement of phosphate buffer solutions

Final report

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02 December 2025

Summary

The CCQM key comparison CCQM-K99.1 is a subsequent comparison to CCQM-K99. It aims to demonstrate the capability of Korean Research Institute of Standards and Science (KRISS) to measure the pH of phosphate buffer solutions. The result of Physikalisch-Technische Bundesanstalt (PTB) was used as a link to the original comparison CCQM-K99.

In this comparison, a measurement method is restricted to the use of the primary method of pH (Harned cell method). Measurements of pH were performed at 15 °C, 25 °C, and 37 °C. The results from KRISS were in good agreement with the reference value, providing evidence to support the respective CMC claims.

Table of Contents

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2 List of Participants

Table 1. List of participants.

Institute	Acronym	Country	Contact person	Email
Korea Research Institute of Standards and Science	KRISS	Korea	Min-Ah Oh	minah.oh@kriss.re.kr
Physikalisch-Technische Bundesanstalt	PTB	Germany	Frank Bastkowski	Frank.Bastkowski@ptb.de

3 Time Schedule

Invitation	April 2025
Registration Deadline	30 April 2025
Sample Preparation	April and May 2025
Sample Shipment	May 2025
Reporting Deadline	11 July 2025
Draft A	September 2025
Draft B report	December 2025

4 Description of Samples

The solutions used for the comparison have been produced by PTB. A phosphate buffer solution with a nominal pH value of approximately 7 at 25 °C has been prepared from deionized water, potassium dihydrogen phosphate, and disodium hydrogen phosphate. The solution has been homogenized, filled in 1 L high-density polyethylene (HDPE) bottles, and closed with screw cap and Parafilm.
Bottle labels indicate “CCQM-K99.1”, “phosphate buffer”, the nominal pH value, the filling date, and the bottle number. 15 bottles were prepared, and 12 bottles were sent to KRISS excluding 3 bottles for PTB. The bottles have been prepared on 7 May 2025 and arrived at KRISS on 19 May 2025.

4.1 Homogeneity

Three bottles were selected for homogeneity testing: the first (bottle #1), the middle (bottle #9), and the last (bottle #15) in the bottling sequence. The primary pH measurement method was used. The standard deviation of the measured values was 0.0009, which is smaller than the typical measurement uncertainty. Since aqueous electrolyte solution can be assumed sufficiently homogeneous within-bottle, the within-bottle homogeneity has not been measured. Verification of the between-bottle homogeneity is sufficient for this comparison. The results of the individual measurements are shown in Table 2.

Table 2. Results of homogeneity evaluation.

Bottle #	Date of measurement	Temperature / °C	pa°	Standard uncertainty (u(pa°))
1	21 May 2025	25	7.2944	0.0012
9	22 May 2025	25	7.2930	0.0016
15	23 May 2025	25	7.2947	0.0018

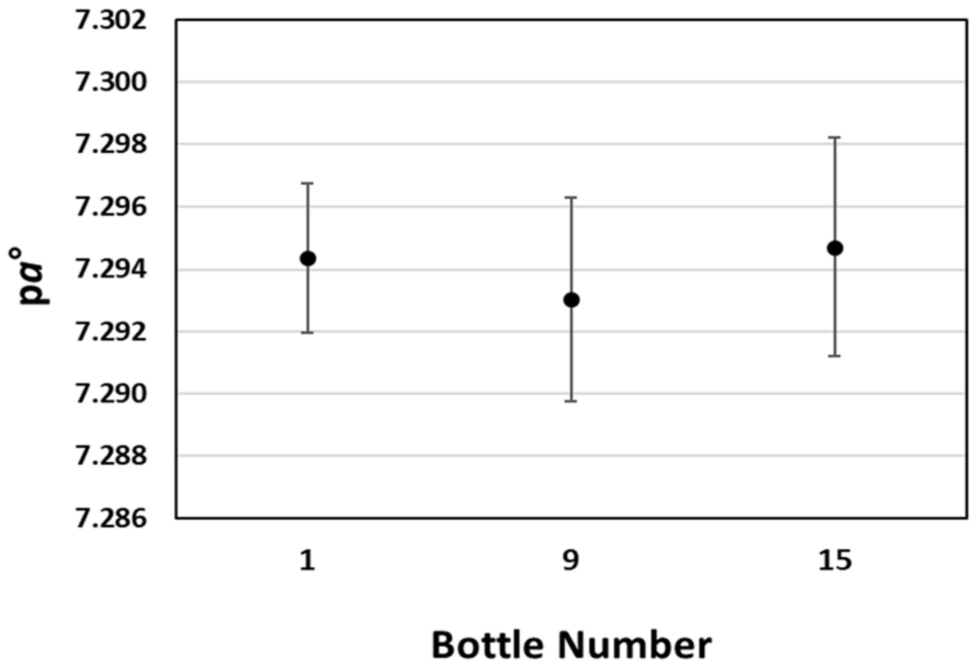

Figure 1. Results of pa° from the homogeneity evaluation with expanded uncertainties (k = 2).

4.2 Stability

Ten bottles were measured to verify stability of the samples. The stability assessment was carried out over the entire duration of the comparison measurement period using primary pH measurement method. The results are given in Table 3.

Table 3. Results of the stability evaluation.

Bottle #	Date of measurement	15 °C		25 °C		37 °C	
		p*a*°	***u*(p*a*°)**	**p*a*°**	***u*(p*a*°)**	**p*a*°**	***u*(p*a*°)**
1	21 May 2025	7.3263	0.0013	7.2944	0.0012	7.2724	0.0013
9	22 May 2025	7.3257	0.0014	7.2930	0.0016	7.2723	0.0017
15	23 May 2025	7.3270	0.0016	7.2947	0.0018	7.2723	0.0018
3	28 May 2025	7.3265	0.0012	7.2938	0.0013	7.2724	0.0013
6	10 Jun 2025	7.3263	0.0013	7.2935	0.0013	7.2728	0.0013
10	12 Jun 2025	7.3264	0.0014	7.2930	0.0016	7.2730	0.0014
4	11 Jul 2025	7.3257	0.0018	7.2925	0.0016	7.2723	0.0015
8	16 Jul 2025	7.3251	0.0020	7.2921	0.0019	7.2714	0.0017
13	17 Jul 2025	7.3256	0.0019	7.2927	0.0021	7.2722	0.0016
5	14 Aug 2025	7.3266	0.0011	7.2940	0.0012	7.2724	0.0010
Slope (b_1)		− 0.000 006		− 0.000 012		− 0.000 004	
$s(b_1)$		0.000 006		0.000 009		0.000 005	
$\|b_1\| / (t_{0.95,n-2} \times s(b_1))$		0.44		0.60		0.41	

A linear regression line has been fitted through the results according to ISO 33405:2024. The slope of regression line (b_1) and its standard deviation $s(b_1)$ are shown in Table 3 (Formulas are given in the annex). Since

$$|b_1| < t_{0.95,n-2} \times s(b_1) \qquad (1)$$

and the standard deviation of the stability measurements is of the same order of magnitude as the standard deviation of the homogeneity measurements, the samples can be assumed sufficiently stable over the measurement period. n is the number of measurements and $t_{0.95,n-2}$ the corresponding student-*t* factor at a 95 % level of confidence and $n-2$ degrees of freedom.

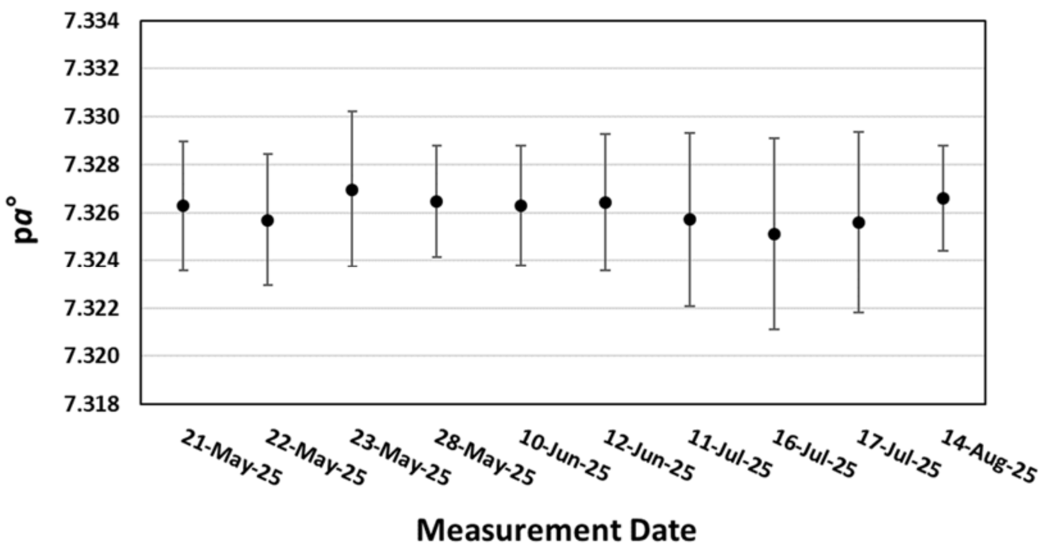

Figure 2. Results of p*a*° at 15 °C from the stability evaluation with expanded uncertainties (*k* = 2).

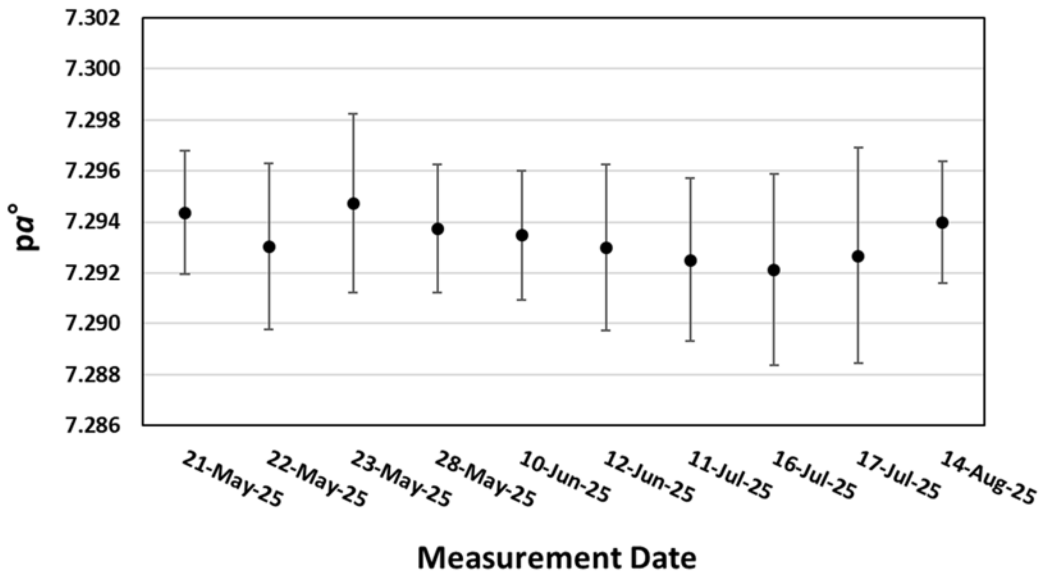

Figure 3. Results of p*a*° at 25 °C from the stability evaluation with expanded uncertainties (*k* = 2).

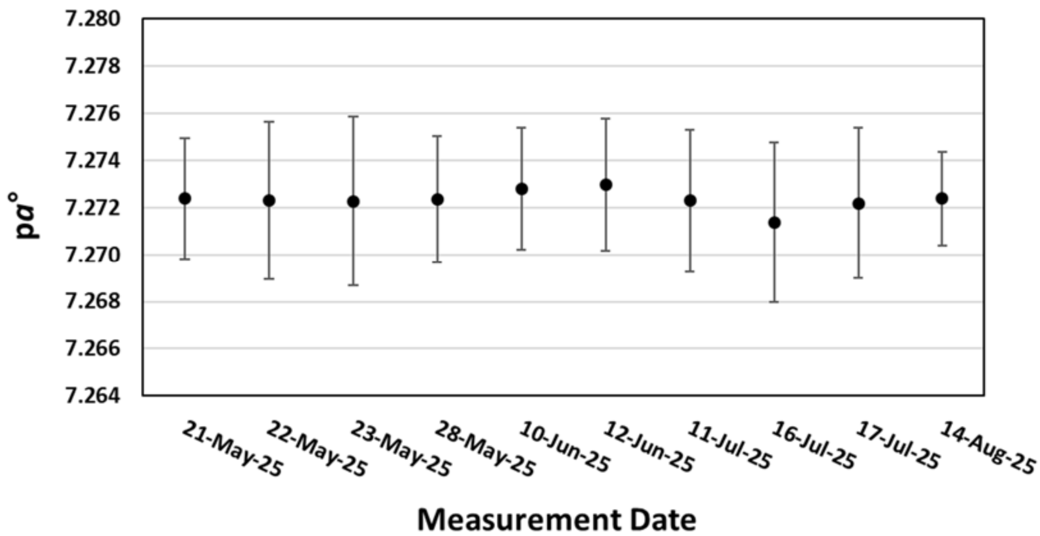

Figure 4. Results of p*a*° at 37 °C from the stability evaluation with expanded uncertainties (*k* = 2).

4.3 Bottle integrity

The packaging material was removed and the bottles were inspected for visible damage or leakage. The bottles were equilibrated in the weighing room overnight. Afterwards, each bottle was weighed using a balance with a resolution of 0.01 g to verify its integrity during shipment without removing Parafilm seal. The weighing results, along with pressure, temperature, and relative humidity at the time of weighing, were recorded in the Weighing-Excel sheet that had been sent to each participant by email in advance. Bottle masses were automatically corrected for air-buoyancy and compared with those measured before shipment. Figure 5 shows the differences between masses measured at KRISS and those measured at PTB. All relative changes are lower than 0.003 %, which are acceptable for key comparisons on pH measurements.

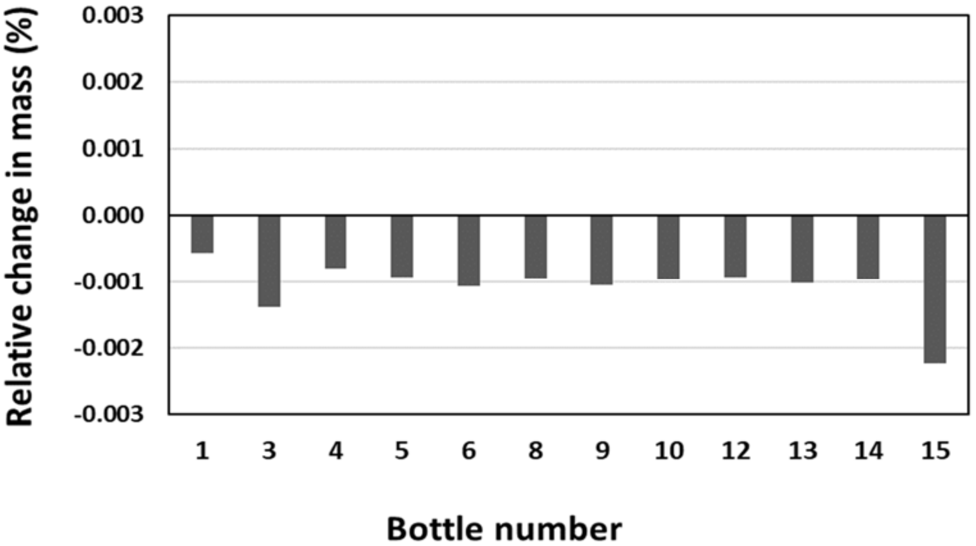

Figure 5. Relative changes in mass on shipping.

5 Correspondence with Institutes

Table 4. Timetable of measurements and submission of reports.

Institute	Bottle Number	Received	Measured	Reported
KRISS	3, 6, 10	19 May 2025	28 May – 13 Jun	04 Jul
PTB	7, 11	-	24 Jun	04 Jul

The samples have been prepared at PTB and evaluated for stability and homogeneity at KRISS. To ensure enough homogeneity of samples, KRISS formally notified PTB upon completion of the homogeneity assessment (26 May 2025). Only after this notification were the reporting measurements conducted at PTB. For integrity of comparison, password-protected files were first exchanged between the institutes. The reporting date was defined as the date on which the protected files were sent. After confirming that both institutes had successfully received the files, the corresponding passwords were then exchanged (07 Jul 2025).

6 Instructions for Measurement

The bottles should be stored at temperatures between 20 °C and 25 °C, however, they were not to be stored above 25 °C. The lids and caps of the bottles were only to be opened immediately before the measurements. If possible, the caps should be re-sealed with Parafilm following each opening.
Each participant had to measure pH of the samples with respect to 15 °C, 25 °C, and 37 °C. It was expected that the highest-level method available at the institute was used.

7 Results

7.1 Reported Results

Table 5 lists the reported results. Figure 6, 7, and 8 show the results graphically.

Table 5. Reported pa° and their standard uncertainties (k = 1).

Institute	15 °C		25 °C		37 °C	
	p*a*°	***u*(p*a*°)**	**p*a*°**	***u*(p*a*°)**	**p*a*°**	***u*(p*a*°)**
KRISS	7.3265	0.0013	7.2936	0.0014	7.2725	0.0014
PTB	7.3271	0.0009	7.2945	0.0009	7.2732	0.0009

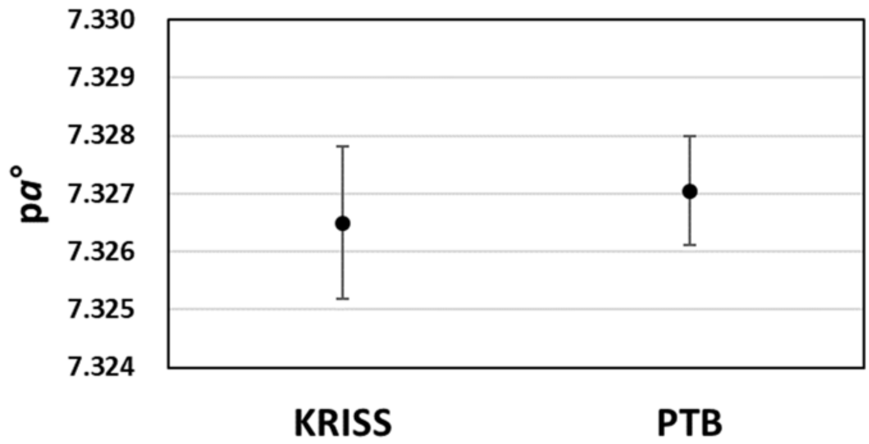

Figure 6. Reported pa^0 results of a buffer solution at 15 °C with standard uncertainties (k = 1).

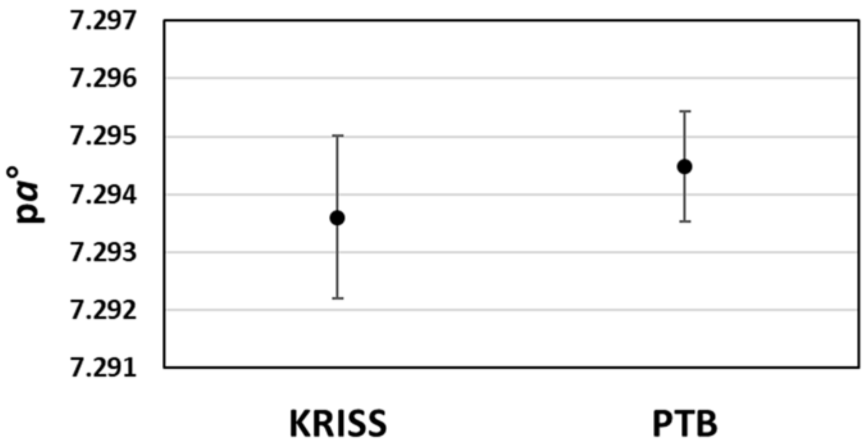

Figure 7. Reported pa^0 results of a buffer solution at 25 °C with standard uncertainties (k = 1).

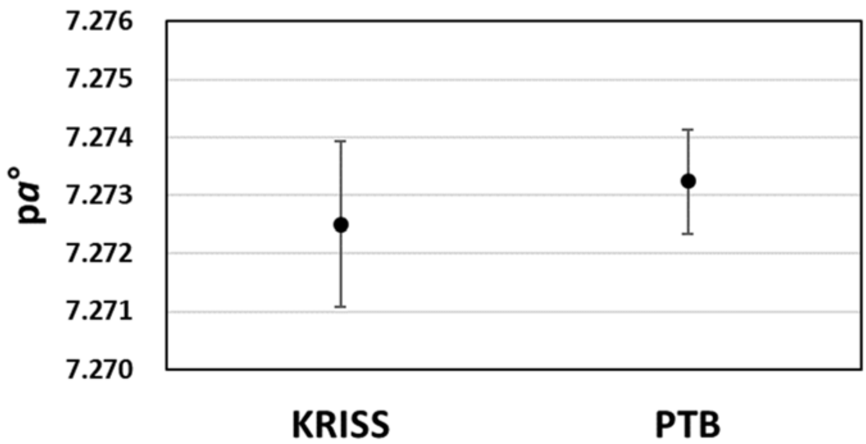

Figure 8. Reported pa^0 results of a buffer solution at 37 °C with standard uncertainties (k = 1).

7.2 Results of Further Analysis or Investigations

The reported results are consistent. No further investigations have been conducted.
Other information reported by the participants is given in Table 6, 7, and 8.

Table 6. HCl molality and method of standardization.

Institute	**HCl molality / mol/kg**	**Standardization technique for HCl**
KRISS	0.01000	Coulometry + gravimetric dilution
PTB	0.0100191	Coulometry

Table 7. Standard potential of the Ag/AgCl electrodes and their standard uncertainty (k = 1) at each temperature.

Institute	15 °C		25 °C		37 °C	
	E^0 / V	$u(E^0)$	E^0 / V	$u(E^0)$	E^0 / V	$u(E^0)$
KRISS	0.228545	0.000044	0.222329	0.000045	0.214123	0.000045
PTB	0.228881	0.000047	0.222683	0.000049	0.214431	0.000048

Table 8. Slope of the regression line of the acidity function at each temperature.

Institute	15 °C	25 °C	37 °C
KRISS	-0.99	-0.95	-0.95
PTB	-1.13	-1.12	-1.09

8 Estimators for the Key Comparison Reference Value (KCRV)

The results were linked to the key comparison reference value of CCQM-K99 through the results of PTB as the linking laboratory.

9 Degrees of Equivalence (DoE) based on the Proposed KCRV

The DoE of participant ($\mathrm{DoE}_{\mathrm{NMI,K99.1}}$) in this comparison was calculated using the results of the linking laboratory ($\mathrm{p}a^0_{\mathrm{PTB,K99.1}}$) and participating institute ($\mathrm{p}a^0_{\mathrm{NMI,K99.1}}$) as well as the DoE of PTB in CCQM-K99 ($\mathrm{DoE}_{\mathrm{PTB,K99}}$), according to the equation (2).

$$\mathrm{DoE}_{\mathrm{NMI,K99.1}} = \mathrm{p}a^0_{\mathrm{NMI,K99.1}} - \mathrm{p}a^0_{\mathrm{PTB,K99.1}} + \mathrm{DoE}_{\mathrm{PTB,K99}} \tag{2}$$

To calculate the uncertainty of the degrees of equivalence ($u(\mathrm{DoE}_{\mathrm{NMI,K99.1}})$), equation (3) was used.

$$u^2\left(\mathrm{DoE}_{\mathrm{NMI,K99.1}}\right) = u^2\left(\mathrm{p}a^0_{\mathrm{NMI,K99.1}}\right) + u^2\left(\mathrm{p}a^0_{\mathrm{PTB,K99.1}}\right) + u^2\left(\mathrm{DoE}_{\mathrm{PTB,K99}}\right) \tag{3}$$

Equation (3) assumes that the results of the linking laboratory and participant were not correlated.
The results are listed in Table 9. The table also states the uncertainty weighed DoE (E_n value), which is calculated using equation (4).

$$E_n(x_i) = \frac{DoE_i}{U(DoE_i)} \tag{4}$$

A result is considered consistent with the KCRV if $|E_n(x_i)| \leq 1$. Table 9 also shows minimal expanded uncertainties U_{minCMC} consistent with the proposed KCRV, which makes the submission and review of claims of calibration and measurement capabilities (CMC) easier. If a result is consistent with the KCRV, U_{minCMC} is equivalent with the expanded uncertainty reported by the institute.
The degrees of equivalence are shown together with the original key comparison (CCQM-K99) results in Figure 9, 10, and 11.

Table 9. Degrees of equivalence of pa^0 with expanded uncertainties (k = 2) at each temperature.

Institute i	Temperature / °C	pa^0_i	U(pa^0_i)	DoE$_i$	U(DoE$_i$)	E_n	U_{minCMC}
KRISS	15	7.3265	0.0026	−0.0014	0.0042	-0.32	0.0026
KRISS	25	7.2936	0.0028	−0.0020	0.0043	-0.46	0.0028
KRISS	37	7.2725	0.0029	0.0007	0.0043	0.15	0.0029

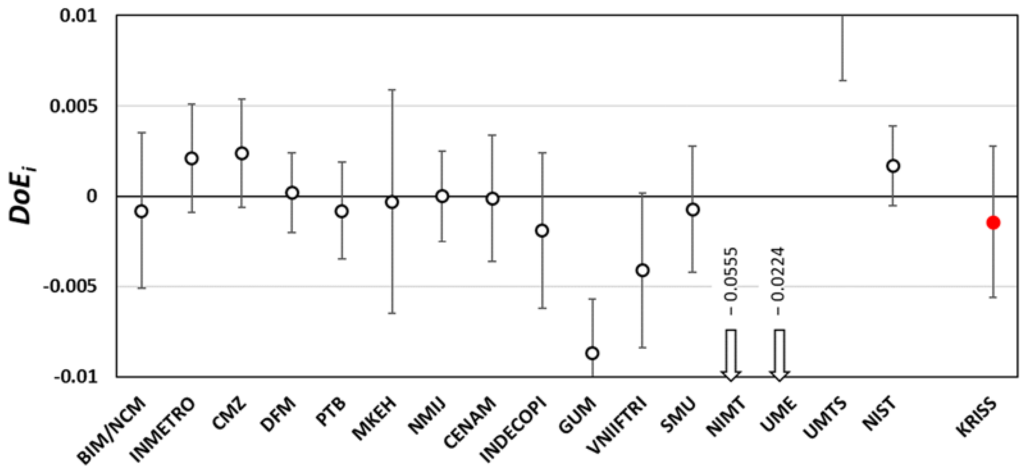

Figure 9. Degrees of equivalence for CCQM-K99 (open black circles) /CCQM-K99.1 (close red circle) at 15 °C with expanded uncertainties (*k* = 2).

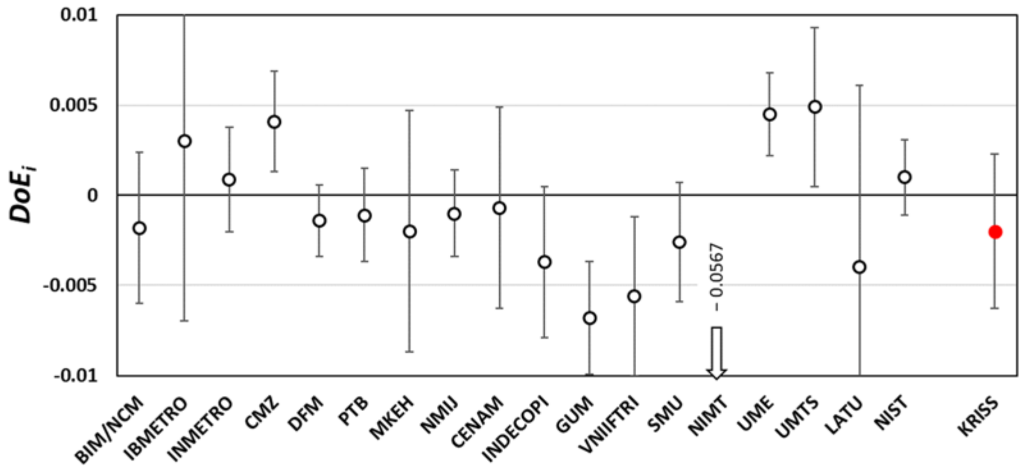

Figure 10. Degrees of equivalence for CCQM-K99 (open black circles) /CCQM-K99.1 (close red circle) at 25 °C with expanded uncertainties (*k* = 2).

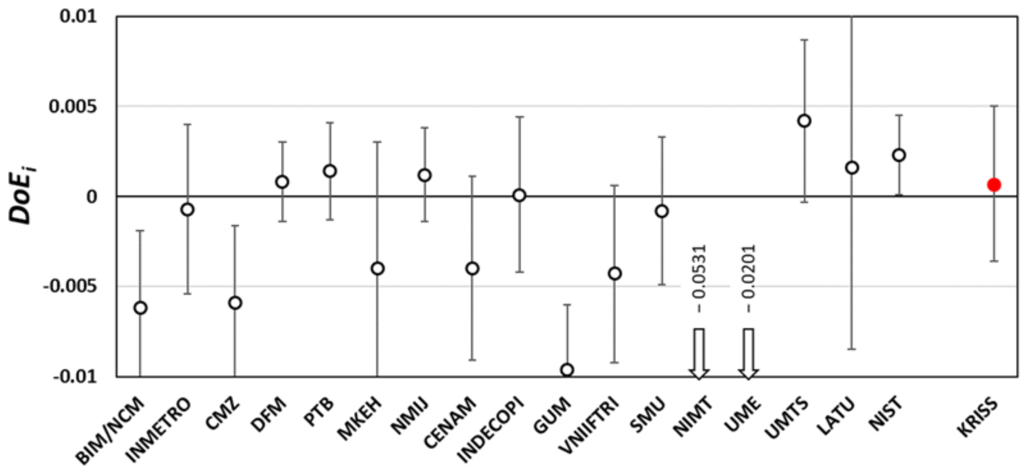

Figure 11. Degrees of equivalence for CCQM-K99 (open black circles) /CCQM-K99.1 (close red circle) at 37 °C with expanded uncertainties (*k* = 2).

10 How Far The Light Shines statement

The results demonstrate equivalence of pH measurements of phosphate buffer with nominal pH value of approximately 7 at 15 °C to 37 °C. Institutes that have successfully participated in the KC can reasonably claim CMCs, usually in service category 6, phosphate buffer in the pH range from 6.4 to 7.6 and in the temperature range from 15 °C to 37 °C. Uncertainties claimed in CMC submission must not be smaller than U_{minCMC} values stated in Table 9, unless exceptions stated in EAWG-CMC guidelines can be applied.

11 Acknowledgements

The coordinating laboratory gratefully acknowledges the contributions of PTB, especially provision of samples.

12 References

[1] JCGM 100:2008 Evaluation of measurement data - Guide to the expression of uncertainty in measurement (GUM) JCGM (available at https://www.bipm.org/en/committees/jc/jcgm/publications).

[2] CCQM/2013-22 CCQM Guidance note: Estimation of a consensus KCRV and associated Degrees of Equivalence (available at https://www.bipm.org/documents/20126/28430045/working-document-ID-5794/49d366bc-295f-18ca-c4d3-d68aa54077b5)

[3] ISO 33405:2024 Reference materials – Approaches for characterization and assessment of homogeneity and stability

[4] Final report on CCQM-K99, Key comparison on pH of an unknown phosphate buffer, 2015.

Annex

Formula

Verification of stability (ISO 33405:2024)

$$b_1 = \frac{\sum_{i=1}^{n} (X_i - \overline{X})(Y_i - \overline{Y})}{\sum_{i=1}^{n} (X_i - \overline{X})^2}$$

$$s(b_1) = \frac{s}{\sqrt{\sum_{i=1}^{n} (X_i - \overline{X})^2}}$$ with $$s^2 = \frac{\sum_{i=1}^{n} (Y_i - b_0 - b_1 X_i)^2}{n-2}$$ and $$b_0 = \overline{Y} - b_1 \overline{X}$$

b_0 (intercept) and b_1 (slope) are the parameters of a linear regression through the stability measurement results X_i (date of measurement) and Y_i (measurement parameter, e.g. pH or pa^0). $\overline{X}$ and $\overline{Y}$ are the means of n stability measurements $i = 1, \cdots, n$. The sample can be considered stable if $|b_1| < t_{0.95,n-2} \times s(b_1)$, with $t_{0.95,n-2}$ being the 95 % student-t factor at $n - 2$ degrees of freedom.

CCQM WG on Electrochemical Analysis and Classical Chemical Methods

CCQM-K99.1 – pH measurement of phosphate buffer solutions

Technical Protocol

23 April 2025

1 Introduction

The CCQM key comparison CCQM-K99.1 is a subsequent comparison to CCQM-K99. It aims to demonstrate the capability of the Korean Research Institute of Standards and Science (KRISS) to measure the pH of phosphate buffer solutions. The result of Physikalisch-Technische Bundesanstalt (PTB) will be used as a link to the original comparison CCQM-K99.
In this comparison, a measurement method is restricted to the use of the primary method of pH (Harned cell method). Measurements of pH will be performed at 15 °C, 25 °C, 37 °C.

2 Coordinating Laboratory and Contact Person

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4 Description of Samples

The solutions used for the comparison have been produced by PTB. A phosphate buffer solution with a nominal pH value of approximately 7 at 25 °C has been prepared from deionized water, potassium dihydrogen phosphate, and disodium hydrogen phosphate. The solution has been homogenized, filled in 1 L high-density polyethylene (HDPE) bottles, and closed with screw cap and Parafilm.
Bottle labels indicate “CCQM-K99.1”, “phosphate buffer”, the nominal pH value, the filling date, and the bottle number. KRISS receives the number of bottles of solutions requested. Before shipment, each bottle weighs with a balance having 0.01 g resolution. These results will be compared with the bottle weight measured upon arrival at KRISS to verify the integrity of the sample. Weighing results, pressure, temperature, and relative humidity at the time of weighing shall be filled in the Weighing-Excel sheet that is sent together with the tracking number. The bottles have been shipped by courier and packed in aluminized plastic bags. The tracking number has been reported by email to the contact person of the laboratory. The contents are stated as “non-hazardous aqueous solution” with a value of 1 € per bottle. Specific customs requirements stated by the KRISS have been considered.
The homogeneity and stability of the sample will be evaluated by KRISS, taking 3 systematically selected bottles. Stability will be measured by the primary Harned cell method after receipt in 3-week intervals throughout the whole measurement period.
Hydrochloric acid and chloride ion sources will not be provided. It is recommended to dry the alkali chloride at no less than 400 °C for at least 2 hours and then store it over a desiccant prior to use.
The mass fraction of water will be provided by PTB.

5 Actions after Receipt of Samples

- The packaging material must be removed after arrival of the samples and the bottles must be inspected for visible damage or leakage.
- The bottles shall be equilibrated in the weighing room overnight. Each bottle shall be weighed with a balance having 0.01 g resolution to verify its integrity during shipment. Do not remove the Parafilm or the label from the bottles. Weighing results, pressure, temperature, and relative humidity at the time of weighing shall be filled in the Weighing-Excel. Bottle masses will be automatically corrected for air-buoyancy. Compare the corrected masses with those stated by PTB in the Weighing-Excel sheet. If the discrepancy is larger than 0.2 g, please investigate for possible leakage and inform PTB. A replacement will be shipped as soon as possible.
- Confirm receipt of samples to the PTB within a week after arrival.

- Within two weeks after arrival, KRISS evaluates the homogeneity of the samples and notifies PTB when it is complete. The measurement results must not be shared at this time. Each participant must begin the measurement after completing the homogeneity evaluation.

6 Instruction for Measurement

- The bottles should be stored at temperatures between 20 °C and 25 °C, however, they must not be stored above 25 °C. The lids and caps of the bottles may only be opened immediately before the measurements. If possible, the caps should be re-sealed with Parafilm following each opening.
- Each participant must measure pH of the samples with respect to 15 °C, 25 °C, 37 °C. It is expected that the primary method of pH is used. However, lower-level methods can be additionally used and reported as additional information.
  - Recommended values of constants are:

    Molar gas constant, R = 8.314 4626 J mol^{-1} K^{-1}

    Faraday constant, F = 96 485.33212 C mol^{-1}
  - The following conditions are used for primary measurements:

    The measurements must be evaluated using the standard pressure of 101 325 Pa.

    The standard potential of the Ag/AgCl electrodes should be determined using hydrochloric acid (aqueous HCl solution) having a molality value close to 0.01 mol kg^{-1}. The actual molality value must be traceable to the SI.

    Alkali chloride (sodium chloride or potassium chloride) should be added to prepare at least three different buffer solutions with molalities in the range of 0.005 mol kg^{-1} to 0.02 mol kg^{-1}.

7 Reporting

A measurement report must be provided, containing the following information:

- Name and address of the laboratory performing the measurements
- Name(s) of the operator(s)
- Date of receipt of samples
- Identification of the samples (bottle numbers) measured.
- Date(s) of measurement.
- Mass of each bottle (without buoyancy correction), pressure, temperature, and relative humidity at time of weighing.
- Description of the method used, including a photo of the experimental setup, if available.
- Complete uncertainty budget according to the *Guide to the Uncertainty in Measurement*. The uncertainty budget of primary measurements must include the following contributions:
  - uncertainty of temperature measurement
  - uncertainty of standard potential of Ag/AgCl electrodes
  - uncertainty of cell potential measurement
  - uncertainty of HCl molality
  - uncertainty of partial pressure of H_2

- uncertainty of chloride molality
- uncertainty of calculation of acidity function at zero chloride molality
- other contributions resulting from the specific set-up and measurement procedure of the participant

The uncertainty budget of secondary measurements must include the following contributions:

- uncertainty of the pH measurement standard used
- measurement repeatability
- uncertainty of calibration curve, or uncertainty due to the potential difference between the sample and the standard when measured
- uncertainty of potential measurement as a function of time
- statement that the uncertainty of Bates-Guggenheim Convention is not included
- other contributions resulting from the specific set-up and measurement procedure of the participant

- The measurement results with the associated standard uncertainties, expanded uncertainties and the corresponding coverage factors *k*, referring to a 95 % probability interval. Note that *k* is 2 if an infinitive number of degrees of freedom can be reasonably assumed.
- The route of traceability

An Excel template will be provided for reporting. It is recommended to use the template. Please be aware that only a single result may be provided for the solution at each temperature. Other results may be added (e.g. those of additional secondary measurements). However, such results must clearly be identified as additional information. If relevant information cannot reasonably be included in the Excel-file it can be provided in a Word document. The report(s) must be sent to the coordinating laboratory by e-mail before **11 July 2025**. For integrity of results, report(s) have to be locked with the password. The coordinating laboratory will confirm the receipt of the report. If the confirmation does not arrive within one week, please contact the coordinating laboratory to identify the problem.

8 Key Comparison Reference Value

The key comparison reference value (KCRV) will be calculated following the CCQM-13/22 guidelines. The choice of the best estimator will be based to the actual distribution of the results.

9 How Far The Light Shines Statement

The results demonstrate equivalence of pH measurements of phosphate buffer with nominal pH value of approximately 7 at 15 °C to 37 °C. Institutes that have successfully participated in the KC can reasonably claim CMCs, usually in service category 6, phosphate buffer in the pH range from 6.4 to 7.6 and in the temperature range from 15 °C to 37 °C.