Asia Pacific Metrology Programme (APMP)
APMP.QM-K18.2016 Key Comparison on pH Measurement of Carbonate Buffer
Final report (December 17, 2020)

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Abstract

This key comparison is being performed to evaluate the degree of equivalence of measurement procedures to support the participants' claims of Calibration and Measurement Capabilities (CMCs) and to evaluate the capabilities of participants for the determination of the pH of carbonate buffer solutions.

This is the fourth APMP key comparison on pH measurement following APMP.QM-K9/P16 (phosphate), APMP.QM-K19/P25 (borate) and APMP.QM-K91/P29 (phthalate).

The results have the linkage to CCQM-K18.2016 (carbonate buffer) and were evaluated by comparing the results of the Physikalisch-Technische Bundesanstalt (PTB) and the National Metrology Institute of Japan (NMIJ) performing Harned cell method. The results of PTB and NMIJ were used for the definition of the Key Comparison Reference Value (KCRV). The ensuing pH value was calculated based on the Bates-Guggenheim convention to compare the results of primary and secondary methods.

In this comparison measurements of pH were performed only at the temperature of 25 °C.

The results demonstrated by most participants are in better agreement than those in CCQM-K18.2016.

Metrology area

Amount of substance

Branch

Electrochemistry

Subject

Determinations of the acidity function at zero chloride molality by primary Harned cell method or related pH by secondary methods with differential potentiometric cell or glass electrode for an unknown carbonate buffer, pH ~10.0 at 25 °C.

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Purpose

This key comparison is being performed to evaluate the degree of equivalence of measurement procedures to support the Calibration and Measurement Capabilities (CMCs) and to evaluate the capabilities of participants for the determination of the pH of carbonate buffer solutions.

This is the fourth APMP key comparison on pH measurement following APMP.QM-K9/P16 (phosphate), APMP.QM-K19/P25 (borate) and APMP.QM-K91/P29 (phthalate).

The purpose of the key comparison is to give an opportunity to National Metrology Institutes (NMIs) or Designated Institutes (DIs) which did not participate previously in the CCQM comparisons, especially to those which usually employ the glass-electrode method for pH measurements.

The comparison scope covers the measurements of an acidity function or pH using either the primary method with a Harned cell, the secondary differential potentiometric cell method or the secondary method with a glass electrode. It is only allowed to participate using a secondary method instead of a primary one if this is the highest metrological level of measurements of NMIs or DIs and if the CMCs are based on this method.

The results have the linkage to CCQM-K18.2016 (carbonate buffer) and were evaluated by comparing the results of the Physikalisch-Technische Bundesanstalt (PTB) and the National Metrology Institute of Japan (NMIJ) performing the primary Harned cell method. The results of PTB and NMIJ were used as the Key Comparison Reference Value (KCRV). The ensuing pH value was calculated based on the Bates-Guggenheim convention to compare the results of the secondary methods.

In this comparison measurements of pH were performed only at the temperature of 25 °C.

Time schedule

Proposal: APMP meeting at Singapore in 2018
Registration deadline: 31 July 2019
Dispatch of samples: 6 and 7 January 2020
Reporting deadline: 12 June 2020
Draft A report: 3 August 2020
Discussion: EAWG meeting on 12 October 2020
Discussion: APMP meeting on 11 November 2020
Draft B report: 13 November 2020
Final report: 17 December 2020

Coordinating laboratory

Contact person: Toshiaki Asakai (t-asakai@aist.go.jp)

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Participants

Table 1. List of participants in key comparison APMP.QM-K18.2016.

Acronym	Economy	Institute	Contact	Method
CENAM	Mexico MX	Centro Nacional de Metrología	José Luis Ortiz Aparicio Judith Velina Lara Manzano	Harned
GLHK	Hong Kong HK	Government Laboratory, Hong Kong	Samuel M.F. Lo Desmond K.F. Poon	Glass
IBMETRO	Bolivia BO	Instituto Boliviano de Metrología	Mabel Delgado Paola Avendaño	Differential
INM	Colombia CO	Instituto Nacional de Metrología de Colombia	Ronald Cristancho Amaya Henry Torres Quezada	Harned
INMETRO	Brazil BR	Instituto Nacional de Metrologia, Qualidade e Tecnologia	Fabiano Barbieri Gonzaga Leonardo da Silva Pardellas	Harned
MUSSD	Sri Lanka LK	Measurement Units, Standards and Services Department	S. D. I. Dias D. Gunawardana	Glass
NIM	P.R.China CN	National Institute of Metrology, China	Xiu Hongyu Wu Bing	Harned
NIMT	Thailand TH	National Institute of Metrology (Thailand)	Nongluck Tangpaisarnkul Patumporn Rodruangthum	Harned
NMIJ	Japan JP	National Metrology Institute of Japan	Igor Maksimov Toshiaki Asakai	Harned
PTB	Germany DE	Physikalisch-Technische Bundesanstalt	Frank Bastkowski Beatrice Sander	Harned
UMTS	Ukraine UA	SE "UKRMETRTESTSTANDART"	Vladimir V. Gavrilkin Anton V. Petrenko	Harned
VNIIFTRI	Russia RU	All-Russian Scientific Research Institute for Physical-Engineering and Radiotechnical Metrology	Sergey Prokunin Darya Vengina Vladimir Dobrovolskiy	Harned

Sample preparation

The carbonate buffer solution with pH around ~10.0 at 25 °C was been prepared using the ultrapure water with the electrical resistivity 18 MΩ cm, reagents of dissodium carbonate (Na_2CO_3, > 99.8 %, CAS 497-19-8) and sodium hydrogen carbonate ($NaHCO_3$, > 99.7 %, CAS 114-55-8) as the original materials. Dissodium carbonate was dried at 250 °C for 4 h and cooled down to the room temperature in the desiccator with silica-gel adsorbent. Sodium hydrogen carbonate was kept in the desiccator with silica-gel over 5 h prior to the following weighting.

An approximately 50 L sample solution for the APMP.QM-K18.2016 comparison was prepared at November 12, 2019, by dissolving the above-mentioned reagents in the Nalgene polypropylene bottle. The composition of solution was close to that of standard carbonate buffer with the slightly altered molalities of solutes from 0.025 mol kg^{-1} nominal values. The solution was later subdivided into 1 L high density polyethylene bottles at November 25, 2019. The bottles were numbered, weighted and sealed in the aluminized plastic bags.

The mass fraction of water in the solution was $w(H_2O) = 0.995274$.

The homogeneity of the solution was measured before the shipment by the precise pH meter PHL-90 and primary Harned cell method; the stability was checked throughout the measurement period by primary method.

Each participant received two bottles with the tracking information emailed to the contact persons.

Hydrochloric acid and chloride ion reagent were not provided by the coordinating laboratory. It was 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.

Solution homogeneity

Homogeneity of the bottled buffer solutions was checked at 25 °C by measuring the values of pH of 5 bottles with a precise pH meter PHL-90 with a combined glass electrode, and 2 bottles by primary Harned cell method. The precise pH meter was a custom-built one (DKK-TOA Corporation, Tokyo, Japan) with the minimum resolution 0.0001.

The results of the homogeneity test between the bottles are presented in Table 2 and Fig. 1. The bottles were numbered according to the order of bottling. The samples used by the pH meter for above-mentioned check were taken from the middle of comparison batch. The differences of pH values given in Table 2 were calculated versus the mean values for each method, respectively. The combined standard uncertainties for the glass electrode method $u(\Delta pH)$ were roughly estimated based on the reproducibility of the standard deviation.

The calculated standard deviation using all data presented in Table 2 was less than 0.0005; therefore, the buffer was homogeneous enough for the key comparison.

Table 2. Results of the homogeneity assessment for the APMP.QM-K18.2016 buffer.

Bottle No.	ΔpH	*u*(ΔpH)	Method
1	−0.00001	0.0011	Harned
between 1 and 2	−0.0004	0.0010	Glass
between 8 and 9	−0.0006	0.0005	Glass
between 16 and 17	0.0004	0.0003	Glass
between 24 and 25	0.0007	0.0005	Glass
between 40 and 41	0.0004	0.0006	Glass
41	0.00001	0.0011	Harned

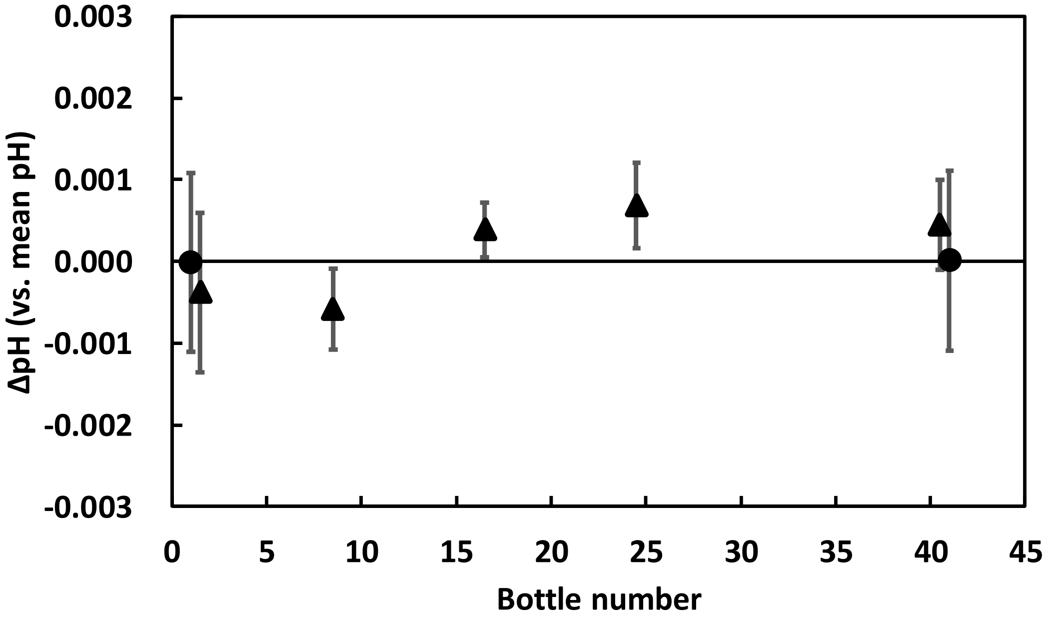

Fig. 1 Results of the homogeneity assessment for the APMP.QM-K18.2016 buffer.
●: primary Harned cell method; ▲: glass electrode method
Each bar corresponds to the combined standard uncertainty

Solution stability

The stability of the sample solutions was assessed at 25 °C by Harned cell method over the duration of the key comparison from November 2019 to June 2020. Each point in the stability assessment represents the independent measurement result from a single bottle of the carbonate buffer by pa^0 determination from 4 solutions with chloride molalities from 0.005 mol kg^{-1} to 0.020 mol kg^{-1}. The buffer stability results are presented in Table 3 and Fig. 2. All the points lay within the ±0.001 range from the average pa^0; therefore, the sample solutions were stable enough over the period of the key comparison.

Table 3. Results of the stability assessment for the APMP.QM-K18.2016 buffer.

Date	Bottle No.	pa^0	Δpa^0	U(pa^0)
29 Nov. 2019	1	10.1279	0	0.0022
3 Dec. 2019	41	10.1282	0.0003	0.0022
29 May 2020	10	10.1275	−0.0004	0.0026
23 June 2020	20	10.1278	−0.0001	0.0023

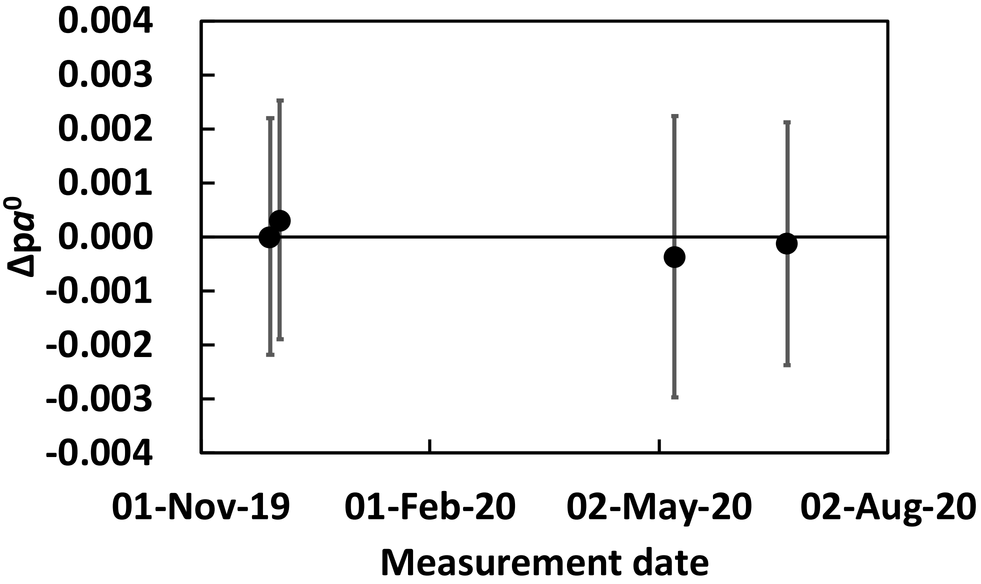

Fig. 2 Results of the stability assessment for the APMP.QM-K18.2016 buffer. Each bar corresponds to the expanded uncertainty.

Sample delivery

The samples were shipped by coordinating laboratory on 6 January 2020 via EMS (Express Mail Service) and 7 January 2020 via OCS (Overseas Courier Service Co., Ltd.). The samples for IBMETRO and UMTS were delivered by OCS due to out of service by EMS; the rest of samples were delivered by EMS. All participants had received two bottles until 31 January 2020. The timetable for the sample deliveries and reporting is summarized in Table 4.

VNIIFTRI had received two bottles (No. 23 and 39) on 14 January 2020. The reported mass of a bottle No. 39 was lighter than original one before the shipment by 0.47 % relative. Therefore, the coordinating laboratory dispatched another spare bottle No. 6 on 27 January 2020, which VNIIFRI received on 4 February 2020.

No visible signs of any damage to the samples were reported to the coordinating laboratory by any participant including VNIIFTRI. To ensure the integrity of the received samples, each participant reported: the ambient pressure, temperature, relative humidity, balance reading, and the calculated mass of each bottle after air buoyancy correction. The relative change in bottle masses is shown in Fig. 3. All relative changes in bottle mass were acceptable for the comparison on pH.

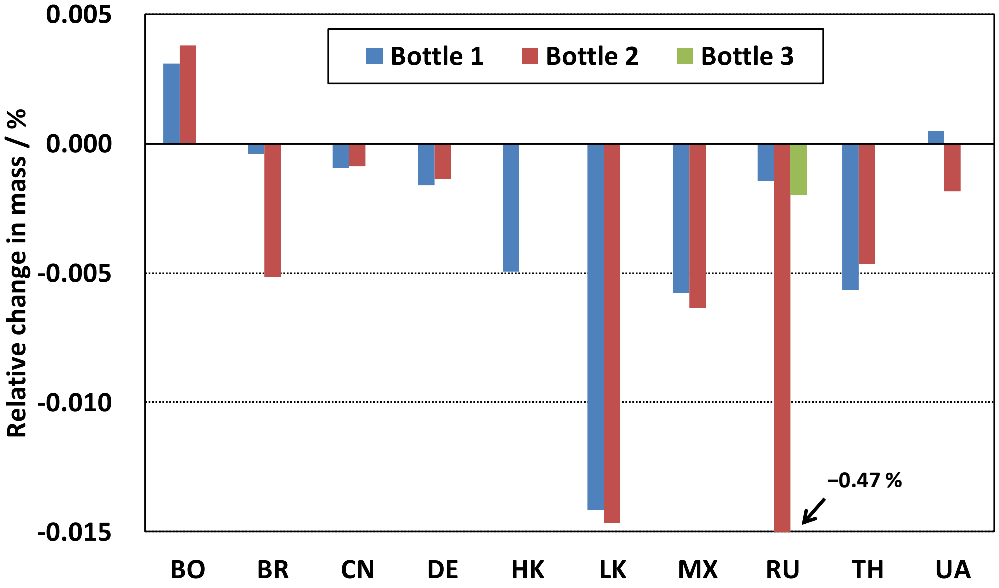

Fig. 3 Relative change in bottle masses before and after the shipment

Communication with participants

5 Nov 2019	The coordinating laboratory announced to all participants that the shipment of the samples was postponed from December to early January.
19 Dec 2019	INM informed the coordinating laboratory that INM had to desist from taking part in the APMP comparison due to the internal reorganization.
24 Jan 2020	VNIIFTRI reported the mass of a bottle (No. 39) which was lighter than that before the shipment by 0.47 % relative. The coordinating laboratory dispatched another spare bottle No. 6 on 27 Jan 2020.
11 Feb 2020	PTB as a linking laboratory with CCQM-K18.2016 informed the coordinating laboratory that their Harned cell system had some problems. PTB suggested the coordinating laboratory to find another institute to serve as a linking laboratory.
13 Feb 2020	SMU was asked to be as a linking laboratory instead of PTB; however, they could not. NMIJ decided to be a single linking laboratory if PTB could not.
21 Apr 2020	The coordinating laboratory asked the participants about the current status of work and the influence of COVID-19.
28 Apr 2020	PTB informed that its Harned cell system was started to work well, and that PTB was able to perform as a linking laboratory with CCQM-K18.2016.
1 May 2020	The coordinating laboratory informed the participants that the reporting deadline was extended from 10 May 2020 to 12 June 2020 due to the global quarantine.
16 July 2020	MUSSD submitted its revised report, the adjustment due to some miscalculations.
21 July 2020	UMTS submitted its revised report, the correction due to some miscalculations.
3 Aug 2020	The results were disclosed as Draft A report to the participants.

Timetable of Measurements and Submission of Reports

The dates of the sample receipts, measurements and reporting are given in Table 4. Most reports were received by the deferred reporting deadline, 12th June 2020.

Table 4. Timetable of shipments and measurements.

Acronym	Bottle No.	Shipped	Received	Measured	Reported Revised
CENAM	29, 35	6-Jan	10-Jan	13-Jan	4-June
GLHK	13, 25	6-Jan	9-Jan	22-Apr 28-Apr	11-June
IBMETRO	4, 19	7-Jan	21-Jan	5, 8, 9, 10-June	12-June
INMETRO	12, 28	6-Jan	31-Jan	6, 21-Feb 13-Mar	2-Apr
MUSSD	3, 27	6-Jan	24-Jan	11-Feb	12-June 16-July
NIM	15, 32	6-Jan	10-Jan	25-31-Jan	17-Mar
NIMT	7, 22	6-Jan	18-Jan	20-Apr 30-Apr	10-May
PTB	8, 21	6-Jan	17-Jan	5-May	11-June
UMTS	11, 34	7-Jan	20-Jan	17-Apr	13-June 21-July
VNIIFTRI	23, 39 6	6-Jan 27-Jan	14-Jan 3-Feb	24-Jan 10-Feb	19-Mar 8-Apr

Measurement Technique

A highest metrological measurement method is required for each participant to perform pH measurements in the key comparison. Harned cell method is the primary measurement method for pH, and it is used for the calculation of the key comparison reference value (KCRV). Use of the secondary differential potentiometric cell or of the secondary method with a glass electrode is allowed, if this is the highest metrological level of measurements available for participant. Table 1 provides the measurement technique used by each participant.

Primary method (Harned cell method)

The primary measurement method for pH (Harned cell) is based on the measurement of the potential difference of "Cell 1" without liquid junction:

$$\mathrm{Pt}\ |\ \mathrm{H_2(g,}\ p^{\circ})\ |\ \mathrm{buffer}, m_{\mathrm{Cl}}\ |\ \mathrm{AgCl}\ |\ \mathrm{Ag} \qquad \text{(Cell 1)}$$

where m_{Cl} is the chloride ion molality added to the chloride free buffer to be measure. The potential difference $E_{\mathrm{Cell.1}}$ of "Cell 1" corrected at the standard pressure, p°, is varied with the hydrogen ion activity, a_{H}, according to Equation 1:

$$E_{\mathrm{Cell.1}} = E^{\circ} - \frac{RT\ \ln 10}{F} \cdot \left(\frac{a_{\mathrm{H}}}{m^{\circ}}\right) \cdot \left(\frac{m_{\mathrm{Cl}}\ \gamma_{\mathrm{Cl}}}{m^{\circ}}\right) \qquad \text{(eq. 1)}$$

where E° is the standard potential of the Ag/AgCl electrode, R the ideal gas constant, T the thermodynamic temperature, F the Faraday constant, $m^{\circ} = 1\ \mathrm{mol\ kg^{-1}}$, m_{Cl} the chloride ion molality, and γ_{Cl} the activity coefficient of the chloride ion.

The standard potential of the Ag/AgCl electrodes is determined in "Cell 2" and obtained according to Equation 2:

$$\mathrm{Pt}\ |\ \mathrm{H_2(g,}\ p^{\circ})\ |\ m_{\mathrm{HCl}}\ |\ \mathrm{AgCl}\ |\ \mathrm{Ag} \qquad \text{(Cell 2)}$$

$$E^{\circ} = E_{\mathrm{Cell.2}} - \frac{2RT\ \ln 10}{F} \cdot \lg\left(\frac{m_{\mathrm{HCl}}\ \gamma_{\pm\mathrm{HCl}}}{m^{\circ}}\right) \qquad \text{(eq. 2)}$$

The nominal molality of the HCl, $m_{\mathrm{HCl}} = 0.01\ \mathrm{mol\ kg^{-1}}$, is usually used for the determination of the standard potential of the Ag/AgCl electrodes. The mean activity coefficient of the HCl as the measurement temperature for this nominal molality is given in the reference[1].

Values for the acidity function, pa, are calculated for each measured $E_{\mathrm{Cell.1}}$ value according to Equation 3:

$$\mathrm{p}a = \frac{E_{\mathrm{Cell.1}} - E^{\circ}}{RT\ \ln 10} \cdot F + \lg\left(\frac{m_{\mathrm{Cl}}}{m^{\circ}}\right) \qquad \text{(eq. 3)}$$

In the primary procedure for pH, pa is measured as a function of m_{Cl}. The reported result for the key comparison, the acidity function at zero chloride molality pa^0 is obtained from linear extrapolation of the set of values for the acidity function pa to $m_{\mathrm{Cl}} = 0$. The reported result for the key comparison APMP.QM-K18.2016 is pa^0 at 25 °C.

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[1] R. G. Bates and R. A. Robinson, "Standardization of silver-silver chloride electrodes from 0 to 60 °C", *J. Sol. Chem.* 9 (1980) 455–456.

Secondary method (with differential potentiometric cell or glass electrode)

A secondary method with differential potentiometric cell was performed by IBMETRO; a secondary method with glass electrode was performed by GLHK and MUSSD. Both secondary potentiometric methods consist of measurements of the potential difference between the key comparison buffer and a primary standard solution with the same nominal composition. The following “Cell 3” is used in the differential potentiometric cell method:

$$\mathrm{Pt} \mid \mathrm{H_2}(\mathrm{g},\ p^\circ) \mid \mathrm{buffer}\ S_1 \parallel \mathrm{buffer}\ S_2 \mid \mathrm{H_2}(\mathrm{g},\ p^\circ) \mid \mathrm{Pt} \qquad \text{(Cell 3)}$$

where S_1 and S_2 represents two quasi-identical buffers (the key comparison buffer and a primary standard solution), | | a physical barrier constructed of a porous diaphragm that separates two buffers. The pH of an unknown buffer (the key comparison buffer), pH(S_2), is given by Equation 4:

$$\mathrm{pH}(S_2) = \mathrm{pH}(S_1) - \left(E_{\mathrm{Cell.3}} - E_{\mathrm{j}}\right) \cdot \frac{F}{RT\ \ln 10} \qquad \text{(eq. 4)}$$

where $E_{\mathrm{Cell.3}}$ is the potential difference determined in “Cell 3”, E_{j} is the liquid junction potential that forms between the physically separated S_1 and S_2 buffer solutions. Provided that S_1 and S_2 are quasi-identical in composition, $|\ \mathrm{pH}(S_2) - \mathrm{pH}(S_1)\ | \leq \pm 0.02$, and $3 < \mathrm{pH}(S) < 11$, then the relationship $E_{\mathrm{j}} \leq \pm 0.1\ E_{\mathrm{Cell.3}}$ is assumed.

Many commercial pH glass electrodes include the following cell, “Cell 4”:

$$\mathrm{Ag} \mid \mathrm{AgCl} \mid \mathrm{conc.\,KCl} \parallel \mathrm{buffer} \mid \mathrm{glass} \mid \mathrm{dilute\ HCl} \mid \mathrm{AgCl} \mid \mathrm{Ag} \qquad \text{(Cell 4)}$$

The glass electrode is affected with the hydrogen ion activity of buffers, then the potential difference between two Ag/AgCl electrodes at both ends is changed according to Equation 4 in practical. In many cases, a pH meter is calibrated with two different primary standard solutions, and then an unknown buffer solution is measured with the pH meter.

Conversion means are necessary if reported values are pH values not the acidity function. The Bates-Guggenheim Convention was used to convert each other according to Equation 5:

$$\log \gamma_{\mathrm{Cl}}^{\circ} = -\frac{A\sqrt{I}}{1+1.5\sqrt{I}} \qquad \text{(eq. 5)}$$

where A represents the Debye-Hückel Constants, I the ionic strength. The Debye-Hückel Constant at 25 °C is equal to 0.5108[2]; consequently, the value of log $\gamma^{\circ}_{\mathrm{Cl}}$ at 25 °C was equal to −0.10956.

The uncertainty of $\gamma^{\circ}_{\mathrm{Cl}}$ was not taken-into-account because its contribution to the results is constant, but it should be added to the pH uncertainty for actual calibration and measurement purposes.

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[2] OIML R 54: 1981, “International Recommendation: pH Scale for Aqueous Solutions”, International Organization of Legal Metrology, Paris.

Results and Discussion

The APMP.QM-K18.2016 key measurements were performed only at 25 °C. Results from all participants are given in Table 5 and shown in Fig. 4. The digits of the standard uncertainties of the reported values were reduced to two significant digits[3].

Table 5. Results at 25 °C of APMP.QM-K18.2016.

Acronym	Calibration standard	pa^0	log γ^0_{Cl}	Reported / calculated pH	u(pH) / u(pa^0)	U(pH) / U(pa^0)
CENAM	Primary	10.1236	−0.10956	10.0141	0.0057	0.011
GLHK	Glass NIST 186g NIST 191d	---	---	10.0165	0.0077	0.015
IBMETRO	Differential NIST 191d	---	---	10.008	0.005	0.010
INMETRO	Primary	10.1261	−0.10956	10.0165	0.0009	0.0018
MUSSD	Glass DAkkS / DIN 19266 ZENTRUM and Xylem	---	---	10.0103	0.0075	0.015
NIM	Primary	10.1259	−0.10956	10.0163	0.0015	0.0030
NIMT	Primary	10.11614	−0.10956	10.0066	0.0037	0.0074
NMIJ	Primary	10.12807	−0.10956	10.0185	0.0012	0.0024
PTB	Primary	10.13110	−0.10956	10.02154	0.00077	0.0016
UMTS	Primary	10.1168	−0.10956	10.0072	0.0020	0.0040
VNIIFTRI	Primary	10.12892	−0.10956	10.0194	0.0020	0.0039

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[3] ISO/IEC Guide 98-3: 2008, “Uncertainty of measurement - Part 3: Guide to the expression of uncertainty in measurement (GUM: 1995)”, International Organization for Standardization, Geneva.

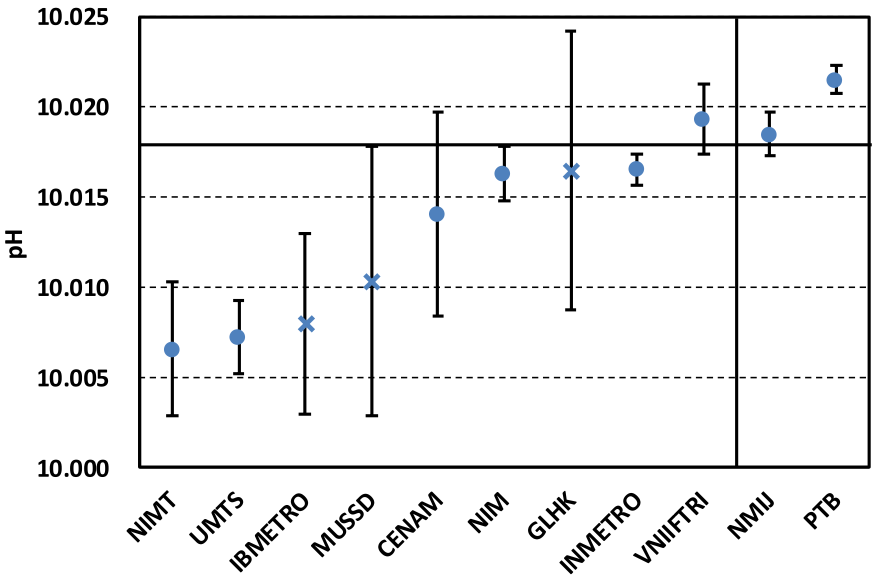

Fig. 4 Results at 25 °C of APMP.QM-K18.2016.
●: primary; x: secondary.
Each bar corresponds to the combined standard uncertainty.
The bold horizontal line indicates the KCRV of this comparison calculated from the results of NMIJ and PTB, used further for the linkage to CCQM-K18.2016 (see the section of "Calculation of the KCRV" for the details)

Other information reported by the participants using the primary Harned cell method: the measurement methods for HCl standardization are given in Table 6; the standard potentials are shown in Table 7 and Figs. 5; the pa^0 values and slopes are presented in Figs. 6 and 7. The digits of the uncertainties of the reported values were reduced to two significant digits.

Table 6. Information on the assay of HCl reported by the primary cell participants

Acronym	Method	mol kg^{-1}	u(mol kg^{-1})
CENAM	Coulometric titration	0.009 174	0.000 008
GLHK	---	---	---
IBMETRO	---	---	---
INMETRO	Coulometric titration	0.010 000 0	0.000 003 2
MUSSD	---	---	---
NIM	Coulometric titration	0.010 018 7	0.000 005
NIMT	NMIJ CRM 3201-a08	0.010 02	0.000 04
NMIJ	Coulometric titration	0.010 000	0.000 003
PTB	Coulometric titration	0.010 016 9	0.000 003 7
UMTS	Coulometric titration	0.010 060 05	0.000 000 65
VNIIFTRI	Coulometric titration	0.009 96	0.000 01

Table 7. Information on the Ag/AgCl standard potential *E*°, its standard uncertainty *u*(*E*°) and the slope of the p*a* extrapolation to the zero chloride molality $b_{\mathrm{Cl}} = 0\ \mathrm{mol\ kg^{-1}}$

Acronym	*E*° / V	*u*(*E*°) / V	p*a* slope
CENAM	0.219 218	0.000 048	−1.8099
GLHK	---	---	---
IBMETRO	---	---	---
INMETRO	0.222 510	0.000 026	−0.7478
MUSSD	---	---	---
NIM	0.222 56	0.000 04	−0.6716
NIMT	0.222 75	0.000 21	−0.7334
NMIJ	0.222 544	0.000 048	−0.9384
PTB	0.222 493	0.000 049	−1.0008
UMTS	0.222 217	0.000 018	−4.4564
VNIIFTRI	0.222 246	0.000 074	−0.9472

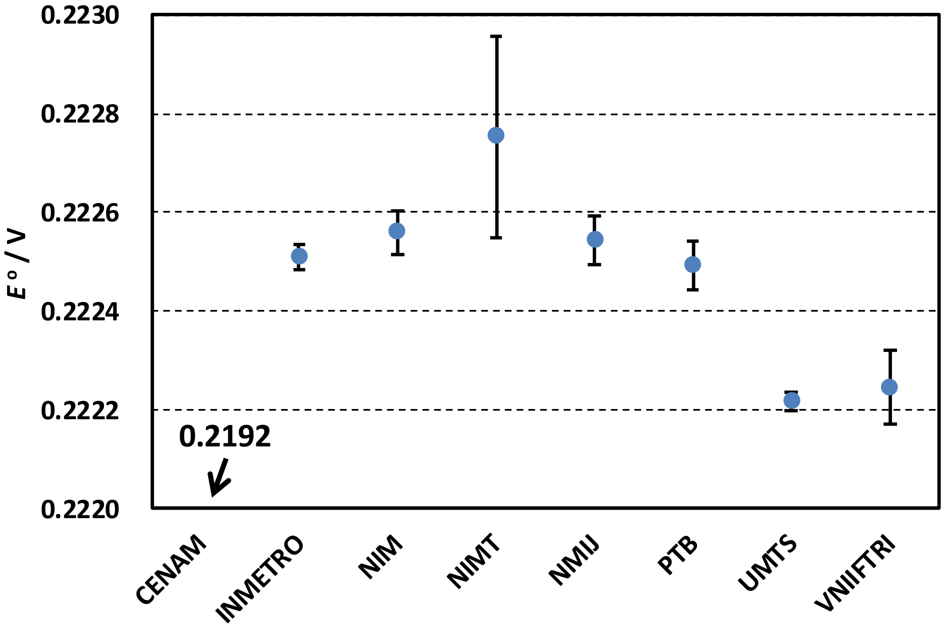

Fig. 5 Reported values of Ag/AgCl standard potential and its combined standard uncertainty

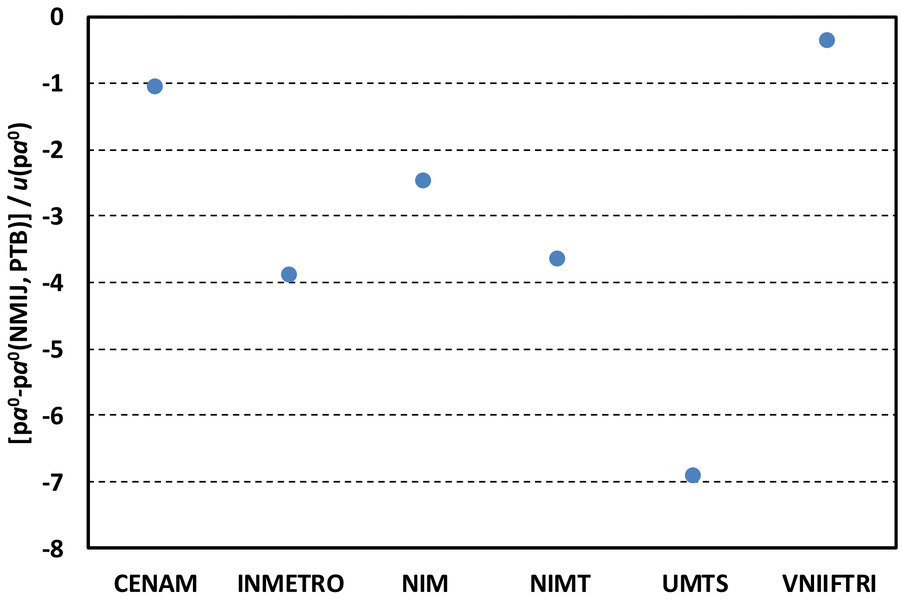

Fig. 6 Results of the inspection for anomalous pa^0 values

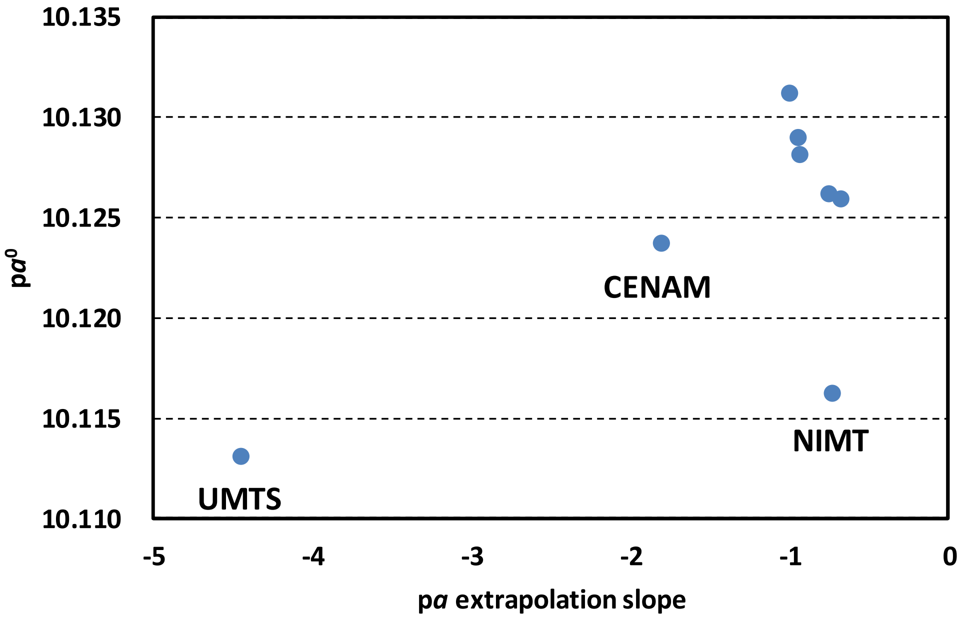

Fig. 7 Comparison of the pa and its slope

Concerning the reported Ag/AgCl standard potentials, they agree well to the literature reference value[4] and are close to each other except for CENAM's one. The standard potential of CENAM is slightly far from the others, but this deviation has no impact within the framework of the primary measurement procedure and CENAM's pa is close to the median.

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[4] R. G. Bates and J. B. Macaskill, "Standard potential of the silver-silver chloride electrode", *Pure Appl. Chem.* 50 (1978) 1701–1706.

The inspection for anomalous pa^0 values shown in Fig. 6 could be one of indications that shows the possibility of the underestimation of the individual participant uncertainty or the anomalous reported pa^0 value. For this estimation, the relative consistency is described by the function: $[pa^0_i - pa^0(\text{average of NMIJ and PTB})] / u(pa^0_i)$ with the average of pa^0 values of NMIJ and PTB being equal to 10.1296. The calculated value of UMTS is slightly far from zero. Fig. 6 suggests that:

- the pa^0 result reported by UMTS is anomalously lower than those of NMIJ and PTB, or the reported $u[pa^0]$ is underestimated.

A similar evaluation was suggested for the value reported by UMTS in the original key comparison CCQM-K18.2016.

Figure 7 shows a relationship between pa^0 and the pa extrapolation slope with all slope values being negative, as in previous CCQM-K18.2016 comparison. More negative pa extrapolation slopes generally show a tendency to make pa^0 values higher. The result of UMTS, however, is the most notable exception. This trend was observed also for this laboratory in the original key comparison CCQM-K18.2016.

The results in CCQM-K18.2016 were spread in the pa^0 range of 0.03 from 10.095 to 10.125. The results demonstrated by most participants in this key comparison are in better agreement than in previous one.

Calculation of the KCRV, its Uncertainty, and the Degrees of Equivalence

NMIJ and PTB participated in the key comparison CCQM-K18.2016 (carbonate buffer) and the reported values were consistent with the KCRV listed in Table 8. As mentioned in the technical protocol, both NMIs serve as the linking laboratories with the original comparison in this study. Therefore, the arithmetic mean value of the results of NMIJ and PTB is used to calculate the KCRV of APMP.QM-K18.2016.

Table 8. Results at 25 °C of CCQM-K18.2016.

Acronym	pa^0: CCQM	$u(pa^0)$: CCQM	$U(pa^0)$: CCQM	D_i: CCQM	$u(D_i)$: CCQM	$u'(D_i)$: CCQM
NMIJ	10.1172	0.0012	0.0024	0.0015	0.0035	0.0031
PTB	10.1187	0.0008	0.0016	0.0030	0.0034	0.0029
KCRV	10.1157	0.0017	0.0034	---	---	---
D_{mean}: CCQM	---	---	---	0.0023	---	0.0021

The consistency of the mean value of NMIJ and PTB with the KCRV of CCQM-K18.2016 was calculated according to the following equations:

$$u'(D_\mathrm{i})\text{: CCQM} = \sqrt{u(D_\mathrm{i})^2 - [u(pa^0)\text{: KCRV}]^2} \qquad \text{(eq. 6)}$$

$$u'(D_\mathrm{i})_\mathrm{mean}\text{: CCQM} = \frac{\sqrt{u'(D_\mathrm{NMIJ})^2 + u'(D_\mathrm{PTB})^2}}{2} \qquad \text{(eq. 7)}$$

$$D_{\mathrm{mean}}\mathrm{:CCQM} = \frac{D_{\mathrm{NMIJ}} + D_{\mathrm{PTB}}}{2} \qquad \text{(eq. 8)}$$

The degrees of equivalence and their uncertainties of APMP.QM-K18.2016 were calculated according to the following equations and given in Table 9.

$$\mathrm{pH_{mean}:APMP} = \frac{\mathrm{pH_{NMIJ}} + \mathrm{pH_{PTB}}}{2} \qquad \text{(eq. 9)}$$

$$D_{\mathrm{i}}\mathrm{:APMP} = \mathrm{pH_i} - [\mathrm{pH_{mean}:APMP}] + [D_{\mathrm{mean}}\mathrm{:CCQM}] \qquad \text{(eq. 10)}$$

$$u(\mathrm{pH_{mean}:APMP}) = \frac{\sqrt{[u(\mathrm{pH_{NMIJ}})]^2 + [u(\mathrm{pH_{PTB}})]^2}}{4} \qquad \text{(eq. 11)}$$

$$u(D_{\mathrm{i}})\mathrm{:APMP} = \sqrt{[u(\mathrm{pH_i})\mathrm{:APMP}]^2 + [u(\mathrm{pH_{mean}:APMP})]^2 + [u(pa^0)\mathrm{:KCRV}]^2 + [u'(D_{\mathrm{mean}})\mathrm{:CCQM}]^2} \qquad \text{(eq. 12)}$$

$$E_{\mathrm{n}} = \frac{[D_{\mathrm{i}}\mathrm{:APMP}]}{2\times[u(D_{\mathrm{i}})\mathrm{:APMP}]} \qquad \text{(eq. 13)}$$

The minimum expanded uncertainties ($U(\mathrm{CMC_{min}})$) of APMP.QM-K18.2016 were calculated based on "EAWG guideline for claims of Calibration and Measurement Capabilities, v12" as follows:

(a) The best estimate $\mathrm{pH_i}$ reported by an institute i in the supporting key comparison is assumed to be consistent with the key comparison reference value $\mathrm{pH_{KCRV}}$ of the key comparison, if

$$|D_{\mathrm{i}}| \leq U(D_{\mathrm{i}}) \ \text{ with } \ D_{\mathrm{i}} = \mathrm{pH_i} - \mathrm{pH_{KCRV}} \qquad \text{(eq. 14)}$$

(b) The minimum standard measurement uncertainty $u(\mathrm{CMC_i})$ that is consistent with results in comparisons is (with reference to document CCQM/09-15):

$$u(\mathrm{CMC_i}) = u(\mathrm{pH_i}) \ \text{ when } \mathrm{pH_i} \text{ is consistent with } \mathrm{pH_{KCRV}}, \qquad \text{(eq. 15)}$$

$$u(\mathrm{CMC_i}) = \sqrt{u^2(\mathrm{pH_i}) + \frac{D_{\mathrm{i}}^2}{4} - u^2(D_{\mathrm{i}})} \ \text{ when } \mathrm{pH_i} \text{ is inconsistent with } \mathrm{pH_{KCRV}} \qquad \text{(eq. 16)}$$

Degrees of equivalence, expanded uncertainties, and minimum expanded uncertainties for CMC claims in APMP.QM-K18.2016 (carbonate buffer at 25 °C) are given in Table 9 and Fig. 8.

Table 9. Degrees of equivalence and expanded uncertainties of APMP.QM-K18.2016 on pH for carbonate buffer at 25 °C.

Acronym	D_i: APMP	$u(D_i)$: APMP	$U(D_i)$: APMP	D_i / $u(\mathrm{pH}_i)$	$U(\mathrm{CMC}_{\mathrm{min}})$	E_n
CENAM	−0.0037	0.0063	0.0126	−0.6509	0.0113	−0.29
GLHK	−0.0013	0.0082	0.0164	−0.1653	0.0154	−0.08
IBMETRO	−0.0098	0.0057	0.0115	−1.9549	0.0100	−0.85
INMETRO	−0.0012	0.0029	0.0059	−1.3716	0.0018	−0.21
MUSSD	−0.0074	0.0080	0.0159	−0.9982	0.0149	−0.47
NIM	−0.0014	0.0032	0.0064	−0.9563	0.0030	−0.23
NIMT	−0.0112	0.0046	0.0093	−3.0255	0.0097*	−1.20
UMTS	−0.0105	0.0034	0.0069	−5.2672	0.0089*	−1.53
VNIIFTRI	0.0016	0.0034	0.0068	0.8139	0.0039	0.23

* These reported values are not consistent with $\mathrm{KCRV}_{\mathrm{APMP}}$; therefore, the minimum expanded uncertainty for the CMC claim is the value calculated according to eq. 16. The other reported values are consistent with $\mathrm{KCRV}_{\mathrm{APMP}}$. The minimum expanded uncertainty for the CMC claim, therefore, is the expanded uncertainty reported by the participant.

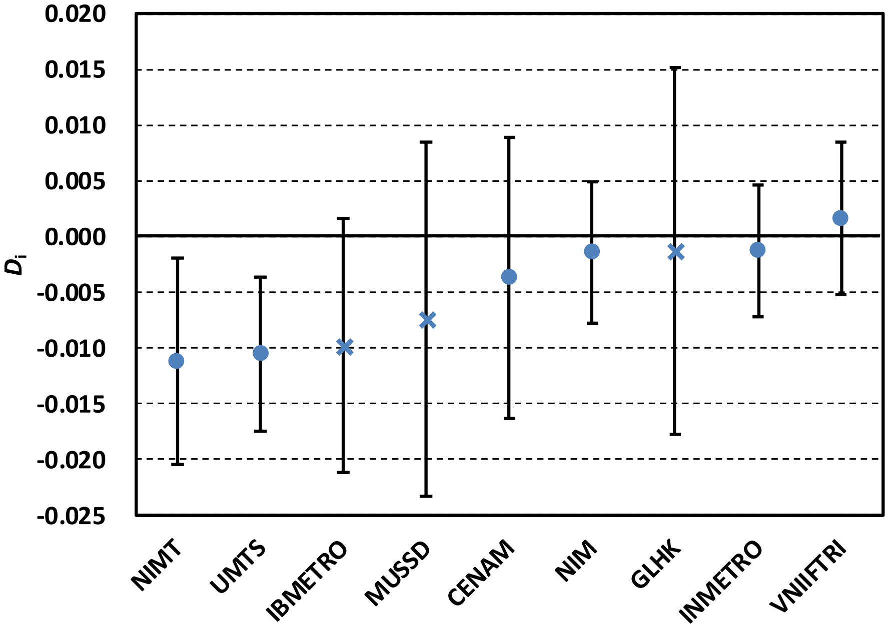

Fig. 8 Degrees of equivalence and expanded uncertainties of APMP.QM-K18.2016 on pH for carbonate buffer at 25 °C. ●: primary; x: secondary

How far the light shines

Carbonate buffer is an 'extended capability' buffer that is difficult to measure by primary Harned cell method due to the change of measurand with CO_2 loss. The CMC claim of carbonate buffer is underpinned by participation in the key comparison testing that particular buffer.

Participants that successfully took part in the APMP.QM-K18.2016 key comparison demonstrate their capability to measure the pH of carbonate buffer by the primary Harned cell method, the secondary differential potentiometric cell method, and the secondary glass electrode method in the pH range 9.5 to 10.5 at 25 °C. Participants that successfully took part in this key comparison by the secondary glass electrode method may claim wider measurement ranges than 9.5 to 10.5 at 25 °C when provided the uncertainty and the calibration procedure are appropriate.

Conclusions

The APMP.QM-K18.2016 key comparison is suitably been linked to CCQM-K18.2016. Comparability of measurement results was successfully demonstrated by many participating NMIs/DIs for the measurement of pH of a carbonate buffer within related expanded uncertainties. The results demonstrated by most participants are in better agreement than those in the original key comparison CCQM-K18.2016. It is expected that the performance of each participant in the present key comparison is representative for measurement of pH of a carbonate buffer with the same technique as used in the present comparison.

Acknowledgment

The coordinating laboratory gratefully acknowledges the contributions of PTB as a linking laboratory and of all participants for their supports in this comparison.

Asia Pacific Metrology Programme (APMP)
APMP.QM-K18.2016 Key Comparison on pH Measurement of Carbonate Buffer
Technical Protocol (May 29, 2019)

Purpose

This key comparison is being performed to evaluate the degree of equivalence of measurement procedures, and support the Calibration and Measurement Capabilities (CMCs), and maintain the capabilities of participants for the determination of the pH of carbonate buffer solutions.

This is the fourth APMP key comparison on pH measurement following APMP.QM-K9/P16 (phosphate), APMP.QM-K19/P25 (borate) and APMP.QM-K91/P29 (phthalate).

The purpose of the key comparison is to give an opportunity to the National Metrology Institutes (NMIs) or Designated Institutes (DIs) which did not participate in the CCQM comparisons, especially to those which usually employ the glass-electrode method for pH measurements.

The comparison scope covers the measurements of an acidity function or pH using either the primary method with a Harned cell[1], the secondary differential potentiometric cell method[2] or the secondary method with a glass electrode. It is only allowed to participate by using a secondary instead of a primary method if this is the highest metrological standard in the NMIs or DIs and if the CMCs are based on this method.

The results will have the linkage to the CCQM-K18.2016 (carbonate buffer) and be evaluated by comparing the results of Physikalisch-Technische Bundesanstalt (PTB) and National Metrology Institute of Japan (NMIJ) performing Harned cell method. The average of the results of PTB and NMIJ will be used as the Key Comparison Reference Value (KCRV). The ensuing pH value will be calculated on the Bates-Guggenheim convention to compare the results by secondary method.

In this comparison measurements of pH will be performed only at 25 °C.

Time schedule

Proposal:	APMP meeting at Singapore in 2018
Registration deadline:	31 July 2019
Dispatch of samples:	Late 2019
Reporting deadline:	10 May 2020
Draft A report:	August 2020
First discussion:	APMP meeting in 2020
Draft B report:	August 2021
Approval of draft B report:	APMP meeting in 2021

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[1] R. P. Buck *et al*. “Measurement of pH. Definition, standards, and procedures (IUPAC Recommendations 2002)”, *Pure appl*. *Chem*. 74 (2002) 2169−2200.

[2] F. G. K. Baucke, “Differential-potentiometric cell for the restandardization of pH reference materials”, *J. Electroanal*. *Chem*. 368 (1994) 67−75.

Description of sample

The carbonate buffer solution with pH around 10.0 at 25 °C will be prepared from deionized water, sodium hydrogen carbonate ($NaHCO_3$, CAS 114-55-8), and disodium carbonate (Na_2CO_3, CAS 497-19-8) as the starting material. The sodium hydrogen carbonate will not be specially treated. The disodium carbonate will be dried at 250 °C for 2 h and stored over silica gel until use.

The molality of APMP.QM-K18.2016 sample would be slightly different from that one of the standard buffer solution of the IUPAC Recommendations 2002. The mass fraction of water in the solution $w(H_2O)$ will be given on the bottle label.

The homogeneity of the solution will be checked before the shipment by precise glass electrode method and its stability will be determined throughout the measurement period by Harned cell.

Each participant will receive the buffer in a 1 L HDPE numbered bottle sealed in an aluminized plastic bag. The number of bottles received by each participant will be:

- For Participants using the primary (Harned cell) method: 2 bottles
- For Participants using a secondary method: 1 bottle

Shipment to all participants will be done at the same time by courier. The tracking information will be e-mailed to the contact persons. The contents are described as “Non-hazardous aqueous solution” and the value is given as 1 US dollar.

Hydrochloric acid and chloride ions source will not be provided for Harned cell measurements. It is recommended to dry the alkali chloride at no less than 400 °C for at least 2 hours and then store over a desiccant prior to use.

Actions at receipt of the sample

- Inspect the received box, bags and bottles for visible damage or leakage.
- If damage is found, report to the coordinating laboratory by e-mail, as soon as possible, about the situation of problems you have encountered. If no damage is found, place the bottle in the bag until the measurements at ambient conditions 25 °C ± 5 °C.
- Confirm the sample receipt by e-mail to the coordinating laboratory.
- Report the weighing data to the coordinating laboratory as soon as the data available.

  Allow the bottles to equilibrate in the weighing laboratory for two days before performing the weighing. Remove the aluminized plastic bag immediately before weighing. Do not remove the tape or the label. Use 1000 kg m^{-3} for the density of the bottles filled with sample solution.

  Report the weighing result (balance reading) and bottle mass (corrected for air buoyancy) for each bottle in the measurement report (summary sheet). Also report the ambient atmospheric pressure, relative humidity and temperature at the time the bottle was weighed.

Instructions for measurements

- Inspect the bags and bottles and check the integrity again before measurements.
- Participants are requested to measure the buffer solution within four weeks after receiving of the solution.
- The measurements are performed only at 25 °C.
- Recommended values of constants are[3]:

Molar gas constant, R = 8.314 459 8(48) J mol^{-1} K^{-1}

Faraday constant, F = 96 485.332 89(59) C mol^{-1}

- The following conditions are used for Harned cell measurements:

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

The standard potential of the Ag/AgCl electrodes must be determined using hydrochloric acid (aqueous HCl solution) with the SI traceability known molality close to 0.01 mol kg^{-1}.

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

Reporting

Please fill in the relevant report sheet and the relevant reporting form for the type of measurement you have done. These must be sent by e-mail to the coordinating laboratory before the reporting deadline. The coordinating laboratory will confirm the receipt of the report by e-mail to the contact person of the participant no later than two weeks after the receipt. If no confirmation is received, please contact the coordinating laboratory in order to identify the problem. The participants must report standard uncertainties calculated according to the Guide to the Expression of Uncertainty in Measurement (GUM)[4].

The report must contain at least the following information:

Name, acronym and address of the laboratory performing the measurements

Name(s) of the analyst(s)

Date of receipt of solutions

Identification of the samples measured

Results from weighing the bottles

Date(s) of the measurement(s)

Description of the method used

Description of the instrumentation, the cell and the electrodes

Measurement result and its standard uncertainty

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[3] P. J. Mohr *et al*. "CODATA recommended values of the fundamental physical constants: 2014", *Rev*. *Mod*. *Phys*. 88 (2016) 035009.

[4] JCGM 100: 2008, "Evaluation of measurement data - Guide to the expression of uncertainty in measurement". http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf

- Primary measurements

The participants are requested to report the value of the acidity function at zero chloride molality (which is determined from values of the acidity function from several measurements) and the associated standard uncertainties.

The participants are requested to report also such numerical results as molalities, cell voltages, acidity functions and data for the extrapolation to zero chloride molality including a plot of the acidity function versus the chloride molality.

If several measurements are made, please make copies of reporting form.

Please give detailed uncertainty budgets for the standard potential of the Ag/AgCl electrodes and for the buffer cell voltage.

Please give an example of the calculations you do to calculate the molality of chloride in the buffer, the corrected voltage in an HCl cell, the standard potential of the Ag/AgCl electrodes, the extrapolation on time if you used, and an individual acidity function value.

- Secondary measurements

Participants performing secondary pH measurements are requested to report the value of pH. The secondary measurement report form should contain at least fundamental information mentioned above.

If you have used the secondary differential potentiometric cell method, information the participants should include would be: an example plot of measured potential difference as a function of time, numerical values of potential difference and temperatures including the respective standard deviations. Please give a detailed uncertainty budget, each or final results and the source of the tractability.

If you have used the secondary method with a glass electrode, information the participants should include would be: voltages and temperatures including the respective standard deviations for the measurements in standard buffers for calibrating the electrode, a table for reporting the calculated slope, intercept of the calibration function, and a plot of measured voltages as a function of pH for the calibration function. Please give a detailed uncertainty budget, each or final results and the source of the tractability.

Call for Participants

The participation is open to all interested NMIs or DIs that perform the determination in the APMP region and other RMOs though the principal purpose of the present comparison is to support the institutes in the APMP.

Coordinating laboratory

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