CCQM WG on Electrochemical Analysis and Classical Chemical Methods
CCQM-K19.2018 Key Comparison on pH of an unknown Borate Buffer
Final report (24 November 2021)

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Abstract

This key comparison CCQM-K19.2018, as a repetition of the previous study CCQM-K19 from 2005, was performed to evaluate the degree of equivalence of measurement procedures of participating National Metrology Institutes (NMIs) and Designated Institutes (DIs) for the determination of pH of borate buffer solutions. The nominal pH value of the buffer was 9.2 at 25 °C and the suggested measurement temperatures were 5 °C, 15 °C, 25 °C, 37 °C and 50 °C. Good agreement of the results is demonstrated by most participants.

Metrology area

Amount of substance

Branch

Electrochemistry

Subject

Determinations of the acidity function at zero chloride molality by the primary Harned cell method or of the related pH value by secondary methods with a differential potentiometric cell or glass electrode for an unknown borate buffer (pH ~9.2 at 25 °C) at 5 °C, 15 °C, 25 °C, 37 °C and 50 °C.

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Purpose

This key comparison has been 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 borate buffer solutions.

This comparison was a repetition of the key comparison CCQM-K19 from 2005.

The comparison was open to NMIs or DIs of member or associate states of the Meter Convention. Only one result per temperature was accepted for report by each participant. No measurement method was prescribed for the comparison, but it was expected to be the highest metrological level of measurements available at each institute. Only results, obtained by the primary method, were used to calculate the Key Comparison Reference Value (KCRV).

In this comparison measurements of pH were performed at temperatures 15 °C, 25 °C and 37 °C with supplementary option of measurements at 5 °C and 50 °C.

Time schedule

Announcement of study: 20 April 2019, EAWG meeting, Sèvres
Invitation for participation: June 2019
Registration deadline: 31 July 2019
Dispatch of samples: August 2020
Reporting deadline: 29 January 2021
Draft A1 report: 26 March 2021
First discussion: 20 to 21 April 2021, EAWG virtual meeting
Draft A2 report: 25 July 2021
Second discussion: 12 to 13 October 2021, EAWG virtual meeting
Draft B report: 15 October 2021
Final report: 24 November 2021

Coordinating laboratories and their roles

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1. NMIJ has announced the upcoming study in April 2019 in Sèvres. VNIIFTRI has prepared the formal invitation and has sent it to the CCQM-EAWG Chair for distribution.
2. VNIIFTRI has prepared the solution, carried out its homogeneity and stability characterization and shipped the samples to the participants.
3. NMIJ will present the comparison results for first discussion at the EAWG meeting, then VNIIFTRI will report the data of stability and homogeneity, based on the final pH values of the samples.
4. NMIJ will prepare the draft A and draft B reports including the calculations of candidate KCRVs and the degrees of equivalence.

Participants

Table 1 List of participants in key comparison CCQM-K19.2018.

Acronym	Country	Institute	Contact	Method
BFKH	Hungary HU	Government Office of the Capital City Budapest	Nagy Dániel Nagyné Szilágyi Zsófia	Primary
BIM	Bulgaria BG	Bulgarian Institute of Metrology	Lyudmila Dimitrova Katya Bezeva	Primary
CENAM	México MX	Centro Nacional de Metrología	José Luis Ortiz Aparicio Judith Velina Lara Manzano	Primary
CMI	Czech Republic CZ	Czech Metrology Institute	Matilda Roziková Martina Vicarova	Primary
GUM	Poland PL	Central Office of Measures	Joanna Dumańska Monika Pawlina	Primary
IBMETRO	Bolivia BO	Instituto Boliviano de Metrología	Mabel Delgado Paola Avendaño	Differential
INMETRO	Brazil BR	Instituto Nacional de Metrologia, Qualidade e Tecnologia	Fabiano Barbieri Gonzaga Leonardo da Silva Pardellas	Primary
INTI	Argentina AR	Instituto Nacional de Tecnología Industrial	Mabel Puelles Hernán Lozano	Glass
IPQ	Portugal PT	Instituto Português da Qualidade, I.P.	Raquel Quendera	Primary
LATU	Uruguay UY	Laboratorio Tecnológico del Uruguay	Simone Fajardo Elizabeth Ferreira	Differential
NIM	P.R.China CN	National Institute of Metrology, China	Xiu Hongyu Wu Bing	Primary
NIMT	Thailand TH	National Institute of Metrology (Thailand)	Nongluck Tangpaisarnkul Patumporn Rodruangthum	Primary
NMIJ	Japan JP	National Metrology Institute of Japan	Igor Maksimov Toshiaki Asakai	Primary
PTB	Germany DE	Physikalisch-Technische Bundesanstalt	Frank Bastkowski Beatrice Sander	Primary
SMU	Slovakia SK	Slovak Institute of Metrology	Zuzana Hanková Michal Máriássy	Primary
UkrCSM	Ukraine UA	State Enterprise All-Ukrainian State Research and production Center of Standardization Metrology, Certification and Consumers' Rights Protection (Ukrmetrteststandart)	Vladimir Gavrilkin Anton Petrenko	Primary
VNIIFTRI	Russia RU	Russian Metrological Institute of Technical Physics and Radio Engineering	Narine Oganyan Sergey Prokunin	Primary

Sample preparation and bottling

The comparison solution was prepared by dissolution of 3.8065 g of sodium tetrabrate $Na_2B_4O_7{\cdot}10H_2O$ per one kilogram of deionized water for the total volume of batch 52 L. The pH value of the borate buffer was around 9.2 and the mass fraction of water in the solution was $w(H_2O) = 0.99650$.

The homogeneity of the solution before the shipment of samples and its stability throughout the whole measurements' period were confirmed by the primary Harned cell method.

Basically, each participant received 4 bottles with the volume of 500 mL for the primary method measurements and 2 bottles for the secondary one.

Hydrochloric acid and chloride ion reagent were not provided by the coordinating laboratories. 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

The homogeneity of the material was tested before the shipment of samples; the pH values at 25 °C had the experimental standard deviation equal to 0.0004 for six tested bottles.

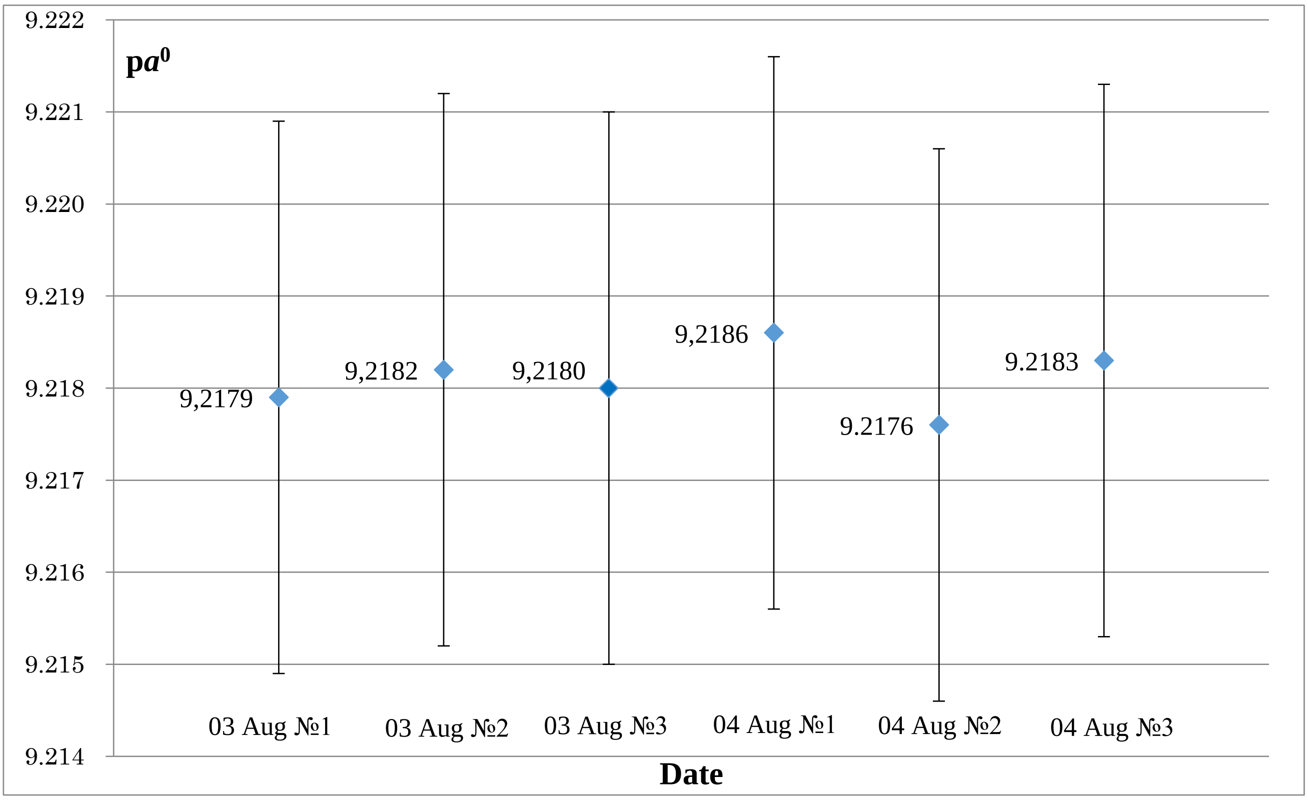

Fig. 1 Results of homogeneity test.

The limits of expanded uncertainty corresponds to $k = 2$.

Solution stability

The stability of the solution was confirmed by the Harned cell method from August 2020 to January 2021. The values of the acidity function obtained at 25 °C were equal to 9.2170, 9.2158, 9.2204, 9.2200, 9.2154, 9.2187 and 9.2188.

The resulted standard deviation being less than ±0.003, the solution was considered to be stable for the measurements' period.

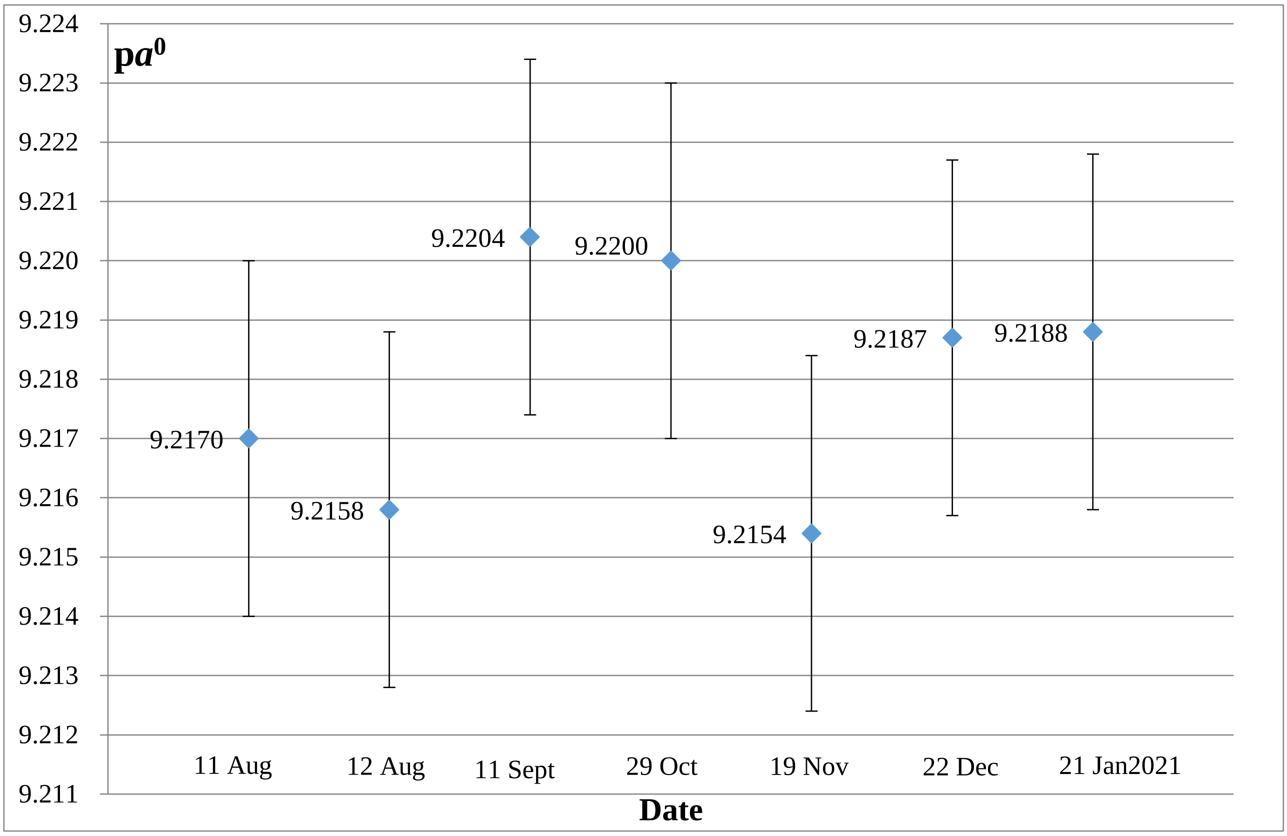

Fig. 2 Results of test for long-term-stability.

Sample delivery

The samples were shipped by VNIIFTRI on 20 August 2020 via UPS (United Parcel Service of America, Inc.) and 28 August 2020 via UPS (United Parcel Service of America, Inc.). The timetable for sample deliveries and reporting are summarized in Table 2.

No visible signs of any damage to the samples were reported to the coordinating laboratories. 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.

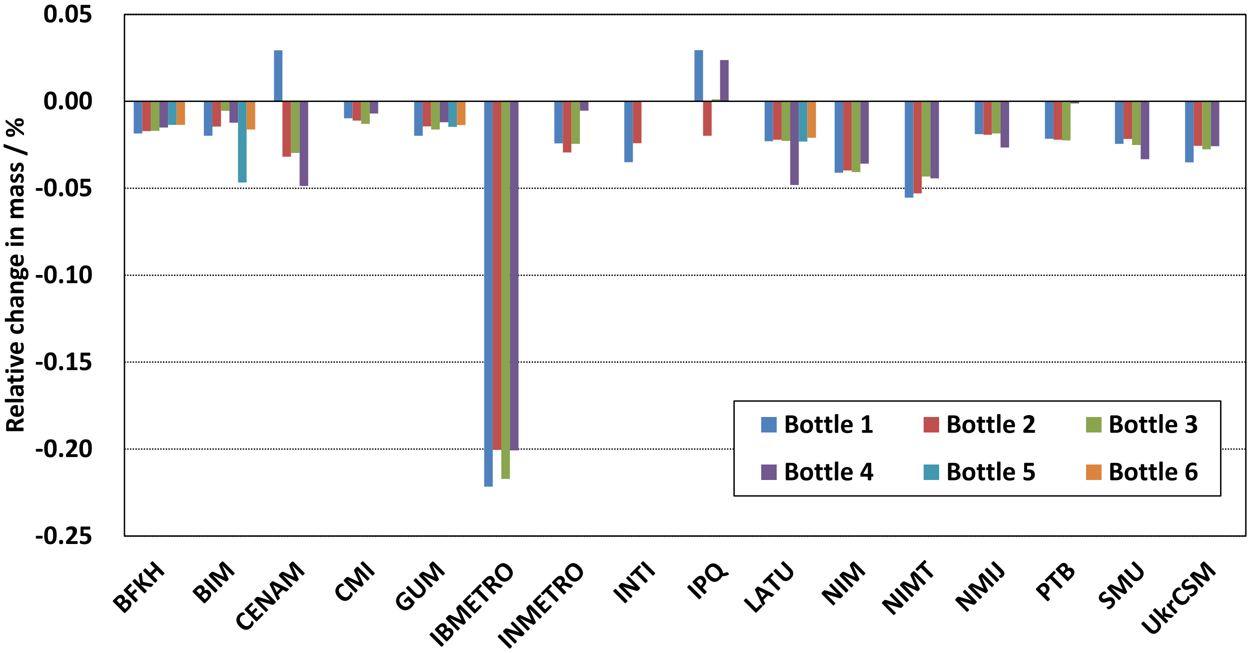

Fig. 3 Relative change in bottle masses after the shipment

Communication with participants

20 Jan 2020	The coordinating laboratories announced to all participants that the shipment of the samples was delayed.
19 Mar 2020	The sample solutions were ready to be shipped; however, the coordinating laboratories decided to postpone the shipping for a few months to avoid any troubles with shipment limitations as a result of the COVID-19 pandemic, and announced it to all participants.
21 Apr 2020	The coordinating laboratories asked the participants about implications due to the pandemic and for adjusting the schedule.
27 July 2020	The borders of Russia were re-opened for the international mail services. The coordinating laboratories asked the participants again about the current status.
6 Aug 2020	The coordinating laboratories decided to start the dispatch of samples and to fix 31 of November as the targeted reporting deadline. The EAWG chair asked the participants again about the possibility to perform the measurements until the targeted deadline.
26 Aug 2020	INMETRO informed that the package with the samples arrived in Brazil, but its delivery requires supplementary tax payment. The coordinating laboratory (VNIIFTRI) handled this issue and paid the taxes.
3 Sept 2020	NMIJ asked the coordinator (VNIIFTRI) to supply additional sample solutions (2 L) for the purpose to expand the measurements to 5 °C and 50 °C.
14 Sept 2020	CENAM informed about the customs problem with parcel clearing and asked for the supplementary invoice. The coordinating laboratory (VNIIFTRI) handled this issue and sent the required papers.
23 Nov 2020	IPQ informed about the four-weeks-delay with its report of results due to the implications of the COVID-19 pandemic.
26 Nov 2020	UkrCSM informed about over one-month-delay with its report of results due to the implications of the COVID-19 pandemic.
9 Dec 2020	The coordinating laboratories asked the participants about their current status for adjusting the schedule.
9 Dec 2020	CMI informed about sending its results within two weeks.
10 Dec 2020	UkrCSM replied about sending its results before 20 Dec 2020.
11 Dec 2020	CENAM declared withdrawal from the ongoing CCQM comparison due to some technical problems with the measurements by the primary method.
14 Dec 2020	IBMETRO informed about sending its results on 21 Dec 2020.
17 Dec 2020	IPQ informed that they expected to send their results by the end of Jan 2021.
24 Dec 2020	The coordinating laboratories announced to postpone the reporting deadline to January 29, 2021.

Timetable of Measurements and Submission of Reports

The dates of the sample receipts, measurements and reporting are given in Table 2.

Table 2 Timetable of shipments and measurements.

Acronym	Bottle No.	Shipped	Received	Measured	Reported Revised
BFKH	37, 56, 76, 83, 99, 102	20.08.2020	24-Aug	19-Nov	30-Nov
BIM	21, 28, 45, 54, 70, 81	20.08.2020	25-Aug	24-Nov 25-Nov 26-Nov	30-Nov
CENAM	6, 18, 63, 87	28.08.2020	24-Sept	---	---
CMI	36, 39, 66, 104	20.08.2020	25-Aug	29-Oct 16-Dec	17-Dec 28-Dec
GUM	1, 9, 23, 43, 55, 86	28.08.2020	1-Sept	15-Oct 26-Oct	1-Dec
IBMETRO	7, 25, 78, 96	28.08.2020	No information	25-Nov 26-Nov 18-Dec 19-Dec	24-Dec
INMETRO	4, 12, 30, 74	20.08.2020	9-Sept	7-Oct 22-Oct 28-Oct	19-Nov
INTI	42, 89	20.08.2020	27-Aug	5-Oct	1-Dec
IPQ	29, 52, 64, 90	20.08.2020	27-Aug	No information	No information
LATU	8, 27, 32, 69, 88, 100	20.08.2020	2-Sept	20-Nov 26-Nov 27-Nov 30-Nov	30-Nov 19-Mar
NIM	19, 41, 95, 98	20.08.2020	28-Aug	19-Sept	28-Oct
NIMT	15, 22, 79, 101	28.08.2020	10-Sept	23-Nov 24-Nov 25-Nov	30-Nov
NMIJ	26, 35, 51, 91	20.08.2020	27-Aug	8-Sept 14-Sept	10-Nov
PTB	10, 46, 53, 75	20.08.2020	25-Aug	15-Sept	6-Nov
SMU	5, 61, 84, 103	20.08.2020	28-Aug	10-Sept	29-Sept
UkrCSM	17, 77, 80, 105	20.08.2020	4-Sept	9-Dec 10-Dec	29-Jan
VNIIFTRI	60,31	---	---	11-Sept	27-Nov

Measurement Technique

The highest metrological measurement methods were required for each participant to perform pH measurements in the key comparison. The Harned cell method is the primary measurement method for pH and only its results were 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 was 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 “Cell1” without liquid junction:

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

where m_{Cl} is the chloride ion molality added to the chloride free buffer to be measured. 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:

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

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

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 at the different measurement temperatures 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 results for the key comparison CCQM-K19.2018 are pa^0 at different measurement temperatures.

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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 and LATU; a secondary method with glass electrode was performed by INTI. 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 differential electrochemical cell, “Cell 3”, is used in the differential potentiometric cell method:

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

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), $\mathrm{pH(S_2)}$, is given by Equation 4:

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

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, $|\ \mathrm{pH(S_2)} - \mathrm{pH(S_1)}\ | \le \pm 0.02$, and $3 < \mathrm{pH(S)} < 11$, then the relationship $E_j \le \pm 0.1\ E_{\mathrm{Cell.3}}$ is assumed.

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

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

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 become necessary when the reported values are pH values instead of acidity function ones. The Bates-Guggenheim Convention was used to convert pH according to Equations 5 and 6:

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

$$\mathrm{p}a^{0} = \mathrm{pH} + \log \gamma^{\circ}_{\mathrm{Cl}} \qquad \text{(eq. 6)}$$

where A represents the Debye-Hückel Constants, I the ionic strength. The values of $\log \gamma^{\circ}_{\mathrm{Cl}}$ were −0.058639 at 15 °C, −0.059596 at 25 °C and −0.060844 at 37 °C.

The uncertainty of $\gamma^{\circ}_{\mathrm{Cl}}$ was not needed to consider in this comparison because the participants used the same value.

Results and Discussion

The measurements in CCQM-K19.2018 were performed at 15 °C, 25 °C and 37 °C with supplementary option of measurements at 5 °C and 50 °C. Results from all participants are given in Table 3 and shown in Figs. 4-1 to 4-5. The digits of the standard uncertainties of the reported values were reduced to two significant digits[2].

Table 3 Results pa^0 determination, CCQM-K19.2018.

Acronym	Method	15 °C pa^0 $u(pa^0)$	25 °C pa^0 $u(pa^0)$	37 °C pa^0 $u(pa^0)$	5 °C pa^0 $u(pa^0)$	50 °C pa^0 $u(pa^0)$
BFKH	Primary	9.3110 0.0027	9.2125 0.0031	9.1255 0.0019	---	---
BIM	Primary	9.3147 0.0018	9.2245 0.0019	9.1356 0.0018	---	---
CENAM	---	---	---	---	---	---
CMI	Primary	9.3012 0.0012	9.2032 0.0012	9.1189 0.0014	---	---
GUM	Primary	9.3096 0.0014	9.2177 0.0013	9.1296 0.0013	9.4236 0.0016	9.0537 0.0014
IBMETRO	Dif.-pot.*	---	9.268 0.005	---	---	---
INMETRO	Primary	9.3149 0.0010	9.2234 0.0014	9.1344 0.0013	---	---
INTI	Glass*	---	9.2244 0.040	---	---	---
IPQ	---	---	---	---	---	---
LATU	Dif.-pot.*	9.3277 0.0056	9.2351 0.0056	9.1497 0.0053	---	---
NIM	Primary	9.3135 0.0017	9.2205 0.0017	9.1292 0.0017	---	---
NIMT	Primary	9.3147 0.0053	9.2125 0.0042	9.1267 0.0044	---	---
NMIJ	Primary	9.3113 0.0011	9.2195 0.0011	9.1317 0.0011	---	---
PTB	Primary	9.3116 0.0007	9.2205 0.0007	9.1327 0.0006	9.4247 0.0007	9.0586 0.0006
SMU	Primary	9.3150 0.0013	9.2232 0.0016	9.1344 0.0018	---	9.0595 0.0017
UkrCSM	Primary	9.3457 0.0024	9.2484 0.0024	9.1548 0.0028	9.4654 0.0026	9.0822 0.0022
VNIIFTRI	Primary	9.3134 0.0017	9.2204 0.0017	9.1325 0.0017	9.4253 0.0017	9.0582 0.0018

*The values of pH were reported by IBMETRO, INTI and LATU which used the secondary methods with differential potentiometric cell or glass electrode. The reported values were converted to pa^0 by adding to pH the value of trace activity coefficient of chloride ions, $\log \gamma^{\circ}_{\mathrm{Cl}}$, equal to −0.058639 for 15 °C, −0.059596 for 25 °C and −0.060844 for 37 °C.

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[2] 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.

The reported uncertainties for pH did not include the contribution of Bates-Guggenheim Convention for calculation of log $\gamma^{\circ}_{\mathrm{Cl}}$.

Traceability sources of standard buffers used in these secondary methods were:
- NIST SRM 187e (Sodium Tetraborate Decahydrate (Borax) pH Standard) for IBMETRO;
- NIST SRM 186 (pH Standards Potassium Dihydrogen Phosphate (186-I-g) and Disodium Hydrogen Phosphate (186-II-g)), NIST SRM 188 (Potassium Hydrogen Tartrate (pH Standard)) and NIST SRM 191 (Sodium Bicarbonate (191d-I) and Sodium Carbonate (191d-II) (pH Standard)) for INTI;
- NIST SRM 187e (Sodium Tetraborate Decahydrate (Borax) pH Standard) for LATU.

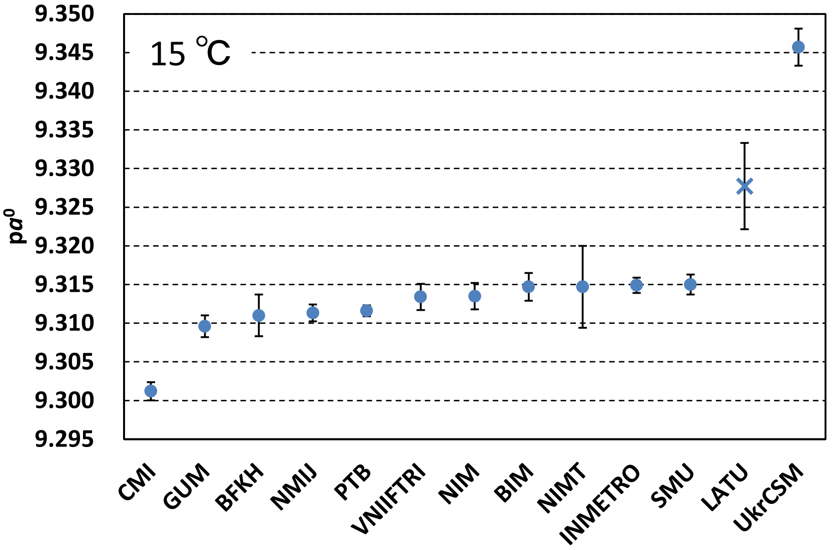

Fig. 4-1 Results of pa^0 determination at 15 °C, CCQM-K19.2018.
●: primary; x: secondary.
Each bar corresponds to the combined standard uncertainty.

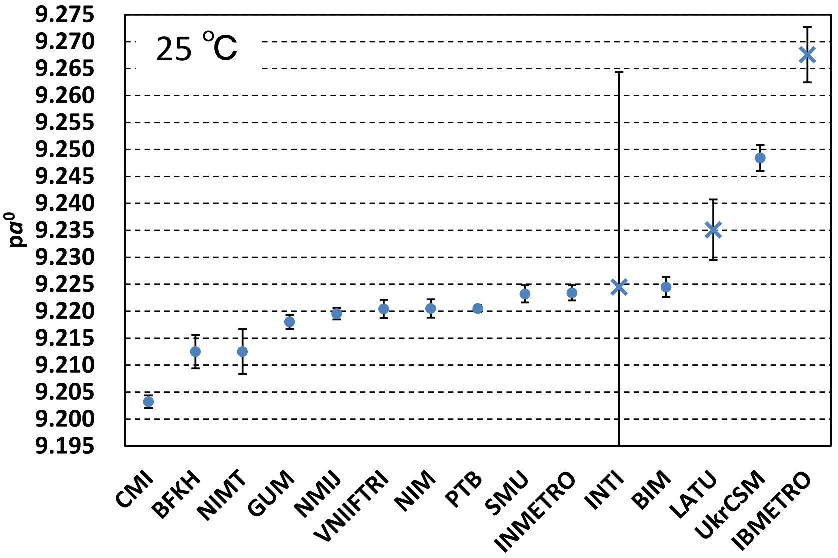

Fig. 4-2 Results of pa^0 determination at 25 °C, CCQM-K19.2018.
●: primary; x: secondary.
Each bar corresponds to the combined standard uncertainty.

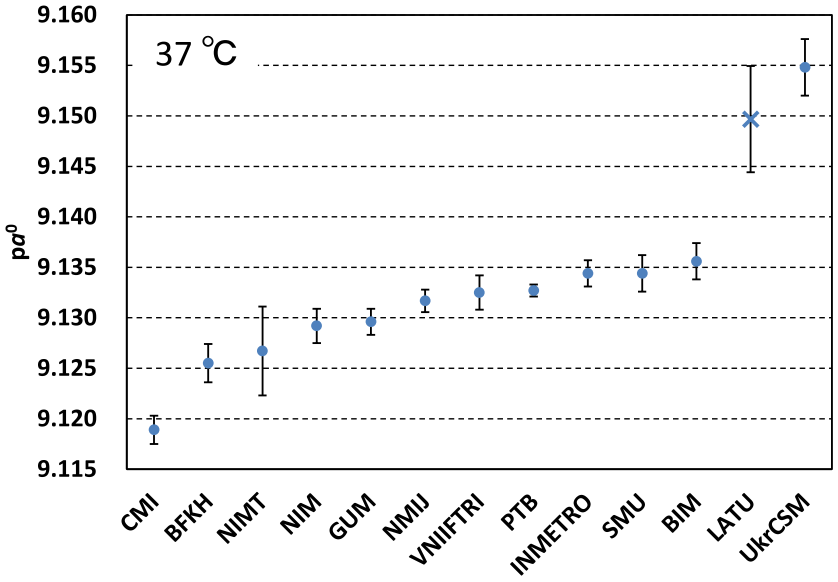

Fig. 4-3 Results of pa^0 determination at 37 °C, CCQM-K19.2018.
●: primary; x: secondary.
Each bar corresponds to the combined standard uncertainty.

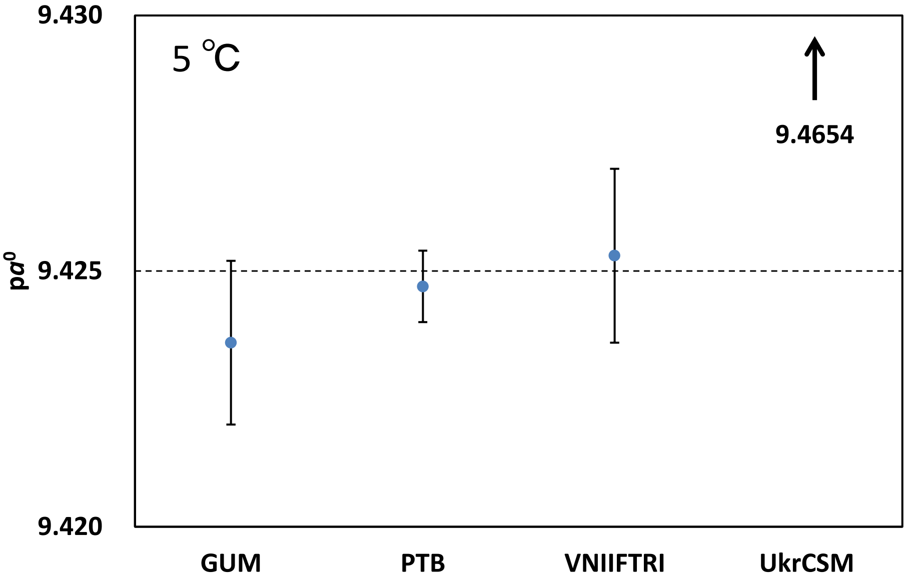

Fig. 4-4 Results of pa^0 determination at 5 °C, CCQM-K19.2018.
●: primary.
Each bar corresponds to the combined standard uncertainty.

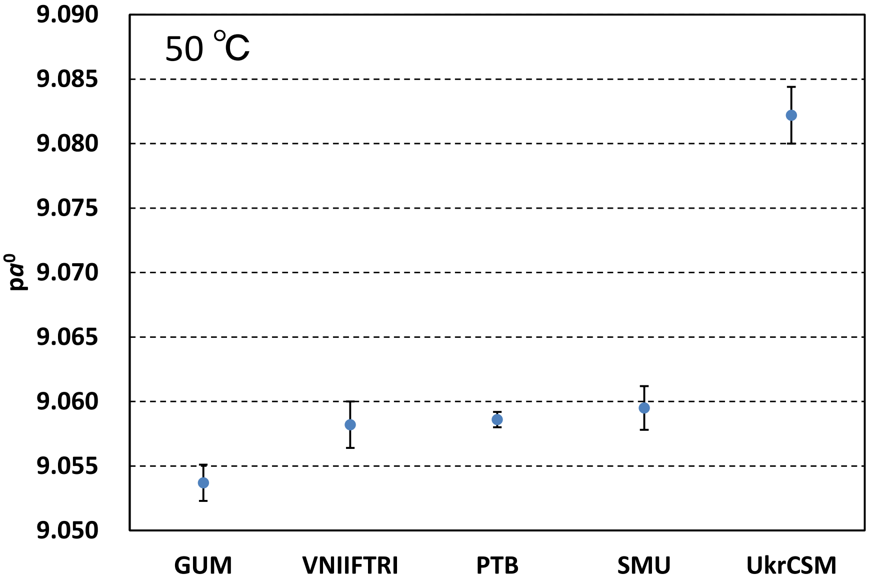

Fig. 4-5 Results of pa^0 determination at 50 °C, CCQM-K19.2018.
●: primary.
Each bar corresponds to the combined standard uncertainty.

Other information reported by the participants using the primary Harned cell method: the measurement methods for HCl standardization are given in Table 4; the standard potentials are shown in Table 5 and Figs. 5-1 to 5-5; the pa^0 values and slopes are presented in Figs. 6-1 to 6-5 and Fig. 7-1 to 7-5. The digits of the uncertainties of the reported values were reduced to two significant digits.

Table 4 Information on the assay of HCl reported by participants using the primary cell

Acronym	Method	Molality, mol kg^{-1}	u(mol kg^{-1})
BFKH	Coulometric titration	0.010 0676	0.000 0053
BIM	Titrimetric method with NaOH (Sigma-Aldrich)	0.010 20	0.000 017
CENAM	---	---	---
CMI	Coulometric titration	0.010 000 0	0.000 001 0
GUM	Coulometric titration	0.010 000 1	0.000 002 1
IBMETRO	---	---	---
INMETRO	Coulometric titration	0.010 000	0.000 002
INTI	---	---	---
IPQ	---	---	---
LATU	---	---	---
NIM	Coulometric titration	0.010 000	0.000 005
NIMT	NMIJ CRM 3201-a07 (0.1 mol/kg HCl)	0.010 00	0.000 04
NMIJ	Coulometric titration	0.010 000	0.000 003
PTB	Coulometric titration	0.010 016	0.000 002
SMU	Coulometric titration	0.009 998 9	0.000 005 8
UkrCSM	Coulometric titration	0.010 001 9	0.000 007 2
VNIIFTRI	Coulometric titration	0.010 00	0.000 01

Table 5 Information on the Ag/AgCl standard potential E°, its standard uncertainty $u(E^\circ)$ and the slope of the pa extrapolation to the zero chloride molality $b_{\mathrm{Cl}} = 0\ \mathrm{mol\ kg^{-1}}$

Acronym	15 °C E° / V $u(E^\circ)$ / V pa slope	25 °C E° / V $u(E^\circ)$ / V pa slope	37 °C E° / V $u(E^\circ)$ / V pa slope	5 °C E° / V $u(E^\circ)$ / V pa slope	50 °C E° / V $u(E^\circ)$ / V pa slope
BFKH	0.228 808 0.000 386 −0.4498	0.222 759 0.000 039 −0.4219	0.213 578 0.000 040 −0.5047	---	---
BIM	0.22855 0.0001 −0.4267	0.22234 0.0001 −0.4237	0.21424 0.0001 −0.454	---	---
CENAM	---	---	---	---	---
CMI	0.227 97 0.000 025 8.5821	0.221 71 0.000 025 12.882	0.213 05 0.000 026 13.599	---	---
GUM	0.228 704 0.000 023 0.1491	0.222 520 0.000 025 0.1807	0.214 358 0.000 027 0.2119	0.234 213 0.000 032 0.1158	0.204 669 0.000 032 0.3654
IBMETRO	---	---	---	---	---
INMETRO	0.228 751 0.000 021 −0.2516	0.222 487 0.000 019 −0.1686	0.214 366 0.000 030 −0.0415	---	---
INTI	---	---	---	---	---
IPQ	---	---	---	---	---
LATU	---	---	---	---	---
NIM	0.228 652 0.000 042 −0.1022	0.222 500 0.000 045 −0.1370	0.214 473 0.000 044 −0.0977	---	---
NIMT	0.228 955 0.000 046 −0.5281	0.222 729 0.000 080 −0.3930	0.214 023 0.000 026 −0.4558	---	---
NMIJ	0.228 699 0.000 044 −0.2408	0.222 580 0.000 044 −0.2103	0.214 434 0.000 044 −0.1727	---	---
PTB	0.228 993 0.000 086 -0.272	0.222 804 0.000 080 -0.255	0.214 584 0.000 077 -0.205	0.234 514 0.000 082 -0.296	0.204 832 0.000 074 -0.157
SMU	0.228 719 0.000 045 −0.2470	0.222 533 0.000 046 −0.2673	0.214 291 0.000 047 −0.3153	---	0.204 412 0.000 048 −0.2539
UkrCSM	0.228 680 0.000 039 −0.848	0.222 333 0.000 040 −0.761	0.214 031 0.000 041 −0.982	0.233 939 0.000 037 −1.148	0.203 456 0.000 043 −0.652
VNIIFTRI	0.229165 0.000074 −2.6732	0.222465 0.000074 −0.5844	0.215079 0.000074 −1.9131	0.234738 0.000074 −0.8706	0.205335 0.000074 −3.2551

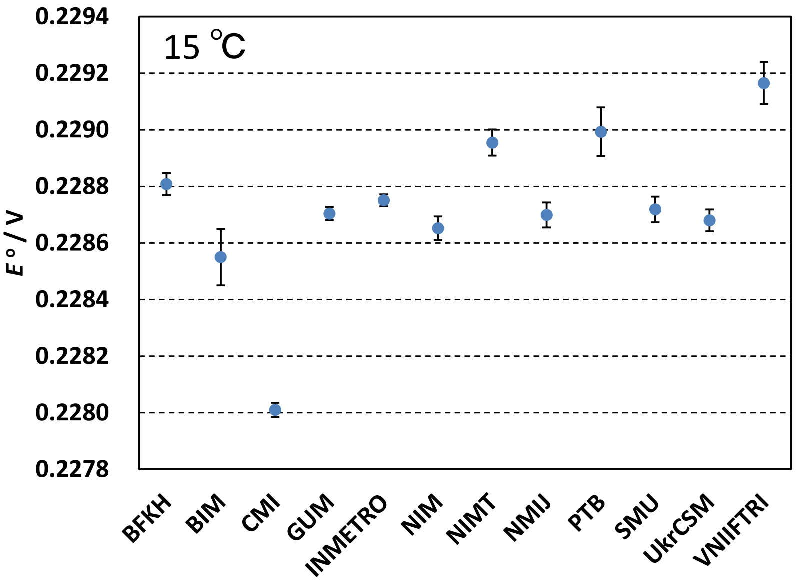

Fig. 5-1 Reported values of Ag/AgCl standard potential and their combined standard uncertainties at 15 °C.

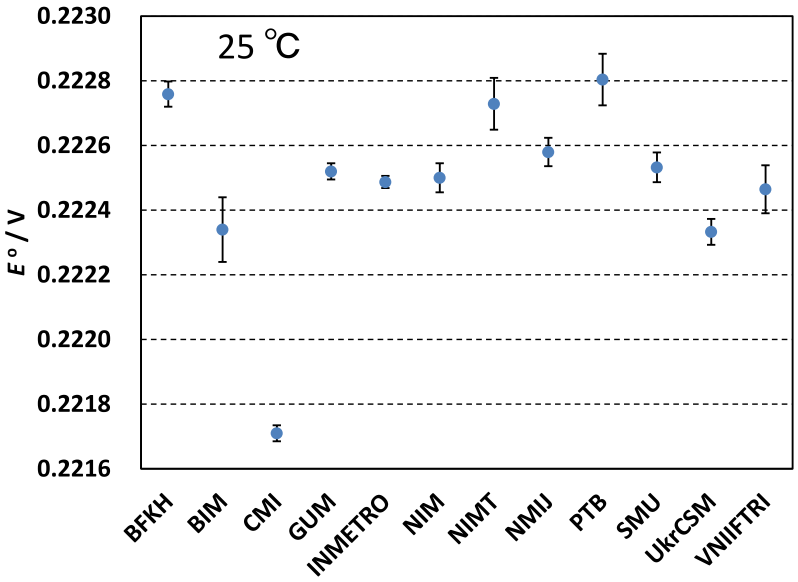

Fig. 5-2 Reported values of Ag/AgCl standard potential and their combined standard uncertainties at 25 °C.

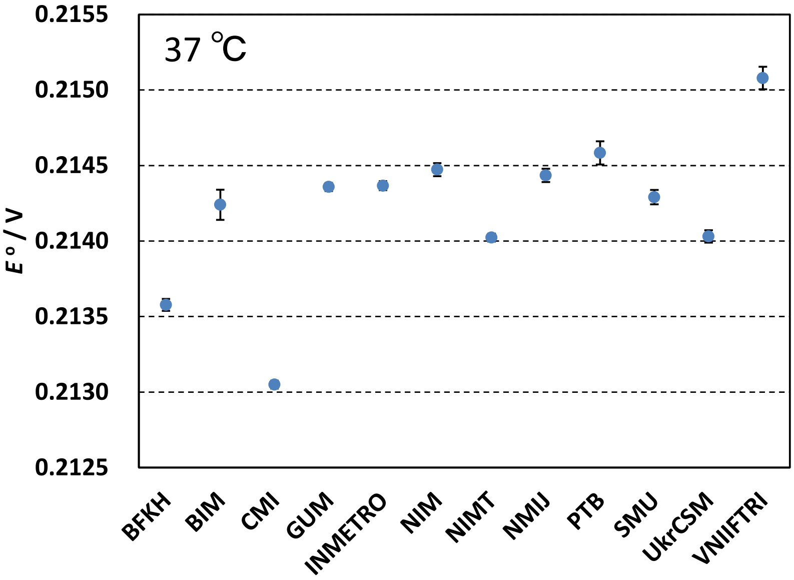

Fig. 5-3 Reported values of Ag/AgCl standard potential and their combined standard uncertainties at 37 °C.

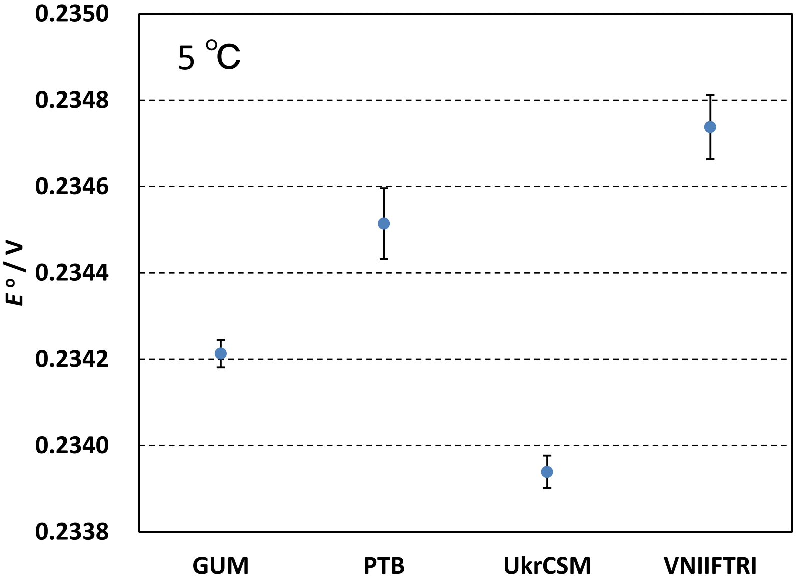

Fig. 5-4 Reported values of Ag/AgCl standard potential and their combined standard uncertainties at 5 °C.

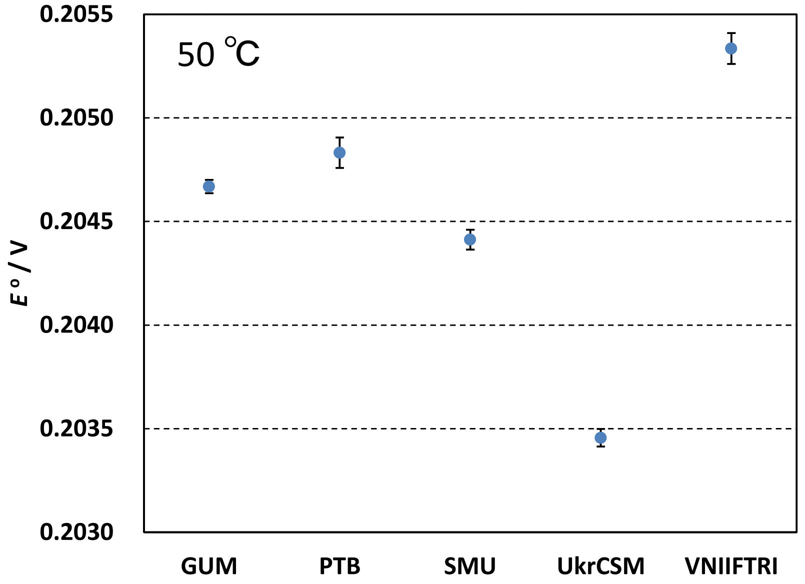

Fig. 5-5 Reported values of Ag/AgCl standard potential and their combined standard uncertainties at 50 °C.

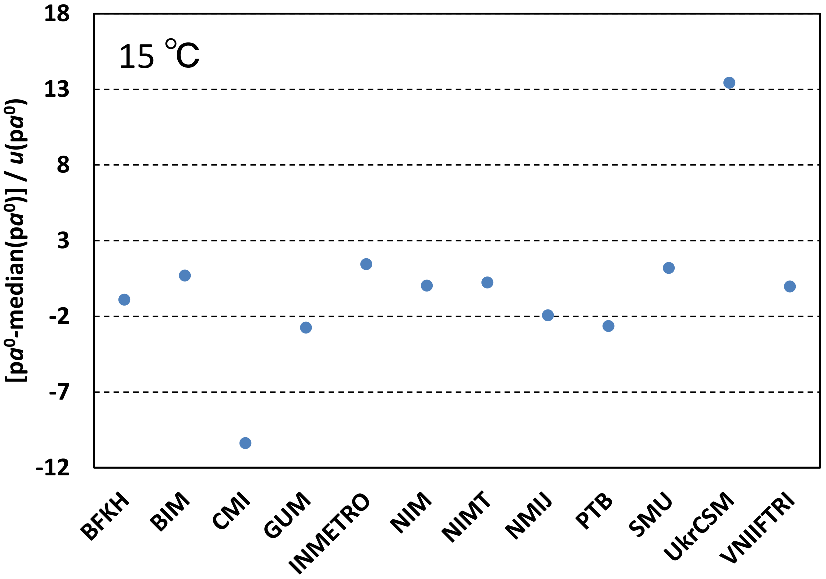

Fig. 6-1 Results of the inspection for anomalous pa^0 values at 15 °C.

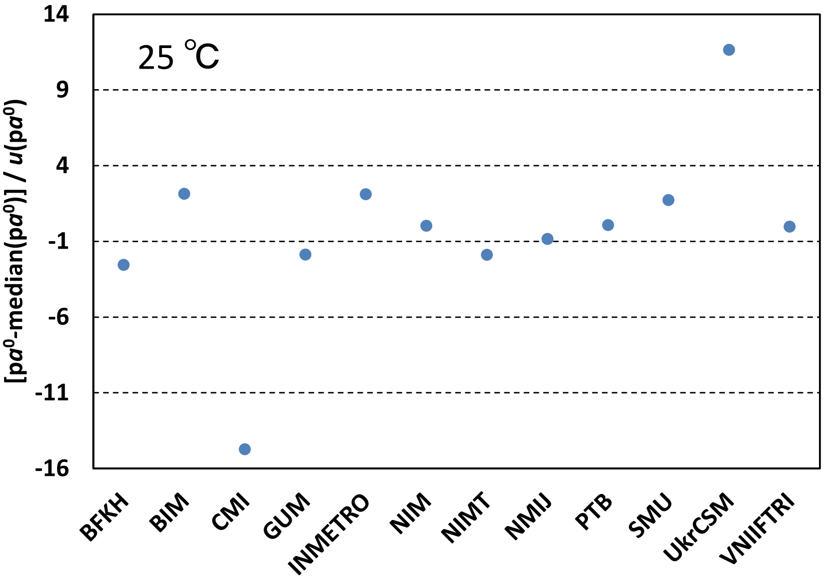

Fig. 6-2 Results of the inspection for anomalous pα^0 values at 25 °C.

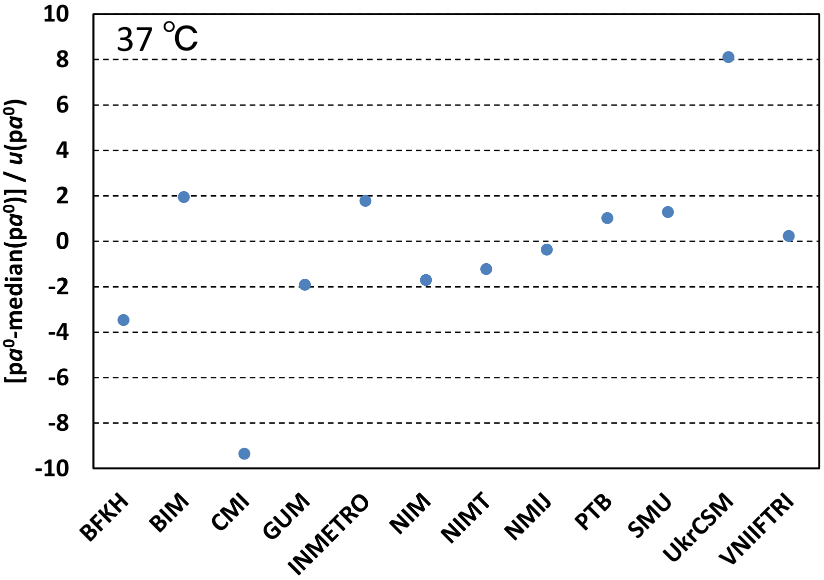

Fig. 6-3 Results of the inspection for anomalous pα^0 values at 37 °C.

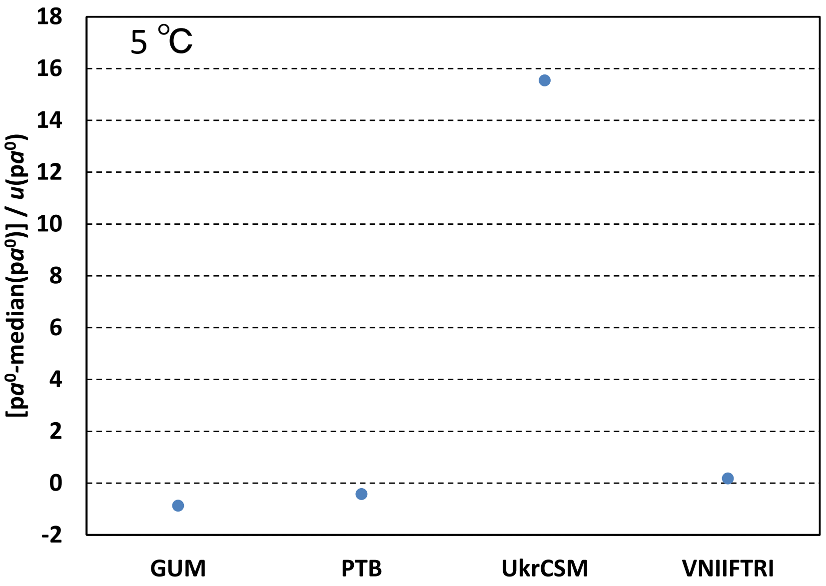

Fig. 6-4 Results of the inspection for anomalous pa^0 values at 5 °C.

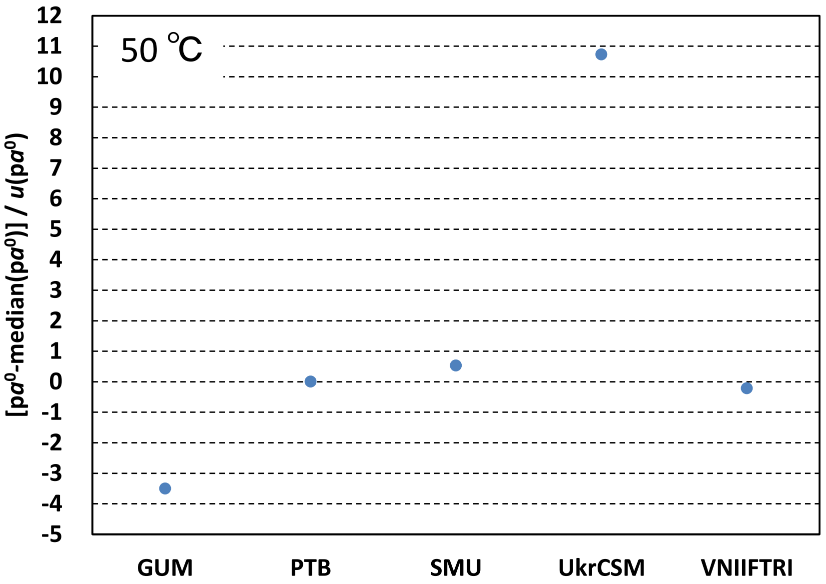

Fig. 6-5 Results of the inspection for anomalous pa^0 values at 50 °C.

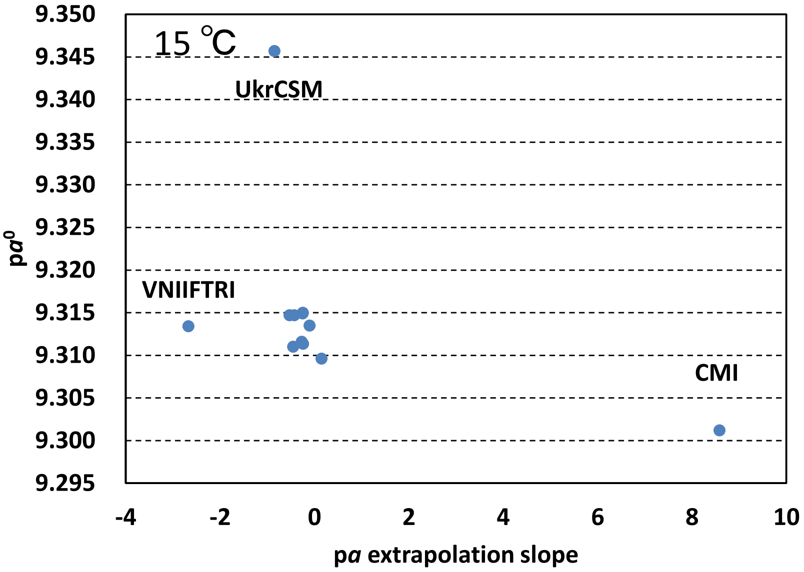

Fig. 7-1 Comparison of the p*a* and its slope at 15 °C.

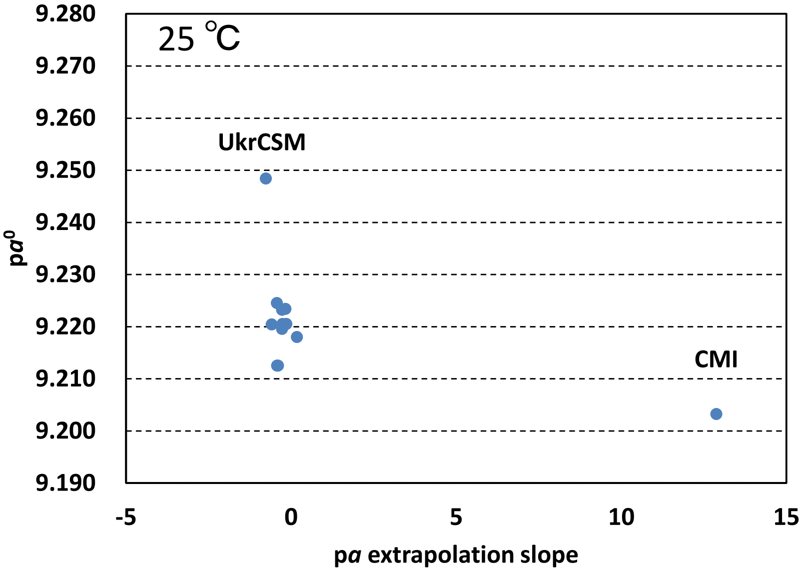

Fig. 7-2 Comparison of the p*a* and its slope at 25 °C.

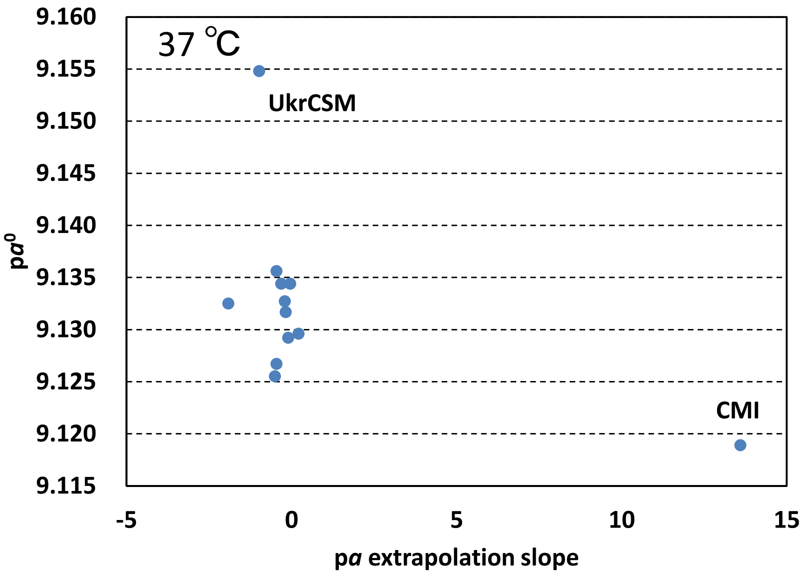

Fig. 7-3 Comparison of the p*a* and its slope at 37 °C.

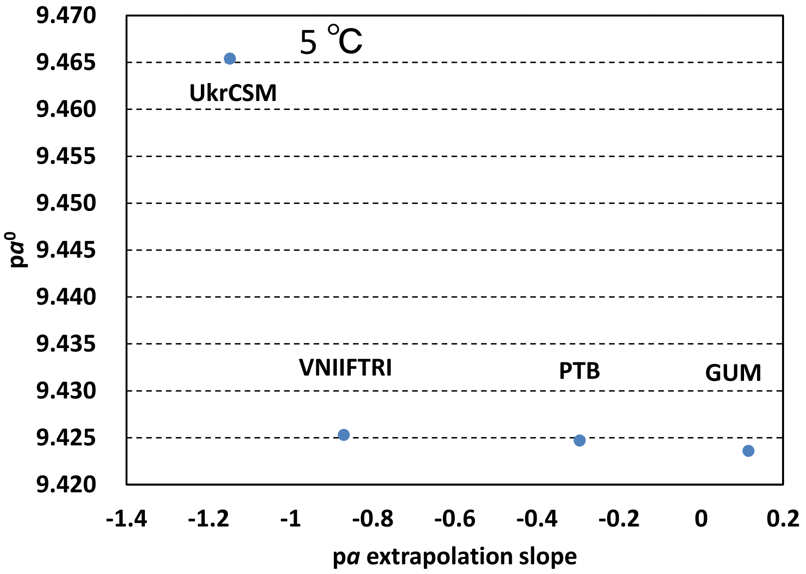

Fig. 7-4 Comparison of the p*a* and its slope at 5 °C.

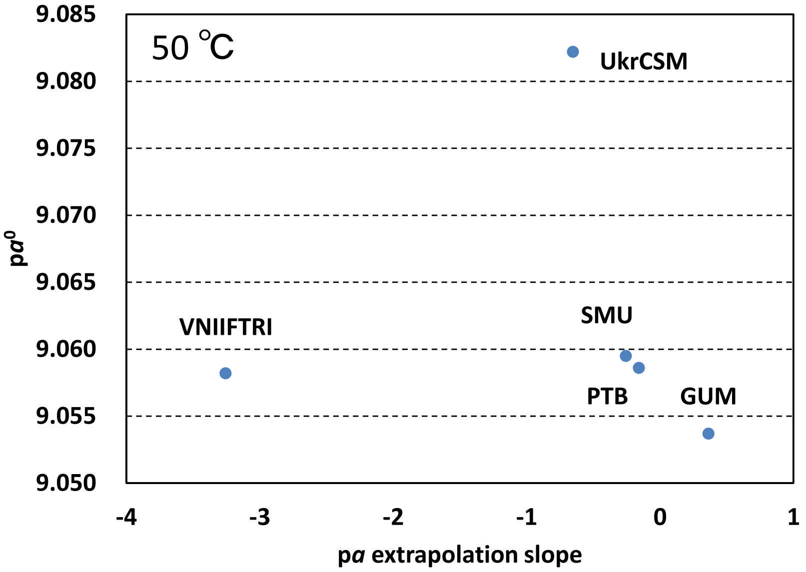

Fig. 7-5 Comparison of the pa and its slope at 50 °C.

In general, the reported Ag/AgCl standard potentials agree quite well to the literature reference value[3] and are close to each other except for CMI's one. The standard potentials of CMI are significantly smaller than the others. Although this deviation has no impact within the framework of the primary measurement procedure, CMI's pa values are significantly lower than the median as well.

The inspection for anomalous pa^0 values shown in Figs. 6-1 to 6-5 could indicate the underestimation of uncertainty of an the anomalous pa^0 value of a participant. For this estimation, the relative consistency is described by the function: [p$a^0{}_i$ – median (pa^0)] / u(p$a^0{}_i$). The calculated value of CMI and UkrCSM is far from zero. Figures 6-1 to 6-5 suggest that:

- the pa^0 result reported by CMI is anomalously lower than the median of the participants' results, or the reported u[pa^0] is underestimated.
- the pa^0 result reported by UkrCSM is anomalously higher than the median of the participants' results, or the reported u[pa^0] is underestimated.

Figures 7-1 to 7-5 show a relationship between pa^0 and the pa extrapolation slope. More positive pa extrapolation slopes generally show a tendency to make pa^0 values lower. The result of CMI had such a tendency.

The results of most participants lay within 0.01 in pH, and are in good agreement.

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

Calculation of the KCRV and Uncertainty

Four possibilities for determination of the KCRV are listed in Tables 6-1 and 6-2[4,5]. For each estimator, only the pa^0 results determined by the primary measurement technique are used in the calculation and only results obtained using primary method were used to calculate candidate KCRVs.

EAWG (EAWG meeting of April 20th, 2021) decided to omit the results of CMI and UkrCSM from the calculation of the KCRV with both concerned institutes kindly accepting this correction. CMI informed that they found that the reason of deviation in their results being the rough calculation error. UkrCSM noticed some unidentified problem with the measurements procedure.

Table 6-1a Values of candidate estimators for the KCRV for CCQM-K19.2018.

Estimator	15 °C		25 °C		37 °C	
	Value, pa^0	$u(\mathrm{p}a^0)$ $U(\mathrm{p}a^0)$	Value, pa^0	$u(\mathrm{p}a^0)$ $U(\mathrm{p}a^0)$	Value, pa^0	$u(\mathrm{p}a^0)$ $U(\mathrm{p}a^0)$
Arithmetic Mean	9.3148	0.0030 0.0060	9.2206	0.0031 0.0061	9.1322	0.0025 0.0049
Weighted Mean*	9.3123	0.0020 0.0040	9.2193	0.0023 0.0046	9.1316	0.0015 0.0031
Median / MAD$_E$	9.3135	0.0038 0.0076	9.2205	0.0039 0.0077	9.1321	0.0031 0.0062
DerSimonian -Laird	9.3145	0.0030 0.0060	9.2206	0.0030 0.0060	9.1321	0.0023 0.0046
Birge ratio	5.24		5.81		4.06	

* The uncertainty of the weighted mean is corrected for the observed dispersion of Birge ratio.

Table 6-1b Values of candidate estimators for the KCRV for CCQM-K19.2018
(CMI and UkrCSM excluded).

Estimator	15 °C		25 °C		37 °C	
	Value, pa^0	$u(\mathrm{p}a^0)$ $U(\mathrm{p}a^0)$	Value, pa^0	$u(\mathrm{p}a^0)$ $U(\mathrm{p}a^0)$	Value, pa^0	$u(\mathrm{p}a^0)$ $U(\mathrm{p}a^0)$
Arithmetic Mean	9.3130	0.00062 0.0012	9.2195	0.00132 0.0026	9.1312	0.00107 0.0021
Weighted Mean*	9.3126	0.00059 0.0012	9.2205	0.00073 0.0015	9.1321	0.00072 0.0014
Median / MAD$_E$	9.3135	0.00088 0.0018	9.2205	0.00153 0.0031	9.1321	0.00141 0.0028
DerSimonian -Laird	9.3128	0.00068 0.0014	9.2204	0.00085 0.0017	9.1317	0.00091 0.0018
Birge ratio	1.45		1.82		1.82	

* The uncertainty of the weighted mean is corrected for the observed dispersion of Birge ratio.

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[4] CCQM13-22: 2013, "CCQM Guidance note: Estimation of a consensus KCRV and associated Degrees of Equivalence, v10".

[5] NIST Consensus Builder: 2017, National Institute of Standards and Technology, MD, USA.

Table 6-2a Values of candidate estimators for the KCRV for CCQM-K19.2018.

Estimator	5 °C		50°C	
	Value, pa^0	u(pa^0) U(pa^0)	Value, pa^0	u(pa^0) U(pa^0)
Arithmetic Mean	9.4348	0.0102 0.0204	9.0624	0.0050 0.0101
Weighted Mean*	9.4267	0.0052 0.0103	9.0592	0.0028 0.0055
Median / MAD$_E$	9.4250	0.0128 0.0256	9.0586	0.0063 0.0126
DerSimonian -Laird	9.4345	0.0101 0.0201	9.0623	0.0049 0.0098
Birge ratio	8.83		5.61	

* The uncertainty of the weighted mean is corrected for the observed dispersion of Birge ratio.

Table 6-2b Values of candidate estimators for the KCRV for CCQM-K19.2018 (CMI and UkrCSM excluded).

Estimator	5 °C		50°C	
	Value, pa^0	u(pa^0) U(pa^0)	Value, pa^0	u(pa^0) U(pa^0)
Arithmetic Mean	9.4245	0.00050 0.0010	9.0575	0.00130 0.0026
Weighted Mean*	9.4246	0.00032 0.0006	9.0580	0.00097 0.0019
Median / MAD$_E$	9.4247	0.00064 0.0013	9.0584	0.00060 0.0012
DerSimonian -Laird	9.4246	0.00021 0.0004	9.0575	0.00128 0.0026
Birge ratio	0.54		1.93	

* The uncertainty of the weighted mean is corrected for the observed dispersion of Birge ratio.

By considering the Birge ratios and the number of participants for the KCRV calculations, the coordinating laboratories recommended “the weighted mean with dispersion” at 15 °C, 25 °C, 37 °C and 50 °C; “the weighted mean without dispersion” at 5 °C. The recommendations were agreed by the participants.

The following equations were used for the KCRVs (KCRV) and their standard uncertainties (*u*(KCRV))[4]:

$$\mathrm{KCRV} = \sum_{i=1}^{m} w_i\, x_i \qquad (\mathrm{eq.}\,7)$$

where

$$w_i = \frac{\left(\frac{1}{u(x_i)}\right)^2}{\sum_{j=1,m}\left(\frac{1}{u(x_j)}\right)^2} \qquad (\mathrm{eq.}\,8)$$

a) Uncorrected for observed dispersion:

$$\frac{1}{u^2(\mathrm{KCRV})} = \sum_{i=1}^{m} \frac{1}{u^2(x_i)} \qquad (\mathrm{eq.}\,9)$$

b) Corrected for observed dispersion:

$$u_{\mathrm{corr}}^2(\mathrm{KCRV}) = \frac{\chi_{\mathrm{obs}}^2}{m-1} u^2(\mathrm{KCRV}) \qquad (\mathrm{eq.}\,10)$$

where

$$\chi_{\mathrm{obs}}^2 = \sum_{i=1}^{m} \frac{(x_i - \mathrm{KCRV})^2}{u^2(x_i)} \qquad (\mathrm{eq.}\,11)$$

Table 7 KCRV and its standard uncertainty for CCQM-K19.2018.

15 °C KCRV, pa^0 *u*(KCRV)	25 °C KCRV, pa^0 *u*(KCRV)	37 °C KCRV, pa^0 *u*(KCRV)	5 °C KCRV, pa^0 *u*(KCRV)	50 °C KCRV, pa^0 *u*(KCRV)
9.31263 0.00059	9.22050 0.00073	9.13210 0.00072	9.42462 0.00060	9.05801 0.00097

Calculation of the Degrees of Equivalence

The degree of equivalence for each participant, d_i, is given by:

$$d_i = \mathrm{pa}_i^0 - \mathrm{KCRV} \qquad \text{(eq. 12)}$$

For the results used in calculation of the KCRV, the standard uncertainty for the degree of equivalence, $u(d_i)$, is given by:

a) Uncorrected for observed dispersion:

$$u(d_i) = \sqrt{u^2(x_i) - u^2(\mathrm{KCRV})} \qquad \text{(eq. 13)}$$

b) Corrected for observed dispersion:

$$u_{\mathrm{corr}}(d_i) = \sqrt{u_{\mathrm{corr}}^2(\mathrm{KCRV}) + (1 - 2w_i)u^2(x_i)} \qquad \text{(eq. 14)}$$

For the results determined by the secondary method and other results, which were not used in calculation of the KCRV, $u(d_i)$, is given by:

$$u(d_i) = \sqrt{u^2(x_i) + u^2(\mathrm{KCRV})} \quad \text{or} \quad \sqrt{u^2(x_i) + u_{\mathrm{corr}}^2(\mathrm{KCRV})} \qquad \text{(eq. 15)}$$

The expanded uncertainties, $U(d_i)$, are calculated with a coverage factor, k, equal to 2.

Minimum standard uncertainties ($u(\mathrm{CMC}_{\mathrm{min}})$) of CCQM-K19.2018 were calculated based on “EAWG guideline for claims of Calibration and Measurement Capabilities, v13” as follows:

The best estimate x_i reported by an institute i in the supporting key comparison is assumed to be consistent with the KCRV of the key comparison, if

$$|d_i| \leq U(d_i) \qquad \text{(eq. 16)}$$

then, the minimum standard measurement uncertainty $u(\mathrm{CMC}_{\mathrm{min}})$ is given by:

$$u(\mathrm{CMC}_{\mathrm{min},i}) = u(x_i) \qquad \text{(eq. 17)}$$

The best estimate x_i reported is assumed to be inconsistent with the KCRV of the key comparison, if

$$|d_i| > U(d_i) \qquad \text{(eq. 18)}$$

then, the minimum standard measurement uncertainty $u(\mathrm{CMC}_{\mathrm{min}})$ is given by:

$$u(\mathrm{CMC}_{\mathrm{min},i}) = \sqrt{u^2(d_i) + \left(\frac{d_i}{2}\right)^2} \qquad \text{(eq. 19)}$$

The expanded uncertainties, $U(\mathrm{CMC}_{\mathrm{min},i})$, are calculated with a coverage factor, k, equal to 2.

The values of E_{n} are given by:

$$E_{\mathrm{n}} = \frac{d_i}{\sqrt{U^2(x_i) + U^2(\mathrm{KCRV})}} \qquad \text{(eq. 20)}$$

Table 8-1 Degrees of equivalence and expanded uncertainties of CCQM-K19.2018 on pH for borate buffer at 15 °C.

Acronym	d_i	$U(d_i)$	$d_i / u(\mathrm{p}a^0)$	$U(\mathrm{CMC_{min}})$	E_n
BFKH	−0.0016	0.0054	−0.60	0.0054	−0.29
BIM	0.0021	0.0036	1.15	0.0036	0.55
CMI	−0.0114	0.0026	−9.69	0.0059*	−4.33
GUM	−0.0030	0.0029	−2.16	0.0021*	−1.00
INMETRO	0.0023	0.0021	2.27	0.0015*	0.98
LATU	0.0151	0.0112	2.71	0.0094*	1.35
NIM	0.0009	0.0034	0.51	0.0034	0.24
NIMT	0.0021	0.0106	0.39	0.0106	0.19
NMIJ	−0.0013	0.0022	−1.18	0.0022	-0.52
PTB	−0.0010	0.0015	−1.47	0.0014	−0.56
SMU	0.0024	0.0027	1.82	0.0026	0.83
UkrCSM	0.0331	0.0049	13.78	0.0167*	6.69
VNIIFTRI	0.0008	0.0035	0.44	0.0035	0.21

* The reported values are inconsistent with KCRV.

Table 8-2 Degrees of equivalence and expanded uncertainties of CCQM-K19.2018 on pH for borate buffer at 25 °C.

Acronym	d_i	$U(d_i)$	$d_i / u(\mathrm{p}a^0)$	$U(\mathrm{CMC_{min}})$	E_n
BFKH	−0.0080	0.0063	−2.58	0.0051*	−1.26
BIM	0.0040	0.0039	2.11	0.0028*	0.98
CMI	−0.0173	0.0028	−14.79	0.0088*	−6.27
GUM	−0.0025	0.0028	−1.92	0.0026	−0.84
IBMETRO	0.0471	0.0104	9.17	0.0241*	4.54
INMETRO	0.0029	0.0030	2.07	0.0028	0.92
INTI	0.0040	0.0798	0.10	0.0798	0.05
LATU	0.0146	0.0113	2.60	0.0092*	1.29
NIM	0.0000	0.0035	0.00	0.0034	0.00
NIMT	−0.0080	0.0085	−1.90	0.0084	−0.94
NMIJ	−0.0010	0.0024	−0.90	0.0022	−0.37
PTB	0.0000	0.0017	0.00	0.0014	0.00
SMU	0.0027	0.0033	1.69	0.0032	0.77
UkrCSM	0.0279	0.0050	11.63	0.0142*	5.56
VNIIFTRI	−0.0001	0.0036	−0.06	0.0035	−0.03

* The reported values are inconsistent with KCRV.

Table 8-3 Degrees of equivalence and expanded uncertainties of CCQM-K19.2018 on pH for borate buffer at 37 °C.

Acronym	d_i	$U(d_i)$	d_i / $u(\mathrm{p}a^0)$	$U(\mathrm{CMC_{min}})$	E_n
BFKH	-0.0066	0.0039	−3.47	0.0038*	−1.62
BIM	0.0035	0.0037	1.94	0.0036	0.90
CMI	-0.0132	0.0032	−9.36	0.0068*	−4.17
GUM	-0.0025	0.0028	−1.92	0.0026	−0.84
INMETRO	0.0023	0.0028	1.77	0.0026	0.77
LATU	0.0176	0.0106	3.34	0.0103*	1.65
NIM	-0.0029	0.0035	−1.71	0.0034	−0.79
NIMT	-0.0054	0.0089	−1.23	0.0088	−0.61
NMIJ	-0.0004	0.0024	−0.38	0.0022	−0.16
PTB	0.0006	0.0015	1.00	0.0012	0.32
SMU	0.0023	0.0037	1.28	0.0036	0.59
UkrCSM	0.0227	0.0058	8.11	0.0117*	3.93
VNIIFTRI	0.0004	0.0036	0.23	0.0035	0.11

* The reported values are inconsistent with KCRV.

Table 8-4 Degrees of equivalence and expanded uncertainties of CCQM-K19.2018 on pH for borate buffer at 5 °C.

Acronym	d_i	$U(d_i)$	d_i / $u(\mathrm{p}a^0)$	$U(\mathrm{CMC_{min}})$	E_n
GUM	-0.0010	0.0030	−0.64	0.0032	−0.30
PTB	0.0001	0.0008	0.11	0.0014	0.04
UkrCSM	0.0408	0.0054	15.68	0.0206*	7.64
VNIIFTRI	0.0007	0.0032	0.41	0.0034	0.19

* The reported values are inconsistent with KCRV.

Table 8-5 Degrees of equivalence and expanded uncertainties of CCQM-K19.2018 on pH for borate buffer at 50 °C.

Acronym	d_i	$U(d_i)$	d_i / $u(\mathrm{p}a^0)$	$U(\mathrm{CMC_{min}})$	E_n
GUM	-0.0043	0.0031	−3.08	0.0027*	−1.27
PTB	0.0006	0.0018	0.98	0.0012	0.26
SMU	0.0015	0.0037	0.88	0.0034	0.38
UkrCSM	0.0242	0.0048	11.00	0.0123*	5.03
VNIIFTRI	0.0002	0.0039	0.10	0.0036	0.05

* The reported values are inconsistent with KCRV.

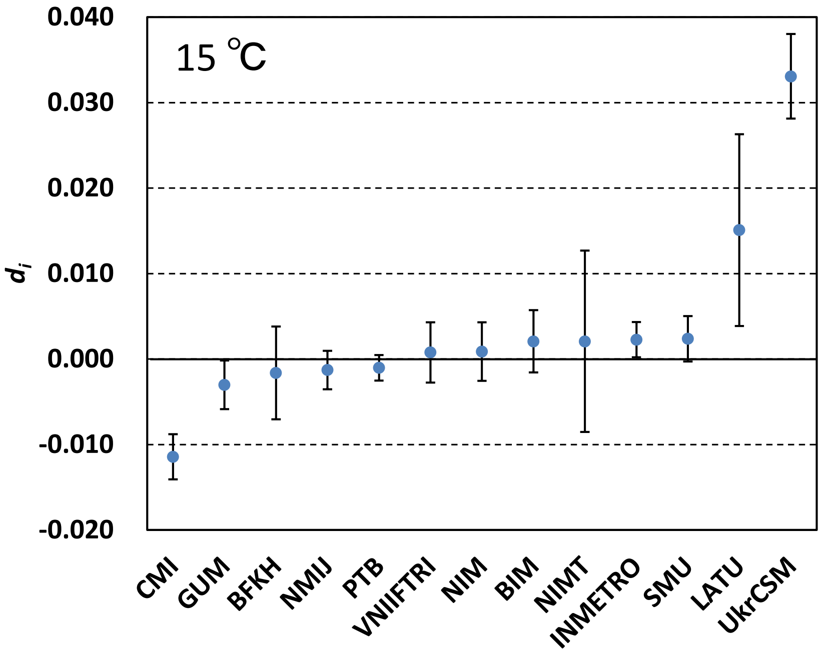

Fig. 8-1 Unilateral degrees of equivalence and expanded uncertainties (*k* = 2) at 15 °C for CCQM-K19.2018.

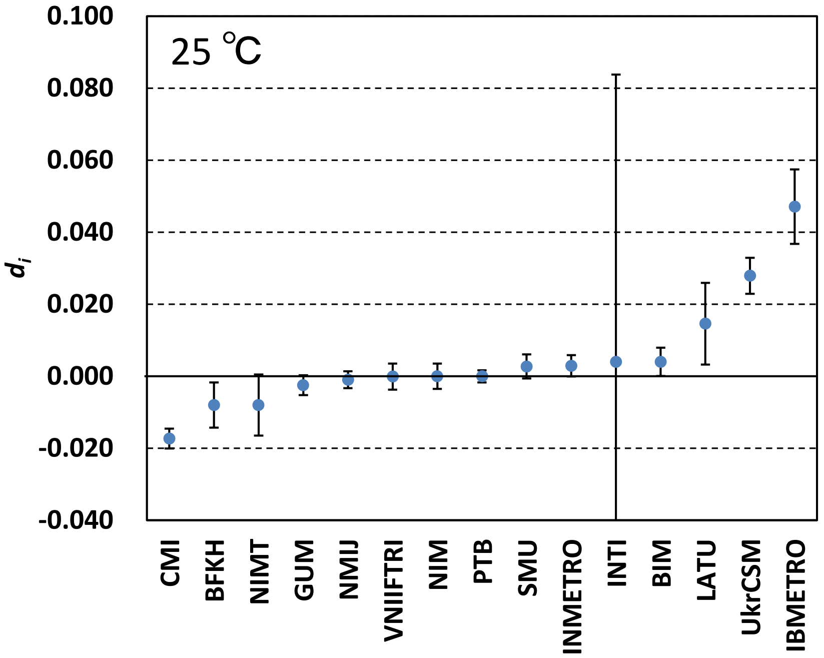

Fig. 8-2 Unilateral degrees of equivalence and expanded uncertainties (*k* = 2) at 25 °C for CCQM-K19.2018.

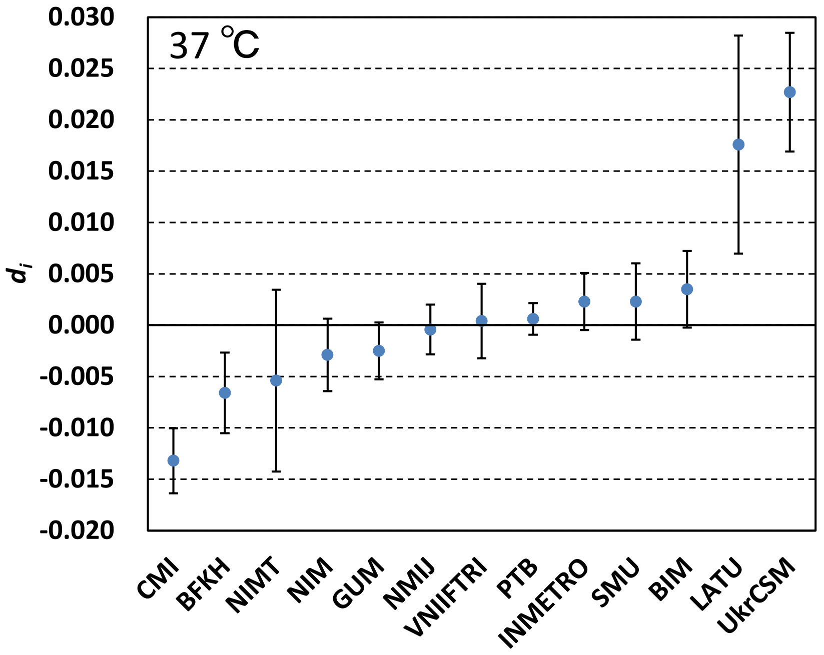

Fig. 8-3 Unilateral degrees of equivalence and expanded uncertainties (*k* = 2) at 37 °C for CCQM-K19.2018.

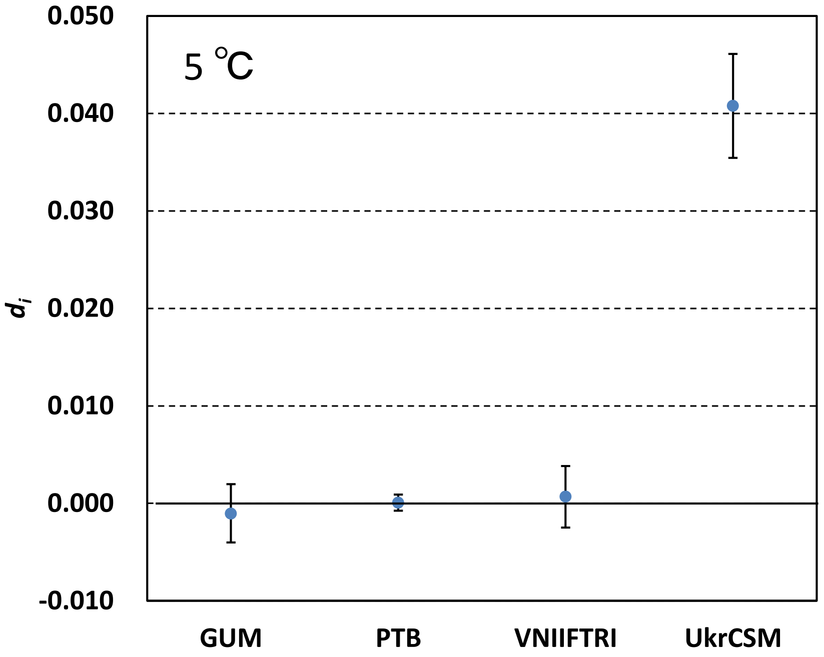

Fig. 8-4 Unilateral degrees of equivalence and expanded uncertainties (*k* = 2) at 5 °C for CCQM-K19.2018.

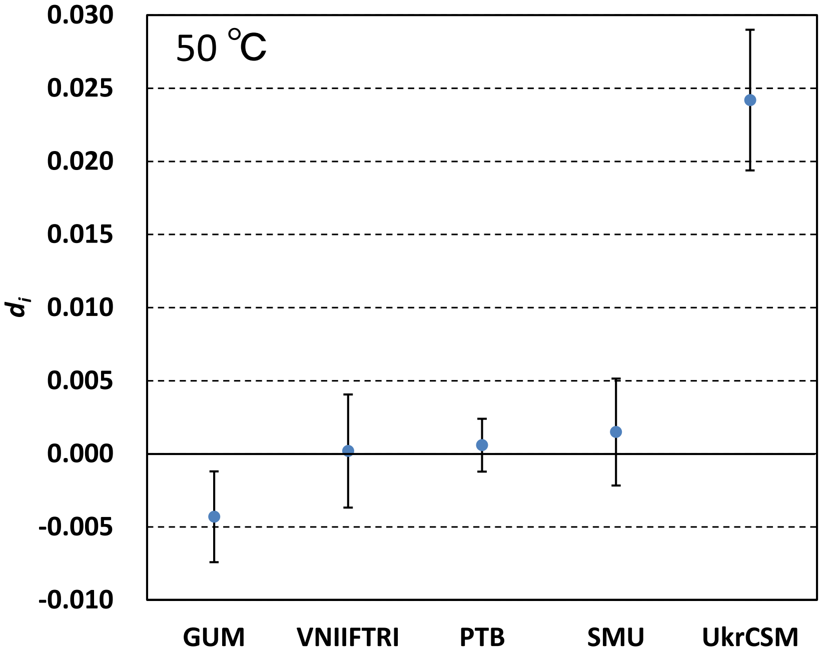

Fig. 8-5 Unilateral degrees of equivalence and expanded uncertainties (k = 2) at 50 °C for CCQM-K19.2018.

How far the light shines

Borate buffer solution is widely used in an alkaline pH range and is a ‘core capability’ buffer in primary Harned cell measurements. Participants that successfully took part in the CCQM-K19.2018 key comparison demonstrate their capability to measure the pH of borate buffer by the primary Harned cell method, the secondary differential potentiometric cell method, or the secondary glass electrode method in the pH range 8.5 to 9.5 at the temperature range 5 °C to 50 °C. The corresponding measurement uncertainties for each temperature must be assessed in reviewing CMC claims. Participants that successfully took part in this key comparison by the secondary glass electrode method may claim wider measurement ranges than 8.5 to 9.5 when provided the uncertainty and the calibration procedure are appropriate.

Conclusion

Comparability of measurement results was successfully demonstrated by many participating NMIs for the measurement of pH of a borate buffer within related expanded uncertainties. It is expected that the performance of each participant in the present key comparison is representative for measurement of pH of a borate buffer with the same technique as used in the present comparison.

Acknowledgment

The coordinating laboratory gratefully acknowledges the contributions of all participants and of the members of the CCQM-EAWG for their support in this comparison.

CCQM WG on Electrochemical Analysis and Classical Chemical Methods
CCQM-K19.2018 Key Comparison on Borate Buffer
Technical Protocol (18 April 2019)

Purpose

This key comparison is being performed to evaluate the degree of equivalence of national standard measurement procedures for the measurement of the pH of borate buffer solutions under the umbrella of the CIPM-MRA.

The comparison is a repetition of the key comparison CCQM-K19 from 2005.

The comparison is open to the National Metrology Institutes (NMI) or Designated Institutes (DI) of member or associate states of the Meter Convention. Only one result per institute (per temperature) is accepted. No measurement method is prescribed for the comparison, but it is expected that the highest level method at each institute is used. Only independent results, obtained by the primary method, will be used to calculate the Key Comparison Reference Value (KCRV).

In this comparison measurements of pH will be performed at 15 °C, 25 °C, 37 °C and optionally at 5 °C and 50 °C.

Time schedule

Oral invitation: April 2019 at EAWG meeting in Sèvres
Written invitation: June 2019
Registration deadline: 31 July 2019
Dispatch of samples: January 2020
Reporting deadline: 01 March 2020
Show results and
first discussion: EAWG meeting April 2020
Draft A report: July 2020
Draft B report: Late 2020
Approval of draft B report: EAWG meeting April 2021

Description of sample

The borate buffer solution with pH around ~ 9.2 at 25 °C will be prepared from deionized water and sodium tetraborate decahydrate ($Na_2B_4O_7 \cdot 10H_2O$, recrystallization pharma grade 99.0 to 103.0 % and kept in a desiccator over a solution of saturated KBr). The mass fraction of water in the solution will be given on the bottle label.

The homogeneity of the solution will be checked before shipment and the stability will be determined throughout the measurement period by Harned cell measurements

Each participant will receive 1 L high density polyethylene (HDPE) bottles which are numbered andsealed in aluminized plastic bags. 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. VNIIFTRI will ship the solutions by TNT or, on request, by another courier company. The tracking information will be emailed to the contact people. The contents are described as “Non-hazardous aqueous solution” and the value is given as 1 EUR.

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.

Actions at receipt of the sample

- Inspect the received box, bags and bottles for visible damage or leakage.
- If damage is found, report the problems you have encountered to the coordinating laboratories, NMIJ and VNIIFTRI, by email as soon as possible. If no damage is found, place the bottle in the bag and close the bag with tape. Store the bottle until the measurements at ambient conditions 25 °C ± 5 °C.
- Confirm the sample receipt by email to the coordinating laboratories, NMIJ and VNIIFTRI.
- Report the weighing data to the coordinating laboratories, NMIJ and VNIIFTRI, as soon as the data are 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 neither remove the tape nor the label from the bottles. 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 having received the solution.

- The measurements are performed at 15 °C, 25 °C, 37 °C and, optionally, at 5 °C and 50 °C.

- Recommended values of constants are[1]:

Molar gas constant, R = 8.314 4626 (18) J mol^{-1} K^{-1}

Faraday constant, F = 96 485.33212 (33) 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} that is traceble 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}.

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 email to the coordinating laboratories, NMIJ and VNIIFTRI, before the reporting deadline. The coordinating laboratory NMIJ will confirm the receipt of the report by email to the contact person of the participant no later than two weeks after the receipt. If no confirmation is received, please contact the coordinating laboratories 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)[2].

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

Technical details (depending on the procedure used):

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[1] To calculate we used the new data given in: Convocation of the General Conference on Weights and Measures (26th meeting), Versailles, 13-16 November 2018, p. 29.

[2] 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. Those values will be used further in the calculation of the KCRV and evaluation of degree of equivalence of each participant.

  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, and an individual acidity function value.

- Secondary measurements

  Participants performing secondary pH measurements are asked to use the template provided together with this technical protocol, however, they might use their own report form. The secondary measurement report form must contain the 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 and the source of the traceability.

  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 and the source of the traceability.

Coordinating laboratories and their roles

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1. VNIIFTRI and NMIJ will register the project. NMIJ will prepare an oral invitation in April 2019 in Sèvres. VNIIFTRI will prepare a written invitation and send to CCQM-EAWG Chair for e-mail posting.
2. VNIIFTRI will prepare the solution, carry out homogeneity and stability characterization and ship the samples to the participants.
3. NMIJ will present the comparison results for first discussion at the EAWG meeting, then VNIIFTRI will give a presentation on the subject of the samples stability and homogeneity and show established value of the samples pH.
4. NMIJ will prepare the draft A and draft B reports including the calculations of possible KCRVs and the degrees of equivalence