Key Comparison CCQM–K18.2016
pH of carbonate buffer

Final report
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Abstract

Key comparison (KC) CCQM-K18.2016 was performed to evaluate the degree of equivalence between pH measurement results on an unknown carbonate buffer reported by participating National Metrology Institutes and Designated Institutes (NMI/DIs). The participants used the highest metrological method existing at their institution. The nominal buffer pH was 10.0 and was determined only at 25 °C. Good agreement of the results is demonstrated by most participants.

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Metrology Area

Amount of Substance

Branch

Electrochemistry

Subject

Determination of the acidity functions at zero chloride molality of an unknown carbonate buffer, pH ≈ 10, by Harned cell or differential potentiometric cell measurements at 25 °C.

Time schedule

Owing to an equipment failure at the coordinating laboratory, shipment of the comparison samples was delayed from the dates outlined in the KC Technical Protocol (KC-TP) and the reporting deadline was extended. A delay in sample receipt caused another extension of the reporting deadline. The following time schedule reflects the updated comparison schedule and not what was originally proposed.

Dispatch of the samples:	12 January 2017
Deadline for receipt of the report:	24 March 2017
Presentation of the results:	EAWG Meeting, 24 April 2017
Discussion of Draft A report:	EAWG Meeting, 16 April 2018

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Summary

CCQM–K18.2016 was an activity of the Electrochemical Analysis Working Group (EAWG) of the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM). The KC was coordinated by the National Institute of Standards and Technology (NIST, USA), with contribution from Danish Fundamental Metrology Ltd (DFM, DK) in preparation of the KC-TP (Technical Protocol) and initial coordination efforts. CCQM-K18.2016 is a repetition of CCQM-K18 [1] conducted by the EAWG in 2006.

All participants applied either the primary method [2] for pH or the secondary differential potentiometric cell [3]. The reported result from the primary cell is the acidity function extrapolated to zero chloride molality, $\mathrm{p}a^0$. The Key Comparison Reference Value (KCRV) and its uncertainty are determined using results from the primary cell. The reported result from the secondary differential cell is pH.

Participants

The list of participants is given in Table 1.

Table 1. Table of participants in CCQM-K18.2016

Participant	Acronym	Country	Person(s)	Measurement Technique
Instituto Nacional de Metrologia, Qualidade e Tecnologia	INMETRO	Brazil (BR)	Fabiano Barbieri Gonzaga	Primary cell
Bulgarian Institute of Metrology	BIM	Bulgaria (BG)	Lyudmila Dimitrova	Primary cell
Czech Metrology Institute	CMI	Czech Republic (CZ)	Alena Vospelova, Matilda Rozikova	Primary cell
Danish Fundamental Metrology Ltd	DFM	Denmark (DK)	Alan Snedden	Primary cell
Laboratoire National de Métrologie et d'Essais	LNE	France (FR)	Daniela Stoica	Primary cell
Physikalisch-Technische Bundesanstalt	PTB	Germany (DE)	Beatrice Sander, Frank Bastkowski	Primary cell
Government Office of the Capital City Budapest	BFKH	Hungary (HU)	Beáta Jakusovszky	Primary cell
National Metrology Institute of Japan	NMIJ	Japan (JP)	Toshiaki Asakai, Igor Maksimov, Sachiko Onuma, Toshihiro Suzuki	Primary cell
Centro Nacional de Metrología	CENAM	Mexico (MX)	Jazmin Montero Ruiz, José Luis Ortiz-Aparicio	Primary cell
Central Office of Measures (Główny Urząd Miar)	GUM	Poland (PL)	Monika Pawlina, Wladyslaw Kozlowski	Primary cell
National Scientific and Research Institute for Physical-technical and Radio-technical Measurements	VNIIFTRI	Russia (RU)	Sergey V. Prokunin, Vladimir I. Dobrovolskiy, Alexey V. Aprelev	Primary cell
Slovak Institute of Metrology	SMU	Slovak Republic (SK)	Zuzana Hanková, Michal Máriássy	Primary cell
National Institute of Metrology (Thailand)	NIMT	Thailand (TH)	Patumporn Rodruangthum	Primary cell
Tübitak National Metrology Institute	UME	Turkey (TR)	Emrah Uysal, Lokman Liv, Nuri Nakiboglu	Primary cell
State Enterprise All-Ukrainian State Research and production Center of Standardization, Metrology, Certification and Consumers' Rights Protection	UMTS	Ukraine (UA)	Vladimir Gavrilkin, Anton Petrenko, Oleksandra Manska	Primary cell
National Institute of Standards and Technology	NIST	USA (US)	Jason F. Waters, Regina A. Easley	Primary cell
Instituto Nacional de Metrologia de Colombia	INM	Colombia (CO)	Ronald Cristancho Amaya, Henry Torres Quezada	Secondary differential cell
Instituto Nacional de Calidad	INACAL	Perú (PE)	Galia Tincona, Javier Vasquez	Secondary differential cell
Laboratorio Tecnológico del Uruguay	LATU	Uruguay (UY)	Simone Fajardo	Secondary differential cell

Sample Preparation and Bottling

The carbonate buffer solution was prepared from 18 MΩ cm ultra-pure water, sodium hydrogen carbonate ($NaHCO_3$, CAS 114-55-8), and sodium carbonate (Na_2CO_3, CAS 497-19-8) as the starting material. The sodium hydrogen carbonate was dried for a period of 3 days in a sealed glass desiccator over anhydrous magnesium perchlorate at room temperature. The sodium carbonate was dried at 275 °C for 2 h and stored over anhydrous magnesium perchlorate until use.

The CCQM-K18.2016 buffer was prepared as a 0.026 mol kg^{-1} equimolal buffer, which differed slightly from the standard 0.025 mol kg^{-1} equimolal buffer composition [2]. The calculated mass fraction of water, w_{H2O}, of the final solution was 0.99500 g g^{-1}. A high-density polyethylene (HDPE) carboy with a nominal volume of 50 dm^3 was used to prepare a single solution of the equimolal carbonate buffer. With the carboy cap firmly shut, the buffer was homogenized overnight by rocking.

After the homogenization, cleaned and dried HDPE bottles were filled and the junction between the cap and bottle was sealed with Parafilm. Bottles for the KC were 1 dm^3 and filled with approximately 1020 g of buffer. Bottles for assessment of the buffer homogeneity were 50 cm^3 and were filled with approximately 60 g of buffer. All bottles were filled in a single day.

After the bottles were filled and the caps sealed, the buoyancy corrected masses of the filled-bottles with the cap, label and Parafilm wrap were recorded. The prepared bottles stood undisturbed for 5 days before the masses were re-determined. The bottle masses were all found to agree to within 0.001 % to 0.002 %. Once the bottle masses were confirmed to be stable, the bottles were individually sealed in Mylar foil bags.

Solution Homogeneity

Homogeneity of the bottled buffer solution was checked by measuring the pH of 11 samples. The buffer samples for homogeneity assessment were filled concurrently, in a semi-randomized order, with the bottles for the KC. An Orion 8103BN ROSS[1] combination semi-micro glass pH electrode and a Keithley 6514 electrometer were used to assess bottle homogeneity. Each bottle was measured in duplicate. The homogeneity results are reported as the difference in the mean bottle pH (*n* = 2) from the overall mean pH (*n* = 12). The bottle homogeneity results are presented in Table 2 and Figure 1.

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

Bottle Number	ΔpH	*u*[ΔpH]
1	0.0009	0.0026
4	0.0005	0.0007
6	-0.0006	0.0007
11	-0.0004	0.0015
21	0.0000	0.0021
32	-0.0001	0.0006
39	-0.0002	0.0020
47	0.0002	0.0027
52	0.0001	0.0022
58	-0.0004	0.0004

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[1] Certain commercial products are included in this paper to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the authors and their affiliated institutions, nor does it necessarily imply that the materials or equipment identified are necessarily the best available for the purpose.

61	-0.0008	0.0017
62	0.0008	0.0005

The estimate of the combined standard uncertainty includes: drift in the glass electrode potential, drift in the temperature measurement, the standard uncertainty of the temperature measurement, and the estimated standard uncertainty of the electrode slope.

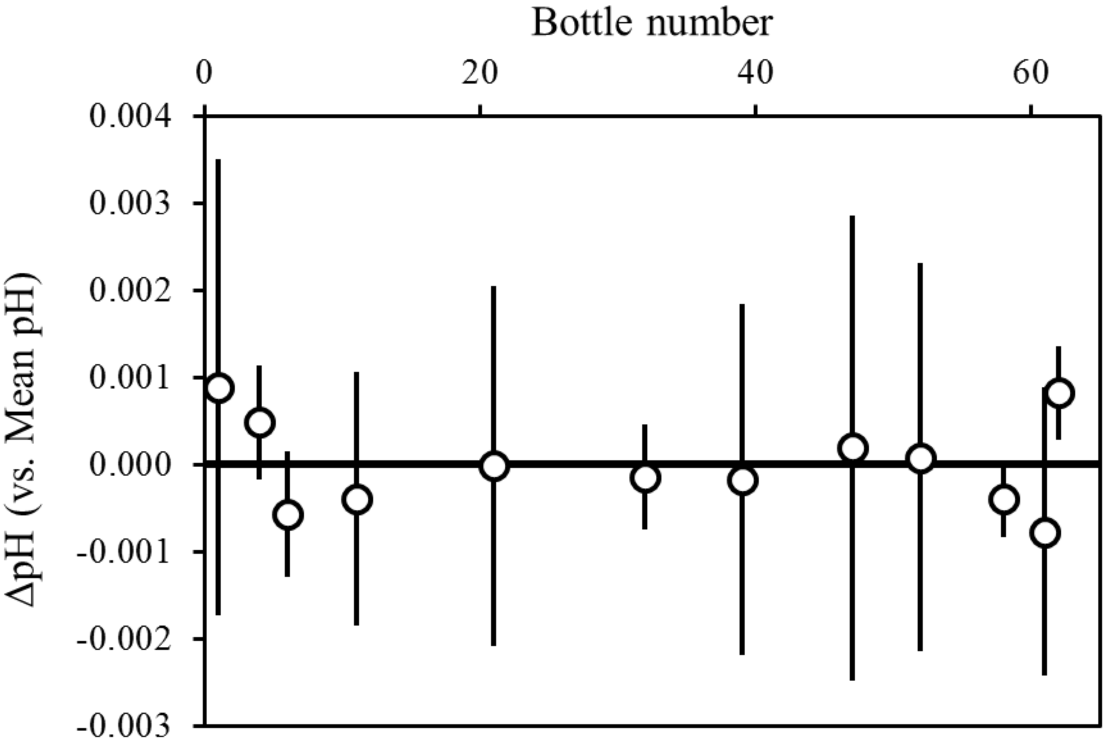

Figure 1. Results of the homogeneity assessment for the CCQM-K18.2016 buffer. Error bars represent the standard ($k = 1$) uncertainty.

Solution Stability

Stability of buffer solution was assessed over the duration of the comparison measurement period (originally scheduled from January 2017 through March 2017 but extended to April 2017) by monitoring $\mathrm{p}a^0$ using the primary pH measurement method. Each point in the stability assessment (see Figure 2) represents the measurement result from a single bottle of the carbonate buffer. The measurement result was determined from 4 solutions prepared with chloride molalities of 0.005 mol kg^{-1}, 0.010 mol kg^{-1}, and 0.015 mol kg^{-1}. The fourth solution was prepared as a replicate at one of the chloride molalities. Initially, 6 bottles were designated for the buffer stability assessment. An additional measurement of a single bottle of buffer was added to the stability assessment when the comparison measurement period was extended to April 2017. The buffer stability results are presented in Table 3 and Figure 2.

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

Date	Bottle #	$\mathrm{p}a^0$	$u[\mathrm{p}a^0]$	$U[\mathrm{p}a^0]$
5-Jan-17	2	10.1180	0.0014	0.0029
6-Jan-17	60	10.1188	0.0016	0.0032
16-Feb-17	5	10.1199	0.0011	0.0022
17-Feb-17	30	10.1193	0.0016	0.0032
27-Mar-17	57	10.1172	0.0019	0.0038
28-Mar-17	49	10.1183	0.0008	0.0016
11-May-17	14	10.1172	0.0015	0.0029

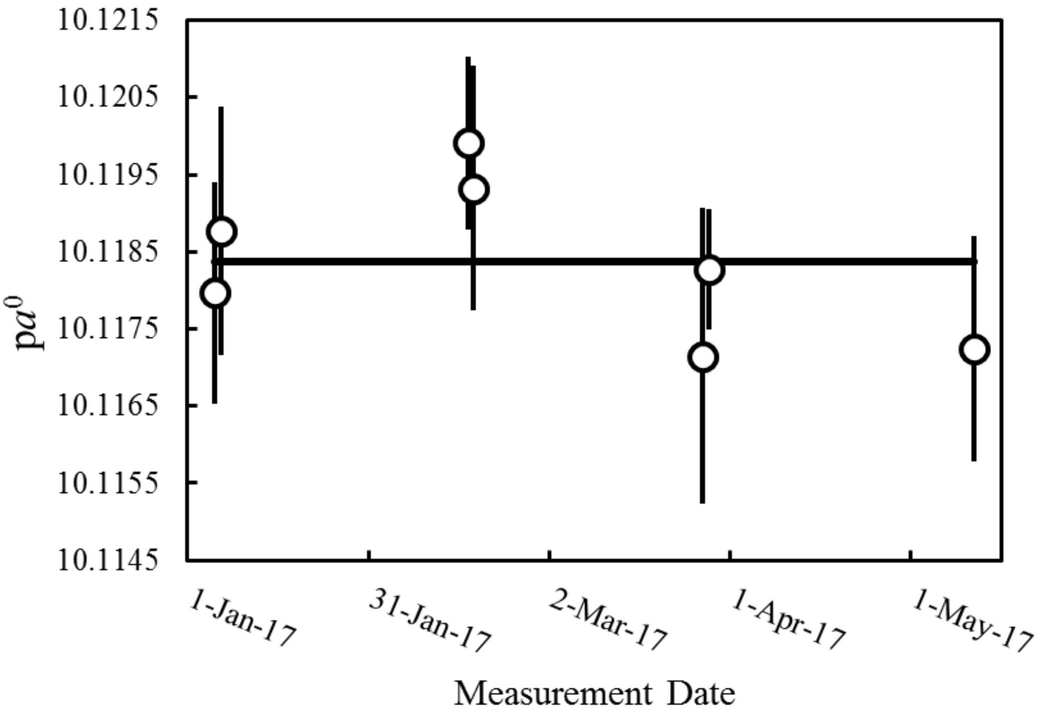

Figure 2. Results of the stability assessment for the CCQM-K18.2016 buffer. Error bars represent the standard (k = 1) uncertainty.

Sample Delivery and Verification of Mass Stability of Shipped Bottles

The sample bottles were shipped between 12 January 2017 and 13 January 2017. Except when an additional bottle was requested, participants using the primary cell received two 1 dm^3 HDPE numbered bottles and participants using the secondary cell received a single 1 dm^3 HDPE numbered bottle. The shipping and receipt dates of the samples are given in Table 4.

With two exceptions, all samples were delivered with little complication between 16 January 2017 and 19 January 2017. Samples sent to CENAM were delayed by customs inspection but were delivered on 24 January 2017. The initial set of samples sent to VNIIFTRI were unable to clear customs authorities and were ultimately returned to NIST, but the returned package was never received by NIST. A second set of samples was sent via a courier arranged by VNIIFTRI on 12 March 2017. The samples were ultimately delivered on 3 April 2017.

No visible signs of damage to the samples were reported to the coordinating laboratory by any participant of the KC. To ensure the integrity of the received samples, each participant reported: the calculated mass of each bottle as received, m_{received}; the balance reading, m'; and the ambient pressure, p, and temperature, T, at the time m' was determined. Values of m_{received} were corrected for air buoyancy using the formula used at the given NMI/DI. Values of $m_{\mathrm{recieved,NIST}}$ were determined with the formula used by the coordinating laboratory and the reported m', p and T. The relative change in bottle mass was calculated for values of m_{received} and $m_{\mathrm{recieved,NIST}}$. The relative change in bottle masses determined using $m_{\mathrm{recieved,NIST}}$ are shown in Figure 3. All relative changes in bottle mass were less than 0.01 %, the maximum allowed drift defined in the KC-TP.

Table 4. Timetable of samples and report with comments. Unless noted, all dates are in 2017.

Participant	Country	Shipped	Received	Measured	Reported, Revised	Comments
BFKH	HU	12-Jan	16-Jan	29-Mar	7-Apr	Reported technical problems that delayed submission of the report.
BIM	BG	12-Jan	16-Jan	10-Mar	24-Mar	
CENAM	MX	12-Jan	24-Jan	Not reported	24-Mar	Submitted results for both primary cell and secondary differential cell; only primary cell results are considered.
CMI	CZ	12-Jan	16-Jan	4-Apr	4-Apr	Reported personnel problems that delayed submission of the measurement report.
DFM	DK	12-Jan	16-Jan	15-Feb	21-Mar, 24-Mar	Revised report to correct values to the requested units: mV to V; V/d to V/h.
GUM	PL	12-Jan	16-Jan	15-Mar	24-Mar	
INMETRO	BR	13-Jan	18-Jan	23-Feb	6-Mar	
LNE	FR	12-Jan	16-Jan	23-Feb	23-Mar	
NIMT	TH	12-Jan	16-Jan	13-Mar	24-Mar	
NIST	US	N/A	N/A	3-Mar	24-Mar	
NMIJ	JP	12-Jan	16-Jan	26-Jan	27-Feb	Measurement report sent to DFM and forwarded to NIST.
PTB	DE	12-Jan	16-Jan	15-Feb	23-Mar	
SMU	SK	12-Jan	16-Jan	21-Mar	23-Mar	
UME	TR	13-Jan	19-Jan	Not reported	24-Mar	
UMTS	UA	12-Jan	17-Jan	27-Mar	31-Mar	Reported technical problems that delayed submission of the report.
VNIIFTRI	RU	4-Mar	3-Apr	17-Apr	21-Apr	Multiple delays in shipping.
INACAL	PE	12-Jan	19-Jan	Not reported	27-Mar	Report deadline was confused with that of CCQM-K143/P181.
INM	CO	13-Jan	17-Jan	Not reported	2-Feb	
LATU	UY	12-Jan	17-Jan	21-Mar	24-Mar	Measurement report sent to DFM and forwarded to NIST.

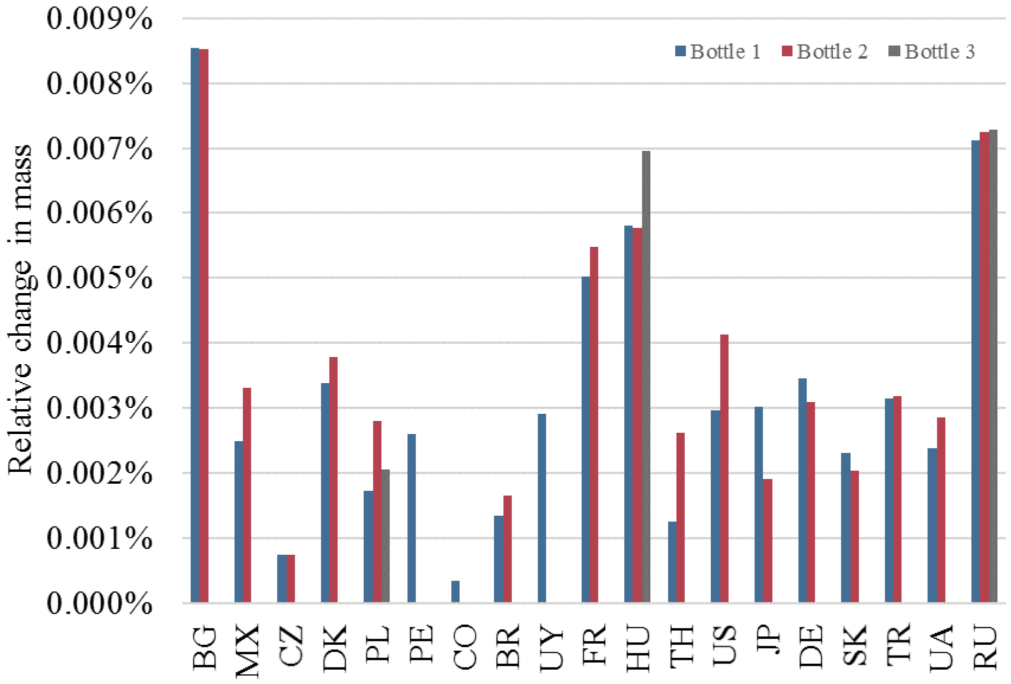

Figure 3. Relative change in bottle mass.

Timetable of Measurements and Submission of Reports

The dates of receipt of the samples and reporting dates are given in Table 4.

All reports were received by the deadline, 24 March 2017, with the following exceptions:

The previously discussed issues in shipping to VNIIFTRI caused a delay in the receipt of their comparison samples until 3 April 2017 and it was necessary to grant VNIIFTRI an extension of the deadline. The measurement report and results were received on 21 April 2017.

The measurement report and results from INACAL were received 27 March 2017 after a mix-up of the CCQM-K18.2016 measurement report deadline with the deadline of CCQM-K143/P181.

Submission of the measurement report and results from BFKH (report and results received 7 April 2017), CMI (report and results received 4 April 2017), and UMTS (report and results received 31 March 2017) were delayed because of technical/personnel problems.

Measurement Technique

Use of the highest metrological standard available to each participant was required. Use of the secondary differential potentiometric cell or of the secondary glass electrode was allowed if the participant CMCs are based upon a secondary method. Table 1 provides the measurement technique used by each participant.

Primary technique

The primary measurement technique for pH [2] consists of measurements of the potential, E_I, at the standard pressure, $p°$, of 101 325 Pa in the electrochemical cell without liquid junction, Cell I

$$\mathrm{Pt} \mid \mathrm{H_2}(\mathrm{g}, p°) \mid \text{buffer} + b_{\mathrm{Cl}} \mid \mathrm{AgCl} \mid \mathrm{Ag}, \qquad \text{(Cell I)}$$

where b_{Cl} is the chloride molality added to the buffer. Measurements of the potential, E_{II}, were also made in the electrochemical cell without liquid junction, Cell II

$$\mathrm{Pt} \mid \mathrm{H_2}(\mathrm{g}, p°) \mid b_{\mathrm{HCl}} \mid \mathrm{AgCl} \mid \mathrm{Ag}, \qquad \text{(Cell II)}$$

where the molality of HCl, b_{HCl}, used is nominally 0.01 mol kg^{-1}. The standard Ag | AgCl reference electrode potential, $E°$, is calculated from E_{II} according to Eq 1:

$$E° = E_{\mathrm{II}} + 2k \log \frac{b_{\mathrm{HCl}} \gamma_{\pm \mathrm{HCl}}}{b°} . \qquad (1)$$

In Eq 1, $\gamma^{\pm}_{HCl}$ is the mean activity coefficient of HCl at the nominal molality of b_{HCl} and $b°$= 1 mol kg^{-1}. The quantity k is the Nernst slope and equals $R\ T \ln 10 / F$. Recommended values and uncertainties of R and F (the ideal gas constant and the Faraday constant) used in the comparison, which were given by the KC-TP, are from [4]. The nominal measurement temperature was 25 °C, but the precise thermodynamic temperature, T, and its uncertainty, $u[T]$, were determined by each participant.

The carbonate buffer is not stable during the primary pH measurement. During the measurement, a portion of the carbon dioxide, CO_2, is removed from the buffer by the hydrogen gas stream. Loss of CO_2 shifts the equilibrium between the HCO_3^- and CO_3^{-2} in the buffer and a linear extrapolation of the determined potential to the hydrogen flow start time is generally required [1,5,6].

Values for the acidity function, pa, are calculated for each measured E_I value using Eq 2:

$$\mathrm{p}a = \frac{(E_\mathrm{I} - E°)}{k} + \log \frac{b_\mathrm{Cl}}{b°} \quad . \tag{2}$$

The acidity function at $b_\mathrm{Cl} = 0$ mol kg^{-1}, pa^0, for the given temperature is obtained from the linear extrapolation of the set of values for pa to $b_\mathrm{Cl} = 0$ mol kg^{-1}. The reported result for the primary pH measurement technique for the KC is pa^0.

Secondary techniques

The secondary differential potentiometric method for pH consists of measurements of the potential difference between the KC buffer and a primary standard pH buffer with the same nominal composition. The differential electrochemical cell, Cell III

$$\mathrm{Pt} \mid \mathrm{H_2}(\mathrm{g}, p) \mid \mathrm{buffer, S} \parallel \mathrm{buffer, S'} \mid \mathrm{H_2}(\mathrm{g}, p) \mid \mathrm{Pt}, \qquad \text{(Cell III)}$$

was used, where || represents a physical barrier constructed of a porous diaphragm, p denotes the identical partial pressure of hydrogen at the Pt electrodes, and S and S′ are the respective primary standard and unknown buffer solutions. The pH of the unknown buffer, pH(S′), is given by Eq 3

$$\mathrm{pH(S')} = \mathrm{pH(S)} - \frac{E_\mathrm{III} - E_j}{k} \tag{3}$$

where E_III is the potential difference determined in Cell III, E_j is the liquid junction potential that forms between the physically separated S and S′ buffer solutions, and k was defined in the description of Eq 1. Provided that $[\mathrm{pH(S')} - \mathrm{pH(S)}] \leq \pm 0.02$ and that $3 \leq \mathrm{pH(S)} \leq 11$, then the relationship $E_j \leq \pm 0.1\ E_\mathrm{III}$ is assumed and pH(S′) can then be determined [3].

No participants submitted results using the secondary glass electrode technique; discussion of the measurement techniques of this method is not necessary for this report.

Results and Discussion

The CCQM-K18.2016 KC measurements were performed only at 25 °C. Results from all participants are given in Table 5 and shown in Figure 4.

The general pattern of the results displayed in Figure 4 is characterized by over-dispersion of the data with a few extreme values.

Other information reported by the participants using the primary measurement technique is given in: Table 6, the HCl method of standardization, the determined molality, b_HCl, and its standard uncertainty, $u[b_\mathrm{HCl}]$; and Table 7, the standard potential, $E°$, its standard uncertainty, $u[E°]$, and the uncertainty of the extrapolation to obtain pa^0. Measurement information for the secondary differential cells is provided in Table 8.

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

Method	Participant	Country	pa^0	$u[\mathrm{p}a^0](k=1)$	$U[\mathrm{p}a^0](k=2)$
Primary cell	BFKH	HU	10.1210	0.0022	0.0044
Primary cell	BIM	BG	10.1234	0.0021	0.0042
Primary cell	CENAM	MX	10.1020	0.009	0.018
Primary cell	CMI	CZ	10.1217	0.0014	0.0028
Primary cell	DFM	DK	10.1149	0.0011	0.0022
Primary cell	GUM	PL	10.1095	0.0023	0.0046
Primary cell	INMETRO	BR	10.1118	0.0012	0.0024
Primary cell	LNE	FR	10.1140	0.002	0.004
Primary cell	NIMT	TH	10.1100	0.0026	0.0052
Primary cell	NIST	US	10.1179	0.0016	0.0032
Primary cell	NMIJ	JP	10.1172	0.0012	0.0023
Primary cell	PTB	DE	10.1187	0.0008	0.0015
Primary cell	SMU	SK	10.1143	0.0013	0.0027
Primary cell	UME	TR	10.1208	0.0023	0.0046
Primary cell	UMTS	UA	10.0977	0.0019	0.0038
Primary cell	VNIIFTRI	RU	10.1241	0.0020	0.0040
Secondary differential cell[a]	INACAL	PE	10.1202	0.0020	0.0040
Secondary differential cell[a]	INM	CO	10.1426	0.0030	0.0060
Secondary differential cell[a]	LATU	UY	10.1189	0.0023	0.0045

[a] The reported value was pH and is converted to pa^0 by subtracting the value for the trace activity coefficient of Cl, $\gamma_{\mathrm{Cl}}^{\circ}$, which is determined using the recommended procedures for determination of pH by the primary cell [2]. The reported uncertainties were for pH, but without considering the uncertainty contribution from $\gamma_{\mathrm{Cl}}^{\circ}$.

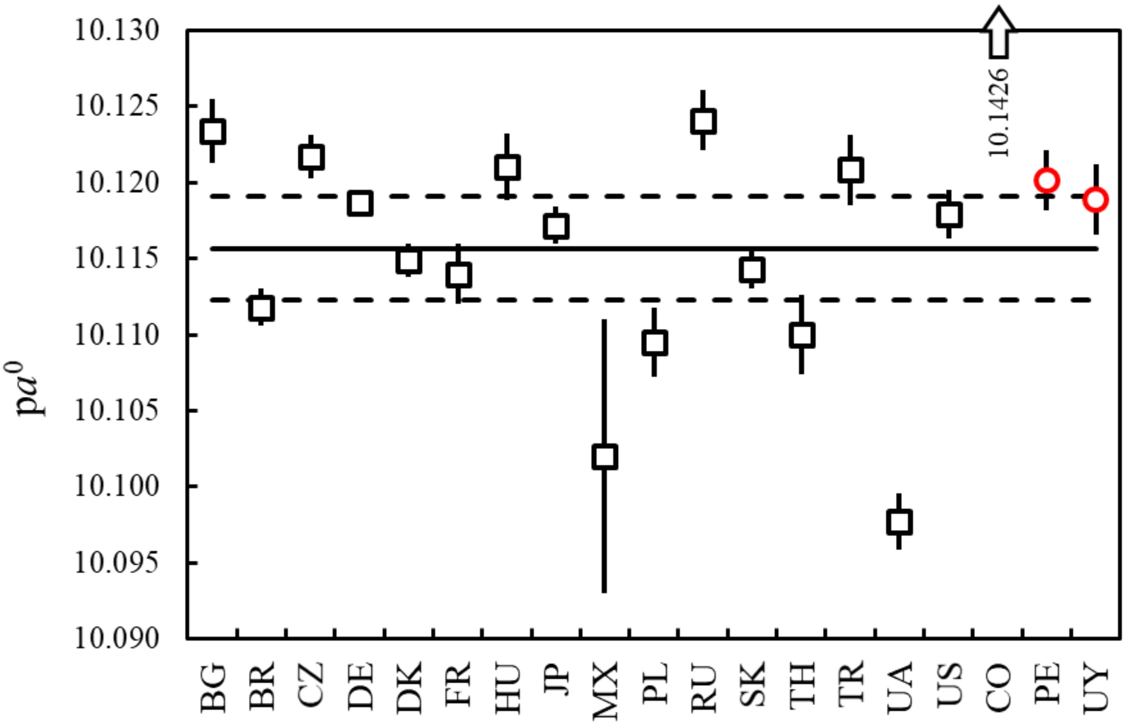

Figure 4. Results of CCQM-K18.2016 at 25 °C. Error bars correspond to the standard (k = 1) uncertainties. Primary cell results are shown as open black squares; secondary differential cell results are shown as open red circles.

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

Participant	Method for HCl Assay	b_{HCl} / mol kg^{-1}	$u[b_{\mathrm{HCl}}]$ / mol kg^{-1}
BFKH	Coulometric titration	0.009994	2.00E-06
BIM	Potentiometric titration against NIST SRM 723e	0.010006	2.00E-05
CENAM	Coulometric titration	0.009995	4.43E-06
CMI	Not reported	0.0099996	5.80E-06
DFM	Coulometric titration, traceable to SMU and gravimetric dilution	0.009999	4.63E-06
GUM	Coulometric titration	0.010005	2.10E-06
INMETRO	Coulometric titration	0.009989	1.80E-06
LNE	Potentiometric titration, traceable to high purity Ag (NRC-CNRC)	0.010001	7.60E-06
NIMT	Not reported	0.010001	3.10E-06
NIST	Coulometric titration	0.010006	1.80E-06
NMIJ	Coulometric titration and gravimetric dilution	0.010000	3.00E-06
PTB	Coulometric titration	0.010034	4.00E-06
SMU	Coulometric titration and gravimetric dilution	0.010000	5.80E-06
UME	Coulometric titration	0.010405	5.77E-06
UMTS	Coulometric titration	0.009999	1.03E-05
VNIIFTRI	FSUE «UNIIM» GSO 9654-2010	0.0099806	1.00E-05

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

Participant	$E°$ / V	$u[E°]$ / V	p*a* slope
BFKH	0.223260	7.61E-04	-1.9659
BIM	0.222300	8.90E-05	-1.6242
CENAM[1]	0.222288	5.53E-04	1.7057
CMI	0.222492	7.63E-04	-0.9643
DFM[2]	0.222599		-0.8184
GUM	0.222346	4.55E-05	-0.7810
INMETRO	0.222619	2.33E-05	-0.5874
LNE[3]	0.222550	6.80E-05	-0.8266
NIMT	0.222725	2.07E-05	-0.8210
NIST	0.222381	4.29E-05	-1.1471
NMIJ	0.222454	4.73E-05	-1.0354
PTB	0.222521	3.27E-05	-0.8743
SMU	0.222449	4.60E-05	-0.6864
UME	0.221514	5.70E-05	-0.5527
UMTS	0.222936	6.70E-05	-3.0510
VNIIFTRI	0.221824	7.43E-05	-1.2098

[1] The p*a* slope represents the mean value as multiple slopes were provided in the measurement results.

[2] Employed a scheme to calculate uncertainty where $u[E°]$ is not determined. The uncertainty of pa^0 is calculated in two steps: in the first step the molalities of the hydrochloric acid for the Harned cells and the chloride in buffer molalities (all with their associated uncertainties) is calculated; in the second step, the uncertainty of the acidity function at zero chloride molality is calculated.

[3] Individual $E°$ values, corresponding to a single Ag/AgCl electrode, were used to obtain each p*a* value. The reported $E°$ and $u[E°]$ is representative of a single electrode and not the entire set of electrodes used in the comparison.

Table 8. Information reported for the secondary differential cells.

Participant	pH	u[pH][1]	U[1] (k = 2)	P. S.[2]	pH (P.S., 25 °C)[2]	u[pH (P.S., 25 °C)][1,2]
INM	10.0330	0.0032	0.0063	CENAM DMR324	10.021	0.003
INACAL	10.0106	0.0020	0.0040	NIST SRM 191d	10.0137	0.0015
LATU	10.0093	0.0023	0.0045	NIST SRM 191d	10.0137	0.0015

[1] The pH measurement uncertainty without contribution from the Bates-Guggenheim convention.

[2] Information for the primary standard (P.S.) pH buffer.

CENAM submitted results for both the primary and secondary cells. Only the result from the primary cell is considered in this comparison. For the CENAM secondary value, the reported pH result and standard uncertainty (excluding the contribution from the Bates-Guggenheim convention) was 10.0191 ± 0.0141, which converts to pa^0 = 10.1286 ± 0.0141.

Consistency check of reported data

Inspection of the relative consistency between the participant reported pa^0 value and its uncertainty is shown in Figure 5. For this inspection, the relative consistency is described by the function: $[\mathrm{p}a^0_i - \mathrm{median}(\mathrm{p}a^0_{\text{primary cell}})] / u(\mathrm{p}a^0_i)$ [7]. Similar plots are generated if other estimators of the central value of pa^0 are used.

Figure 5 suggests there are 2 anomalous results:

- the pa^0 result reported by UMTS (UA) is too low, or the reported $u[\mathrm{p}a^0]$ is underestimated;
- the pa^0 result reported by INM (CO) is too high, or the reported $u[\mathrm{p}a^0]$ is underestimated.

The data supplied by the primary cell participants suggest a relationship between pa^0 and the pa extrapolation slope, see Figure 6. In general, more negative pa extrapolation slopes are associated with larger values of pa^0. The most notable exception to this trend is the UMTS (UA) result.

Except for CENAM (MX), all the pa extrapolation slopes are negative. Despite this difference, the CENAM result follows the observed trend between pa^0 and the pa extrapolation slope, see Figure 6.

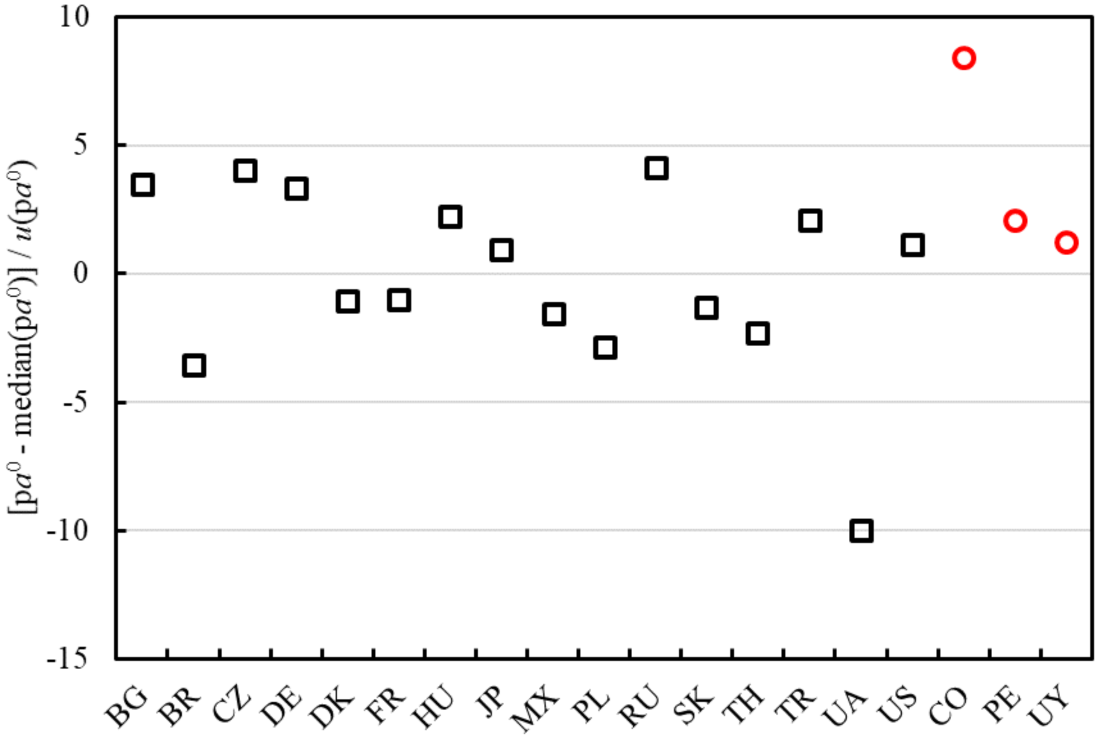

Figure 5. Result of the inspection for anomalous pa^0 values. Relative results of the secondary results are shown (open red circles), but not used in calculation of the median(pa^0).

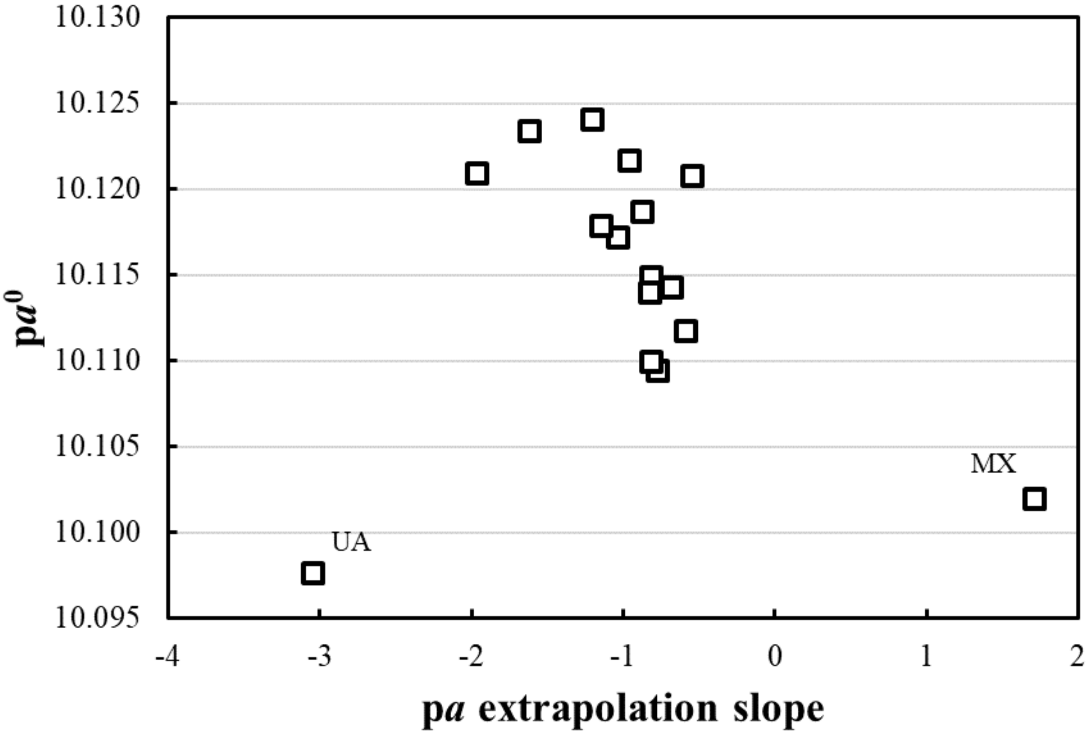

Figure 6. Comparison of the p*a* intercept and slope.

Calculation of the KCRV and Uncertainty

There are several possibilities for determination of the KCRV. These possibilities are listed in Table 9. 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 the KCRV.

Table 9. Values of candidate estimators for the KCRV for CCQM-K18.2016.

Estimator	Value	$u(k = 1)$	$U(k = 2)$
Arithmetic Mean	10.1149	0.0019	0.0037
Weighted Mean[1]	10.1163	0.0014	0.0027
DerSimonian-Laird	**10.1157**	**0.0017**	**0.0034**
Median/MAD$_E$	10.1161	0.0023	0.0047

[1] The Birge ratio is 3.592 and the weighted mean standard uncertainty is corrected for the observed dispersion.

At $k = 1$, the differences between the estimators are not significant, especially for the differences between the Weighted Mean, DerSimonian-Laird and Median estimators. For all estimators included in Table 9, the range in the determined standard uncertainties is 0.0009 units.

The DerSimonian-Laird estimator, x_{DL}, was selected as the KCRV. The KCRV and its standard uncertainty, $u(\mathrm{KCRV})$, were calculated using the equations [7]:

$$\mathrm{KCRV} = \sum_{i=1}^{p} \widetilde{w}_i \, x_i \; ,$$

$$u(\mathrm{KCRV}) = \left[\sum_{i}^{p} \frac{\widetilde{w}_i^2\ (x_i\ -\ x_{\mathrm{DL}})^2}{1\ -\ \widetilde{w}_i}\right]^{1/2}\ ,$$

where

$$\widetilde{w}_i = \frac{(u_i^2 + \lambda)^{-1}}{\sum_{j=1}^{p}\left(u_j^2 + \lambda\right)^{-1}}\,,$$

$$\lambda = max\left[0, \frac{\sum_{i=1}^{p} w_i\ (x_i\ -\ \overline{x_{\mathrm{w}}})^2\ -\ p + 1}{W_1 - \frac{W_2}{W_1}}\right],$$

$$\overline{x_w} = \frac{1}{W_1}\sum_{i=1}^{p} w_i\, x_i\ ,$$

$$W_1 = \sum_{i=1}^{p} w_i\ ,$$

$$W_2 = \sum_{i=1}^{p} w_i^2\ ,$$

and

$$w_i = \frac{1}{u_i^2}\,.$$

Values of the KCRV and *u*(KCRV) calculated with these equations were confirmed by comparison with output from the NIST Consensus Builder [8] and the R [9] 'metRology' package [10].

Calculation of the Degrees of Equivalence

For each participant, *i*, the degree of equivalence, D_i, is determined by

$$D_i = \mathrm{p}a_i^0 - \mathrm{KCRV}\,.$$

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

$$u(D_{\mathrm{i}}) = [u^2(\mathrm{p}a_i^0) + \lambda - u^2(\mathrm{KCRV})]^{1/2}\,.$$

For the results determined by the secondary differential cell, which were not used in calculation of the KCRV, $u(D_i)$ is determined by

$$u(D_i) = [u^2(pa_i^0) + \lambda + u^2(\mathrm{KCRV})]^{1/2}\,.$$

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

Table 10. Degrees of Equivalence, D_i, and Standard Uncertainty, $u(D_i)$, for CCQM-K18.2016.

Participant	Country	Method	D_i	$u(D_i)$
BIM	BG	Primary	0.0078	0.0055
INMETRO	BR	Primary	-0.0038	0.0053
CMI	CZ	Primary	0.0061	0.0053
PTB	DE	Primary	0.0031	0.0052
DFM	DK	Primary	-0.0007	0.0053
LNE	FR	Primary	-0.0016	0.0055
BFKH	HU	Primary	0.0054	0.0056
NMIJ	JP	Primary	0.0016	0.0053
CENAM	MX	Primary	-0.0136	0.0104
GUM	PL	Primary	-0.0061	0.0056
VNIIFTRI	RU	Primary	0.0085	0.0055
SMU	SK	Primary	-0.0013	0.0053
NIMT	TH	Primary	-0.0056	0.0058
UME	TR	Primary	0.0052	0.0056
UMTS	UA	Primary	-0.0179	0.0055
NIST	US	Primary	0.0023	0.0054
INM	CO	Secondary	0.0270	0.0065
INACAL	PE	Secondary	0.0046	0.0060
LATU	UY	Secondary	0.0033	0.0061

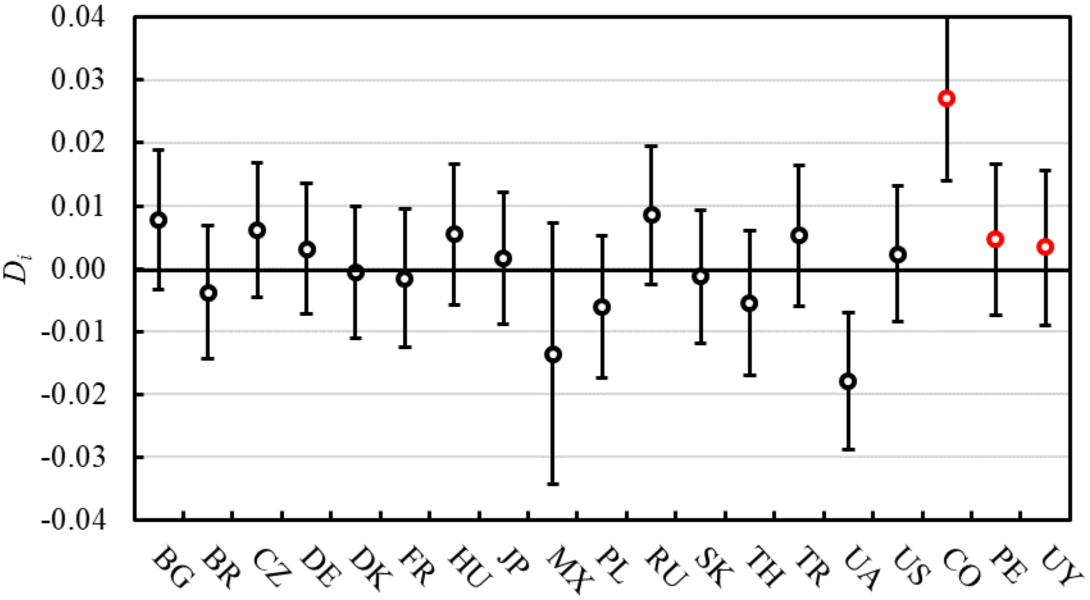

Figure 7. Unilateral degrees of equivalence and expanded (k = 2) uncertainties for CCQM-K18.2016.

How far the light shines

Carbonate reference buffer solutions are widely used as pH standards in alkaline pH range. Participants that successfully took part in the CCQM-K18.2016 key comparison demonstrate their capability to measure the pH of carbonate buffer in the pH range (25 °C) 9.5 to 10.5.

Conclusion

Nineteen NMI/DIs participated in CCQM-K18.2016, pH of carbonate buffer. Of the participants, sixteen submitted results by the primary method of measurement and three by the secondary differential cell. Good agreement was found for most participants. The spread of reported values for the primary cell was only slightly less than in CCQM-K18 (2006) [1].

Comparison of CCQM-K18.2016 and CCQM-K18 (2006)

After removing outlying results, the spread of results, defined as [max(pa^0) – min(pa^0)], in the CCQM-K18 (2006) comparison was 0.0292 [1]. For CCQM-K18.2016: the overall spread for all results is 0.0449; and the overall spread for the primary cell results was 0.0264. Table 11 compares the different KCRV estimators for the two CCQM KCs on carbonate buffer.

Table 11. Comparison of the central value estimators and uncertainties for CCQM-K18 and CCQM-K18.2016.

Estimator	Comparison	Value	$u(k = 1)$	$U(k = 2)$
Median[1]	K18 (2006)	10.1985	0.0019	0.0038
Arithmetic Mean	K18 (2006)	10.1984	0.0025	0.0050
Weighted Mean	K18 (2006)	10.2002	0.0021	0.0042
MM-Median	K18 (2006)	10.1990	0.0020	0.0040
Median	K18.2016	10.1161	0.0023	0.0047
Arithmetic Mean	K18.2016	10.1149	0.0019	0.0037
Weighted Mean	K18.2016	10.1162	0.0014	0.0027
DerSimonian-Liard	K18.2016	10.1157	0.0017	0.0034

[1] The median, with omission of a single outlying result, was selected as the CCQM-K18 (2006) KCRV [1].

Acknowledgment

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