

Final report on CCQM-K19.1

pH of borate buffer

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Abstract

The subsequent key comparison CCQM-K19.1 has been carried out in 2010 as a follow-up comparison to CCQM-K19. Three laboratories (NMIJ, PTB and SMU) took part in both comparisons. Their results are consistent. The assigned uncertainties are reliable and in the same order. These results provide the link to CCQM-K19.

As well as the original comparison the subsequent key comparison was organised to demonstrate the capability of the interested National Metrology Institutes to measure the pH value of an unknown borate buffer by a primary method at 15 °C, 25 °C and 37 °C. Eight laboratories took part in CCQM-K19.1. The participants either were not able to participate in the original comparison or participate only in the Pilot Study CCQM-P82 running in parallel to CCQM-K19. In one case the laboratory expressed doubts on the integrity of the sample provided in CCQM-K19.

The result in CCQM-K19.1 is the acidity function at zero chloride molality, AF^0 of the unknown borate buffer solution.

Most participants in the key comparison CCQM-K19.1 demonstrated improved capabilities. This especially applies for the laboratories original taken part in the pilot study CCQM-P82. In some cases previous results could be confirmed. The hidden reasons for that have still to be clarified.

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Metrology Area

Amount of Substance

Branch

Electrochemistry

Subject

Determination of the acidity functions at zero chloride molality of an unknown borate buffer, nominal pH ~ 9.2 by Harned cell measurement at 15 °C, 25 °C, and 37 °C.

Participants and acronyms

Acronym	Participant	Country	Analyst
INMETRO	Instituto Nacional de Metrologia, Normalização e Qualidade Industrial	BR	Paulo Paschoal Borges, Júlio Cesar Dias, Fabiano Barbieri Gonzaga
NIM	National Institute of Metrology, China	CN	Xiu Hongyu; Wu Bing
PTB	Physikalisch-Technische Bundesanstalt	DE	Beatrice Adel, Janine Meyer, Jessica Matzke
DFM	Danish Fundamental Metrology	DK	Pia Tønnes Jakobsen
LNE	Laboratoire National de métrologie et d'Essais	FR	Rachel Champion
NMIJ	National Metrology Institute of Japan	JP	Masaki Ohata, Igor Maksimov, Akiharu Hioki
SMU	Slovensky Metrologicky Ustav	SK	Anna Mathiasova, Leos Vyskocil
NIST	National Institute of Standards and Technology	US	Kenneth W. Pratt

Comparison background

Borate buffer is widely used to calibrate pH electrodes in the alkaline range. A buffer solution of 0.01mol/kg disodium tetraborate decahydrate is one of the primary reference pH buffer solutions recommended by IUPAC².

The key comparison CCQM-K19.1 has been carried out subsequent to the comparison CCQM-K19 which was completed in 2006³. In parallel to CCQM-K19 the pilot study CCQM-P82 was organized.

CCQM-K19.1 was originally initiated by INMETRO as a bilateral follow-up comparison with PTB. Finally eight NMI took part in CCQM-K19.1. INMETRO and LNE as participants in CCQM-P82 used the opportunity to demonstrate their progress in pH measurements on the primary level. NIST reported in CCQM-K19 an unusual large measurement uncertainty for the results. The reasons for the deviations could not explained absolutely certain. NIM, China is experienced in pH measurements but could only take part in CCQM-K19.1. The Danish Primary Laboratory (DPL) successfully took part in the CCQM-K19. Meanwhile the primary set-up for pH in Denmark moved to DFM, Denmark.

² Buck RP et al. 2002 Pure Appl. Chem. 74(11) 2169–2200

³ http://www.bipm.org/exalead_kcdb/exa_kcdb.jsp?_p=AppB&_q=CCQM-K19&x=0&y=0Guide

Three NMI (PTB, NMIIJ and SMU) participated in CCQM-K19 and CCQM-K19.1. They are acting as anchor laboratories providing the link to CCQM-K19.

The result reported by the participants of CCQM-K19.1 is the acidity function at zero chloride molality, AFO , of the unknown borate buffer. All participants applied the primary method for pH (Harned cell measurement) as defined in the IUPAC Recommendations. The measurement temperatures were 15 °C, 25 °C, and 37 °C. The nominal pH of the buffer at 25 °C is pH~9.2.

CCQM-K19.1 and CCQM-K19 are activities of the Electrochemical Working Group (EAWG) of the CCQM. Both comparisons were coordinated by the PTB, Germany. The sample preparation, sample homogeneity test and shipment for CCQM-K19.1 was done by INMETRO, Brazil.

Time Schedule

Dispatch of the samples	21 January 2010
Deadline for receipt of the report	01 April 2010
Presentation of the results	13 April 2010
Draft A report	30 September 2010
Draft B report	30 October 2010
Improved draft B report	15 March 2011

The technical protocol of the comparison and the preliminary schedule were discussed at the meeting of the CCQM-EAWG on 5 November 2009 in Rio de Janeiro, Brazil.

The samples were characterized in January 2010. Before shipment, INMETRO measured the pH of the sample from 3 randomly chosen bottles to estimate the homogeneity of the batch. Differential potentiometry was used by INMETRO to monitor the sample solutions during the whole measurement period.

Each participant received three 1 liter HDPE bottles sealed into plastic bags. The mass of the bottles (corrected to air buoyancy) and the mass fraction of water was reported to the participants. The erroneous mass fraction of water stated on the bottles has been corrected by email at 21 January 2010 together with the message on the dispatch of the samples.

All participants measured the pH value of the samples in the period from 28 January to 3 March 2010.

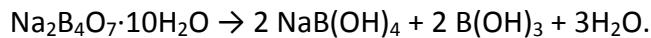
The results of the comparison were presented at the CCQM EAWG meeting at BIPM in Paris at 13 April 2010. It was agreed to establish a robust link via the three laboratories NMIIJ, PTB and SMU. The results of these participants were consistent in both comparisons. The draft A report was discussed at the autumn CCQM EAWG meeting 2010 in Børas Sweden.

Sample preparation

The samples were produced in January 2010 at INMETRO from 44273.3 ± 0.1 g of purified water and 190.395 ± 0.001 g of disodium tetraborate decahydrate (Merck). Each 1 L HDPE bottle was filled with about 1 kg of the buffer solution. The bottles were closed and the caps secured with Parafilm®. Finally, the bottles were sealed into plastic bags. INMETRO stated the mass fraction of water to be 0.995718 g/g and the molality of the buffer solution to be 0.011276 mol/kg. For these calculations the crystal water content was not taken into account. The participants prepared their measurement solutions according to these specifications.

Remark: The borate buffer is prepared from a hydrated salt generally described as $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (borax).

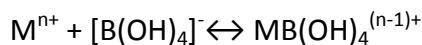
When dissolved in water disodium tetraborate decahydrate is converted into boric acid and the borate ion^{4 5}



At these concentrations boric acid exists as undissociated boric acid B(OH)_3 at $\text{pH} < 5$, whereas at $\text{pH} > 12.5$, the metaborate ion $[\text{B(OH)}_4]^-$ becomes the main species in solution.

Both species are present at $\text{pH } 5-12.5$. At higher boron concentrations ($c(\text{B}) \geq 0.025 \text{ mol/kg}$) the formation of polynuclear species $\text{B}_3\text{O}_3(\text{OH})_4^-$, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$, $\text{B}_3\text{O}_3(\text{OH})_5^{2-}$, and $\text{B}_5\text{O}_6(\text{OH})_4^-$ becomes significant.

In the presence of metal ions (e.g. Na, Mg, and Ca), ion pair complexes are formed.



These ion pair complexes are expected to be present in solutions of disodium tetraborate, disodium octaborate and buffered solutions of boric acid and boric oxide. (Ingri N (1963) cited in⁶)

Sample homogeneity and stability

INMETRO evaluated the homogeneity of the whole batch. The sample quality was monitored during the whole measurement period from 7 January 2010 to the 16 March 2010. A differential potentiometric cell⁷ was used to run these studies. The set-up consists of two half cells with identical platinum hydrogen electrodes. A porous glass disc diaphragm separates both half cells. The cell is constructed such that the hydrogen partial pressure at the platinum electrodes is identical. One bottle was selected and the buffer was filled as reference in one of the two half cells. In four runs the other half cell was filled with buffer from four randomly selected testing bottles. The difference in pH results from the difference in cell potential measured between the buffer in the "reference" bottle and the buffer in the "testing" bottles. The homogeneity study was carried out on 7 January 2010 on four bottles. The differences of pH between the bottles were less than 0.001 and, therefore, the batch was considered to be homogeneous. A second homogeneity test was carried at the end of the measurement period. The differences in pH between another randomly chosen reference bottle and four other bottles also not accede 0.001. Bottles #33 and #34 were measured twice to check the reproducibility of the measurements under the condition of taken buffer from one bottle repeatedly. The difference in pH was within 0.001.

The relative measurements done by differential potentiometry are not sufficient to indicate the stability of the samples. Information on the stability of the buffer solution is estimated from the differences in pH measured between a randomly chosen reference and one testing

⁴F. A. Cotton and G Wilkinson, Advanced Inorganic Chemistry, 5th Edition, Wiley Interscience, New York, 1988, p 361

⁵J. D. Lee, Concise Inorganic Chemistry, Springer 1996, p. 379

⁶http://echa.europa.eu/doc/trd_substances/disodium_tetraborate_anhydrous/ann_xv_trd/trd_austria_trisodiumtetraborate.pdf

see also: European chemical agency: ANNEX XV – IDENTIFICATION OF SVHC

http://echa.europa.eu/doc/consultations/svhc/svhc_axvrep_denmark_cmr_tetraboron_disodium.pdf

⁷ Baucke F G K (1994) J. Electroanal. Chem 68: 67-75

bottles stored at high (50 °C) and one bottle stored at low (4 °C) temperatures since their production. The difference in pH measured at 4 February for both samples was about 0.001. An additional uncertainty contribution due to the stability of the sample has not been taken into account. The test results are summarized in table 1.

Date	Reference Bottle	Testing Bottle	$\Delta E / \mu\text{V}$	$ \Delta\text{pH} $
07/01/2010	25	34	-5	< 0.0001
		06	-34	0.0006
		34	-30	0.0005
		22	-39	0.0007
04/02/2010	02	17 ^a	-58	0.0010
		41 ^a	65	0.0011
16/03/2010	19	07	25	0.0004
		33	-62	0.0010
		43	29	0.0005
		33	-24	0.0004

^a Samples #17 and #41 were stored at 4 °C and 50 °C, respectively, since their production. All other samples were stored at room temperature (22 ± 1 °C).

Tab 1 Monitoring of the samples by differential potentiometry.

Shipment and travel events

The time schedule is summarized in table 2. All participants received their sample uneventfully within January 2010. The participants were asked for weighing the bottles for integrity check. The reported results identified a problem. Some of the participants obviously removed the plastic bag from the sample before weighing and some participants did not. After INMETRO provided data for both cases the sample integrity could be confirmed for all samples, as listed in table 3 and in figure 1. Only the differences in mass weighted at INMETRO and at the NIST are slightly exceeding 0.1 g.

NIST used for calculations the mass fraction water $w(\text{H}_2\text{O}) = 0.99621$ which was given on the sample. Later this value was corrected by INMETRO (email from 21 January 2010) to $w(\text{H}_2\text{O}) = 0.995718$.

According to NIST the difference in pH resulting from using the wrong mass fraction water is only $\Delta(\text{pH}) = 0.00021$ for all measurement temperatures. This difference is within the measurement uncertainty.

Participant	Bottle No	Sample arrived	Sample measured
INMETRO	21, 36, 12	18 Jan	9 Feb-3 March
NIM	4, 18, 35	28 Jan	19 Feb-2 March
PTB	9, 20, 29	22 Jan	18 Feb
DFM	14, 24, 26	21 Jan	17 Feb-19 Feb
LNE	8, 23, 32	21 Jan	28 Jan-1 Feb
NMIJ	3, 27, 38	22 Jan	28 Jan- 23 Feb
SMU	11, 37, 40	22 Jan	9 Feb
NIST	15, 28, 42	30 Jan	11 March

Tab 2 Measurement time schedule.

Participant	Bottle #	Difference in mass /g
INMETRO	12	0.080
INMETRO	21	0.056
INMETRO	36	0.068
NIM	4	0.073
NIM	18	0.074
NIM	35	0.073
PTB	9	0.021
PTB	20	0.025
PTB	29	0.023
DFM	14	0.053
DFM	24	0.061
DFM	26	0.059
LNE	8	0.035
LNE	23	0.035
LNE	32	0.047
NMIJ	3	0.040
NMIJ	27	0.065
NMIJ	38	0.083
SMU	11	0.050
SMU	37	0.056
SMU	40	0.048
NIST	15	0.130
NIST	28	0.134
NIST	42	0.142

Tab 3 Differences in mass between samples which were weighted at INMETRO and at the NMI.

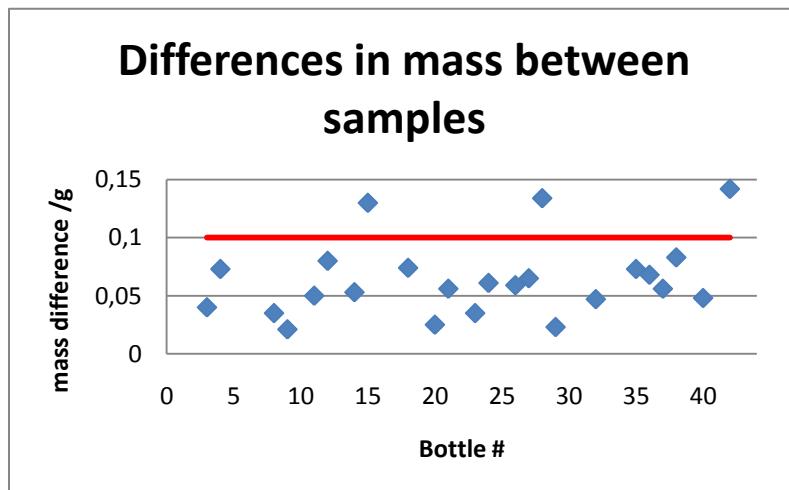


Fig 1 Differences in mass between samples which were weighted at INMETRO and at the NMI.

Results and discussion

Measurement of the acidity function

The acidity function is derived from the potential difference measured in an electrochemical cell without junction (Cell I, Harned cell) at several chloride molalities. The addition of small amounts of chloride is necessary to stabilize the potential of the silver-silver chloride electrode.



The potential difference E of this cell (corrected to 101 325 Pa partial pressure of hydrogen) depends on the hydrogen ion activity, a_{H} according to equation (1)

$$E = E^0 - \frac{RT}{F} \ln(10) \log(a_{\text{H}} / m^0) (m_{\text{Cl}} \gamma_{\text{Cl}} / m^0) \quad (1)$$

E^0 is the standard potential difference of the cell, $m^0 = 1 \text{ mol kg}^{-1}$ is the standard molality, γ_{H} and γ_{Cl} are the activity coefficients of the hydrogen and the chloride ion, R is the molar gas constant, F the Faraday constant and T the thermodynamic temperature.

Equation (1) can be rearranged to give the acidity function AF . All quantities on the right hand side of equation (2) can be measured directly.

$$AF = -\log(a_{\text{H}^+} \gamma_{\text{Cl}^-} / m^0) = (E - E^0) / \left[\frac{RT}{F} \ln(10) \right] \log(m_{\text{Cl}^-} / m^0), \quad (2)$$

$$AF^0 = -\log \left(\gamma_{\text{H}} \gamma_{\text{Cl}} / m^0 \right)_{\text{Cl} \rightarrow 0} \quad (3)$$

$$AF = AF^0 + b_s m_{\text{Cl}} \quad (4)$$

The acidity function AF^0 at zero chloride molality is determined by linear extrapolation of the acidity function AF as a function of the chloride molality according to equation (4). Alkali chloride of certified high quality is added at least three different molalities m_{Cl} in the range of $0.005 \text{ mol} \cdot \text{kg}^{-1}$ to $0.02 \text{ mol} \cdot \text{kg}^{-1}$. It is assumed that a linear extrapolation is appropriate if the change in ionic strength produced by the addition of chloride is restricted to less than 20%.

The constant b_s is an empirical and temperature-dependent constant. For the Faraday constant and for the gas constant the following values are recommended $F = 96\,485.3399(24) \text{ C mol}^{-1}$ and $R = 8.314472(15) \text{ J mol}^{-1} \text{ K}^{-1}$ ⁸. The standard potential E^0 is measured in a cell filled with hydrochloric acid with a molality 0.01 mol kg^{-1} , according to equation (5). The mean activity coefficient γ_{\pm} of the HCl is taken from the literature⁹. The participants were asked to use hydrochloric acid with SI traceable known molality close to $0.01 \text{ mol} \cdot \text{kg}^{-1}$.

$$E^0 = E + \frac{2RT \ln(10)}{F} \cdot \log \left(\gamma_{\text{HCl}} \cdot \gamma_{\text{HCl}} \right)^{-1} \quad (5)$$

⁸ <http://physics.nist.gov/cuu/Constants/index.html>

⁹ R.G. Bates., Robinson R. A., *Solution Chemistry*, 1980, 9, 455

Reported results

The result of the comparison is the intercept of the acidity function extrapolated to zero chloride molality, AF^0 , and its uncertainty u ($k = 1$) at each of the three measurement temperatures 15 °C, 25 °C and 37 °C.

A pH value was not calculated from the results. For a buffer solution of about 0.011 mol·kg⁻¹, the ionic strength is slightly different from $I = 0.02$ mol·kg⁻¹ for the 0.01 mol·kg⁻¹ standard buffer solution. With known ionic strength it is possible to calculate the pH value according to equation (6). The activity coefficient γ_{Cl} at the ionic strength I of the sample buffer is given by the expression (7). A is the Debye-Hückel temperature-dependent limiting slope.¹⁰

$$pH = AF^0 + \log \gamma_{Cl} \quad (6)$$

$$\log \gamma_{Cl} = \frac{-A\sqrt{I}}{1+1.5\sqrt{I}} \quad (7)$$

A key comparison reference value (KCRV) was not calculated. The mean of the results from the anchor laboratories NMIIJ, PTB and SMU has been used to link CCQM-K19.1 to the original comparison CCQM-K19.

The results reported for the sample, disodium tetraborate decahydrate buffer solution are summarized in table 4 and shown in figure 2 to 4.

Participant	AF^0	$u(AF^0)$	AF^0	$u(AF^0)$	AF^0	$u(AF^0)$
	15 °C		25 °C		37 °C	
INMETRO	9.3250	0.0039	9.2367	0.0022	9.1541	0.0041
NIM	9.3385	0.0016	9.2465	0.0017	9.1592	0.0016
PTB	9.3314	0.0011	9.2399	0.0011	9.1522	0.0011
DFM	9.3352	0.00085	9.2432	0.00094	9.1550	0.00098
LNE	9.3236	0.0025	9.2321	0.0020	9.1441	0.0024
NMIJ	9.3305	0.00119	9.2379	0.00117	9.1503	0.00117
SMU	9.3325	0.00110	9.2390	0.00109	9.1505	0.00109
NIST	9.3337	0.00069	9.2409	0.00056	9.1516	0.00078

Tab 4 Results obtained by the participants of the comparison CCQM-K19.1 a follow-up on CCQM-K19. The result is the acidity function extrapolated to zero chloride molality, AF^0 , and its uncertainty u ($k = 1$) at each of the three measurement temperatures 15 °C, 25 °C and 37 °C. The results of the anchor laboratories PTB, NMIIJ and SMU are greyed out.

¹⁰ OIML International Recommendation No 54: pH scale for aqueous solutions. 1981

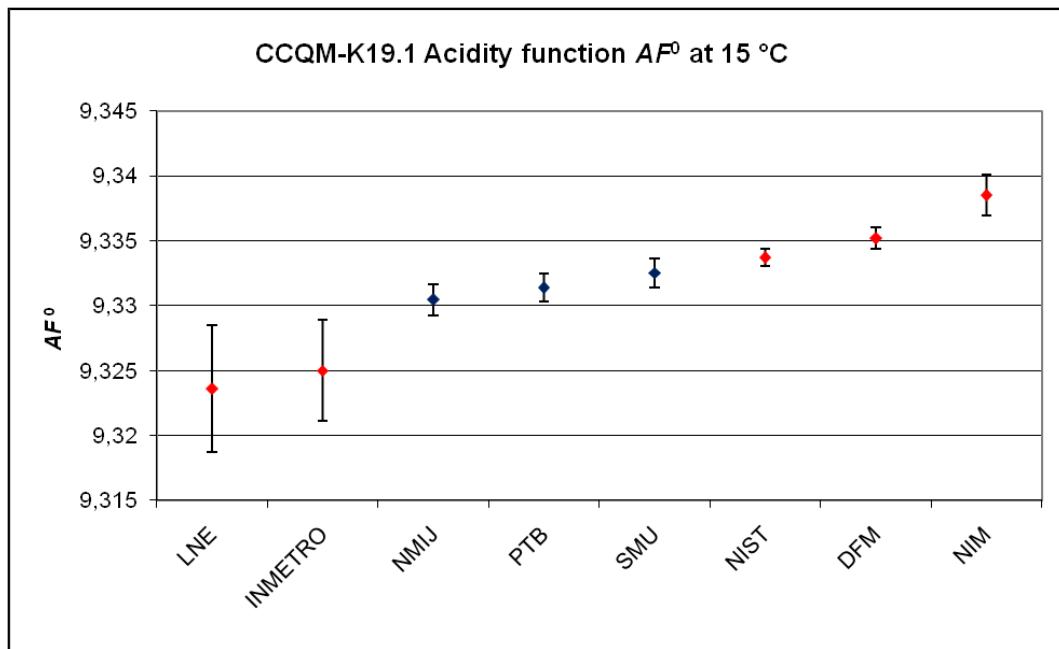


Fig 2 Acidity functions at zero chloride molality at 15 °C measurement temperature.
The uncertainty is the standard uncertainty ($k = 1$). Blue dots: NMJJ, PTB and SMU, the anchor laboratories to CCQM-K19.

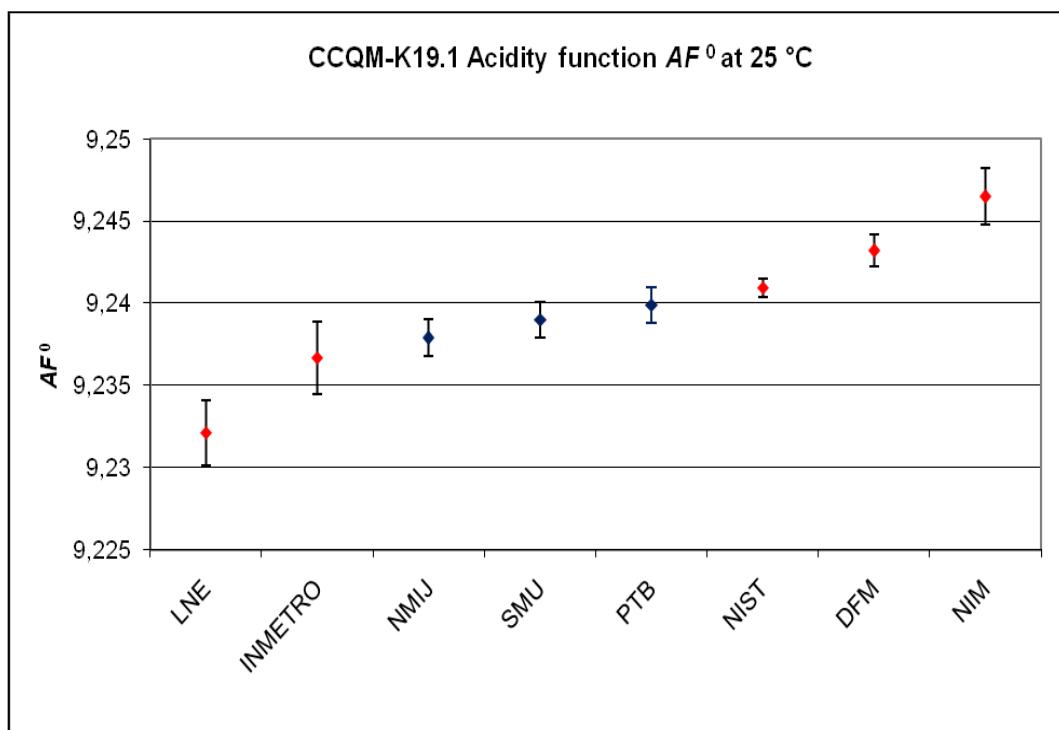


Fig 3 Acidity functions at zero chloride molality at 25 °C measurement temperature.
The uncertainty is the standard uncertainty ($k = 1$). Blue dots: NMJJ, PTB and SMU, the anchor laboratories to CCQM-K19.

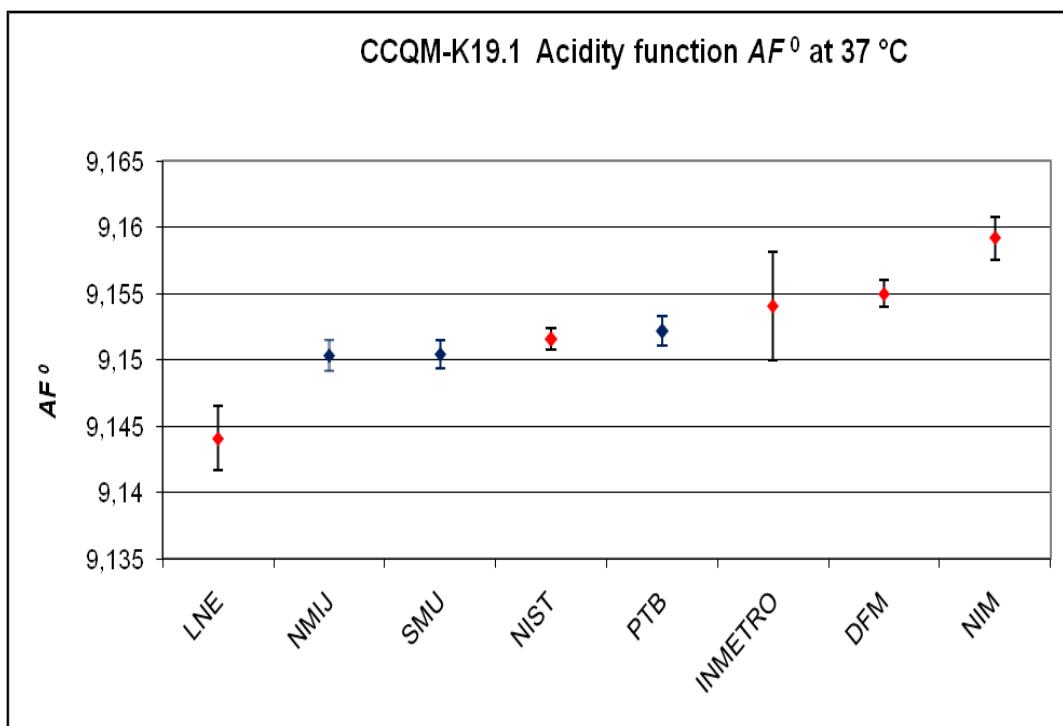


Fig 4 Acidity functions at zero chloride molality at 37 °C measurement temperature. The uncertainty is the standard uncertainty ($k = 1$). Blue dots: NMJJ, PTB and SMU, the anchor laboratories to CCQM-K19.

Measurement uncertainty

All participants delivered an uncertainty budget according to GUM¹¹. To estimate the uncertainty of the acidity function the uncertainty contributions from the determination of the standard potential E^0 is required. The uncertainty of the molality of the hydrochloric acid has been identified as one of the main components contributing to the uncertainty of E^0 . An overview on first the uncertainties associated with the determination of the molality of the hydrochloric acid and second on the uncertainties of the standard potential are given in table 7 and table 8. For the molality determination of the hydrochloric acid coulometric titration was used by all participants except LNE and SMU. LNE applied classical potentiometric titration. SMU used conductometry. In figure 7 the molality of the hydrochloric acid versus the standard potentials of the silver/silver chloride electrodes at 25 °C is plotted for all participants.

Except DFM all institutes estimated the uncertainty of AF^0 from equation (8) by combining the uncertainty of intercept (type A component) and the uncertainty of the acidity function at the smallest amount of added chloride (type B component). It is assumed that the uncertainty of the acidity function $u(AF_{mCl})$ is largest for the acidity function at the smallest amount of added chloride.

$$u(AF^0) = \sqrt{u^2(AF_{mCl}) + u^2(\text{intercept})} \quad (8)$$

The standard uncertainty u (intercept) of the linear least squares fit to get AF^0 is given by equation (9).

¹¹ <http://www.bipm.org/en/publications/guides/gum.html>

$$u(\text{intercept}) = SR \sqrt{\left[\frac{1}{N} + \frac{\bar{m}_{Cl}^2}{\sum_{i=1}^N (m_{Cl} - \bar{m}_{Cl})^2} \right]}, \quad SR^2 = \frac{\sum_{i=1}^N [F_{m_{Cl}} - (AF^0 + b_s \cdot m_{Cl})]^2}{N-2} \quad (9)$$

SR is the residual standard deviation; N the number of measurements used to get AF at different molalities of chloride, b_s is the slope of the regression line.

DFM adopted a scheme of calculating uncertainty based on a method and software developed at this institute¹². For the results from DFM the uncertainty is calculated in two steps. In the first step the molalities of the hydrochloric acid and the chloride added to the sample buffer solution together with all associated uncertainties is calculated. In the second step, the uncertainty of the acidity function at zero chloride molality is calculated.

Table 5 summarizes the standard uncertainties of the intercept of the regression line. In figure 5 the data for u (intercept) are also shown for all participants. If the scatter around the regression line is large, the uncertainty of the intercept can become the major contribution to the overall uncertainty. The slopes of the regression lines are listed in table 6 and shown in figure 6 at the three measurement temperatures. Except for DFM the data are similar.

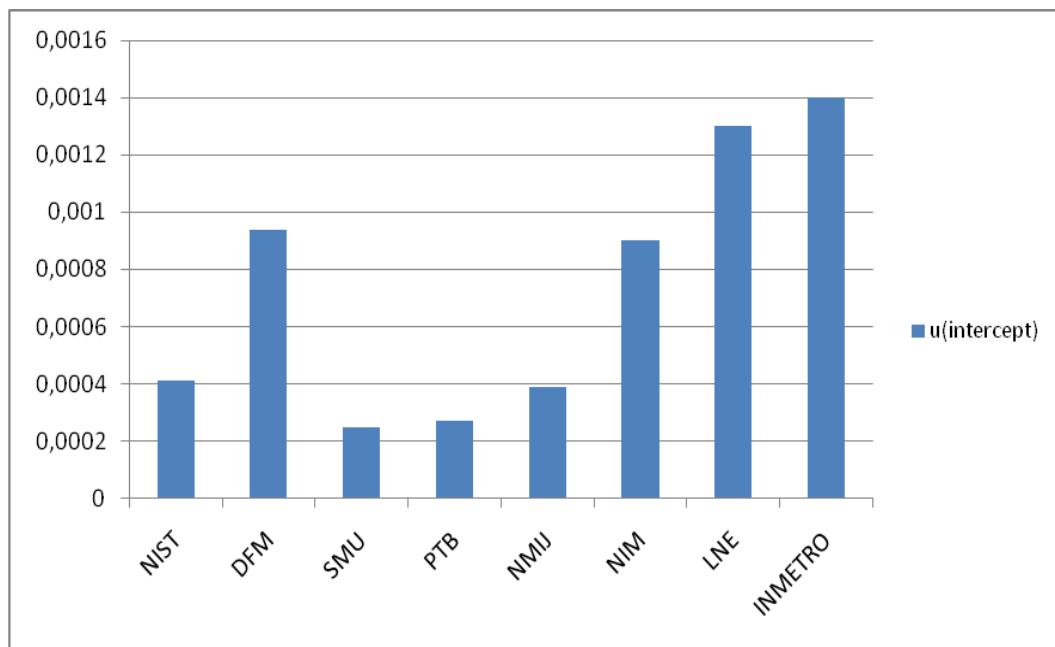


Fig 5 Uncertainty of the intercept of the regression ($k=1$).

¹² Nielsen L, Least-squares estimation using Lagrange multipliers, *Metrologia* 35 (1998), 115-118. Erratum, *Metrologia* 37 (2000), 183

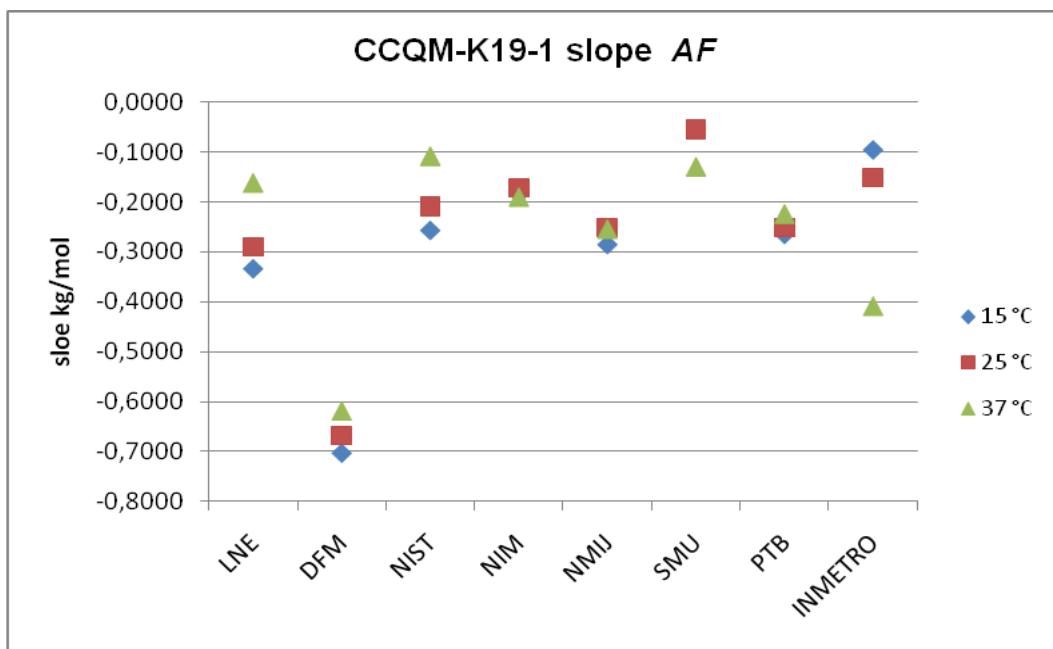


Fig 6 The slopes of the of the regression line at the three measurement temperatures as reported by the participants.

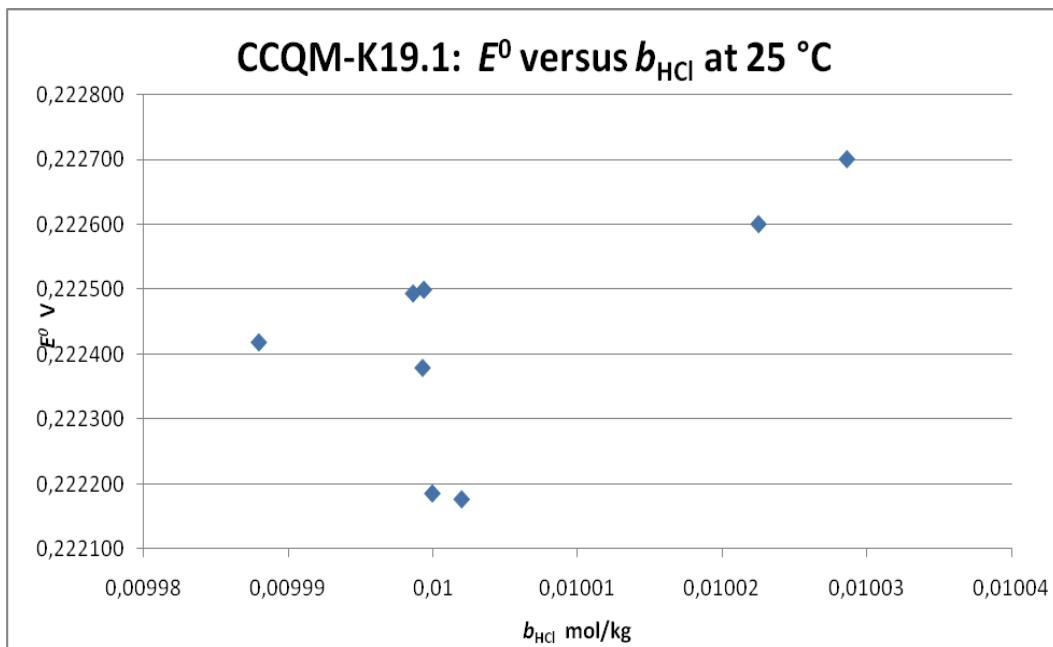


Fig 7 Standard potentials of the silver/silver chloride electrodes as function of the molality of the hydrochloric acid.

Participant	u(intercept) 15 °C	u(intercept) intercept 25 °C	u(intercept) intercept 37 °C
INMETRO	0,0027	0,0014	0,0029
NIM	0,00080	0,00090	0,00080
PTB	0,00032	0,00027	0,00042
DFM	0,00085	0,00094	0,00098
LNE	0,0019	0,0013	0,0018
NMIJ	0,00039	0,00039	0,00047
SMU	0,00023	0,00025	0,00032
NIST	0,00054	0,00041	0,00066

Tab 5 Standard uncertainties of the intercept of the regression to obtain AF^0 .

Participant	Slope /kg/mol/15 °C	Slope /kg/mol/25 °C	Slope /kg/mol/37 °C
INMETRO	-0,097	-0,151	-0,409
NIM	-0,186	-0,172	-0,190
PTB	-0,266	-0,252	-0,224
DFM	-0,703	-0,668	-0,619
LNE	-0,334	-0,290	-0,162
NMIJ	-0,286	-0,252	-0,254
SMU	-0,056	-0,054	-0,129
NIST	-0,258	-0,209	-0,108

Tab 6 The slopes of the of the regression line at the three measurement temperatures as reported by the participants.

Participant	E^0/V	$u(E^0)/V$	E^0/V	$u(E^0)/V$	E^0/V	$u(E^0)/V$
	15 °C		25 °C		37 °C	
INMETRO	0.228941	0.000031	0.222700	0.000031	0.214286	0.000031
NIM	0.228618	0.000078	0.222418	0.000080	0.214280	0.000083
PTB	0.228793	0.000056	0.222600	0.000057	0.214388	0.000060
DFM	0.228376	0.000064	0.222176	0.000065	0.213978	0.000066
LNE	0.228293	0.000068	0.222185	0.000070	0.213724	0.000074
NMIJ	0.228648	0.000051	0.222499	0.000051	0.214339	0.000052
SMU	0.228704	0.000046	0.222493	0.000047	0.214237	0.000048
NIST	0.228549	0.000021	0.222379	0.000019	0.214234	0.000023

Tab 7 Mean values of standard potentials and associated standard uncertainties as reported by the participants.

Participant	$b_{\text{HCl}}/\text{mol/kg}$	$u(b_{\text{HCl}})/\text{mol/kg}$	Analytical method
INMETRO	0.010029	0.0000003	coulometry
NIM	0.009988	0.000015	coulometry
PTB	0.010023	0.000010	coulometry
DFM	0.0100018	0.0000029	coulometry (of ~0.1 mol/kg stock acid) + gravimetric dilution (to ~0.01 mol/kg acid)
LNE	0.009999976	0.000007	potentiometry
NMIJ	0.009999	0.000005	coulometry
SMU	0.009999	0.000006	conductometry
NIST	0.0099993	0.0000016	coulometry

Tab 8 Molality of the hydrochloric acid, the associated uncertainty and the analytical method applied by the participants to determine the standard potential of the silver/silver chloride electrodes as reported by the participants.

The link to CCQM-K19

The results of the common participants NMIJ, PTB and SMU in the original comparison CCQM-K19 and in the subsequent comparison CCQM-K19.1 are consistent. The uncertainties of the results estimated by these participants in both comparisons are reliable and in the same order. The results of the three common participants in CCQM-K19 and CCQM-K19.1 are listed in table 9 and table 10.

AF^0 mean in table 9 and table 10 is the mean value of the acidity functions at zero chloride molality for NMIJ, PTB and SMU obtained in CCQM-K19.1 and in CCQM-K19 at 15 °C, 25 °C and 37 °C. The standard uncertainty $u(k=1)$ for AF^0 mean (K19.1) and AF^0 mean (K19) is estimated from equation (10), where $s(AF^0_i)$ is the standard deviation of the AF^0 values obtained by the common participants in both comparisons (NMIJ, SMU and PTB).

$$u(AF^0 \text{ mean}) = \sqrt{1/N \cdot s^2(AF^0_i)} \quad (10)$$

The Degree of Equivalence DoE (AF^0 mean (K19)) is calculated as AF^0 mean (K19) – AF^0_R (K19). AF^0_R (K19) is the key comparison reference value obtained in CCQM-K19. Table 11 summarized the quantities needed to calculate $D_i(AF^0 \text{ mean (K19)})$.

Participant	AF^0	$u(AF^0)$	AF^0	$u(AF^0)$	AF^0	$u(AF^0)$
	15 °C		25 °C		37 °C	
NMIJ	9.3224	0.0014	9.2303	0.0015	9.1426	0.0013
PTB	9.3214	0.0012	9.2300	0.0012	9.1421	0.0012
SMU	9.3210	0.0012	9.2289	0.0012	9.1415	0.0012
Mean (AF^0)	9.3216	0.00042	9.2297	0.00043	9.1421	0.00032

Tab 9 Results obtained by NMIJ, PTB and SMU in CCQM-K19.

Participant	AF^0	$u(AF^0)$	AF^0	$u(AF^0)$	AF^0	$u(AF^0)$
	15 °C		25 °C		37 °C	
NMIJ	9.3305	0.0012	9.2379	0.0012	9.1503	0.0012
PTB	9.3314	0.0011	9.2399	0.0011	9.1522	0.0011
SMU	9.3325	0.0011	9.2390	0.0011	9.1505	0.0011
Mean (AF^0)	9.3315	0.00058	9.2389	0.00058	9.1510	0.00060

Tab 10 Results obtained by NMIJ, PTB and SMU in CCQM-K19.1.

T/°C	Mean (AF^0)K19	AF^0_R (K19)	$U(AF^0_R$ (K19))(k=2)	DoE (Mean (AF^0)K19)	Mean (AF^0)K19.1
15	9.3216	9.3222	0.0014	-0.0006	9.3315
25	9.2297	9.2300	0.0013	-0.0003	9.2389
37	9.1421	9.1421	0.0024	0	9.1510

Tab 11 Summary of quantities required to link CCQM-K19.1 to CCQM-K19.

The D_i of a participant in the follow-up comparison CCQM-K19.1 relative to the original comparison CCQM-K19 D_i is calculated according to equation (11). Equation (12) gives the corresponding expanded uncertainty ($k = 2$).

$$D_i = AF^0 (\text{NMI (K19.1)}) - \text{Mean} (AF^0) \text{ K19.1} + \text{DoE} (\text{Mean} (AF^0) \text{ K19}) \quad (11)$$

$$U(D_i(\text{NMI})) = 2\sqrt{u(AF^0((\text{NMI(K19.1)}))^2 + u(AF^0(\text{mean(K19.1)}))^2 + u(AF^0_R(\text{K19}))^2} \quad (12)$$

Tables 12 to 14 summarizes the degrees of equivalence D_i (NMI) and the associated expanded uncertainties ($k = 2$).

In Figures 8 to 10 the degrees of equivalence of the participants in CCQM-K19.1 with respect to CCQM-K19 are shown.

Participant	D_i	$U(D_i)$
INMETRO	-0.0071	0.0083
NIM	0.0064	0.0042
DFM	0.0031	0.0031
LNE	-0.0085	0.0057
NIST	0.0016	0.0030

Tab 12 Degree of Equivalence with respect to CCQM-K19 at 15 °C.

Participant	D_i	$U(D_i)$
INMETRO	-0.0025	0.0051
NIM	0.0073	0.0043
DFM	0.0040	0.0033
LNE	-0.0071	0.0048
NIST	0.0017	0.0029

Tab 13 Degree of Equivalence with respect to CCQM-K19 at 25 °C.

Participant	D_i	$U(D_i)$
INMETRO	0.0031	0.0089
NIM	0.0082	0.0046
DFM	0.0040	0.0040
LNE	-0.0069	0.0059
NIST	0.0006	0.0037

Tab 14 Degree of Equivalence with respect to CCQM-K19 at 37 °C.

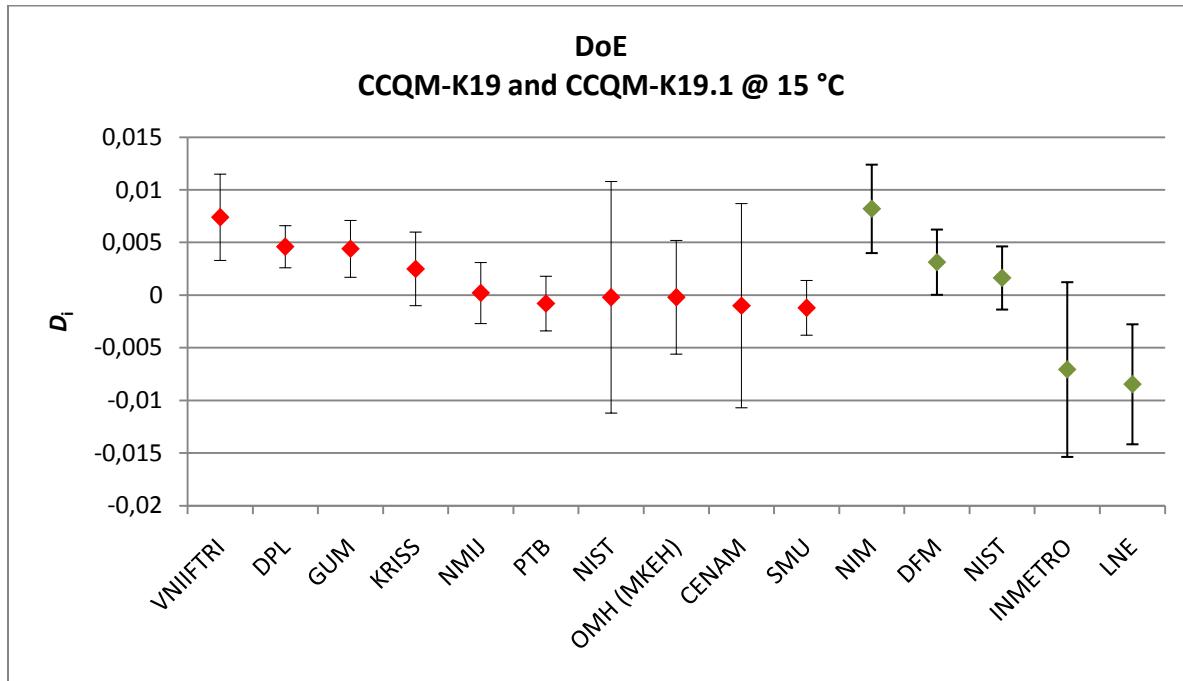


Fig 7 Statement of equivalence for CCQM-K19 and the follow-up comparison CCQM-K19.1. Acidity functions at zero chloride molality at 15 °C. Expanded uncertainty ($k=2$) is given. Red dots indicate CCQM-K19 participants, green dots indicate CCQM-K19.1 participants.

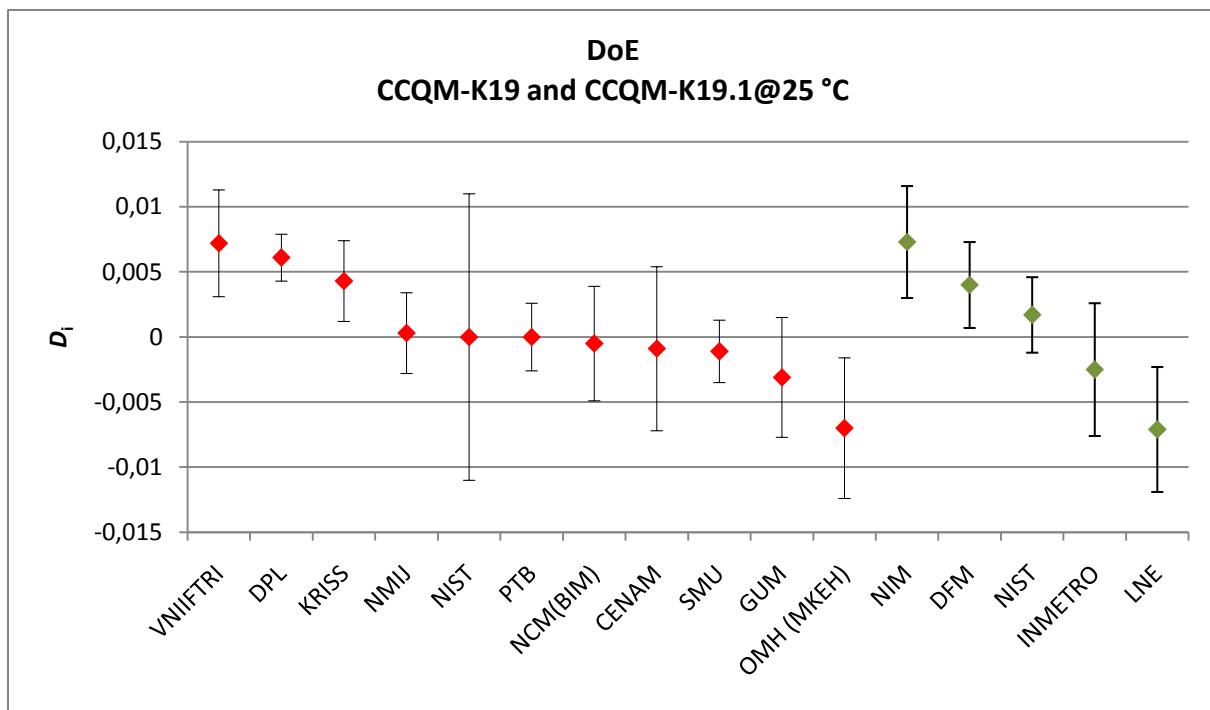


Fig 8 Statement of equivalence for CCQM-K19 and the follow-up comparison CCQM-K19.1. Acidity functions at zero chloride molality at 25 °C. Expanded uncertainty ($k=2$) is given. Red dots indicate CCQM-K19 participants, green dots indicate CCQM-K19.1participants.

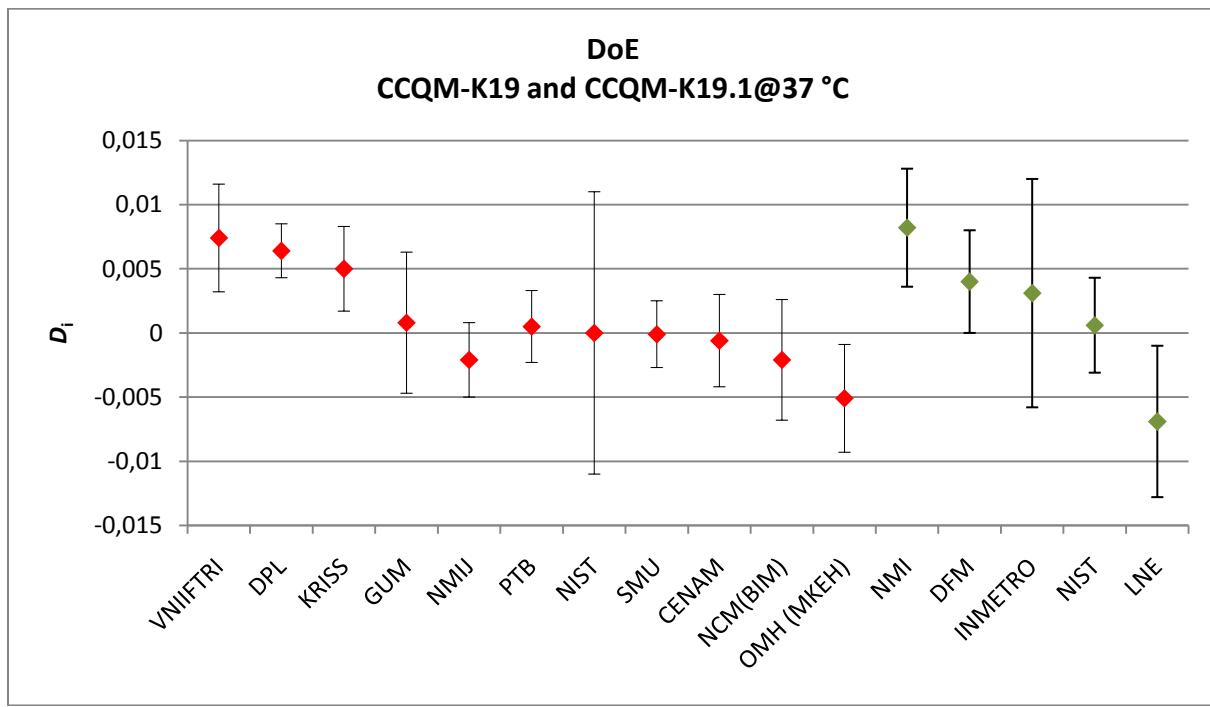


Fig 9 Statement of equivalence for CCQM-K19 and the follow-up comparison CCQM-K19.1. Acidity functions at zero chloride molality at 37 °C. Expanded uncertainty ($k=2$) is given. Red dots indicate CCQM-K19 participants , green dots indicate CCQM-K19.1participants.

How far the light shines

Borate reference buffer solutions are widely used as pH standards for the alkaline range. The participants in the follow-up comparison CCQM-K19.1 have demonstrated their capability to measure the pH of primary buffer solutions in the alkaline range of pH (25 °C) = 8.5 to pH = 9.5.

Acknowledgments

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Invitation to CCQM-K19.1



CCQM Working Group Electrochemical Analysis

CCQM-K19.1 Key Comparison on pH of Borate Buffer

Invitation

The Key Comparison CCQM-K19.1 on pH of Borate Buffer is about to begin. As member of the CCQM you are therefore invited to nominate a participant for this Key Comparison. Please observe the rules specified in the CIPM Guidelines for Key Comparisons for the nominations. The Comparison Protocol, a spreadsheet for the Measurement Report and a Registration Form to be filled out (see below) are being sent with this invitation as a separate attachment.

This invitation is being sent to all participants who agreed to participate in this Key Comparison.

For nominated participant, please provide the following information in the Form:

- CCQM Member laboratory name.
- Name of contact person for the comparison.
- Exact *shipping address* for samples.
- Contact person telephone and telefax numbers.
- Contact person e-mail and possible alternatives.
- Can .doc and .pdf attachments be received at the address? Are there any size limitations on such attachments?

Please return this information by e-mail (preferred), telefax, or e-mail to the supporting laboratory before **20 December 2009**.

Yours Sincerely,

A handwritten signature in blue ink, appearing to read 'Paulo P. Borges'.

Paulo P. Borges

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