Final Report on CCQM – K19

Key comparison on pH

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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, pH ~9.17 by Harned cell measurements at 15 °C, 25 °C and 37 °C.

Laboratories

Contains measurement contribution from

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Abstract

The key comparison CCQM-K19 was carried out to demonstrate the capability of the interested National Metrology Institutes to measure the pH value of an unknown borate buffer by a primary method. The buffer of nominal pH ~ 9.17 was measured at 15 °C, 25 °C and 37 °C. The pilot study CCQM-P82 was performed in parallel in order to allow interested laboratories, mainly newcomers in this field. to compare their capabilities to the more advanced NMI using the same batch of sample.

The comparison was an activity of the Electrochemical Working Group (EAWG) of the CCQM and was coordinated by the Physikalisch - Technische Bundesanstalt, Germany.

All participants applied the primary method for pH [1]. The result for the unknown buffer solution is the acidity function at zero chloride molality, pa^0.

Good agreement of the results was observed for the majorities of participants. The Key Comparison Reference Value (KCRV) was agreed upon during the EAWG meeting in Berlin October 2005 as the median of the reported results. Accordingly the Statements of Equivalence were calculated.

Time schedule

Dispatch of the samples   29 August 2005
Deadline for receipt of the report   01 October 2005
Draft A report   18 October 2005
Draft B report   04 April 2006

Participation in CCQM-K19

The following laboratories participated in the key comparison CCQM-K19 (alphabetical order). Due to technical problems LNE was unable to report valid results. The standard potential of the silver/ silver chloride could not be measured with sufficient reproducibility. Although the bias potential of the electrodes before the measurement was below 30µV differences up to 0.9 mV were observed during measurement. A reason for this behaviour was not find out.

Acronym	Participant	Country	Acronym	Remarks
CENAM	Centro Nacional de Metrologia	Mexico	MX	
DPL	Danish Primary Laboratory for pH	Denmark	DK	
GUM	Central Office of Measure	Poland	PL	
KRISS	Korea Research Institute of Standards and Science	Korea	KR	
íLNE	Laboratoire National d'Essais	France	FR	No results, reported technical problems
NCM	National Centre of Metrology	Bulgaria	BG	
NMJ/AIST	/National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology	Japan	JP	
NIST	National Institute of Standards and Technology	USA	US	
OMH	National Office of Measure	Hungary	HU	
PTB	Physikalisch-Technische Bundesanstalt	Germany	DE	
SMU	Slovak Institute of Metrology	Slovakia	SK	
VNIIFTRI	National Scientific and Research Institute for Physical-technical and >Radio-technical Measurements	Russia	RU	

Table 1. Participants in CCQM-K19.

Purpose of the comparison

Borate buffer is widely used to calibrate pH meter-electrode assemblies in the alkaline range. A buffer solution of 0.01mol/kg di-sodium tetraborate decahydrate is one of the primary reference pH buffer solutions recommended by IUPAC [2].

Measurements of the pH value are only as accurate as the buffers used for calibration of the pH meter electrode assembly. These buffers have to be traceable to the primary pH buffers. The purpose of the present Key comparison is to establish the equivalence of the measurement of the pH value at national metrology institutes.

As a result of the previous comparisons on pH the participating institutes improved their own primary measurement procedures for pH. On the other hand each time the number of participants increased. At the 20th CCQM meeting in 2004 it was decided to initiate a Key Comparison and a Pilot Study in parallel. This way the difference in experience will be taken into account.

The comparison is restricted to the use of the primary method for pH (Harned cell measurements). The measurements have to be performed at three measurement temperatures, 15 °C, 25 °C and 37°C.

Sample

The buffer solution used for the comparison was produced at the laboratory of the German Calibration Service DKD-K-14301 (Merck KGaA) under the supervision of PTB. The source material is from a similar batch as the source material normally used for production of primary pH reference material.

Thermo gravimetric analyses (TGA) at 550°C competed only after making up the samples have shown a weight loss of 47.0 % for the source material. This is a little bit different from the weight loss of 47.23 % expected for di-sodium tetraborate decahydrate. Loss of water means increasing tetraborate molality if the same amount of material is dissolved. It is known from literature that sodium tetraborate decahydrate can loose some of its water of crystallisation while transforming slowly into the pentahydrate [3]. The water content of the pentahydrate is 30.92 %.

The sample was prepared at the end of June 2005 from 100 ± 0.5 kg purified water and 310 ± 1 g borate. The batch size was 100 kg. One kg of buffer solution was filled in 1 L HDPE bottles, respectively. The mass of the closed bottles (corrected to air buoyancy) and the mass fraction of water was reported to the participants. The bottles were sealed in MILAR$^{®}$ bags.

The mass fraction of water in each bottle was **w = 0.99691 g/g with an expanded (k = 2) uncertainty of $U = 37 \cdot 10^{-6}$ g/g** according to a molality of **b = 0.0081mol·kg^{-1}** if the weight loss is not taken into account. The molality of a primary buffer solution prepared from di-sodium tetraborate decahydrate is 0.01 mol·kg^{-1} that is something higher.

Test on homogeneity and stability of the sample batch

Before shipment, the coordinating laboratory performed measurements to estimate the homogeneity and stability of the batch. The stability of the solution was tested during the whole measurement period by differential potentiometric measurements [4].

During three periods one sample was compared to three other samples. Between bottle homogeneity measured from 06-08 September 2005 using random selected bottles. Each time one half cell was filled with the same buffer solution while the buffer in the other half cell was changed. The results are summarized in table 2. The results of pH measurement between the bottles differ less than 0.001, therefore the batch can be considered to be homogeneous.

Sample in first half cell	Sample in second half cell	ΔE /μV	Δ pH
65	0A	-2	< 0.0001
65	0B	2	< 0.0001
65	74	1	< 0.0001
65	75	-11	0.0002

Table 2. Between bottle homogeneity tested by means of differential potentiomentry.

After the test was completed sample 74 was stored in the refrigerator under argon. Sample 65 was stored in the laboratory. The between bottle homogeneity has been measured again from 27-29 September 2005. The pH value of sample 74 and 65 was compared to the pH value of just opened sample 61 and 69. The results are summarized in table 3. The three samples 55, 61 and 69 were unopened up to that time. There was no significant difference in pH between these three samples.
Depending on the filling level in the bottles the samples 74 A, B, C differences in pH was indicated. Sample 74A contained 900 g solution, 74 B 700 g and sample 74C les than 500 ml. Sample 65 contained only 300g buffer solution and was stored in the laboratory without precaution. This result means remaining buffer should not store for later use.
In a third measurement cycle between 09 -10 November the pH of the tetraborate buffer in three bottles 54, 62 and 70 are compared by differential potentiomentry. The difference in pH was again less than pH = 0.0002.
The tests demonstrated the stability of the sample solution over the whole measurement period.

Sample	Sample	ΔE /μV	Δ pH
55	61	2	< 0.0001
55	69	-8	0.0001
55	74 A	12	-0.0002
55	74 B	103	-0.002
55	74 C	192	-0.004
55	65	181	-0.004

Table 3. Influence of the storing conditions on the pH of the tetraborate sample.

Instructions to the participants

Each participant received a copy of the measurement protocol and a datasheet for the batch as well as three 1L HDPE bottles filled with 1kg of borate buffer sealed in MILAR® bags.
The mass of the closed bottles (corrected to air buoyancy) and the mass fraction of water was reported in the datasheet. The bottles were numbered and marked with a number and a nominal value of pH = 9.2 (at 25 °C).
Each participant was asked to use hydrochloric acid and sodium or potassium chloride as is usual in the laboratory for the primary method of pH. It was recommended to dry the alkali chloride at least at 400 °C for two hours.
Shipment to all participating laboratories was performed at the same time. The participants were asked to inspect the sample bottles for damage, leakage or visible contaminants in the solution. No irregularities were reported to the coordinating laboratory. No weight loss exceeding 0.02 g has been observed.
Participants were requested to measure the buffer solution within three weeks of receiving of the solution. This condition has been fulfilled by most of the participants. Table 4 listed the

information given by the participants regarding the receipt of the sample and the date of measurement.

Laboratory	Bottle No	Sample received	Measurement period
CENAM	22, 29, 37	01 Sep 05	06 Sep to 15 Sep
DPL	8, 12, 26	31 Aug 05	07 Sep to 09 Sep
GUM	6, 21, 36	31 Aug 05	03 Oct to 11 Oct
KRISS	20	30 Aug 05	14 Sep. 05
NCM	11, 27, 31	31 Aug 05	07 Sep to 2005-09-27
NMIJ/AISI	3, 18, 25	28 Aug 05	08 Sep, 12 Sep, 21 Sep
NIST	9, 19, 39	02 Sep 05	15 Sep to 16 Sep , 19 Sep to 20 Sep
OMH	1, 16, 24	29 Aug 05	20 Sep to 26 Sep
PTB	59, 73		12 Aug, 16.Sep
SMU	4, 17, 34	30 Aug. 05	7 Sep
VNIIFTRI	14,15, 35	08 Sep 05	20 Sep to 29 Sep

Table 4. Measurement period and date of receiving the samples.

The participants were requested to use the Measurement Report Form prepared by the coordinating laboratory. This form was send at the same time as the samples.
The following details are asked in the form:
— Identification of the samples measured
— Date(s) of measurement(s)
— Method used for the determination of molality of HCl
— Description of the instrumentation, the cell and the electrodes
— Flow rate of hydrogen in one cell
— Volume of buffer in one cell
— Preparation of the Ag/AgCl electrodes, aging, comparison method, storage solution
— Molality of the HCl and its uncertainty
— Cell potentials measured in HCl and in the buffer with added alkali chloride corrected to a partial pressure of hydrogen of 101325. Alkali chloride should be added at at least three different molalities in the range of 0.005 mol/kg to 0.02 mol/kg.
— Standard potential of the Ag/AgCl electrodes, single values and mean, SD of the mean
— Acidity function at each chloride molality
— Slope and intercept of the acidity function extrapolated to zero chloride molality
— Standard uncertainties calculated according to the "Guide to the Expression of Uncertainty in Measurement

Measurement method

Participants are requested to use only the primary method for pH [1]. During sample handling contamination with CO_2 had to be avoided. The standard potential of the Ag/AgCl electrodes had to be measured using HCl with SI traceable known molality very close to 0.01 mol/kg.

The pH measurement is carried out by measuring the potential difference of the electrochemical cell (Cell I, Harned cell) at several chloride molalities necessary in order to stabilize the potential of the silver-silver chloride electrode. The determination of the pH value of the buffer solution involves an extrapolation of the measured potential difference to zero chloride molality.

$$\text{Pt} \mid \text{H}_2 \mid \text{buffer, Cl}^- \mid \text{AgCl} \mid \text{Ag} \qquad \text{(Cell I)}$$

The potential difference E of this cell (corrected to 101.325 kPa partial pressure of hydrogen) depends on the hydrogen ion activity, a_H, the quantity to be measured, in the following way:

$$E = E^0 - [(RT/F)\ln 10]\lg(a_H/m^0)(m_{Cl}\gamma_{Cl}/m^0) \qquad (1)$$

This is the measurement equation.

E^0 is the standard potential difference of the cell i.e. at $a_H = a_{Cl} = 1 \ \text{mol} \cdot \text{kg}^{-1}$, m^0 is the standard molality: $1 \ \text{mol kg}^{-1}$, 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.

A pH measurement of a buffer solution using cell I usually consists of the following steps.

1. The standard potential difference E^0 is determined from a Harned cell filled with hydrochloric acid of fixed molality, according to equation (2). The mean activity coefficient of HCl, $\gamma_{\pm HCl}$, at various temperatures is best known at the molality 0.01 mol kg^{-1} [5]

$$E^0 = E + [(2RT/F)\ln 10](\lg(m_{HCl}/m^0)(\gamma_{\pm HCl})) \qquad (2)$$

   E is corrected to 101.325 kPa partial pressure of hydrogen.

2. Equation (1) can be rearranged to give the acidity function pa so that there are only measurable quantities on the right hand side of equation (3) pa is measured as a function of m_{Cl}.

$$\text{p}a = -\lg(a_{H^+}\gamma_{Cl^-}/m^0) = (E - E^0)/[(RT/F)\ln 10] + \lg(m_{Cl^-}/m^0) , \qquad (3)$$

3. Extrapolation of the acidity function to zero chloride molality.
   The acidity function

$$\text{p}a_0 = -\lg\left(a_H\gamma_{Cl}/m^0\right)_{m_{Cl}\to 0} \qquad (4)$$

   corresponding to zero chloride molality is determined by linear extrapolation according to equation (5) of pa as a function of the chloride molality, using measurements at least three values of m_{Cl} in the range from 0.005 to 0.02 mol·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%.

$$\text{p}a = \text{p}a_0 + bm_{Cl} \qquad (5)$$

   where b is an empirical, temperature-dependent constant.

CCQM-K19 results of the participants

The result of the comparison is the intercept of the acidity function extrapolated to zero chloride molality, pa^0, and its expanded uncertainty (k =2) at each of the three measurement temperatures 15 °C, 25 °C, 37 °C. The coordinating laboratory did not calculate the pH value of the sodium tetraborate buffer solution from the results of the participants.

It is assumed that the deviation in weight loss from the theoretical value indicating a slightly deviant composition of the buffer material. Presumably the dissolution of the partly transformed decahydrate results in different borate species in the solution [6]. Further for a buffer solution of about 0.0081 mol· kg^{-1} the ionic strength will be smaller than $I = 0.02$ mol·kg^{-1} for the 0.01 mol· kg^{-1} standard buffer solution and in the order of $I = 0.016$ mol·kg^{-1}.

Table of results

The results reported for the sample, sodium tetraborate buffer solution are summarized in table 5. Diagrams are summarized in annex A.

Institute	pa^0at15°C	U(pa^0) (k=2)	pa^0at25°C	U(pa^0) (k=2)	pa^0at 37°C	U(pa^0) (k=2)
CENAM	9.3212	0.0148	9.2291	0.0063	9.1401	0.0034
DPL	9.3268	0.0019	9.2361	0.0017	9.1485	0.0017
GUM	9,3266	0.0026	9,2269	0.0046	9,1429	0.0054
KRISS	9.3247	0.0034	9.2343	0.0030	9.1471	0.0031
NCM	9.2955	0.0045	9.2295	0.0044	9.14	0.0045
NIST	9.322	0.011	9.230	0.011	9.142	0.011
NMIJ/AIST	9.3224	0.0028	9.2303	0.0030	9.1426	0.0026
OMH	9.322	0.0054	9.223	0.0054	9.137	0.0040
PTB	9.3214	0.0025	9.2300	0.0025	9.1421	0.0025
SMU	9.3210	0.0025	9.2289	0.0023	9.1415	0.0023
VNIIFTRI	9.3296	0.0040	9.2372	0.0040	9.1495	0.0040

Table 5. Acidity function at zero chloride molality as calculated by the participants of key comparison CCQM-K19.

Laboratory	u(intercept) 15 °C	u(intercept) 25 °C	u(intercept) 37 °C	mean value
CENAM	0.0026	0.0031	0.0014	0.0024
DPL	0.00044	0.00031	0.00034	0.00036
GUM	0.0011	0.0022	0.0026	0.0020
KRISS	0.00042	0.00021	0.00018	0.00027
NCM	-	0.001	0.001	0.001
NMIJ	0.001	0.0011	0.001	0.001
NIST	0.0056	0.0054	0.0055	0.0055
OMH	0.001	0.001	0.001	0.001
PTB	0.00051	0.00045	0.00042	0.00046
SMU	0.0008	0.0006	0.00066	0.00070
VNIIFTRI	0.001	0.001	0.001	0.001

Table 6. Extrapolation to zero chloride molality. Uncertainty associated to the intercept of the regression line.

The intercept of the regression line and the Type A uncertainty associated with this value are listed in table 6. If the scatter around the regression line is large, the uncertainty of the intercept can become the major contribution to the overall uncertainty.

NIST reported an unusual large uncertainty contribution. It is an open question whether the reason for the deviation are caused by the buffer material. The data presented at the CCQM autumn meeting in Berlin 2005 allow the educated guess that there was a difference in the composition of the sample between the three NIST bottles. Thus the high uncertainty stated for the NIST result in CCQM-K19 should not be taken as representative for NIST capabilities. The source of the contamination of one bottle could not be identified.

In Table 7 and 8 the standard potentials of the silver/silver chloride electrodes and the molality of the hydrochloric acid as reported by the participants are summarized together with the standard uncertainties associated with the results. As the method of choice for the determination of the molality of HCl coulometric titration was recommended as a primary method. The decision was left to the participants. Nearly all of the participants determined the amount content of HCl by coulometric titration. Various classical titration methods were used by VNIIFTRI, OMH, GUM, NCM and CENAM.

Laboratory	E^0/V 15 °C	$u(E^0)$ 15 °C	E^0/V 25 °C	$u(E^0)$ 25 °C	E^0/V 37 °C	$u(E^0)$ 37 °C
CENAM	0,2285452	0,000037	0,2223775	0,000033	0,2140166	0,000041
DPL	0,228761	0,000039	0,222579	0,000039	0,214384	0,000039
GUM	0,228254	0,000030	0,22259	0,000037	0,213797	0,000039
KRISS	0,228619	0,000072	0,222437	0,000064	0,214280	0,000064
NCM	0,22234	0,000056	0,22857	0,000058	0,21422	0,00006
NMIJ	0,228488	0,000033	0,222400	0,000033	0,214344	0,000033
NIST	0,228508	0,000014	0,22236	0,000018	0,214207	0,000022
OMH	0,228179	0,000084	0,222129	0,000084	0,213139	0,000084
PTB	0,228854	0,000025	0,222673	0,000031	0,214517	0,000035
SMU	0,228846	0,000039	0,222623	0,000040	0,214391	0,000042
VNIIFTRI	0,228726	0,00015	0,222543	0,00015	0,214370	0,00015

Table 7. Standard potential of the silver/ silver chloride electrode.

Laboratory	HCl molality / mol kg^{-1}	$u(b)$
CENAM	0,0100060	6,05E-06
DPL	0,0100000	1,00E-07
GUM	0,0100160	4,40E-06
KRISS	0,0100132	8,00E-07
NCM	0,0102400	1,00E-05
NMIJ	0,0100004	2,00E-06
NIST	0,0100024	5,80E-07
OMH	0,0100220	1,20E-05
PTB	0,0100200	1,00E-06
SMU	0,0100000	5,80E-06
VNIIFTRI	0,0099270	2,00E-05

Table 8. Molality of the HCl and the associated standard uncertainty.

Uncertainties

All participants delivered the results together with a complete uncertainty budget.

A good estimate for the uncertainty of the acidity function at zero chloride molality of the sample is equation (6).

$$u(\mathrm{p}a_0) = \sqrt{u^2(\mathrm{p}a_{m=0,005}) + u^2(\text{intercept})} \tag{6}$$

The standard uncertainty u(intercept) of the extrapolation of the acidity function, pa, to zero chloride molality by a linear least squares fit at the pa values obtained at the different chloride molalities can be calculated according to equation (7). These two equations are used by the majority of the participants. The NIST and the SMU reported the uncertainty in a slightly different way combining the uncertainty of the acidity function and the intercept in one table.

$$u(\text{intercept}) = s \sqrt{\left[\frac{1}{N} + \frac{\overline{m}_{Cl}^2}{\sum\limits_{i=1}^{N}(m_{Cl} - \overline{m}_{Cl})^2} \right]} \;,\; s^2 = \frac{\sum\limits_{i=1}^{N}\left[\mathrm{p}a_{m_{Cl}} - (\mathrm{p}a_0 + b \cdot m_{Cl})\right]^2}{N-2} \tag{7}$$

s is the residual standard deviation, N the number of measurements used to get pa at different molalities of chloride, b is the slope of the regression line.

The main uncertainty contributions in most cases are the uncertainty in the molality of HCl in the determination of the standard potential E^0 according to equation (2) and the uncertainty of the intercept of the regression line.

Agreement on the KCRV

The NCM from Bulgaria reported difficulties in temperature control of the themostated bath at 15 °C as a reason for the deviation in pa^0 at this measurement temperature. NCM normally does not measure below 20°C. During the autumn meeting of the EAWG in Berlin October 2005 this problem was discussed among the participants. The value pa^0 = 9.2955 at 15°C for NCM is identified as an outlier and therefore not taken into account in the KCRV.

In principle there are at least three possibilities to calculate the key comparison reference value KCRV: the mean, the weighted mean and the median. In table 9 the three values and the associated uncertainties are compared. There are apparent differences between the values. Th median is displaced as red line in the

The weighted mean was calculated according to the approach discussed in the report of the key comparison CCQM-K17 [] according to equations (9) to (12). The weighted mean is sensitive to outliers. Reliable uncertainty statements are required.

$$\mathrm{p}a^0{}_\mathrm{R} = \frac{\sum\limits_{i=1}^{N} w_i \mathrm{p}a^0{}_i}{\sum\limits_{i=1}^{N} w_i} \tag{9}$$

$\mathrm{p}a^0{}_i$ represents the individual results and w_i: the individual weights.

$$w_i = \frac{C}{u_i{}^2} \tag{10}$$

$$C = \frac{1}{\sum\limits_{i=1}^{N} \dfrac{1}{u_i{}^2}} \tag{11}$$

The values of u_i are the individual uncertainties and C is the variance.

$$u\left(\mathrm{p}a^0{}_\mathrm{R}\right)^2 = C \tag{12}$$

A problem with the estimation of the uncertainty according to equation (12) is that a laboratory that quotes an optimistically small uncertainty has a strong influence on the KCRV and makes the uncertainty of the latter unreasonably small [8].

A reasonable estimate of the uncertainty for the KCRV is that of the external consistency concept [9], [10] taking into account the individual uncertainties and the spread of the results according to equation (13).

$$u_\mathrm{R}{}^2 = \frac{\sum\limits_{i=1}^{N} \left(w_i\left(\mathrm{p}a^0{}_i - \mathrm{p}a^0{}_\mathrm{R}\right)^2\right)}{(N-1)\cdot\sum\limits_{i=1}^{N} w_i} \tag{13}$$

The median as a more robust estimator of the KCRV is more insensitive to outliers. To use the median is therefore recommended, if there results reported with significant differences to the results of other participants.

Median was proposed and accepted as the KCRV for CCQM-K19 during the EAWG meeting in Berlin in October 2005.

The median and its uncertainty was estimated applying robust statistics based on the mean absolute distance, MAD [11] according to the equation (14).

$$u = \frac{1,858}{\sqrt{n-1}} \, median\left(\left|pa^0{}_i - \tilde{x}\right|\right)$$ (14)

There $\tilde{x}$ is the median of the reported acidity function at zero chloride molality

The results are also given in graphs in annex. The median is shown as a red line.

	15°C	U (k=2)	25°C	U (k=2)	37°C	U (k=2)
Mean	9.3240	0.0056	9.2305	0.0040	9.1430	0.0037
Weighted mean	9.3243	0.0018	9.2321	0.0023	9.1442	0.0023
Median	9.3222	0.0014	9.2300	0.0013	9.1421	0.0024

Table 9. Comparison of potential KCRV values.

Evaluation of equivalence (according to Appendix B of the MRA)

The equivalence statements are calculated according to the BIPM guidelines. The degree of equivalence (and its uncertainty) between a NMI result and the KCRV is calculated according to the following equations:

D_i is the degree of equivalence between the participant result $x_i = pa^0{}_i$ and the KCRV $x_R = pa^0{}_R$ and U_i
is the expanded uncertainty ($k=2$) of the D_i calculated by the combined uncertainty ($k=1$) of the participant result u_i and the uncertainty ($k=1$) of the KCRV u_R.

The equivalence statement of the CCQM-K19 and the relevant graphical display are presented in the Annex B of this report.

$$D_i = \left(x_i - x_R\right)$$ (15)

$$U_i^2 = 2^2\left(u_i^2 + u_R^2\right)$$ (16)

The degree of equivalence (and its uncertainty) between two participants is given by a pair of terms. This value is calculated on request only according to the following equation (18). Where D_{ij} is the degree of equivalence between two results and U_{ij} is the expanded uncertainty ($k=2$) of the D_{ij} calculated by the combined uncertainty ($k=1$) of the two results.

$$D_{ij} = x_i - x_j = pa^0{}_i - pa^0{}_j$$ (17)

The expanded uncertainty $U_{ij},(k=2)$ is calculated according to equation (18)

$$U_{ij}^2 = 2^2(u_i^2 + u_i^2).$$

(18)

The statements of equivalence are summarized in table 10 to 12.

Laboratory	D_i	U_i
CENAM	-0,0010	0,0097
DPL	0,0046	0,0020
GUM	0,0044	0,0027
KRISS	0,0025	0,0035
NMIJ	0,0002	0,0029
NIST	-0,0002	0,0110
OMH	-0,0002	0,0054
PTB	-0,0008	0,0026
SMU	-0,0012	0,0026
VNIIFTRI	0,0074	0,0041

Table10. Statement of equivalence at 15 °C

Laboratory	D_i	U_i
CENAM	-0,0009	0,0063
DPL	0,0061	0,0018
GUM	-0,0031	0,0046
KRISS	0,0043	0,0031
NCM	-0,0005	0,0044
NMIJ	0,0003	0,0031
NIST	0,0000	0,0110
OMH	-0,0070	0,0054
PTB	0,0000	0,0026
SMU	-0,0011	0,0024
VNIIFTRI	0,0072	0,0041

Table11. Statement of equivalence at 25 °C

Laboratory	D_i	U_i
CENAM	-0,0020	0,0036
DPL	0,0064	0,0021
GUM	0,0008	0,0055
KRISS	0,0050	0,0033
NCM	-0,0021	0,0047
NMIJ	0,0005	0,0029
NIST	-0,0001	0,0111
OMH	-0,0051	0,0042
PTB	0,0000	0,0028
SMU	-0,0006	0,0026
VNIIFTRI	0,0074	0,0042

Table 12. Statement of equivalence at 37 °C.

Discussion

Good agreement was found between the majorities of participants. The results are similar to those in CCQM-K17, significant improvement was observed for some participants compared

to the previous study. NIST reported unusual large uncertainty contribution associated to the intercept of the regression line. It is presumed that one of the buffer solutions delivered to NIST was different in composition to the others. A contamination could not be identified. Stability tests at the coordinating laboratory gave no indication on changes in the composition of the solution during the measurement period.

Acknowledgment

References

1. *Working Documents of the 6th CCQM Meeting*, BIPM, Paris, April 2000
2. R.P. Buck, S. Rondinini, F.G. K. Baucke, M.F. Camoes, A.K. Covington, M.J.T. Milton, T. Mussini, R. Naumann, K.W. Pratt, P. Spitzer, G.S. Wilson: The Measurement of pH-Definition, Standards and Procedures, Report of the Working Party on pH. *Pure Appl. Chem.* 74(11), 2169-2200, 2002
3. R. Naumann, Alexander-Weber, Ch., Baucke, FGK, Fresenius J Anal Chem (1994) 350:119-121
4. FGK Baucke , J Electroanal. Chem. (1994) 368:67-75
5. R. G Bates., Robinson R. A., *Solution Chemistry*,1980, **9**, 455
6. G.G. Manov, Delollis NJ, Lindvall PW, Acree SF, J Research NBS (1946) 36:543
7. P.Spitzer, Hongyu X., Dazhou C., Famnin M., Kristensen H.B., Hjelmer B., Nakamura S., Hwang E., Lee H., Castro E., Mendoza M.M., Kozlowski W., Wyszynska J., Mateuszuk A., Pawlina M., Karpov O.V., Zdorikov N., Seyku E., Maximov I., Vyskocil L., Máriássy M., Pratt K.W., Vospelova A., Giera J., Eberhardt R.[BIPM]
   Final report for CCQM-K17: pH determination on a phthalate buffer by Harned cell measurements
   Metrologia, 2003, 40, *Tech. Suppl.*, 08006 [on-line]
8. Cox, M. G., *A Discussion of Approaches for Determining a Reference Value in the Analysis of Key-Comparison Data*, NPL Report CISE 42/99, 1999
9. DIN 1319-4, *Grundlagen der Messtechnik, Teil 4: Auswertung von Messungen; Messunsicherheit, Beuth Verlag*, Berlin, 1999
10. Dietrich, C.F., *Uncertainty, Calibration and Proability. The Statistics of Scientific and Industrial Measurement, sc. edition*, Adam Hilger, 1991, p. 39-49, p.295-298
11. Jörg W.Müller: Possible Advantages of a Robust Evaluation of Comparisons, J. Res. Natl. Inst. Stand. Technol. 105, 551 (2000) ,Volume 105, Number 4
12. *Guide to the Expression of Uncertainty* (GUM), ISO, Geneva,1993

Annex A

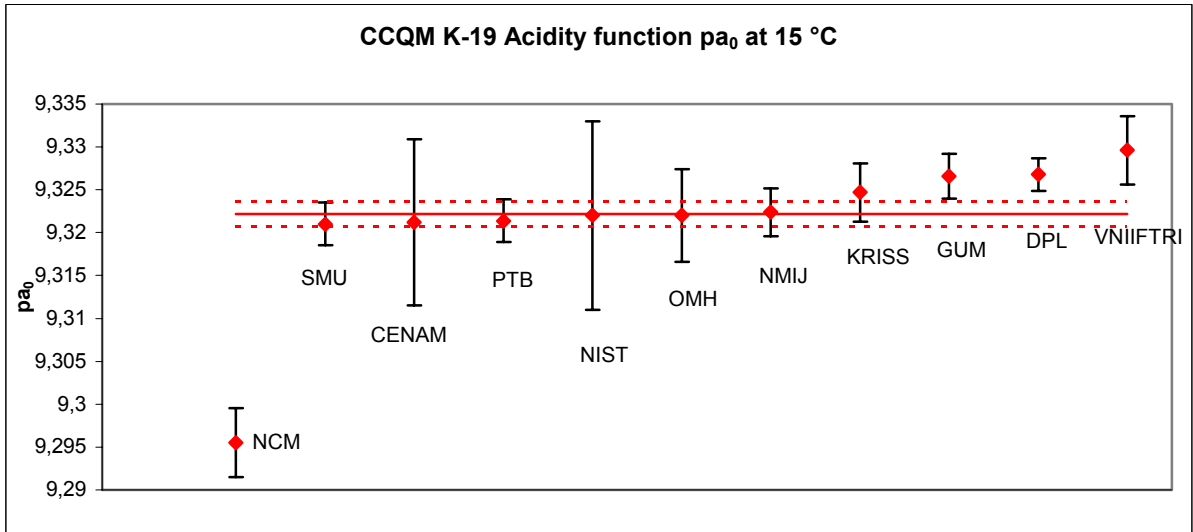**Graphical display of CCQM-K19**
Results and the KCRV

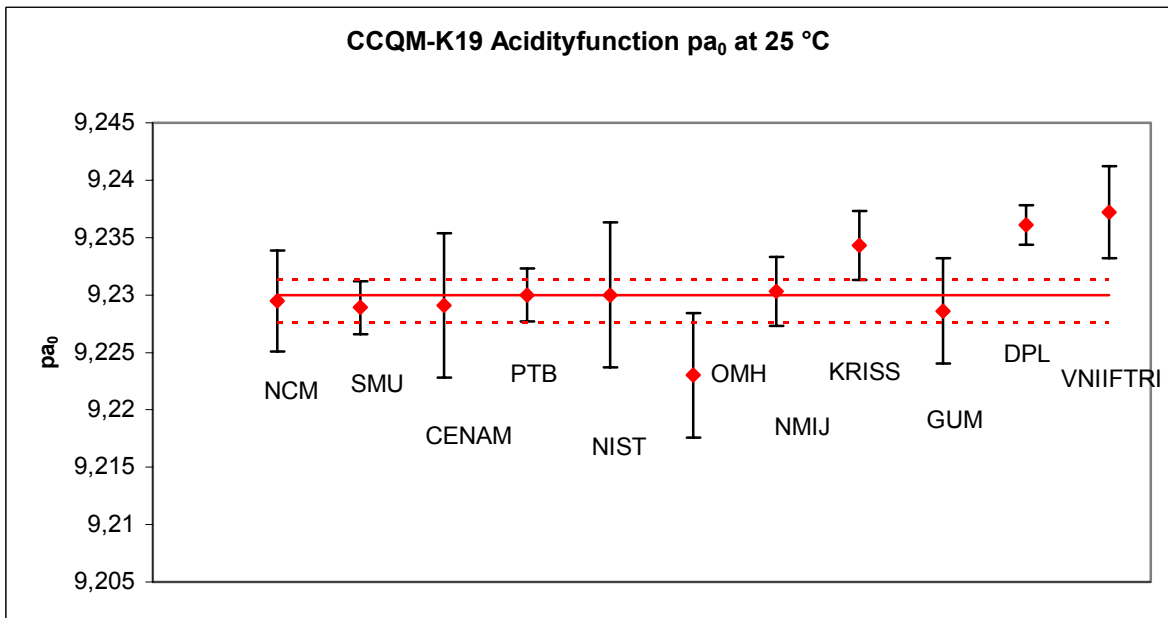Figure A1. Acidity function at zero chloride molality at 15 °C.

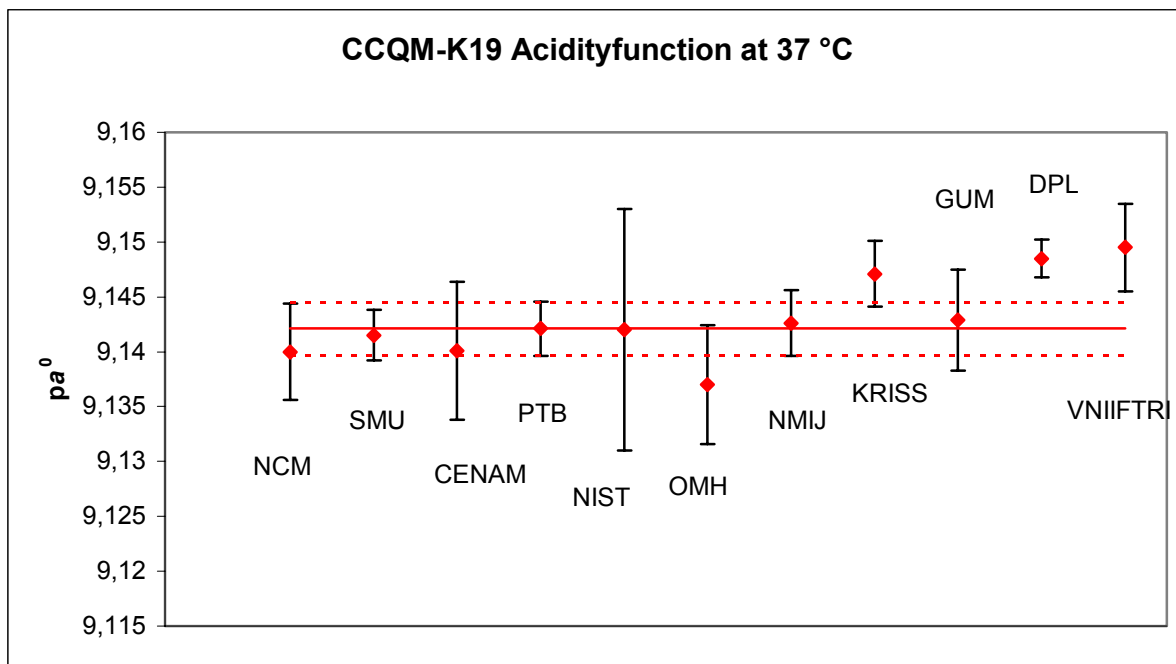Figure A2. Acidity function at zero chloride molality at 25 °C.

Figure 3. Acidity function at zero chloride molality at 37 °C.

Annex B

Statement of equivalence

Equivalence statement for CCQM-K19

Measurand   pH (acidity function at zero molality)

Standard uncertainty of KCRV

15 °C u R = 0.0014

25 °C u R = 0.0013

37 °C u R = 0.0024

The standard uncertainty of the KCRV was calculated on the basis of the MAD according to the equation (14)

$$u = \frac{1,858}{\sqrt{n-1}} median\left(\left|pa^0{}_i - \tilde{x}\right|\right)$$

The KCRV was calculated as the median of all results; at 15 °C the value of NCM was not taken into account. NCM was not able to control the measurement temperature at 15 °C.

The degree of equivalence of each laboratory with respect to the KCRV is given by a pair of numbers:

$Di = (x_i - x R)$ and Ui, its expanded uncertainty ($k = 2$),

Key comparison reference value (KCRV)

15 °C x R = 9.3222

25 °C x R = 9.2300

37 °C x R = 9.1421

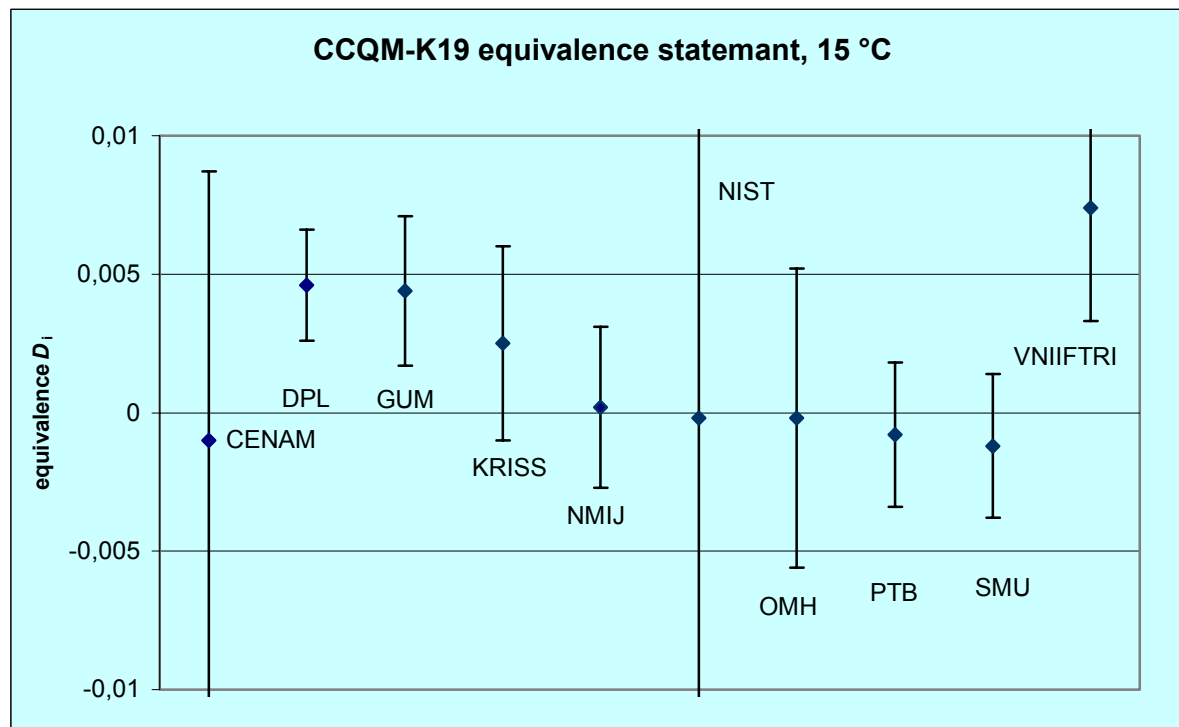Graphical display of the statement of equivalence

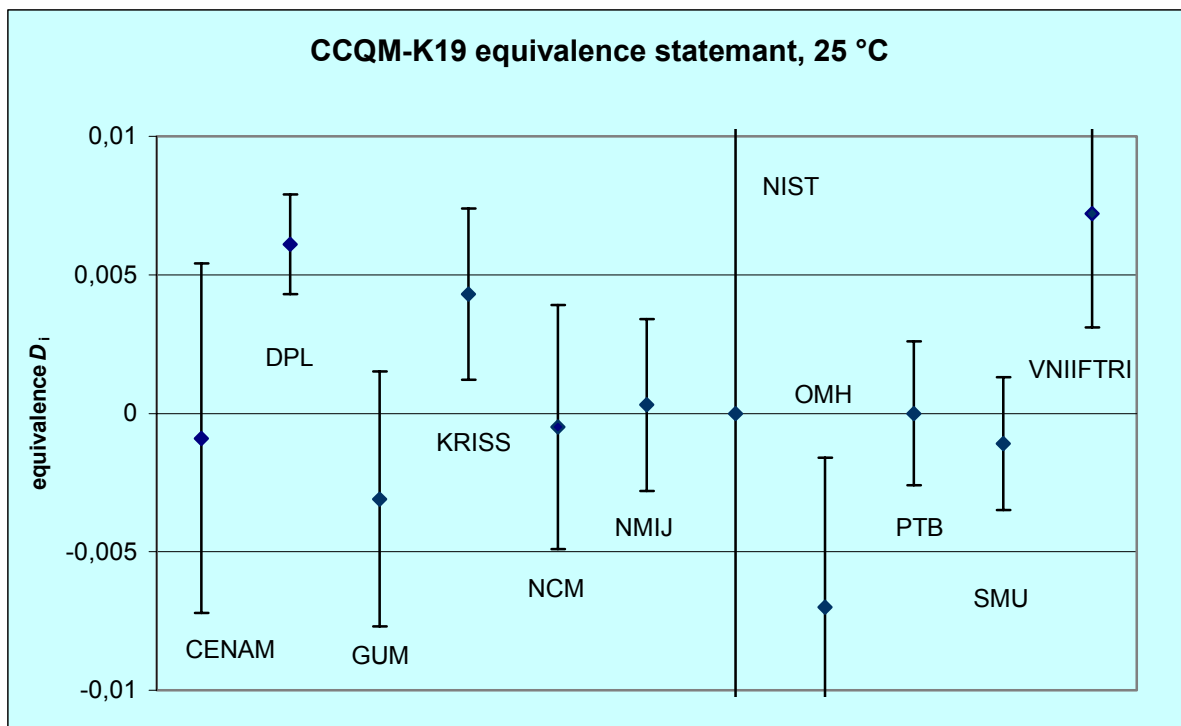Figure B1. Acidity function at zero chloride molality at 15 °C.
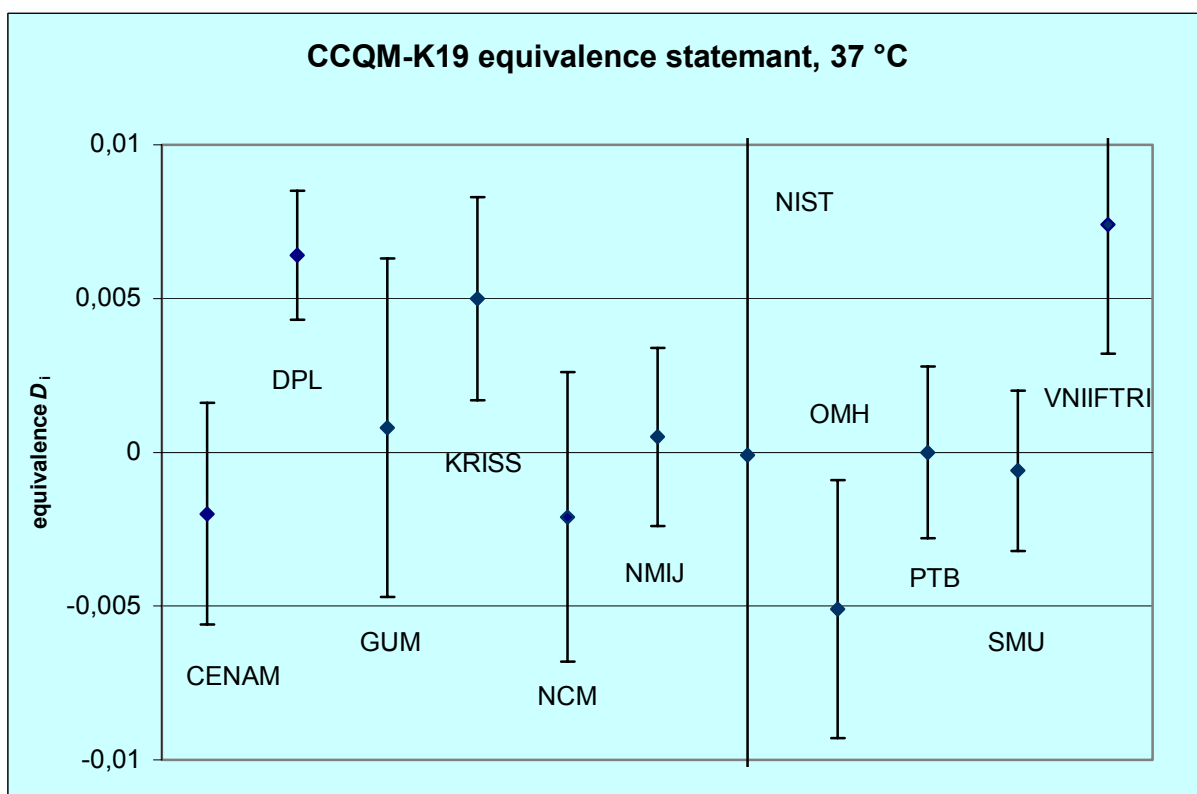
Figure B2. Acidity function at zero chloride molality at 25 °C.

Figure B3. Acidity function at zero chloride molality at 37 °C.