

Report of subsequent key comparison CCQM – K18.1

pH of carbonate buffer

Final Report

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Summary

The subsequent key comparison CCQM-K18.1 was started in order to evaluate the equivalence of metrology institutes as a follow-up of the previous key comparison CCQM-K18 for institutes that could not take part in the comparison at that time or did not consider their results representative for their capabilities. A carbonate buffer of a slightly different composition to that in CCQM-K18 was used.

There were 7 institutes + the coordinating laboratory participating in this subsequent comparison. Most from the participating institutes showed significant improvement, in some cases the new results confirmed the previous ones. The reasons for this have still to be elucidated.

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Introduction

The key comparison CCQM-K18 on pH of carbonate buffer took place in August 2006. Some institutes could not take part in the comparison at that time or did not consider their results representative for their capabilities. Therefore a subsequent key comparison was launched. A carbonate buffer of a slightly different composition to that in CCQM-K18 was used.

All participants applied the primary method for pH. The result for the unknown buffer solution is the acidity function at zero chloride molality p_a^0 .

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 measurements at 25 °C.

Time schedule

Dispatch of the samples: 15 May 2007
 Deadline for receipt of the report: 31 July 2007
 Discussion of results: EAWG meeting, October 2007

Participants

Table 1 *Table of participants*

Acronym	Participant	Country	Analyst
CENAM	Centro Nacional de Metrologia	Mexico	Marcela Monroy; Adrian Reyes
INMETRO	Instituto Nacional de Metrologia, Normalização e Qualidade Industrial	Brasil	Paulo P. Borges; Isabel C. S. Fraga; Bianca S. R. Marques; Júlio C. Dias
DFM	Danish Fundamental Metrology A/S	Denmark	Pia Tønnes Jakobsen
INPL	The National Physical Laboratory of Israel	Israel	Elena Kardash
LNE	Laboratoire National d'Essais	France	Rachel Champion, Paola Fisticaro
NIM	National Institute of Metrology, Division of Metrology in Chemistry	China	Hongyu Xiu
PTB	Physikalisch-Technische Bundesanstalt	Germany	Janine Giera; Petra Spitzer
SMU	Slovenský metrologický ústav	Slovakia	Anna Mathiasova; Leos Vyskocil

Sample description

Sample preparation

The carbonate buffer solution was prepared from deionised water and NaHCO₃ (MERCK) as the starting material. The buffer composition differed from that of the standard buffer solution (pH~10.012).

About 100 g of sodium hydrogen carbonate was dried in a desiccator over silica gel at room temperature. A second portion (about 300 g) was ignited 5 h in a furnace at 300°C with intermittent mixing, to convert it to sodium carbonate:



After cooling in a desiccator about 76,087 g NaHCO₃ was dissolved in 1000 mL hot deionised water. After dissolution, 91,297 g Na₂CO₃ was added and the solution was stirred until the dissolution was complete. The cooled down solution was quantitatively transferred into a 60 L HDPE bottle filled with about 35 L of deionised water.

Water was added slowly to reach the target balance reading, and then the solution was stirred 5 h with a vibration stirrer. Cleaned and dry 1 L HDPE bottles were filled with the prepared solution. The filled bottles were closed using a special key and after weighing they were sealed in a Mylar type foil to prevent access of CO₂.

The mass fraction of water in the solution was $w = 0.995221$ g/g.

Solution homogeneity

Interwoven between the 1 L bottles (after each 5 bottles), several 250 mL bottles were filled for homogeneity check (trend analysis). The solution in 250 mL bottles was measured immediately after filling using a glass electrode. The results are given in Table 2.

Table 2 *Results of homogeneity measurement*

Sample	pH
1	9,990
2	9,991
3	9,989
4	9,990
5	9,991
6	9,990

No observable difference between the bottles was seen, so it can be concluded that no systematic change occurred during the filling process and the solution can be considered homogeneous.

Sample delivery

Each participant received three 1 L HDPE numbered bottles, sealed into foil bags to eliminate the influence of the carbon dioxide from ambient air. Shipment to participants was done by

DHL. The bottles were shipped in a cardboard box by courier and the consignment number was reported by email to the contact person of the receiving laboratory for tracking purposes. The dates of receipt of the samples are given in Table 3.

Table 3 *Date of sample receipt and measurement period*

Institute	Sample received	Measurement period
CENAM	28.5.07	July 10 to 19
DFM	23.5.07	July 7 to 8
INMETRO	31.5.07	July 19
INPL	24.5.07	July 5 to 20
LNE	23.5.07	July 25 and 27
NIM	25.5.07	July 5 to 29
PTB	24.5.07	July 25 and 27
SMU	- - -	July 19 to 24

Check of the bottle integrity

Participants were requested to weigh the received bottles to verify that they were unchanged during the transport. No significant mass deviation above 0.5 g was observed compared to the bottle mass reported by SMU. No leaks were observed.

Results and discussion

The measurement protocol was almost identical to that in CCQM-K18 [1] except the calculation of the reference value. All participants received template file for reporting the results.

Measurement of acidity function

Participants were requested to use only the primary method for acidity function measurement. The standard potential of the Ag/AgCl electrodes had to be measured using HCl of known molality very close to 0.01 mol/kg. The acidity function measurement is carried out by measuring the potential difference of the electrochemical cell without junction (1) (so called Harned cell) at several chloride molalities necessary in order to stabilize the potential of the silver-silver chloride electrode.



The voltage U^* corrected to standard pressure is calculated according to the equation:

$$U^* = U - \frac{\mathbf{RT} \ln 10}{2\mathbf{F}} \log \left(\frac{p - p_w}{p_0} \right) \quad (2)$$

The voltage U^* of cell (1) (corrected to hydrogen pressure of $p_0 = 101.325$ kPa) depends on the hydrogen ion activity¹ a_{H^+} according to the equation:

$$U^* = E^0 - \frac{RT \cdot \ln(10)}{F} \log(a_{H^+} \cdot b_{Cl^-} \cdot \gamma_{Cl^-}) \quad (3)$$

Where:

- U voltage of cell, measured at laboratory pressure
- U^* voltage of cell, corrected to standard pressure $p_0 = 101.325$ kPa
- E^0 standard potential of silver, silver chloride electrode
- T absolute temperature in K
- a_{H^+} activity hydrogen ions
- b_{Cl^-} molality of chloride ions in mol/kg
- γ_{Cl^-} activity coefficient of chloride ions
- p barometric pressure
- p_w pressure of saturated vapour of water

Equation (3) can be rearranged to give the acidity function so that there are only measurable quantities on the right hand side of equation (4), so acidity function is measured as a function of b_{Cl^-} .

$$-\log(a_{H^+} \cdot \gamma_{Cl^-}) = \frac{(U^* - E_{Ag/AgCl}^0) \cdot F}{RT \ln(10)} + \log(b_{Cl^-}) \quad (4)$$

All terms on the right-hand side are known or experimentally accessible. The value of the left-hand side is plotted against the chloride ion molality in the graph. The intercept on the y-axis represents the acidity function value determined (AF^0).

In the measurement of carbonate buffer some CO_2 is eliminated from the buffer by the hydrogen stream, thus modifying pH of the buffer. Therefore the Harned cell voltage will not reach a stable value during the measurement and an extrapolation to the start time of measurement is usually necessary. The voltage drift is almost not detectable only at lowest flow-rates of hydrogen, at the expense of very long stabilisation times.

All the measurements were performed only at one temperature, $25^\circ C$, due to logistical problems with preparation and distribution of more sample bottles. The results are given in Table 4 and Figure 1.

¹ All the activities are relative to activity in standard state

Table 4 Results of key comparison CCQM-K18.1

Institute	Acidity function AF°	U _{AF°} (k=2)
LNE	10,0857	0,0068
NIM	10,0861	0,0036
INMETRO	10,1032	0,0032
PTB	10,1048	0,0029
DFM	10,1076	0,0012
CENAM	10,1092	0,0037
INPL	10,1409	0,0067
SMU	10,1033	0,0030

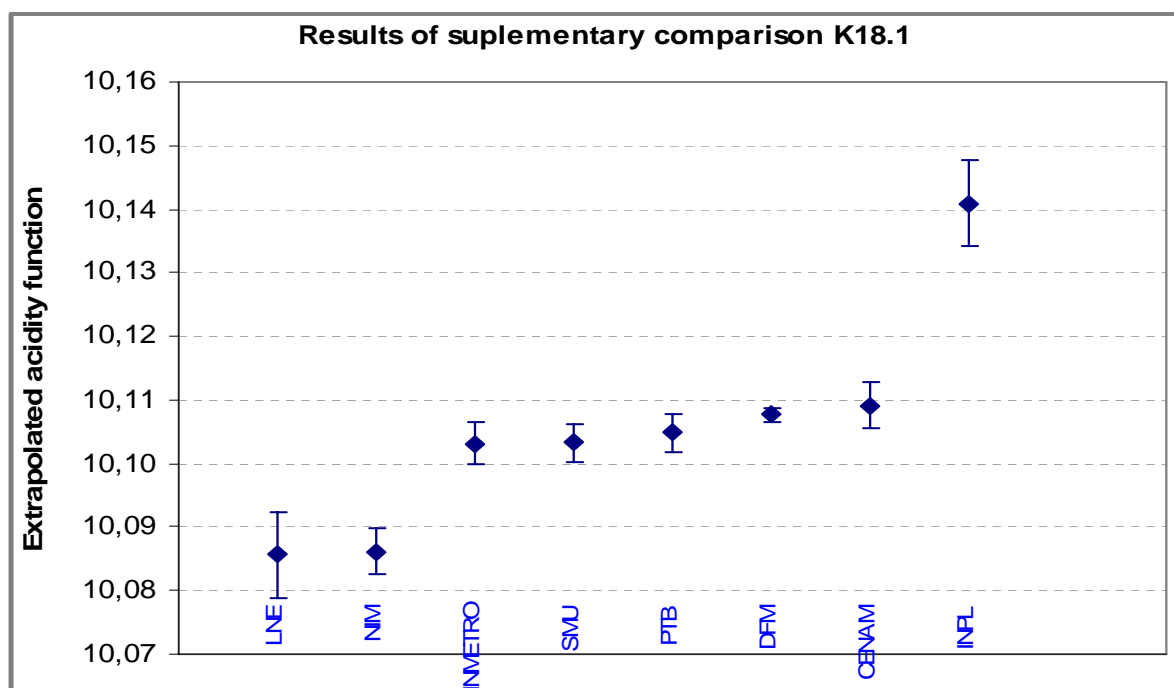


Figure 1 Results of supplementary comparison K18.1

Measurements of standard potential E°

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

$$E^\circ = U^* + \frac{2RT}{F} \cdot \ln(b_{\text{HCl}} \cdot \gamma_{\text{HCl}}^\pm) \quad (5)$$

Table 5 *The standard potential of Ag/AgCl electrodes*

Institute	Standard potential E° [V]	U_{E° (k=2)
CENAM	0,22241	0,00008
INMETRO	0,22234	0,00007
DFM	0,22249	0,00003
INPL	0,22135	0,00036
LNE	0,22241	0,00017
NIM	0,22259	0,00013
PTB	0,22248	0,00009
SMU	0,22239	0,00009

The standard potential values given agree very well with values recalculated by the coordinating laboratory.

Measurement of HCl molality

The molality of HCl used was measured in most cases by coulometric, volumetric or weight titration (Table 6); the participants were in most cases able to prepare solution very close to target molality.

Table 6 *Molality of HCl used and method of determination*

Institute	HCl molality	Methods of analyse
CENAM	0,010034	Gravimetric Potentiometric Titration
DFM	0,009999	Dilution from coulometrically determined HCl
INMETRO	0,010044	Coulometry
INPL	0,009959	Volumetric titrimetry with NaOH
LNE	0,010000	Potentiometric titration
NIM	0,010004	Coulometry
PTB	0,010003	Coulometry
SMU	0,009997	Conductimetry

Degrees of equivalence

The degree of equivalence of the participants of the subsequent comparison relative to the original CCQM-K18 comparison was calculated using the results of the coordinating laboratory according to the equation (6), based on assumption that the deviation of the coordinating laboratory's result from the reference value is constant.

$$D_{NMI} = D_{SMU(K18)} + AF^\circ_{NMI(K18.1)} - AF^\circ_{SMU(K18.1)} \quad (6)$$

D_{NMI} degree of equivalence of the participant of the subsequent comparison

$D_{SMU(K18)}$ degree of equivalence of SMU in CCQM-K18

$AF^\circ_{NMI(K18.1)}$ result of NMI in CCQM-K18.1

$AF^{\circ}_{SMU(K18.1)}$ result of SMU in CCQM-K18.1

For the calculation of uncertainty of the degrees of equivalence equation (7) was used. The analysis of uncertainty budget of SMU results revealed no significant correlation between the uncertainty contribution in both measurements, therefore the full uncertainty of the results is used in the calculations. The meaning of the symbols is analogous to those above and the individual contributions are depicted in Figure 2.

$$U_{D_{(NMI)}} = \sqrt{U_{D_{SMU(K18)}}^2 + U_{AF^{\circ}_{NMI(K18.1)}}^2 + U_{AF^{\circ}_{SMU(K18.1)}}^2} \quad (7)$$

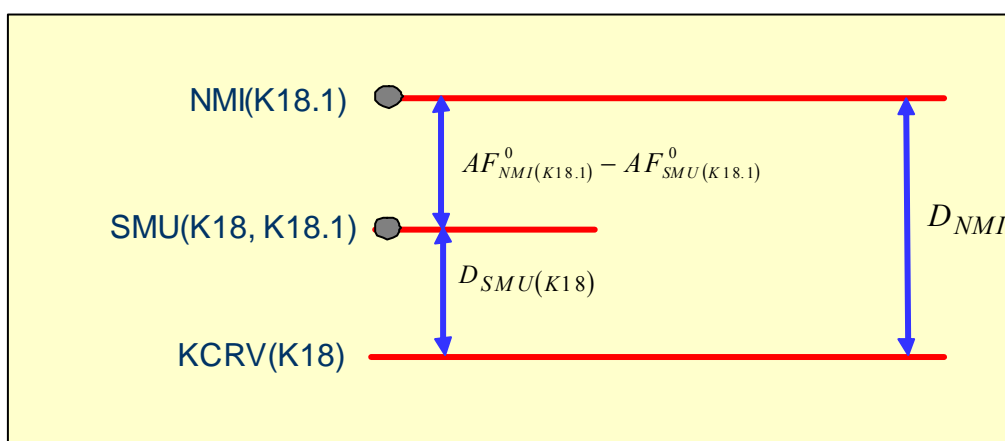


Figure 2 Principle of calculation of degrees of equivalence in subsequent comparison

The degrees of equivalence are given in Table 6. In figure 3 the degrees of equivalence are shown together with the original CCQM-K18 results.

Table 6 Degrees of equivalence

Institute	D	U _D
LNE	-0,0166	0,0088
NIM	-0,0162	0,0067
INMETRO	0,0009	0,0065
PTB	0,0025	0,0064
DFM	0,0053	0,0058
CENAM	0,0069	0,0068
INPL	0,0386	0,0088

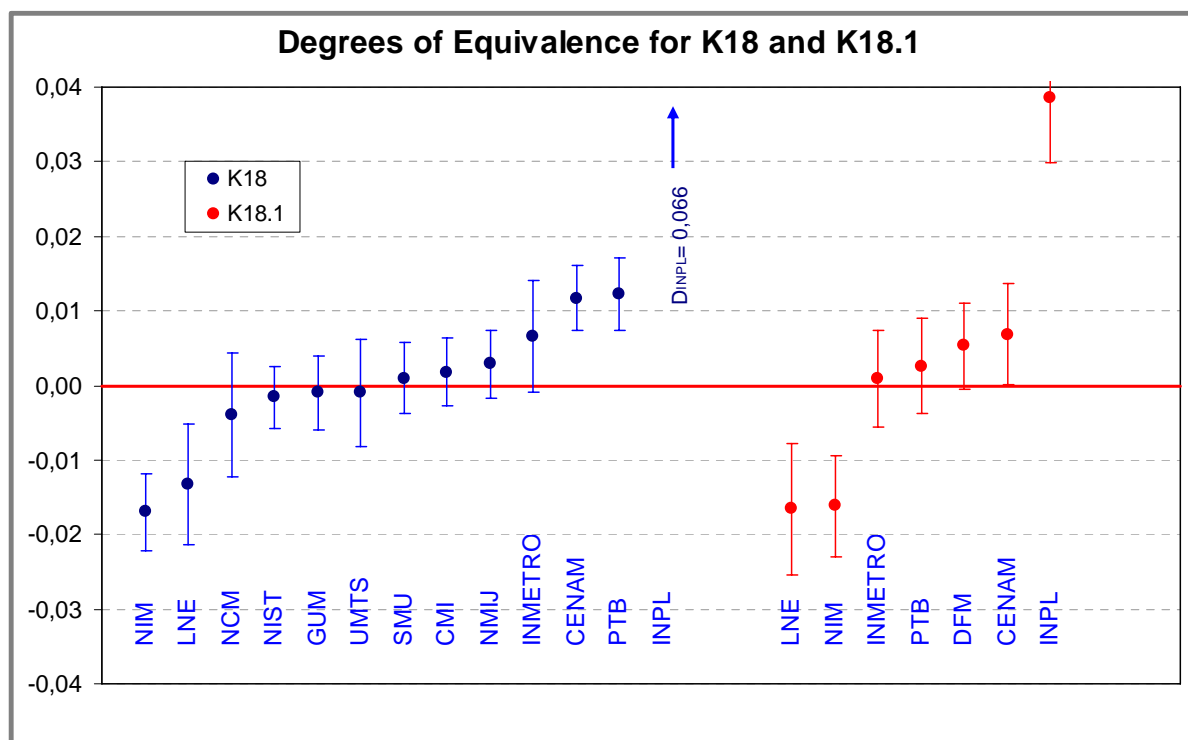


Figure 3 Results with expanded ($k=2$) uncertainties given

Conclusions

There were 7 institutes + the coordinating laboratory participating in this subsequent comparison. Most from the participating institutes showed significant improvement, in some cases the new results confirmed the previous ones. The reasons for this have still to be elucidated.

The carbonate buffer is one of the more difficult ones to measure. Good results in this comparison are relevant to measurement of carbonate buffer; other buffers except phthalate and borate are covered partially.

References

1. Final report of key comparison CCQM-K18: pH of carbonate buffer, Metrologia, 2007, 44, Tech. Suppl., 08011
2. Bates R.G., Robinson R. A.: Standardisation of Silver-Silver Chloride Electrodes from 0 to 60°C, J.Soln.Chem. 9 (1980) 455

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