

Final report on CCQM-K9.2: Subsequent key comparison on pH determination of phosphate buffer by Harned cell measurements

Petra Spitzer¹

Janine Giera, Isabel C. Fraga, Pia Tønnes Jakobsen, Hans D. Jensen, Peter Hyllested, Oleg Karpov, Viatcheslav Kutovoy, Susumu Nakamura, Alena Vospelova, Valentina Zvezdina.,

1. Abstract

CCQM-K9.2 was performed supplementary to the key comparison CCQM-K9 [1] on the pH determination of a phosphate buffer with nominal pH ~ 6.9 (at 25 °C). The sample composition was very similar in both comparisons. Only the source of the starting material used for sample preparation was different. The comparison was restricted to the use of the primary method for pH (Harned cell measurement) as defined in the IUPAC Recommendations [2]. The measurement temperatures were 15 °C, 25 °C, 37 °C.

CCQM-K9.2, CCQM-K.9 and the first supplementary comparison CCQM-K9.1 [5] are activities of the Electrochemical Working Group (EAWG) of the CCQM. All three comparisons were coordinated by the PTB, Germany.

The Danish Primary Laboratory (DPL) successfully took part in the CCQM-K9. Meanwhile the primary set-up for pH in Denmark moved from DPL affiliated to Radiometer Medical to DFM, Denmark. The subsequent comparison allows assessing the degree of equivalence for the measurement of pH at DFM after the move. Due to the interest of other laboratories to demonstrate their progress in pH measurements on the primary level the CCQM-K9.2 supplementary comparison was extended to other participants than DFM, namely NMIJ, VNIIFTRI, INMETRO and CMI.

The reported quantity for CCQM-K9.2 was not the pH of the sample but the acidity function at zero chloride molality (see chapter 12). To calculate the pH value from the acidity function it is necessary to know the ionic strength of the sample buffer solution which was undisclosed by the coordinator.

With the exception of the Czech Metrology Institute, CMI, good agreement in the determined acidity function is found between the participants.

The results reported by DFM and by PTB agree within their measurement uncertainty at all measurement temperatures.

¹ Coordinator

Table of content

1. Abstract	1
2. Table of content	2
3. Subject field	3
4. Subject	3
5. Participants and acronyms	3
6. Comparison background	3
7. Schedule	4
8. Sample preparation	4
9. Shipment and travel events	4
10. Characterisation	4
11. Participants results	4
12. Measurement conditions	5
13. Reported results	6
14. The link to CCQM-K9	7
15. Annex	13
Figures	13
16. References	12
17. Addresses	18

2. Subject field

Amount of substance

3. Subject

Measurand: pH value of phosphate buffer.

Sample: Unknown phosphate buffer: Potassium di-hydrogen phosphate, KH_2PO_4 and disodium hydrogen phosphate, Na_2HPO_4 at a molality of about $0.025 \text{ mol}\cdot\text{kg}^{-1}$, each.

Nominal value: pH ~ 6.9 (at 25 °C)

The values reported by the participants are the acidity function at zero chloride molality at measurement temperatures of 15 °C, 25 °C and 37 °C.

4. Participants and acronyms

Acronym	Participant	Country
CMI	Czech Metrology Institute	Czech Republic
DFM	Danish Fundamental Metrology	Denmark
INMETRO	Intituto Nacional de Metrologia, Normalização e Qualidade Industrial	Brazil
NMIJ	National Metrology Institute of Japan	Japan
PTB	Physikalisch-Technische Bundesanstalt	Germany
VNIIFTRI	National scientific and Research Institute for Physical-Technical and Radiotechnical Measurements	Russia

5. Comparison background

The CCQM-K9 on pH determination of two phosphate buffers was the first key comparison in the field of pH measurements completed in 2000. The Danish Primary Laboratory (DPL) successfully took part in the CCQM-K9 [1] which was coordinated by PTB. Meanwhile the primary set-up for pH in Denmark moved from DPL affiliated to Radiometer Medical to DFM, Denmark. The sample chosen for the supplementary comparison CCQM-K9.2 was similar to sample 1 of CCQM-K9. The supplementary comparison allows assessing the degree of equivalence for the measurement of pH between DPL and DFM.

Harned cell measurements by means of platinum/hydrogen and silver/silver chloride electrodes were performed at three measurement temperatures, 15 °C, 25 °C and 37 °C.

Due to the interest of other laboratories to demonstrate their progress in pH measurements on the primary level the CCQM-K9.2 supplementary comparison was extended to other participants than DFM, namely NMIJ, VNIIFTRI, INMETRO and CMI.

6. Schedule

Dispatch of the samples	6 December 2006
Deadline for receipt of the report	15 January 2007
Draft A report	08 March 2007
Draft B report	11 April 2007
Final report	1 June 2007

7. Sample preparation

The phosphate buffer was prepared at PTB from high purified water, potassium di-hydrogen phosphate, KH_2PO_4 (Merck: A377069) and di-sodium hydrogen phosphate, Na_2HPO_4 (Merck A497570). The buffer composition differed from that of the standard buffer solution (pH ~ 6.9 (at 25 °C)). The mass fraction of water in the phosphate solution was given on the bottle label. Each participant received three 1L numbered HDPE bottles. The bottles were capped with a tamper-evident closure and sealed in aluminized plastic bags.

The bottles were shipped in a cardboard box by courier. Hydrochloric acid and sodium or potassium chloride was not provided. It was recommended to dry the alkali chloride at least at 400 °C for two hours.

8. Shipment and travel events

Acronym	Shipment	Arrival	Remarks
CMI	12 Dec 2006	15 Dec 2006	
DFM	21 Nov 2006	22 Nov 2006	
INMETRO	12 Dec 2006	22 Dec 2006	For one bottle the seal of the aluminized plastic bag was defect, but no leakage was observed
NMIJ	12 Dec 2006	15 Dec 2006	
VNIIFTRI	12 Dec 2006 (17 Dec 2006)	10 Jan 2007	Courier service was not willing to deliver the samples to Moscow. Therefore the samples were shipped only at 17 Dec 2006 to VNIIM St. Petersburg and picked up from VNIIFTRI

9. Characterisation

For stability control the acidity function at zero chloride molality was measured before shipment, during the comparison period and after deadline. The results agreed within the stated expanded uncertainty ($k = 2$) of $U(p\text{a}^0) = 0.002$. The results are displayed in Figure 1.

10. Participants results

Participants reported their results in the period from 12 Jan 2007 to 12 Feb 2007 (VNIIFTRI).

Acknowledgement of receipt of the report was sent to the laboratories soon after receipt.

The results reported by CMI were found to be in disagreement with other results. A message was sent

to the laboratory at 21 Feb 2007 with a request to check the reported values for numerical errors. Not only a revised but a completely new report was submitted by CMI at 8 March 2007. According to the BIPM rules on key comparisons this report had to be rejected [4]. Only CMI results from the original report are included in the final report.

CMI reported in April 2007 to the Convener of the EAWG on on-going measurement problems. The reproducibility of the cell potential measured in hydrochloric acid was still poor and up to 2 mV.

11. Measurement of the acidity function

The participants are requested to use HCl with SI traceable known molality close to a molality of $0.01 \text{ mol}\cdot\text{kg}^{-1}$ in order to measure the standard potential of the Ag/AgCl electrodes. For the Faraday constant and for the gas constant the following values are recommended $F = 96485.3415(39) \text{ C mol}^{-1}$ and $R = 8.314472(15) \text{ J mol}^{-1} \text{ K}^{-1}$.

The measurement of the acidity function is carried out by measuring the potential difference of the electrochemical cell without junction (Cell I, Harned cell) at several chloride molalities necessary in order to stabilize the potential of the silver-silver chloride electrode.



The potential difference E of this cell (corrected to 101.325 kPa partial pressure of hydrogen) depends on the hydrogen ion activity, a_{H} , according to equation (1):

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

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

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 (2) pa is measured as a function of m_{Cl} .

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

The acidity function

$$pa^0 = -\lg(a_{\text{H}}\gamma_{\text{Cl}} / m^0)_{m_{\text{Cl}} \rightarrow 0} \quad (3)$$

corresponding to zero chloride molality is determined by linear extrapolation according to equation (4) of the acidity function pa as a function of the chloride molality. Alkali chloride of certified high quality is added at 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%.

$$pa = pa^0 + bm_{Cl} \quad (4)$$

where b is an empirical, temperature-dependent constant.

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 and 37 °C. The coordinating laboratory calculated the pH value of the phosphate buffer solution from the results of the participants.

12. Reported results

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 sample measurement conditions are summarized in table 1.

Laboratory	Bottle No	Sample measured
CMI	13,14, 15	10 – 15 Dec 2006
DFM	1, 2, 3	30 Nov - 4 Dec 2006
INMETRO	10, 11, 12	9 -11 Jan 2007
NMIJ	7, 8, 9	26 - 8 Dec 2006
PTB	4, 5, 6	2 Nov -18 Jan 2007
VNIIFTRI	16, 17, 18	19 Jan, 25 Jan 2007

Table1. Measurement conditions

In figures 2 to 4 plots of the results as reported by the participants are shown. Acidity functions at different chloride molalities as reported by the participants are displayed in figure 5. The results are summarized in the Tables 2-4 below. pH values are calculated by the coordinator (PTB) (see chapter 13). DFM, PTB, INMETRO and NMIJ determined the molality of the HCl solution needed in the determination of the standard potential of the Ag/AgCl electrodes by coulometry. VNIIFTRI made no statement on its analytical method.

Laboratory	Acidity function pa^0	pH	$U(pa^0)= U(pH)$ ($k = 2$)
CMI	7.0323	6.9245	0.0036
DFM	7.0058	6.8980	0.0016
INMETRO	6.9962	6.8884	0.0062
NMIJ	7.0046	6.8968	0.0026
PTB	7.0055	6.8977	0.0020
VNIIFTRI	7.0086	6.9008	0.0022

Table 2.Reported results at 15 °C; pH values are calculated by the coordinator (PTB)

Laboratory	Acidity function pa^0	pH	$U(pa^0) = U(pH)$ ($k = 2$)
CMI	6.9882	6.8786	0.0036
DFM	6.9738	6.8642	0.0016
INMETRO	6.9689	6.8593	0.0059
NMIJ	6.9715	6.8619	0.0022
PTB	6.9728	6.8632	0.0020
VNIIFTRI	6.9738	6.8642	0.0021

Table 3. Reported results at 25 °C; pH values are calculated by the coordinator (PTB)

Laboratory	Acidity function pa^0	pH	$U(pa^0) = U(pH)$ ($k = 2$)
CMI	6.9682	6.8564	0.0043
DFM	6.9527	6.8409	0.0016
INMETRO	6.9463	6.8345	0.0058
NMIJ	6.9504	6.8386	0.0024
PTB	6.9521	6.8403	0.0020
VNIIFTRI	6.9511	6.8393	0.0026

Table 4. Reported results at 37 °C; pH values are calculated by the coordinator (PTB)

13. The link to CCQM-K9

The key comparison CCQM-K9: “pH determination on two phosphate buffers by Harned cell measurements” [1] was completed in 2000. In CCQM-K9 SMU discovered a calculation error which influenced the measurement result. Therefore in 2001 CCQM-K9.1 was carried out subsequent to CCQM-K9 between PTB and SMU

The chemical composition and the molality of the samples distributed in CCQM-K9.2, CCQM-K9.1 and of sample (1) distributed in CCQM-K9 was very similar. In all cases the molality of the two buffer components, potassium di-hydrogen phosphate and di-sodium hydrogen phosphate were approximately $0.025 \text{ mol}\cdot\text{kg}^{-1}$, each. The ionic strength for the samples was $0.1 \text{ mol}\cdot\text{kg}^{-1}$ at all measurement temperatures. Only the source of the starting material was different. In CCQM-K9 and CCQM-K9.1 the samples were prepared from NIST Standard Reference Materials NIST SRM 186If and NIST SRM186IIf whereas the starting material for the CCQM-K9.2 sample was delivered by Merck company, Germany.

For CCQM-K9 the reported result in the BIPM database [1] was the pH value of the sample. To link the results of the supplementary key comparison CCQM-K9.2 to CCQM-K9 the acidity functions pa^0 reported by the participants in CCQM-K9.2 were converted to pH values. The pH values calculated according to equation (5) are given in Tables 2 to 4. The activity

coefficient γ_{Cl} at the ionic strength I of the sample buffer is given by the expression (6). A is the Debye-Hückel temperature-dependent limiting slope [3]. Values for A at the measurement temperatures are listed in Table 5. The value for A at 37 °C is interpolated from the values at 0°C to 95 °C as given in Tables 2 in [3]. As for CCQM-K9 the uncertainties associated with the Bates-Guggenheim convention are neglected in CCQM-K9.2 also. Small uncertainties associated with the ionic strength are regarded as insignificant.

$$\text{pH} = \text{p}a_0 + \lg \gamma_{Cl} \quad (5)$$

$$\lg \gamma_{Cl} = \frac{-A\sqrt{I}}{1+1.5\sqrt{I}} \quad (6)$$

Temperature °C	A [3]
15	0.5026
25	0.5108
37	0.5214

Table 5. Values for A the Debye-Hückel limiting slope. The value for A at 37 °C is interpolated.

For CCQM-K9 the key comparison reference value, $\text{pH}_R(\text{K9})$, was obtained as the variance-weighted mean of the results from all participants. Within their uncertainty, the performance of the common participants in both comparisons PTB and VNIIFTRI is assumed to be similar in the original comparison CCQM-K9 and in the subsequent comparison CCQM-K9.2. The assumption is fully satisfied as demonstrated in Table 6 and Figure 6 to 8 for the three measurement temperatures of CCQM-K9.2.

Temperature °C	CCQM-K9 VNIIFTRI pH (U(pH))	CCQM-K9 PTB pH (U(pH))	CCQM-K9.2 VNIIFTRI pH (U(pH))	CCQM-K9.2 PTB pH (U(pH))
15	6.8980 (0.0038)	6.8992 (0.0020)	6.9008 (0.0022)	6.8977 (0.0020)
25	6.8640 (0.0036)	6.8643 (0.0020)	6.8642 (0.0021)	6.8632 (0.0020)
37	6.8390 (0.0038)	6.8406 (0.0020)	6.8393 (0.0026)	6.8403 (0.0020)

Table 6. Results of the common participants VNIIFTRI and PTB in both comparisons CCQM-K9 and CCQM-K9.2. The uncertainty U is the expanded uncertainty ($k = 2$)

It was decided by the CCQM Electroanalytical Working Group (EAWG) at their meeting on 16 April 2007 to calculate the degree of equivalence for the participants of CCQM-K9.2 rela-

tive to the original comparison CCQM-K9 taking into account the results of the PTB and VNIIFTRI in both comparisons. $pH(\text{mean}(K9.2))$ is the mean value of $pH(\text{VNIIFTRI})$ and $pH(\text{PTB})$ in CCQM-K9.2, $pH(\text{mean}(K9))$ is the mean of $pH(\text{VNIIFTRI})$ and $pH(\text{PTB})$ in CCQM-K9. The mean values $pH(\text{mean}(K9))$ and $pH(\text{mean}(K9.2))$ together with the associated uncertainties $u(pH(\text{mean}(K9)))$ and $u(pH(\text{mean}(K9.2)))$ are summarized in Table 7. The key comparison reference value (KCRV) of CCQM-K9, $pH_R(K9)$, and the Degrees of Equivalence (DoE) of $pH(\text{mean}(K9))$ with respect to $pH_R(K9)$, $DoE(pH(\text{mean}(K9)))$ are also included in Table 7. The mean values and their uncertainties are calculated according to equation (7), (8) and (9) following the GUM [6]. The degree of equivalence of the mean of $pH(\text{VNIIFTRI})$ and $pH(\text{PTB})$ in CCQM-K9, $pH(\text{mean}(K9))$, $DoE(pH(\text{mean}(K9)))$ is calculated according equation (10).

The equations (7),(8), (9) and (10) are related to CCQM-K9. By fitting in the data for CCQM-K9.2 equations (7), (8), (9) and (10) are also valid for this comparison.

$$pH(\text{mean}(K9)) = (pH(\text{VNIIFTRI}(K9)) + pH(\text{PTB}(K9)))/2 \quad (7)$$

$$u^2(pH(\text{mean}(K9))) = (1/2)^2 \cdot (u(pH(\text{VNIIFTRI}(K9))))^2 + (1/2)^2 \cdot (u(pH(\text{PTB}(K9))))^2 \quad (8)$$

$$u(pH(\text{mean}(K9))) = 1/2 \sqrt{(u(pH(\text{VNIIFTRI}(K9))))^2 + (u(pH(\text{PTB}(K9))))^2} \quad (9)$$

$$DoE(pH(\text{mean}(K9))) = pH(\text{mean}(K9)) - pH_R(K9) \quad (10)$$

Temperature °C	$pH(\text{mean}(K9))$ ($u(pH(\text{mean}(K9)))$)	KCRV(CCQM-K9) $pH_R(K9)$ $u(pH_R(K9))$	DoE ($pH(\text{mean}(K9))$)	$pH(\text{mean}(K9.2))$ ($u(pH(\text{mean}(K9.2)))$)
15	6.8986 (0.0011)	6.8975 (0.00049)	0.0011	6.8992 (0.00074)
25	6.8642 (0.0010)	6.8633 (0.00056)	0.0009	6.8637(0.00073)
37	6.8398 (0.0011)	6.8394 (0.00064)	0.0004	6.8398 (0.00082)

Table7. Summary of quantities required to link CCQM-K9.2 to CCQM-K9.

$pH(\text{mean}(K9))$ and $pH(\text{mean}(K9.2))$ are the mean of $pH(\text{VNIIFTRI})$ and $pH(\text{PTB})$ in CCQM-K9 and CCQM-K9.2, respectively.

$u(pH(\text{mean}(K9)))$, $u(pH(\text{mean}(K9.2)))$ and $u(pH_R(K9))$ are the corresponding uncertainties.

$pH_R(K9)$ is the key comparison reference value agreed for CCQM-K9, sample(1).

$DoE(pH(\text{mean}(K9)))$ is the degree of equivalence of $pH(\text{mean}(K9))$ with respect to $pH_R(K9)$

The degree of equivalence of a participant in the supplementary comparison CCQM-K9.2 relative to the original comparison CCQM-K9, $DoE(\text{NMI})$, was calculated according to equation (11) following the procedure applied in CCQM-K9.1 the first comparison subsequent to CCQM-K9 [5]. Equation (12) was used to calculate the corresponding expanded uncertainty (coverage factor $k = 2$).

$$\text{DoE(NMI)} = \text{pH(NMI (K9.2))} - \text{pH(mean (K9.2))} + \text{DoE(pH(mean (K9)))} \quad (11)$$

$$U(\text{DoE(NMI)}) = 2\sqrt{u(\text{pH}((\text{NMI}(\text{K9.2}))))^2 + u(\text{pH}(\text{mean}(\text{K9.2})))^2 + u(\text{pH}_R(\text{K9}))^2} \quad (12)$$

Where

DoE(NMI) is the degree of equivalence of a participant in CCQM-K9.2 relative to the comparison CCQM-K9.

pH(NMI(K9.2)) is the pH value calculated from the acidity function $\text{p}a^0$, measured by the participant in CCQM-K9.2.

pH(mean (K9.2)) is the mean of pH(VNIIFTRI) and pH(PTB) in CCQM-K9.2 calculated using the data from CCQM-K9.2 and equation (7).

DoE(pH(mean(K9))) is the degree of equivalence of pH(mean(K9)) with respect to $\text{pH}_R(\text{K9})$ calculated according to equation (10).

U(DoE(NMI)) is the expanded uncertainty (coverage factor $k = 2$) associated with the degree of equivalence of a participant in CCQM-K9.2 relative to the comparison CCQM-K9.

u(pH(NMI(K9.2))) is the uncertainty of the pH value calculated from acidity function $\text{p}a^0$, measured by the participant in CCQM-K9.2 (see Tables 2 to 4).

u(pH(mean (K9.2))) the uncertainty of the mean of pH(VNIIFTRI) and pH(PTB) in CCQM-K9.2 is given in Table 7.

u(pH_R(K9)) the uncertainty of the key comparison reference value for sample(1) in CCQM-K9 is given in Table 7.

In Tables 8 to 11a the degrees of equivalence DoE(NMI) and the associated expanded uncertainty ($k = 2$), $U(\text{DoE(NMI)})$ of the results DFM, NMIJ, INMETRO and CMI in CCQM-K9.2 with respect to CCQM-K9 are summarized.

In Figures (9 to 11) the degrees of equivalence of the participants in CCQM-K9.2 with respect to CCQM-K9 are shown.

Temperature °C	DoE(DFM)	U(DoE)(DFM)
15	-0.0001	0.0024
25	0.0014	0.0024
37	0.0015	0.0026

Table 8. Degree of equivalence of DFM with respect to CCQM-K9.

Temperature °C	DFM pH(K9.2) (u(pH(K9.2)))	pH(mean (K9.2)) (u(pH(mean (K9.2))))	DoE (pH(mean(K9)))	u(pH _R (K9))
15	6.8980 (0.0008)	6.8992 (0.00074)	0.0011	0.00049
25	6.8642 (0.0008)	6.8637 (0.00073)	0.0009	0.00056

37	6.8409 (0.0008)	6.8398 (0.00082)	0.0004	0.00064
-----------	-----------------	------------------	--------	---------

Table 8a. Quantities required to calculate the degrees of equivalence DoE(DFM) and the associated expanded uncertainty ($k=2$), U(DoE(DFM)).

Temperature °C	DoE (NMIJ)	U(DoE)(NMIJ)
15	-0.0013	0.0032
25	-0.0009	0.0029
37	-0.0008	0.0032

Table 9. Degree of equivalence of NMIJ with respect to CCQM-K9.

Temperature °C	NMIJ pH(K9.2) (u(pH(K9.2)))	pH(mean (K9.2)) (u(pH(mean (K9.2))))	DoE (pH(mean(K9)))	u(pH _R (K9))
15	6.8968 (0.0013)	6.8992 (0.00074)	0.0011	0.00049
25	6.8619 (0.0011)	6.8637 (0.00073)	0.0009	0.00056
37	6.8386 (0.0012)	6.8398 (0.00082)	0.0004	0.00064

Table 9a. Quantities required to calculate the degrees of equivalence DoE(NMIJ) and the associated expanded uncertainty ($k=2$), U(DoE(NMIJ)).

Temperature °C	DoE (INMETRO)	U(DoE)(INMETRO)
15	-0.0097	0.0065
25	-0.0035	0.0062
37	-0.0049	0.0062

Table 10. Degree of equivalence of INMETRO with respect to CCQM-K9.

Temperature °C	INMETROpH(K9.2) (u(pH(K9.2)))	pH(mean (K9.2)) (u(pH(mean (K9.2))))	DoE (pH(mean(K9)))	u(pH _R (K9))
15	6.8884 (0.0031)	6.8992 (0.00074)	0.0011	0.00049
25	6.8593 (0.0030)	6.8637(0.00073)	0.0009	0.00056
37	6.8345 (0.0028)	6.8398 (0.00082)	0.0004	0.00064

Table 10a. Quantities required to calculate the degrees of equivalence DoE(INMETRO) and the associated expanded uncertainty ($k=2$), U(DoE(INMETRO))

Temperature °C	DoE (CMI)	U(DoE)(CMI)
-------------------	-----------	-------------

15	0.0264	0.0040
25	0.0158	0.0040
37	0.0170	0.0048

Table 11. Degree of equivalence of CMI with respect to CCQM-K9.

Temperature °C	CMI _{pH(K9.2)} ($u(pH(K9.2))$)	pH(mean (K9.2)) ($u(pH(\text{mean}(K9.2)))$)	DoE ($pH(\text{mean}(K9))$)	$u(pH_R(K9))$
15	6.9245 (0.0018)	6.8992 (0.00074)	0.0011	0.00049
25	6.8786 (0.0018)	6.8637(0.00073)	0.0009	0.00056
37	6.8564 (0.0021)	6.8398 (0.00082)	0.0004	0.00064

Table 11a. Quantities required to calculate the degrees of equivalence DoE(CMI) and the associated expanded uncertainty ($k=2$), $U(\text{DoE}(\text{CMI}))$.

14. How far the light shines

pH phosphate reference buffer solutions are the most widely used pH standards. One important field of application is the calibration of equipment for pH measurements in laboratory medicine. With the exception of the CMI the participants in the comparison CCQM-K9.2 supplementary to CCQM-K9 have demonstrated their capability to measure the pH of primary phosphate buffer solutions in the range of pH = 6.0 to pH = 8.0.

15. References

1. http://kcdb.bipm.org/appendixB/appbresults/ccqm-k9/ccqm-k9_final_report.pdf
2. Buck RP et al. 2002 *Pure Appl. Chem.* **74**(11) 2169–2200
3. OIML International Recommendation No 54: pH scale for aqueous solutions, 1981
4. <http://www.bipm.org/utis/en/pdf/guidelines.pdf>
5. http://kcdb.bipm.org/appendixB/appbresults/ccqm-k9/ccqm-k9_s_smu_final_report.pdf
6. Guide to the Expression of Uncertainty in Measurement, ISO 1995

16. Annex

Figures

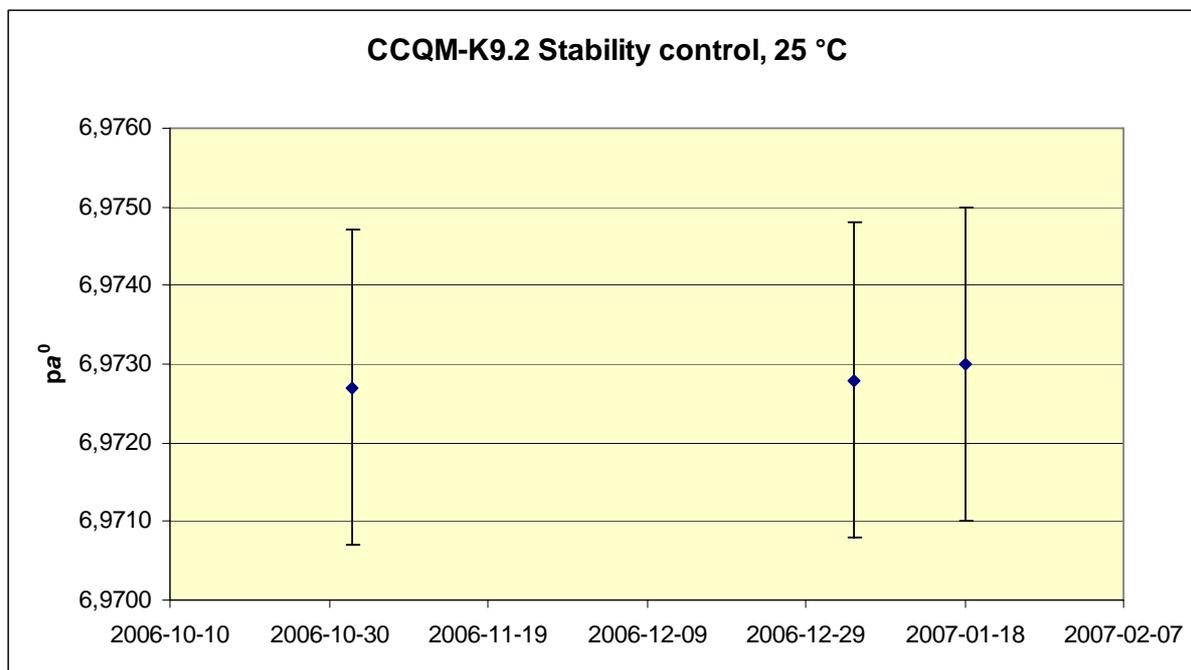


Figure 1. Acidity function at zero chloride molality measured at different time during the comparison period

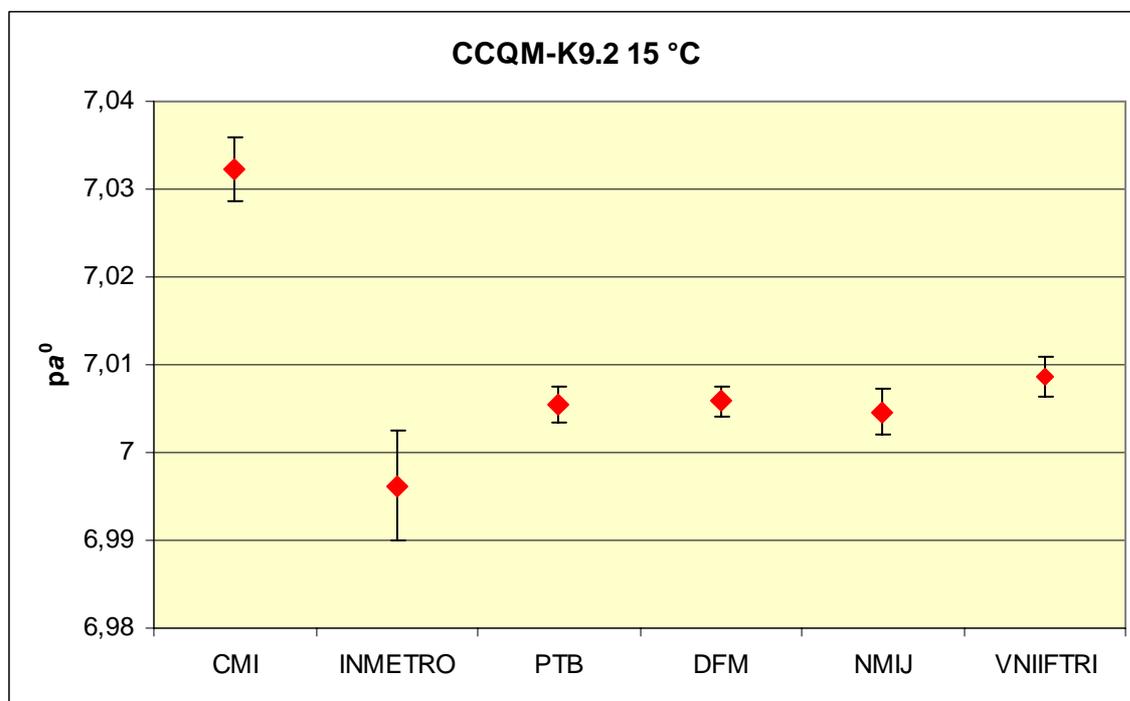


Figure 2. Acidity function at zero chloride molality reported for 15 C and its expanded uncertainty ($k = 2$).

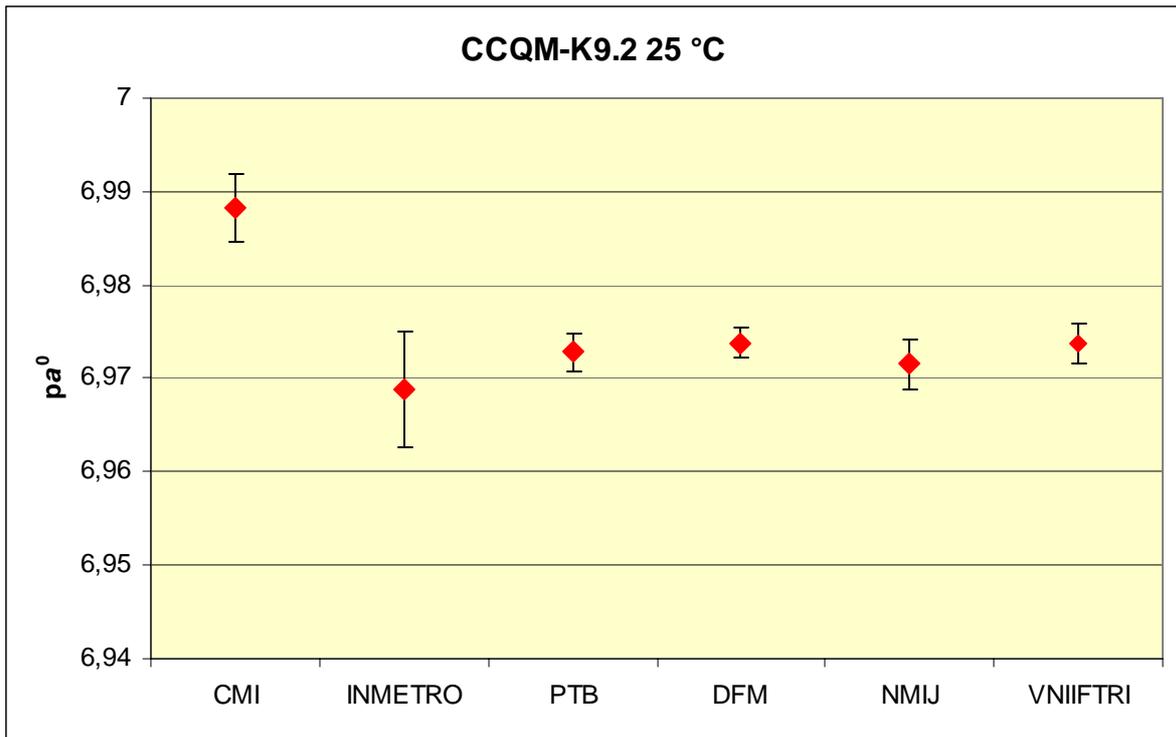


Figure 3. Acidity function at zero chloride molality reported for 25 C and its expanded uncertainty ($k = 2$).

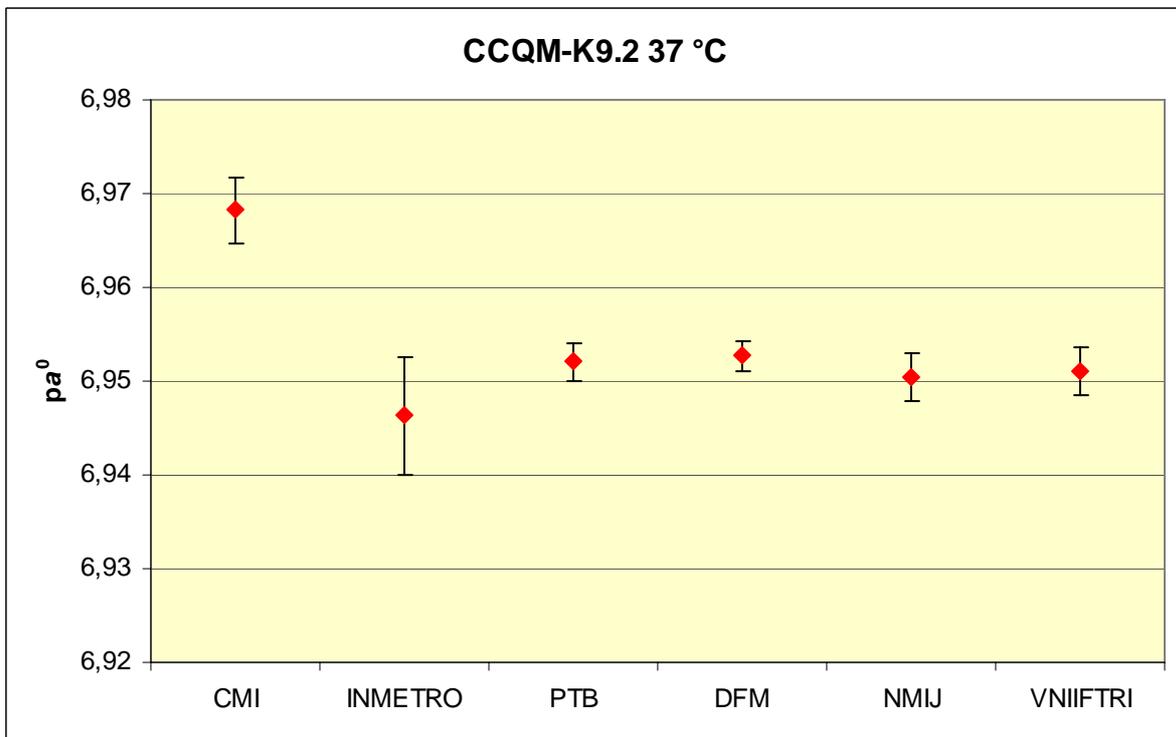


Figure 4. Acidity function at zero chloride molality reported for 37 C and its expanded uncertainty ($k = 2$).

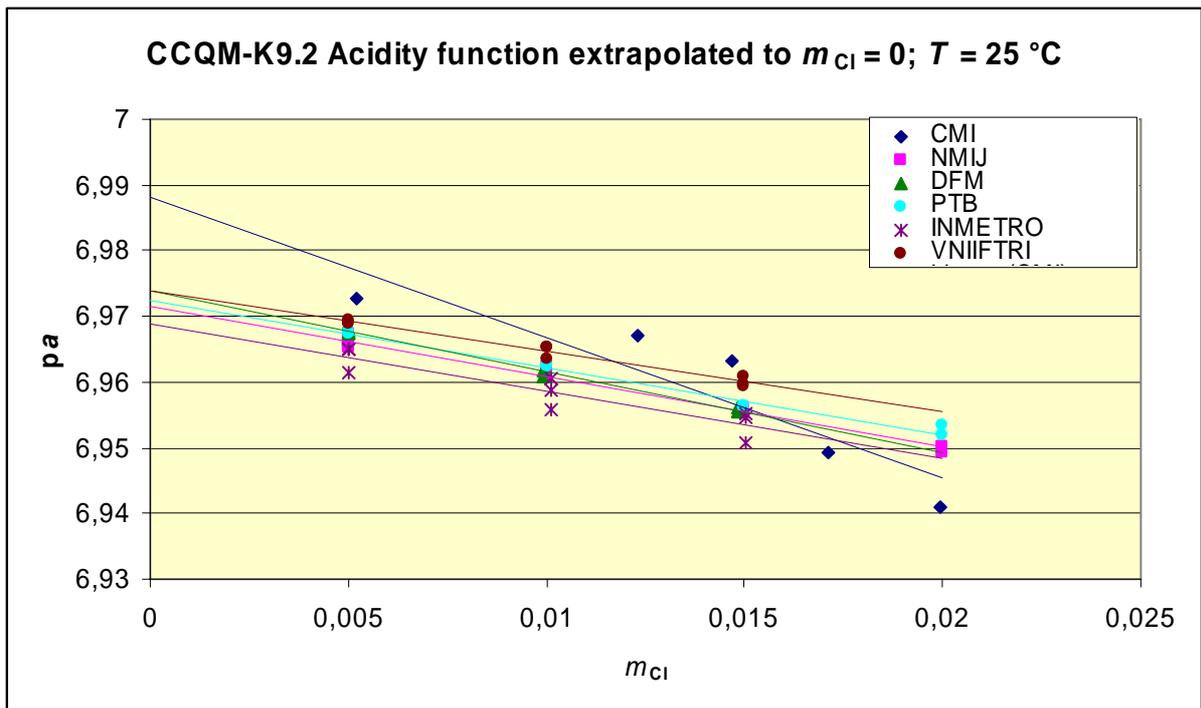


Figure 5 Acidity function at different chloride molalities as reported by the participants.

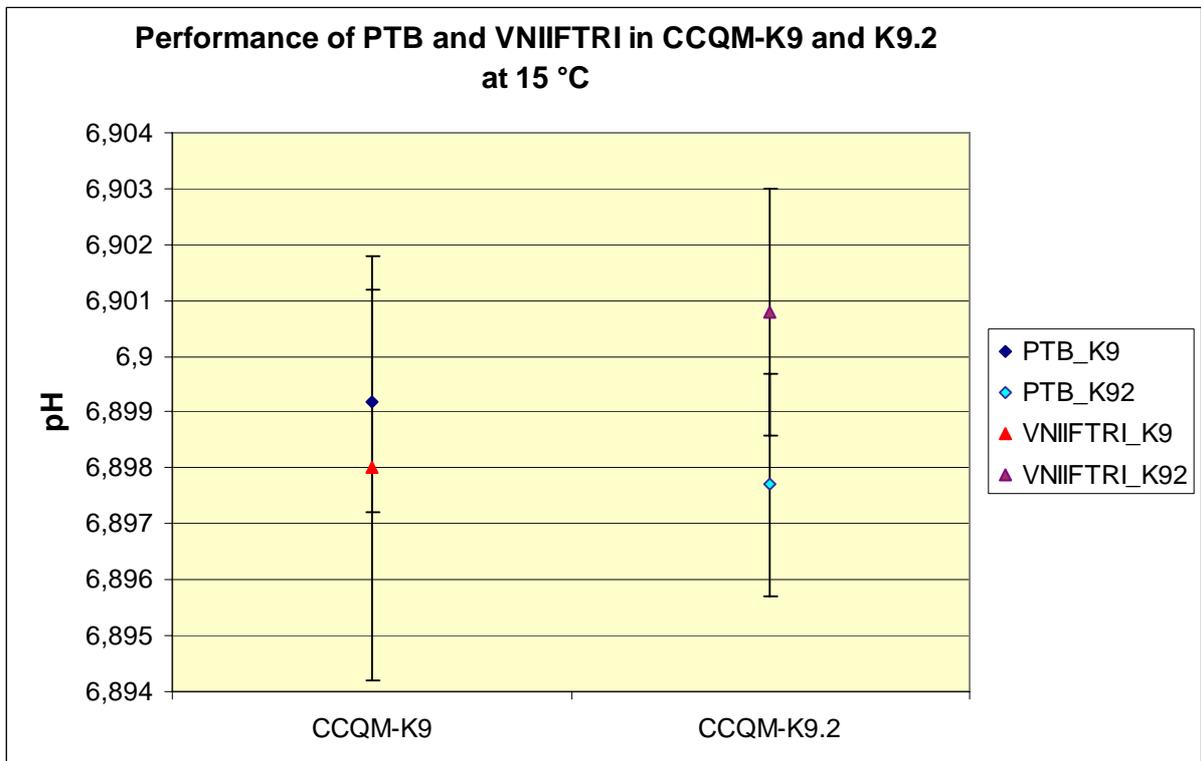


Figure 6. Performance of the common participants in CCQM-K9 and CCQM-K9.2, VNIIFTRI and PTB at 15 °C

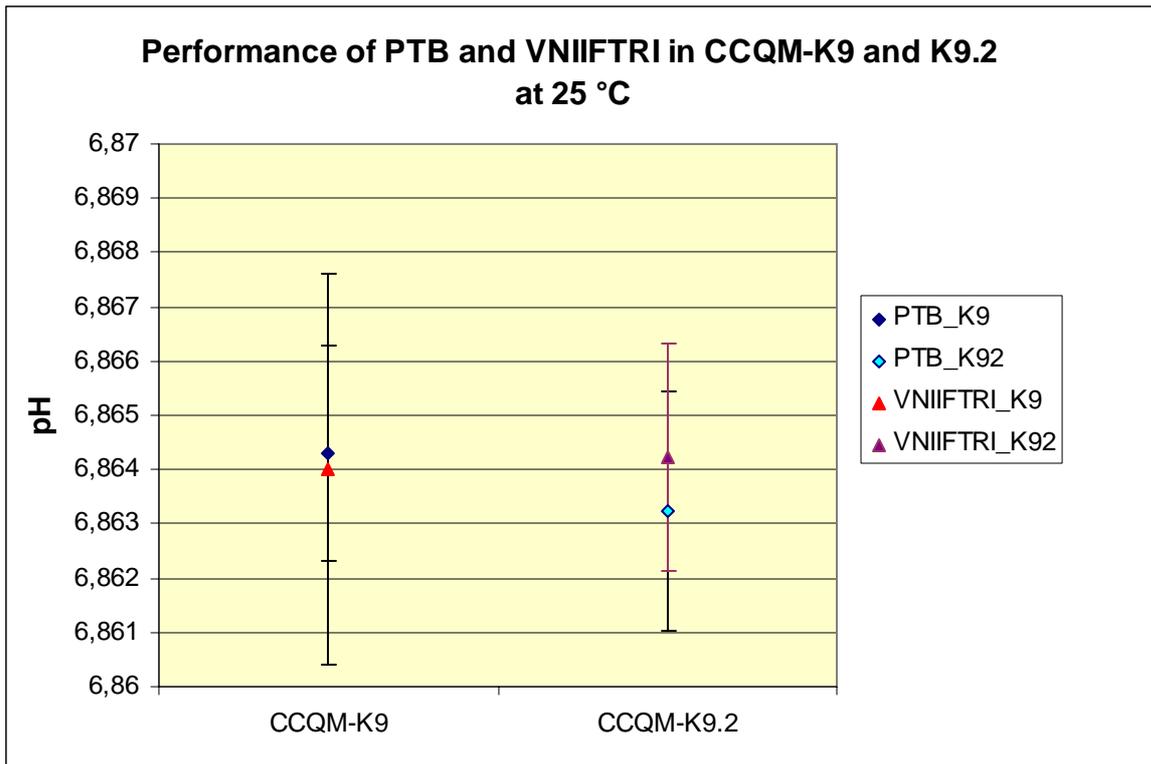


Figure 7. Performance of the common participants in CCQM-K9 and CCQM-K9.2, VNIIFTRI and PTB at 25 °C

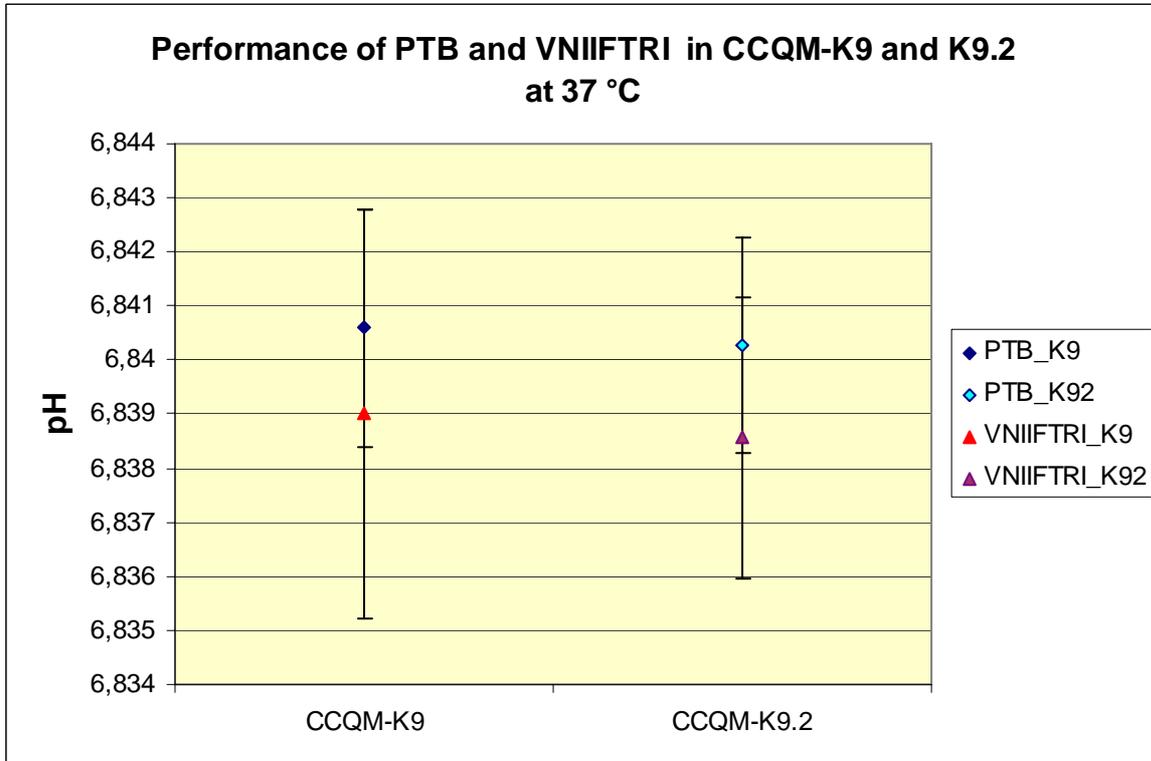


Figure 8. Performance of the common participants in CCQM-K9 and CCQM-K9.2, VNIIFTRI and PTB at 37 °C

CCQM-K9, CCQM-K9.1, CCQM-K9.2
Degree of equivalence D_i and expanded uncertainty U_i ($k = 2$) at 15 °C

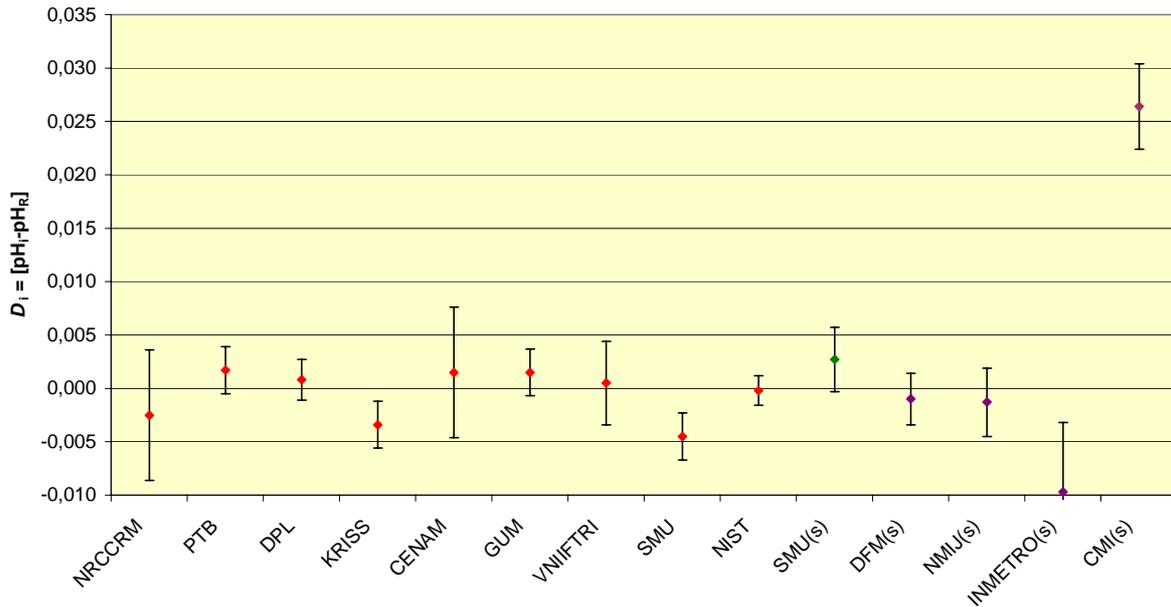


Figure 9. Degrees of equivalence D_i for the participants in CCQM-K9, CCQM-K9.1 and CCQM-K9.2 at 15 °C. Red \blacklozenge indicates the degrees of equivalence for the participants in CCQM-K9, green \blacklozenge indicates the degree of equivalence for SMU resulting from the subsequent bilateral comparison CCQM-K9.1 between SMU and PTB, light green \blacklozenge indicates the degrees of equivalence resulting from the subsequent comparison CCQM-K9.2 between DFM, NMIJ, INMETRO, CMI and PTB and VNIIFTRI.

CCQM-K9, CCQM-K9.1, CCQM-K9.2 Degree of equivalence D_i and expanded uncertainty U_i ($k = 2$) at 25 °C

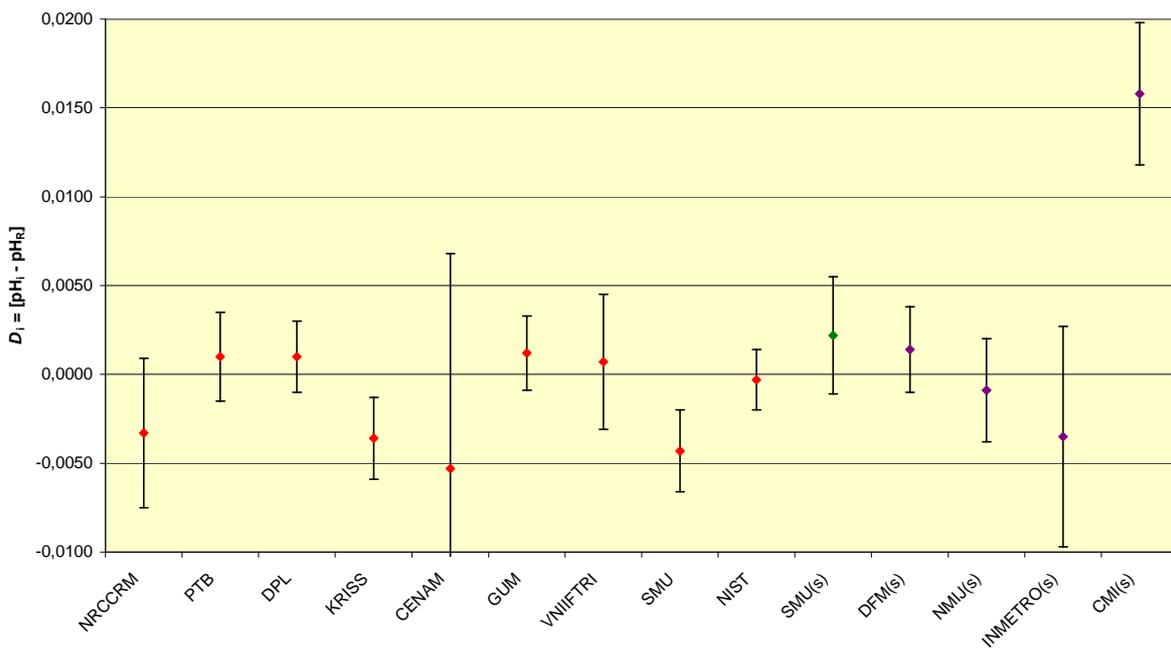


Figure 10. Degrees of equivalence D_i for the participants in CCQM-K9, CCQM-K9.1 and CCQM-K9.2 at 25 °C. Red \blacklozenge indicates the degrees of equivalence for the participants in CCQM-K9, green \blacklozenge indicates the degree of equivalence for SMU resulting from the subsequent bilateral comparison CCQM-K9.1 between SMU and PTB, light green \blacklozenge indicates the degrees of equivalence resulting from the subsequent comparison CCQM-K9.2 between DFM, NMIJ, INMETRO, CMI and PTB and VNIIFTRI.

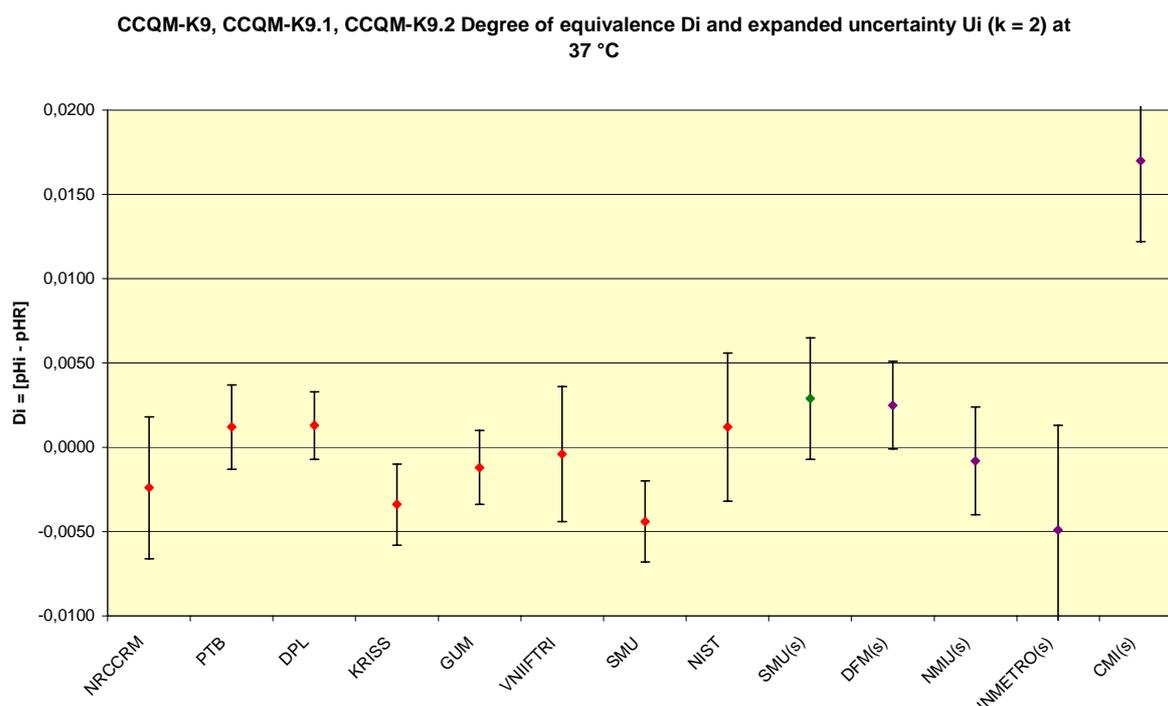


Figure 11. Degrees of equivalence D_i for the participants in CCQM-K9, CCQM-K9.1 and CCQM-K9.2 at 37 °C. Red \blacklozenge indicates the degrees of equivalence for the participants in CCQM-K9, green \blacklozenge indicates the degree of equivalence for SMU resulting from the subsequent bilateral comparison CCQM-K9.1 between SMU and PTB, light green \blacklozenge indicates the degrees of equivalence resulting from the subsequent comparison CCQM-K9.2 between DFM, NMIJ, INMETRO, CMI and PTB and VNIIFTRI.

17. Addresses

DFM

Hans D. Jensen

Danish Institute of Fundamental Metrology

Building 307, Matematiktorvet

DK-2800 Kgs. Lyngby

DENMARK

Tel: +45 4525 5874

Email: hdj@dfm.dtu.dk

CMI

Alena Vospelova
Czech Metrology Institute
Okruzni 31
CZ 638 00 Brno
CZECH Republic
Tel: +420 545 555 322
avospelova@cmi.cz

INMETRO

Isabel C. Fraga,
INMETRO
Divisão de Metrologia Química,
Av. Nossa Senhora das Graças, 50
Xerém, CEP 25250-020, Prédio 04
Duque de Caxias, RJ
BRASIL
Tel +55 21 2679-9069,
icfraga@inmetro.gov.br

NMIJ

Susumu Nakamura
National Metrology Institute of Japan (NMIJ)
in National Institute of Advanced Industrial Science and Technology (AIST)
1-1, Higashi, Tsukuba, Ibaraki
305-8565
JAPAN.
susumu-nakamura@aist.go.jp

VNIIFTRI

Viatcheslav Kutovoi
National Research Institute for Physical-Technical and Radio-technical Measurements
(VNIIFTRI),
141570 Mendeleevo, Moscow Region
RUSSIA
Tel: +7(095 534-00-84)
mera@ftri.extech.msk.ru

PTB

Petra Spitzer

Physikalisch-Technische Bundesanstalt (PTB)

Bundesallee 100

38116 Braunschweig

GERMANY

Tel. +49 531 592 3322

Petra.Spitzer@ptb.de