

CCQM WG on Electrochemical Analysis

Final report on CCQM – K91 Key comparison on pH of an unknown phthalate buffer

22 April 2013

P. Spitzer, F. Bastkowski, B. Adel, L. Dimitrova, F. B. Gonzaga, P. T. Jakobsen, P. Fiscaro, D. Stoica, T. Asakai, I. Maksimov, Z. N.Szilágyi, A.Reyes, M. Monroy, G.T. Canaza, W. Kozlowski, M. Pawlina, V. Kutovoy, L. Vyskocil, A. Mathiasova, T. Nongluck, F. Ficicioglu, V. Gavrilkin, K.W. Pratt, J. Waters

Abstract

Results of the CCQM-K91 key comparison on pH of an unknown phthalate buffer with a nominal pH value of $pH \sim 4.01$ at 25 °C are reported. Measurements are performed at 15 °C, 25 °C, and 37 °C and optional also at 5 °C and 50 °C.

Subject field

Amount of substance

Subject

Determination of the acidity functions at zero chloride molality, $p\alpha^0$, of an unknown phthalate buffer, nominal pH value $pH \sim 4.01$ (25 °C) by Harned cell and differential potentiometric cell measurements, respectively at 15 °C, 25 °C and 37 °C and optional at 5 °C and 50 °C.

Table of Contents

Abstract.....	1
Subject field	1
Subject.....	1
Table of Contents	2
Purpose of the comparison.....	3
Time schedule	3
Coordinating laboratory	3
Participants	4
Sample preparation and distribution	4
Sample homogeneity and stability	5
Timetable of measurements and Comments	8
Problems reported to the coordinator.....	8
Measurement Technique	9
Results and discussion	10
Calculation of the KCRV and its uncertainty	13
Conclusions	16
How far the light shines.....	17
Acknowledgment.....	17
Figures	17

Purpose of the comparison

The key comparison (KC) CCQM-K91 was performed to demonstrate the capability of the participating National Metrology Institutes (NMI) to measure the pH value of unknown phthalate buffer solutions. The buffer of nominal pH ~ 4.01 (25 °C) was measured at 15 °C, 25 °C 37 °C and optional also at 5 °C and 50 °C.

The comparison is a complete repetition of the KC CCQM-K17 from 2001.

The comparison was restricted to the use of either the primary Harned cell¹ or the secondary differential potentiometric cell² method for pH. It was only allowed to participate by using a secondary instead of a primary method if this is the highest metrological standard in the NMI and if the CMCs are based on this method. Only the results obtained by the primary method have been used to calculate the KCRV.

Phthalate buffer is widely used to calibrate pH electrodes in the acid range. A buffer solution of 0.05 mol kg⁻¹ potassium hydrogen phthalate, KHC₈H₄O₄, is one of the primary pH reference buffer solutions recommended by IUPAC. Certified reference materials are issued by several NMIs based on primary measurements.

Time schedule

Dispatch of the samples:	29 July 2011
Deadline for receipt of the report:	30 September 2011
Draft A report distributed	25 October 2011
Discussion of results	EAWG meeting, November 2011
Discussion of Draft A report	EAWG meeting, April 2012
Draft B report distributed	February 2013
EAWG approval of Draft B report	April 2013
Final report	April 2013

Coordinating laboratory

PTB (Physikalisch-Technische Bundesanstalt)
Bundesallee 100
38116 Braunschweig
Germany

Petra Spitzer
Tel: +49 531 592 3130
Fax: +49 531 592 3015
Email: petra.spitzer@ptb.de

Frank Bastkowski
Tel: +49 531 592 3323
Fax: +49 531 592 3015
Email: frank.bastkowski@ptb.de

Beatrice Adel
Tel: +49 531 592 3132
Fax: +49 531 592 3015
Email: beatrice.adel@ptb.de

¹ Buck RP et al. 2002 Pure Appl. Chem. 74(11) 2169–2200

² Baucke FGK (1994) J Electroanal Chem 368:67–75

Participants

No	Country	Institute	Acronym	Contact
1	BG	Bulgarian Institute of Metrology- National Centre of Metrology	BIM-NMC	L. Dimitrova
2	BR	National Institute of Metrology, Quality and Technology	INMETRO	F. B.Gonzaga
3	DK	Danish Fundamental Metrology	DFM	P. T. Jakobsen
4	DE	Physikalisch-Technische Bundesanstalt	PTB	P. Spitzer. F. Bastkowski, B. Adel
5	FR	Laboratoire National de métrologie et d'Essais	LNE	P. Fiscaro, D. Stoica
6	JP	National Metrology Institute of Japan	NMIJ	T. Asakai
7	HU	Hungarian Trade Licensing Office	MKEH	Z. N.Szilágyi
8	MX	Centro Nacional de Metrología	CENAM	A.Reyes, M. Monroy
9	PE	Instituto Nacional de Defensa Competencia y de la Protección de la Propiedad intelectual	INDECOPI	G.T. Canaza
10	PL	Central Office of Measures	GUM	W. Kozłowski, M. Pawlina
11	RU	National Research Institute Physicotechnical and Radio Engineering Measurements	VNIIFTRI	V. Kutovoy
12	SK	Slovenský metrologický ústav	SMU	L. Vyskocil, A. Mathiasova
13	TH	National Institute of Metrology	NIMT	T. Nongluck
14	TR	TUBITAK UME	Tubitak UME	F. Ficicioglu
15	UA	Ukrmetrteststandart	UMTS	V. Gavrilkin
16	US	National Institute of Standards and Technology	NIST	K.W. Pratt

Tab. 1: List of participants in KC CCQM-K91.

Sample preparation and distribution

The phthalate buffer solution was prepared from deionized water and potassium hydrogen phthalate (Merck A112365). The mass fraction of water of the final solution was $w(\text{H}_2\text{O}) = 0,989893 \text{ g g}^{-1}$.

The sample batch was produced at 15 July 2011 in one 100 kg batch at the ZMK (Zentrum fuer Messen und Kalibrieren) facilities in Germany by colleagues from PTB and ZMK.

ZMK is a calibration laboratory accredited by the German accreditation body DAkkS for the quantity pH. The bottles and the buffer starting material were provided by PTB. The samples were bottled during one day. Sealing and weighing was done at PTB.

Each participant received three 1 L high-density polyethylene (HDPE) bottles filled with the sample solution, sealed in aluminized plastic bags and numbered. Shipment to all participants was performed at the same time by courier. Except VNIIFTRI the participants received the samples between 29 July and 16 August. VNIIFTRI received the sample solution only at 9 September.

Hydrochloric acid and sodium or potassium chloride was not provided. It has been recommended to dry the alkali chloride at least at 400 °C for two hours.

To verify that the sample mass are unchanged during transport participants were requested to weight the bottles and to calculate the bottle mass from the balance reading. Figure 1 shows the relative deviation reported by the participants from the bottle mass. The bottle masses were calculated at PTB from the balance reading.

In general, the reported bottle masses agree within 0.02 % with the bottle masses calculated at PTB. The absolute differences in mass in all cases are smaller than 0.4 g except for Indecopi (bottle # 5, 20 and 51) and Tubitak-UME (bottle #17, 34 and 55). Here the deviation is in the order of 1.2 g absolute or 0.1 % relative.

No sample problems were reported to the coordinator.

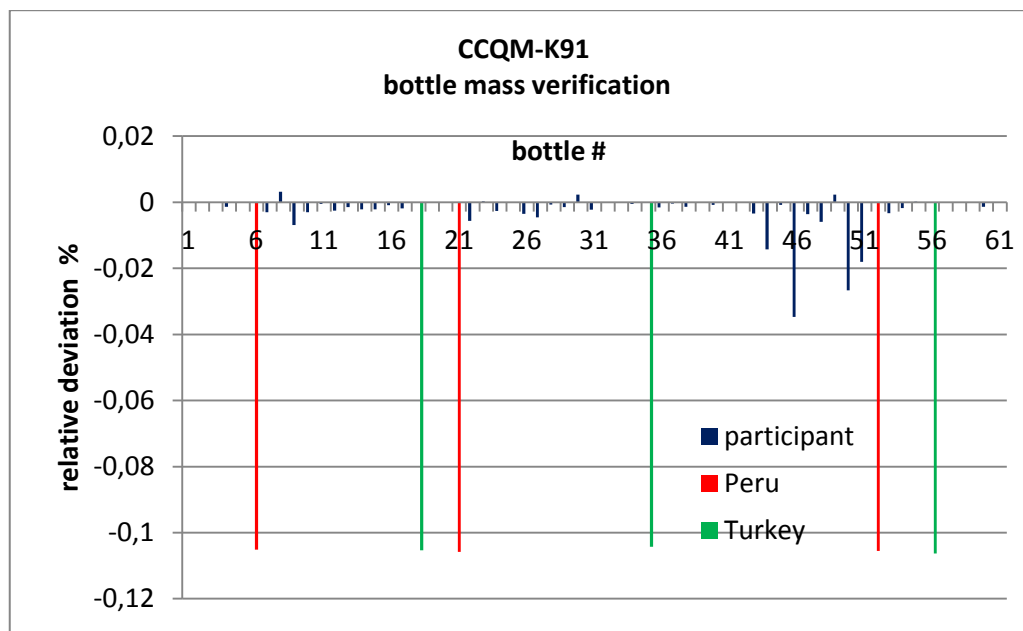


Fig.1: Relative deviation (%) of the bottle mass reported by the participants from the bottle mass calculated at the PTB from balance reading.

Sample homogeneity and stability

Before shipment the homogeneity between the bottles was checked. The stability of the bottled solution was evaluated over the measurement period (01 August -29 September 2011). The primary pH measurement method was used.

For homogeneity testing three times two bottles were selected. For each of the three runs a single sample solution was prepared from the two bottles. The sample solution was divided in three portions. To each portion NaCl was added at $0.005 \text{ mol kg}^{-1}$, $0.010 \text{ mol kg}^{-1}$ and $0.015 \text{ mol kg}^{-1}$. The samples were measured during a period of ten days.

The results are summarized in table 2 and shown in figure 2 for p_a^0 of the bottled buffer solution at 25 °C. The results are shown in table 2 along with the CCQM-K91 results of the coordinating laboratory. To evaluate the stability of the sample solution results of homogeneity testing and of two additionally measurement runs were used. To validate the stability of the samples the p_a^0 of the bottled buffer solution was measured at all measurement temperatures. The results are given in table 3. The sample solution remained stable over the measurement period as demonstrated by the results and shown in figure 3 to 5 for 37 °C, 5 °C and 50 °C. All dates are 2011.

. The measurements at 5 °C and 50 °C only started at 26 July 2011.

Date	Bottle #	$p\alpha^0$	$U(k=2)$
19 July 2011	1/2	4.09423	0.0023
25 July 2011	31/32	4.09417	0.0023
28 July 2011	61/62	4.09424	0.0023
07 Sept 2011	K91 (85/86)	4.09415	0.0023

Tab 2: Homogeneity check at 25 °C at coordinating laboratory before shipment. The measurement result of KC CCQM-K91 of the coordinating laboratory is shown in the last row.

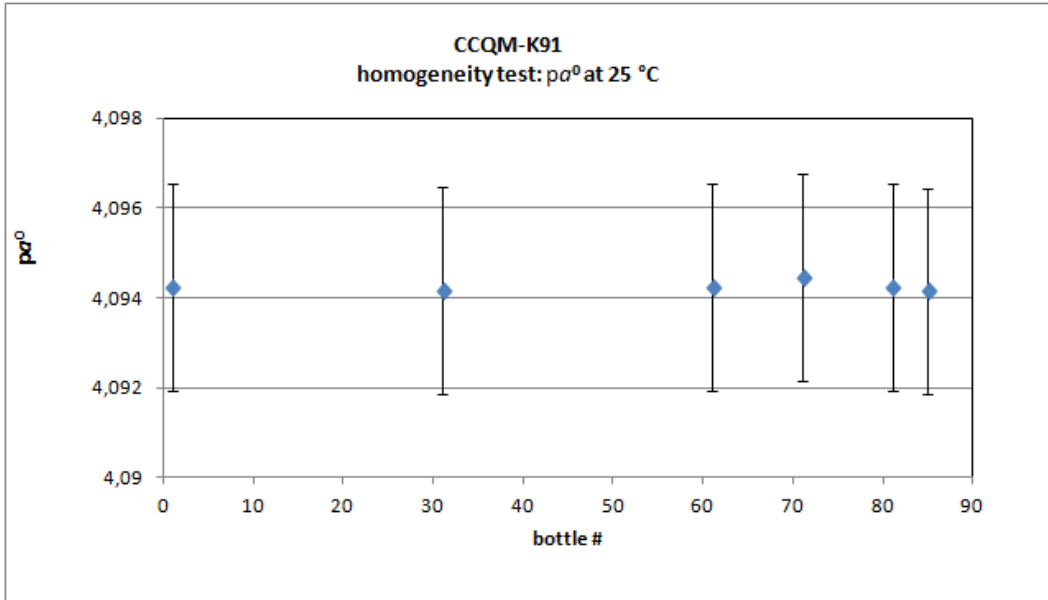


Fig.2: Sample homogeneity at 25 °C. Given is the expanded uncertainty ($k=2$).

Date	Bottle #	$p\alpha^0$ 25 °C	$p\alpha^0$ 15 °C	$p\alpha^0$ 37 °C	$p\alpha^0$ 5 °C	$U(k=2)$	$p\alpha^0$ 50 °C	$U(k=2)$
19. Jul	1/2	4.09423				0.0023		
25. Jul	31/32	4.09417	4.08668	4.11416		0.0023		
28. Jul	61/62	4.09424	4.08681	4.11603	4.08692	0.0023	4.15073	0.0028
03. Aug	71/72	4.09445	4.08592	4.11430	4.08650	0.0023	4.14759	0.0028
16. Aug	81/82	4.09424	4.08560	4.11523	4.08524	0.0023	4.14970	0.0028
07. Sep	KC 91 85/86	4.09415	4.08631	4.11435	4.08838	0.0023	4.14684	0.0028

Tab 3: Sample stability over a 90 days period. The measurement result of KC CCQM-K91 of the coordinating laboratory is shown in the last row.

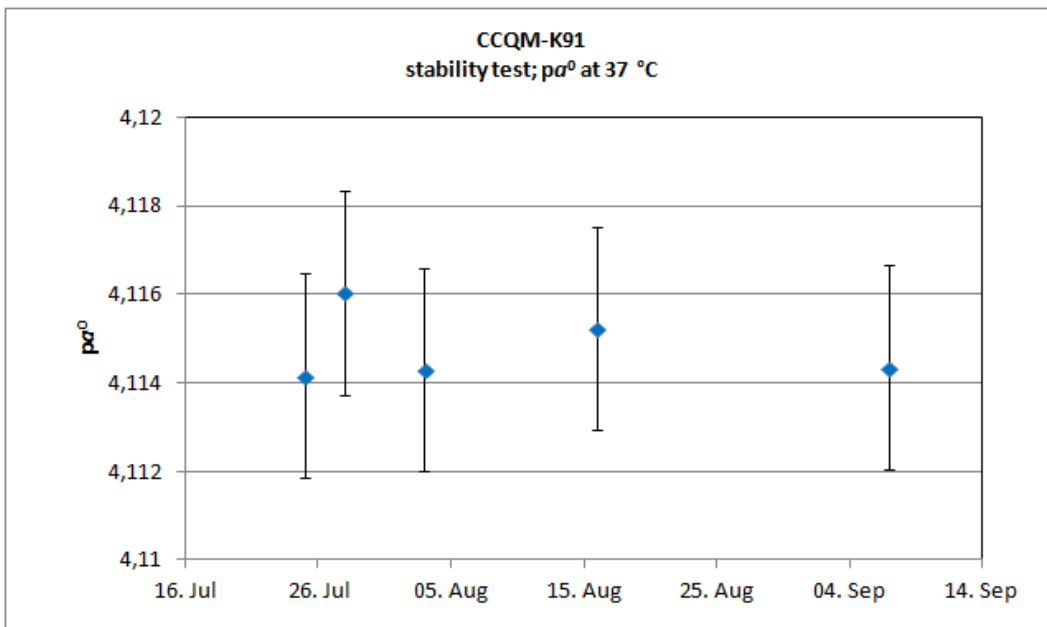


Fig.3: Validation of the sample stability at 37 °C. Given is the expanded uncertainty ($k = 2$).

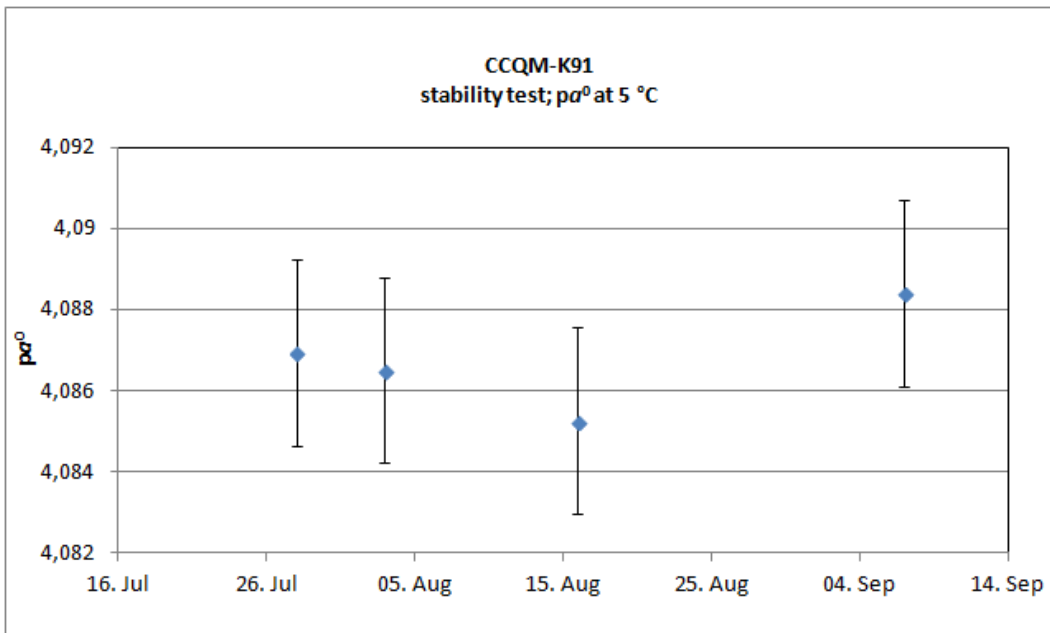


Fig.4: Validation of the sample stability at 5 °C. Given is the expanded uncertainty ($k = 2$).

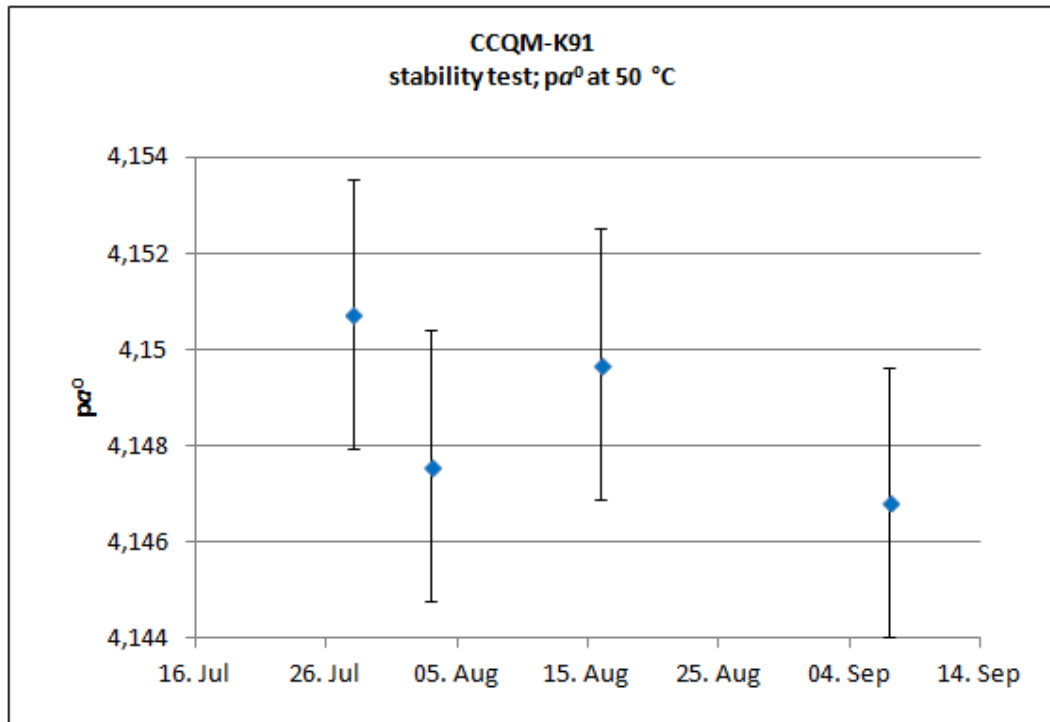


Fig.5: Validation of the sample stability at 50 °C. Given is the expanded uncertainty ($k = 2$).

Timetable of measurements and Comments

NMI	Sample received	Measurement Period	Report Date	Revised Report	Comments
BIM-NCM	03 Aug	18 - 26 Sep	30 Sep	31 Oct	E^0 revised values
INMETRO	03 Aug	3 - 25 Aug	14 Sep		
DFM	29 July	31 Aug – 2 Sep	21 Sep		
PTB	-	7 -9 Sep	11 Sep		
LNE	01 Aug	29 Aug – 2 Sep	22 Sep		
NMIJ	01 Aug	4 -23 Aug	30 Sep		
MKEH	01 Aug	29 Aug	30 Sep		
CENAM	12 Aug	13 – 22 Sep	30 Sep		
Indecopi	16 Aug	19 Aug	30 Sep	1 Nov	$p\alpha^0$ values added
GUM	01 Aug	29 Aug – 2 Sep	30 Sep		
VNIIFTRI	09 Sep	14 Sep	30 Sep	7 Oct	uncertainty budgets added
SMU	03 Aug	20 – 22 Sep	30 Sep		
NIMT	01 Aug	14 – 26 Sep	30 Sep		
Tubitak UME	01 Aug	25 – 29 Sep	30 Sep	25 Oct	malfunction of thermostat unit: no results at 5 °C and 15 °C
UMTS	16 Aug	16 – 25 Sep	30 Sep	11 Oct 14 Nov	revised value for partial pressure of hydrogen malfunction of potential measurement circuit reported
NIST	08 Aug	12 – 15 Sep	26 Sep		

Tab 4: Dates of sample received, measurement period, and comments.

Problems reported to the coordinator

-**Indecopi(PE)**: In the original report only pH as result was stated. In the revised version the $p\alpha^0$ are added.

-**UMTS (UA)**:“Unexpectedly, our results appeared to be biased compared to the results of other participants. It could be possibly caused by the malfunction of our potential measurement circuit. Now

we are trying to find the exact reason. In course of preparation for comparison the instruments calibration was OK (for example, electrode potential was close to mean value of all participants). The most probable reason is a failure of microcircuit in the potential meter.

At any case, our results should not be taken into account in KCRV calculation.”

-**Tubitak UME (TR)** reported problems with their thermostat unit and did not report results at 5 °C and 15 °C.

-**SMU (SK)** gave only an informal result for 5 °C due to instability in this temperature.

-**BIM-NCM (BG)** observed a calculation error in E^0 and sent revised pa^0 values at 31 October one month after the comparison deadline.

-**VNIIFTRI (RU)** added uncertainty calculations in a revised version of the report.

Measurement Technique

The primary measurement method for pH (Harned cell) has been described among others in the report of KC CCQM-K17 on the pH of phthalate buffer³. The primary method for pH is based on the measurement of the potential difference of cell I without liquid junction

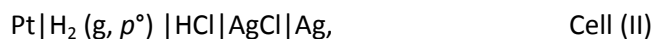


Chloride ions are added to the chloride free buffer at several chloride molalities in order to stabilize the potential of the silver-silver chloride electrode. The potential difference E of cell I depends on the hydrogen ion activity, a_{H} , according to Equation 1:

$$E_1 = E^0 - k \log(a_{\text{H}} / m^0)(m_{\text{Cl}} \gamma_{\text{Cl}} / m^0) \quad (1)$$

In Eq. 1, E^0 is the standard potential of the Ag/AgCl reference electrode, $m^0 = 1 \text{ mol kg}^{-1}$, m_{Cl} and γ_{Cl} the molality and activity coefficient of the chloride ion. k equals $RT \ln 10 / F$, where R , T , and F are the gas constant, the thermodynamic temperature, and the Faraday constant, respectively.

The standard potential of the Ag/AgCl electrodes is simultaneously determined in cell II.



The standard potential E^0 of the Ag/AgCl electrodes are calculated from the measured E_2 values according to Eq. 2. The nominal molality of the HCl is $m_{\text{HCl}} = 0.01 \text{ mol kg}^{-1}$. The mean activity coefficient of the HCl at the measurement temperature for this nominal molality is taken from literature⁴.

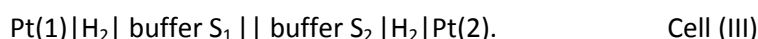
$$E^0 = E_2 - 2k \log(m_{\text{HCl}} \gamma_{\pm \text{HCl}} / m^0) \quad (2)$$

The acidity function pa is calculated for each measured cell potential E_1 using Eq. 3.

$$pa = (E_1 - E^0) / k + \log(m_{\text{Cl}} / m^0) \quad (3)$$

In the primary procedure for pH, pa is measured as a function of m_{Cl} . The reported result for the key comparison, the acidity function at zero chloride molality pa^0 is obtained from linear extrapolation of the set of values for the acidity function pa to $m_{\text{Cl}} = 0$. The reported result for the key comparison CCQM-K91 is pa^0 at each measurement temperature.

As secondary method for pH the differential potentiometry (Baucke cell) was used by Indecopi⁵. For reference buffer solutions with the same nominal composition as that of the primary standard, the differential potentiometric cell (cell III) is the method of choice.



Cell III consists of two identical Pt|H₂ electrodes, Pt(1) and Pt(2); and two quasi-identical buffers, S₁ and S₂, with pH values, pH(S₁) and pH(S₂). A diaphragm, ||, separates S₁ and S₂. The cell is constructed such that the H₂ pressure, p_{H_2} , at Pt(1) and Pt(2) is identical. pH(S₁) is given by Eq.4.

³ http://kcdb.bipm.org/AppendixB/appbresults/ccqm-k17/ccqm-k17_final_report.pdf

⁴ Bates R G and Robinson R A (1980) Solution Chemistry 9 455-456

⁵ Baucke FGK (1994) J Electroanal Chem 368:67-75

$$\text{pH}(S_2) = \text{pH}(S_1) - \frac{E_3 - E_j}{k}, \quad (4)$$

E_j is the liquid junction potential that forms between S1 and S2 at the diaphragm. Provided that S1 and S2 are quasi-identical in composition, $|\text{pH}(S_2) - \text{pH}(S_1)| \leq 0.02$, and $3 < \text{pH} < 11$ $|E_j| < 0.1 |E_3$.

Results and discussion

All participants delivered results. It was agreed previously that only results from primary measurements are used to calculate the key comparison reference value (KCRV).

Only Indecopi (PE) applied a secondary method. Indecopi measured the pH of the sample by differential potentiometry as this is the highest metrological standard in the NMI and as the CMCs are based on this method. The pH value reported by Indecopi is recalculated as $\text{p}a^0$ by assuming an ionic strength of the buffer of $0.0535 \text{ mol kg}^{-1}$. All participants were requested to measure the $\text{p}a^0$ at 15°C , 25°C and 37°C . Eight institutes provided additional results at 5°C and 50°C . The results for the key comparison, $\text{p}a^0$, are given at each measurement temperature in table 5 to 6 below and shown in figures 6 to 10. The uncertainty is the standard uncertainty with $k = 1$. Only for information BIM-NCM revised as well as original results are shown in tables and figures below but only in case they are different.

Tables 7 and 8 summarize the E^0 values at 25°C . The E^0 values at 25°C are shown in figure 11. In table 9 and 10 and the uncertainty of the intercept and the slope of the regression line obtained from linear extrapolation of the acidity function $\text{p}a$ to $m_{\text{Cl}} = 0$ are given. These data are shown in figures 12 to 15. The HCl molality and the method used to standardize the HCl are given in table 11.

NMI	Country	15 °C		25 °C		37 °C	
		$\text{p}a^0$	$u(\text{p}a^0)$ (k = 1)	$\text{p}a^0$	$u(\text{p}a^0)$ (k = 1)	$\text{p}a^0$	$u(\text{p}a^0)$ (k = 1)
BIM-NCM rev	BG	4.0817	0.0040	4.0907	0.0040	4.1133	0.0040
BIM-NCM org	BG	4.0751	0.0040	4.0831	0.0040	4.1058	0.0040
INMETRO	BR	4.0831	0.0015	4.0918	0.0013	4.1131	0.0012
DFM	DK	4.0857	0.0006	4.0940	0.0005	4.1157	0.0005
PTB	DE	4.0863	0.0012	4.0941	0.0012	4.1143	0.0012
LNE	FR	4.0835	0.0022	4.0921	0.0018	4.1112	0.0019
NMIJ	JP	4.0854	0.0012	4.0932	0.0012	4.1151	0.0015
MKEH	HU	4.0847	0.0014	4.0947	0.0014	4.1102	0.0030
CENAM	MX	4.0808	0.0010	4.0904	0.0011	4.1133	0.0012
Indecopi	PE	4.0877	0.0020	4.0923	0.0020	4.1136	0.0020
GUM	PL	4.0852	0.0014	4.0926	0.0016	4.1116	0.0014
VNIIFTRI	RU	4.0856	0.0030	4.0942	0.0038	4.1137	0.0039
SMU	SK	4.0862	0.0010	4.0946	0.0010	4.1162	0.0010
NIMT	TH	4.0815	0.0025	4.0883	0.0025	4.1114	0.0040
Tubitak UME	TR	-	-	4.8085	0.0028	4.0626	0.0190
UMTS	UA	3.9573	0.0021	3.9832	0.0019	3.9970	0.0019
NIST	US	4.0867	0.0006	4.0946	0.0008	4.1153	0.0019

Tab 5: Results at 15°C , 25°C and 37°C . The uncertainty is the standard uncertainty ($k = 1$).

NMI	Country	5 °C		50 °C	
		$\text{p}a^0$	$u(\text{p}a^0)$ (k = 1)	$\text{p}a^0$	$u(\text{p}a^0)$ (k = 1)
BIM-NCM rev	BG	4.0827	0.0040	4.1447	0.0030
BIM-NCM org	BG	4.0750	0.0020	4.1382	0.0020
PTB	DE	4.0884	0.0012	4.1477	0.0014
NMIJ	JP	4.0868	0.0012	4.1446	0.0021
MKEH	HU	4.0818	0.0027	4.1458	0.0031
GUM	PL	4.0831	0.0017	4.1419	0.0014

VNIIFTRI	RU	4.0851	0.0037	4.1559	0.0039
SMU	SK	-	-	4.1513	0.0010
NIMT	TH	4.0792	0.0015	4.1358	0.0055
Tubitak UME	TR	-	-	3.9537	0.0488
UMTS	UA	3.9624	0.0019	4.0311	0.0019
NIST	US	4.0896	0.0006	4.1496	0.0017

Tab 6: Results at 5 °C and 50 °C. The uncertainty is the standard uncertainty ($k = 1$).

NMI	Country	15 °C		25 °C		37 °C	
		E^0/V	$u(E^0)$ ($k=1$)	E^0/V	$u(E^0)$ ($k=1$)	E^0/V	$u(E^0)$ ($k=1$)
BIM-NCM rev	BG	0.228322	0.00020	0.222011	0.00020	0.213719	0.00020
BIM-NCM org	BG	0.22875	0.00020	0.222454	0.00020	0.21418	0.00020
INMETRO	BR	0.228936	0.000085	0.222753	0.000086	0.214599	0.000088
DFM	DK	0.228671	0.000062	0.222506	0.000059	0.214316	0.000062
PTB	DE	0.228688	0.000052	0.222508	0.000052	0.214286	0.000052
LNE	FR	0.228746	0.000175	0.222526	0.000155	0.214293	0.000162
NMIJ	JP	0.228641	0.000035	0.222508	0.000040	0.214364	0.000040
MKEH	HU	0.227959	0.000067	0.220157	0.000069	0.21102	0.000071
CENAM	MX	0.228639	0.000067	0.222383	0.000060	0.214066	0.000088
GUM	PL	0.228351	0.000068	0.222166	0.000071	0.214031	0.000072
VNIIFTRI	RU	0.228536	0.000088	0.222352	0.000107	0.214218	0.000101
SMU	SK	0.228880	0.000046	0.222667	0.000047	0.214381	0.000048
NIMT	TH	0.228991	0.000027	0.222865	0.000027	0.214326	0.000027
Tubitak UME	TR	-	-	0.524718	0.000041	0.5734436	0.000041
UMTS	UA	0.228641	0.000074	0.222384	0.000075	0.214955	0.000079
NIST	US	0.228543	0.000023	0.222396	0.000034	0.214256	0.000038

Tab 7: Standard potential of the Ag/AgCl electrodes at 15 °C, 25 °C and 37 °C as reported by the participants.

NMI	Country	5 °C		50 °C	
		E^0/V	$u(E^0)$ ($k=1$)	E^0/V	$u(E^0)$ ($k=1$)
BIM-NCM rev	BG	0.23380	0.00020	0.20397	0.000140
BIM-NCM org	BG	0.23422	0.00020	0.204454	0.000140
PTB	DE	0.234177	0.000052	0.204471	0.000052
NMIJ	JP	0.234142	0.000046	0.204639	0.000052
MKEH	HU	0.233434	0.000077	0.202258	0.000084
GUM	PL	0.233853	0.000066	0.204327	0.000075
VNIIFTRI	RU	0.234142	0.000067	0.204515	0.000093
SMU	SK	-	-	0.204484	0.000049
NIMT	TH	0.234458	0.000027	0.203507	0.000027
Tubitak UME	TR	-	-	0.580283	0.001564
UMTS	UA	0.234676	0.000074	0.204913	0.000850
NIST	US	0.234045	0.000023	0.204489	0.000025

Tab 8: Standard potential of the Ag/AgCl electrodes at 5 °C and 50 °C as reported by the participants.

NMI	Country	$u(\text{intercept})$			Slope (extrapolation)		
		15 °C	25 °C	37 °C	15 °C	25 °C	37 °C
BIM-NMC rev	BG	0.003	0.004	0.003	-0.629	-0.421	-0.512
BIM-NMC org	BG	0.003	0.004	0.003	-0.65357	-0.41610	-0.51140
CENAM	MX	0.00077	0.00076	0.00081	-0.65670	-0.57740	-0.72264
DFM	DK	0.00056	0.00048	0.00051	-0.69300	-0.67900	-0.69800
GUM	PL	0.00057	0.00098	0.00058	-0.75066	-0.61501	-0.59550
INMETRO	BR	0.00110	0.00090	0.00070	-0.47570	-0.52030	-0.57130
LNE	FR	0.00100	0.00100	0.00110	-0.66060	-0.63700	-0.53480
MKEH	HU	0.00063	0.00286	0.00279	-6.56970	-4.96640	-7.81350
NMIJ	JP	0.00080	0.00070	0.00130	-0.63869	-0.64661	-0.67039
NMIT	TH	0.00527	0.00506	0.00813	-0.89350	-0.85950	-1.15140
NIST	US	0.00046	0.00054	0.00077	-0.59044	-0.61278	-0.56763
PTB	DE	0.00040	0.00032	0.00054	-0.61499	-0.61012	-0.61838
SMU	SK	0.00040	0.00030	0.00040	-0.60855	-0.62893	-0.73113
Tubitak UME	TR	-	-	-	-	-29.119	-0.01600
UMTS	UA	0.00160	0.00130	0.00130	0.00210	0.00190	0.00190
VNIIFTRI	RU	0.00208	0.00279	0.00316	-0.03351	-0.08744	-0.07679

Tab 9: Uncertainty of the intercept and slope of the regression line obtained from linear extrapolation of the acidity function p_a to $m_{Cl} = 0$ at 15 °C, 25 °C and 37 °C.

NMI	Country	<i>u</i> (intercept)		Slope (extrapolation)	
		5 °C	50 °C	5 °C	50 °C
BIM-NCM rev	BG	0.00300	0.00210	-0.0847	-0.639
BIM-NMC org	BG	0.00300	0.00200	-0.0857	-0.6429
GUM	PL	0.00114	0.00065	-0.4047	-0.3883
MKEH	HU	0.00224	0.00253	-5.6401	-7.0092
NMIJ	JP	0.00060	0.00130	-0.6608	-0.7291
NIMT	TH	0.00272	0.01100	-0.6166	-0.5574
NIST	US	0.00041	0.00060	-0.6300	-0.5932
PTB	DE	0.00035	0.00085	-0.5975	-0.6749
SMU	SK	-	0.00043	-	-0.8614
Tubitak UME	TR			-	-0.0161
UMTS	UA	0.00297	0.00421	-8.9200	-17.4000
VNIIFTRI	RU	0.00300	0.00210	-0.0027	-0.1013

Tab 10: Uncertainty of the intercept and slope of the regression line obtained from linear extrapolation of the acidity function p_a to $m_{Cl} = 0$ at 5 °C and 50 °C.

NMI	HCl molality m_{Cl} (mol kg ⁻¹)	Standardization Technique for HCl
BIM-NCM	0.00947	titrimetry (methyl red)
INMETRO	0.010013	coulometry
DFM	0.010000	coulometry+gravimetric dilution
PTB	0.010008	coulometry
LNE	0.0099998	potentiometric titration
NMIJ	0.0099989	coulometry+gravimetric dilution
MKEH	0.010005	potentiometric titration
CENAM	0.01000	coulometry
Indecopi	-	-
GUM	0.010009	potentiometric titration (Tris)
VNIIFTRI	0.01015	coulometry
SMU	0.010000	coulometry
NIMT	0.010002	coulometry+gravimetric dilution
Tubitak UME	0.0108	coulometry
UMTS	0.010012	coulometry
NIST	0.0100042	coulometry

Tab.11: HCl molality and method of standardization.

Calculation of the KCRV and its uncertainty

The key comparison CCQM-K91 (pH of phthalate buffer, pH~4) was a complete repeat of CCQM-K17. CCQM-K17 was performed in 2001⁶.

Three possibilities for determination of the KCRV are listed in Table 12 and 13. For each estimator, the UMTS, Tubitak UME, BIM-NCM and Indecopi results are omitted from the calculation. The differences between the estimators at all temperatures are insignificant. Based on the decision of the EAWG at its

⁶ http://kcdb.bipm.org/appendixB/KCDB_ApB_info.asp?cmp_idy=168&cmp_cod=CCQM-K17&prov=exalead

meeting on 31 April 2012, the weighted mean and its uncertainty were selected as the estimators for the KCRV in CCQM-K91.

This approach is the same as that used to calculate the KCRV in the CCQM-K17.

Estimator	15 °C		25 °C		37 °C	
	Value	$u(k=1)$	Value	$u(k=1)$	Value	$u(k=1)$
Arithmetic mean	4.0846	0.00054	4.0929	0.00057	4.1134	0.0011
Weighed mean	4.0853	0.00052	4.0935	0.00042	4.1147	0.00046
Median	4.0853	0.00055	4.0936	0.00057	4.1135	0.00057
Birge ratio	1.73		1.38		1.37	

Tab.12: Values of candidate estimator for the KCRV at 15 °C, 25 °C and 37 °C for CQQM-K91.

Estimator	5 °C		50 °C	
	Value	$u(k=1)$	Value	$u(k=1)$
Arithmetic mean	4.0849	0.0026	4.1466	0.0027
Weighed mean	4.0875	0.0013	4.1480	0.0015
Median	4.0851	0.0014	4.1468	0.0022
Birge ratio	3.04		2.51	

Tab.13: Values of candidate estimator for the KCRV for CQQM-K91 at 5 °C and 50 °C.

The weighted mean pa_R^0 for CCQM-K91 was calculated using Eq4. Where n is the number of participants, w_i is the normalized weight for participant i , and pa_i^0 is the result for participant i .

$$pa_R^0 = \sum_{i=1}^N w_i pa_i^0 \quad (4)$$

The weight w_i is given by Eq 5 and 6, where $u(x_i)$ is the standard uncertainty for participant i :

$$w_i = \frac{C}{u(x_i)^2}$$

(5)

$$C = \frac{1}{\sum_{i=1}^N \frac{1}{u(x_i)^2}}$$

(6)

The values of $u(x_i)$ are the individual uncertainties and C is the variance. The uncertainty of the weighted mean was determined by the external consistency method (uncertainty –weighted mean). $u_R(pa_R^0)$ is given by Eq 7.

$$u_R(pa_R^0) = \sqrt{\frac{\sum_{i=1}^N w_i (pa_i^0 - pa_R^0)^2}{(N-1)}} \quad (7)$$

As for CCQM-K17 the Birge approach is used again to test if there is the possibility that some or all of the individual uncertainties have been underestimated. When applying this test, the uncertainty of the KCRV as determined from the individual uncertainties stated by the participants (the internal consistency of the data, equation (8)) are compared to the external consistency taking into account how much each result deviates from the KCRV in relation to its uncertainty.

$$u_m(p a_R^0) = \sqrt{C} \tag{8}$$

The Birge ratio $R = u_R/u_m$ calculated for the CCQM-K91 is always larger than one as given in tables 13 and 14, indicating that the external consistency method yields a better estimate of the uncertainty of the results than does the internal consistency method. Therefore the calculated values of $u_R(p a_R^0)$ were taken as the standard uncertainty of the KCRV, $u(\text{KCRV})$. For CCQM-K17 the Birge ratios were: 2.85 (15 °C), 3.08 (25 °C) and 3.02 (37 °C).

The final value of the KCRV and its expanded uncertainty ($k = 2$) is listed for each temperature in table 14.

15 °C		25 °C		37 °C		5 °C		50 °C	
KCRV	$U(k = 2)$	KCRV	$U(k = 2)$	KCRV	$U(k = 2)$	KCRV	$U(k = 2)$	KCRV	$U(k = 2)$
4.0853	0.0011	4.0935	0.00083	4.1147	0.00092	4.0875	0.0027	4.1480	0.0030

Tab. 14: KCRV and its expanded uncertainty, U, for CCQM-K91.

Calculation of the degrees of equivalence

The degree of equivalence for each participant, D_i , and its standard uncertainty, $u(D_i)$, are given by Eq 9 and Eq 10.

$$D_i = (p a_i^0 - \text{KCRV}) \tag{9}$$

$$u(D_i) = \sqrt{u^2(p a_i^0) + u^2(\text{KCRV})} \tag{10}$$

Values for D_i and $u(D_i)$ are given in Table 15 and 16 Figures 16-20 and shown in for each participant except Tubitak UME and UMTS. For BIM-NCM values are given for the original submitted and for the revised values.

NMI	15 °C		25 °C		37 °C	
	D_i	$u(k = 1)$	D_i	$u(k = 1)$	D_i	$u(k = 1)$
BIM-NCM rev	-0.0036	0.0040	-0.0028	0.0040	-0.0014	0.0040
BIM-NCM org	-0.0102	0.0040	-0.0104	0.0040	-0.0089	0.0040
Inmetro	-0.0022	0.0016	-0.0017	0.0012	-0.0016	0.0013
DFM	0.0005	0.0008	0.0005	0.0007	0.0010	0.0007
PTB	0.0010	0.0013	0.0006	0.0013	-0.0004	0.0013
LNE	-0.0018	0.0023	-0.0014	0.0018	-0.0035	0.0020
NMIJ	0.0001	0.0013	-0.0004	0.0013	0.0004	0.0016
MKEH	-0.0006	0.0015	0.0012	0.0015	-0.0045	0.0030
CENAM	-0.0045	0.0011	-0.0031	0.0012	-0.0014	0.0013
GUM	-0.0001	0.0015	-0.0009	0.0017	-0.0031	0.0015
VNIIFTRI	0.0003	0.0030	0.0007	0.0037	-0.0010	0.0040
SMU	0.0009	0.0011	0.0011	0.0011	0.0015	0.0011
NIMT	-0.0038	0.0026	-0.0052	0.0025	-0.0033	0.0040
NIST	0.0014	0.0008	0.0011	0.0009	0.0006	0.0020
Indecopi	0.0024	0.0021	-0.0012	0.0020	-0.0012	0.0021
Tubitak UME	-	-	0.7150	0.0028-	-0.0521-	0.038
UMTS	-0.1280	0.0021-	-0.1103-	-0.0019	-0.1177-	0.0039-

Tab.15: Degrees of equivalence and its uncertainty at 15 °C, 25 °C and 37 °C.

NMI	5 °C		50 °C	
	D_i	$u(k = 1)$	D_i	$u(k = 1)$
BIM-NCM rev	-0.0048	0.0042	-0.0033	0.0033
BIM-NCM org	-0.0125	0.0024	-0.0098	0.0025
PTB	0.0009	0.0018	-0.0003	0.0020
NMIJ	-0.0007	0.0018	-0.0034	0.0026
MKEH	-0.0057	0.0030	-0.0022	0.0034
GUM	-0.0044	0.0022	-0.0061	0.0020
SMU	-	-	0.0033	0.0018
VNIIFTRI	-0.0024	0.0039	0.0079	0.0042
NIMT	-0.0083	0.0020	-0.0122	0.0057
NIST	0.0021	0.0015	0.0016	0.0022
Tubitak UME	-	-	-0.1943	0.0244
UMTS	-0.1250	0.0046	-0.1169	0.0026

Tab.16: Degrees of equivalence and its uncertainty at 5 °C and 50 °C.

Conclusions

In the discussion it was noted that the Pd electrodes are more sensitive to oxygen (back-diffusion) what could cause deviation in one direction. More work is required to be done for temperatures far deviating from 25°C to reduce the spread of results. Some of the participants obviously underestimated their uncertainties especially at measurement temperatures of 5 °C and 50 °C.

Compared to the results obtained for the CCQM-K17 the results are showing smaller variation at the same measurement temperatures. This is shown in figure 21.

How far the light shines

Phthalate reference buffer solutions are widely used as pH standards in acid range. Participants successfully took part in the KC CCQM-K91 demonstrate their capability to measure the pH of primary buffer in the acid range of pH (25°C) = 3.8 to pH = 4.2. Problems occurred at 5 °C and 50 °C measurement temperatures. The spread of results is much higher as at 25 °C. This has to be taken into for CMC claims for pH different from 25 °C.

Acknowledgment

The coordinating laboratory gratefully acknowledges the contributions of all participants and of the members of the CCQM EAWG for their valuable suggestions concerning and the evaluation process.

Figures

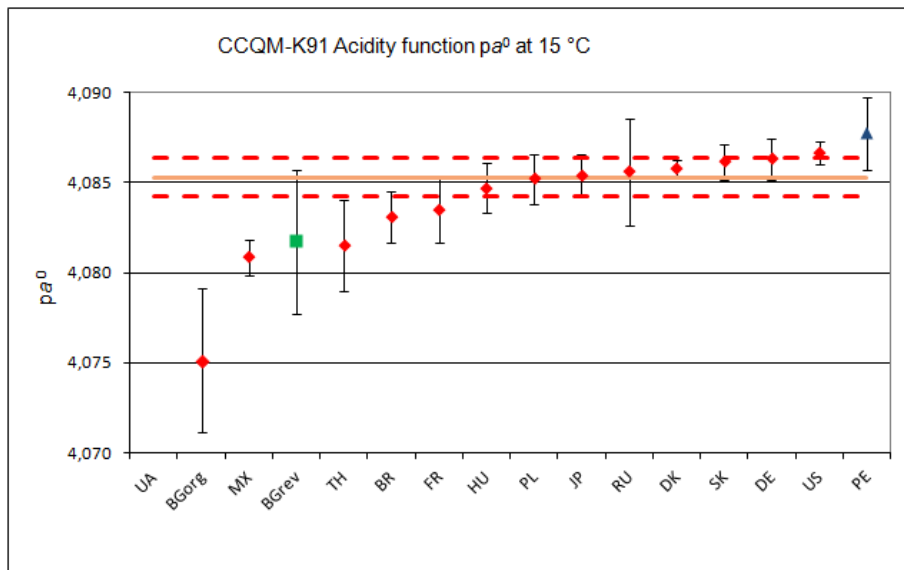


Fig 6: CCQM-K91 p_{a0} at 15 °C. The uncertainty of the results is the standard uncertainty ($k = 1$). The results of TR and UA are not shown. Red line: KCRV and dotted lines uncertainty of the KCRV ($k = 2$).

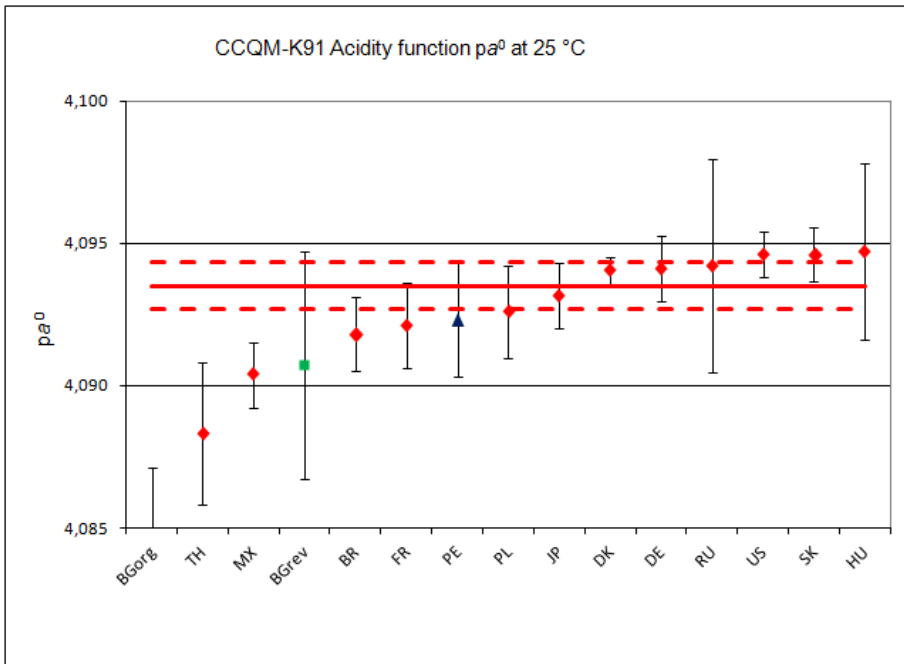


Fig. 7: CCQM-K91 p_a^0 at 25 °C. The uncertainty of the results is the standard uncertainty ($k = 1$). The results of TR and UA are not shown. Red line: KCRV and dotted lines uncertainty of the KCRV ($k = 2$).

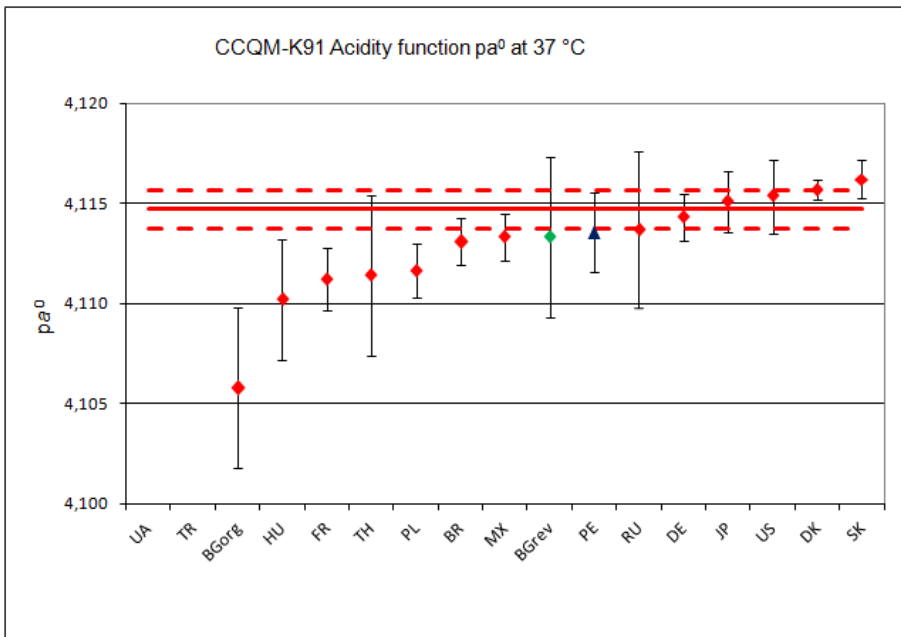


Fig. 8: CCQM-K91 p_a^0 at 37 °C. The uncertainty of the results is the standard uncertainty ($k = 1$). The results of TR and UA are not shown. Red line: KCRV and dotted lines uncertainty of the KCRV ($k = 2$).

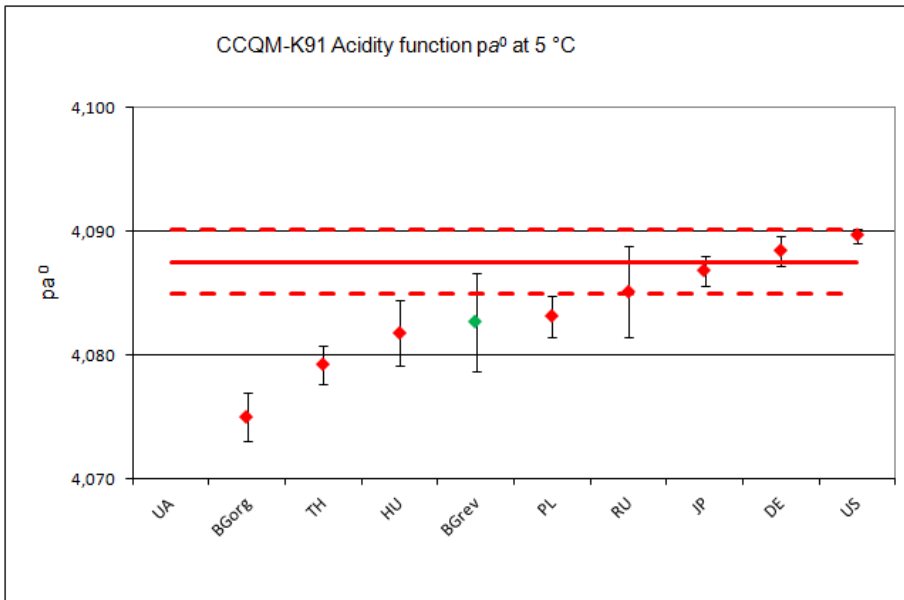


Fig. 9: CCQM-K91 p_a^0 at 5 °C. The uncertainty of the results is the standard uncertainty ($k = 1$). The results of UA are not shown. Red line: KCRV and dotted lines uncertainty of the KCRV ($k = 2$).

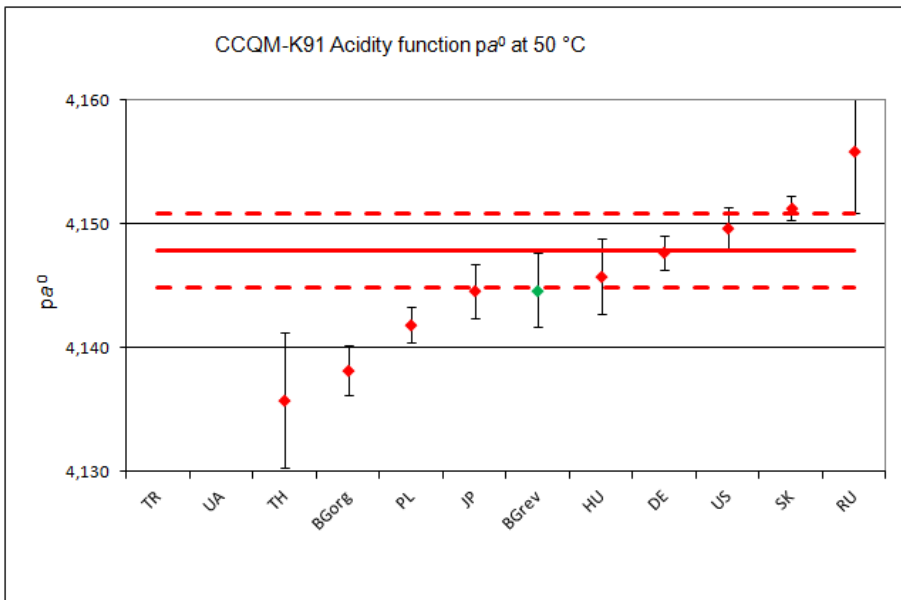


Fig. 10: CCQM-K91 p_a^0 at 50 °C. The uncertainty of the results is the standard uncertainty ($k = 1$). The results of TR and UA are not shown. Red line: KCRV and dotted lines uncertainty of the KCRV ($k = 2$).

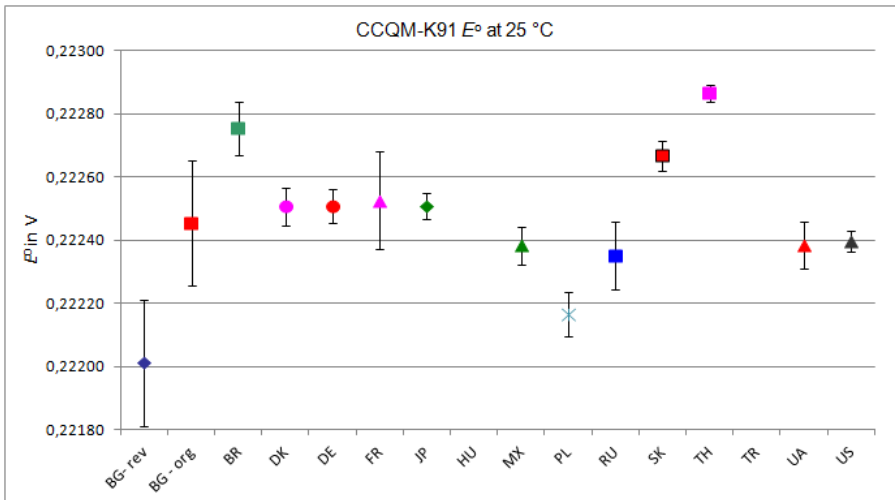


Fig. 11: Standard potential of the Ag/AgCl electrodes at 25 °C. The result of HU is out of range.

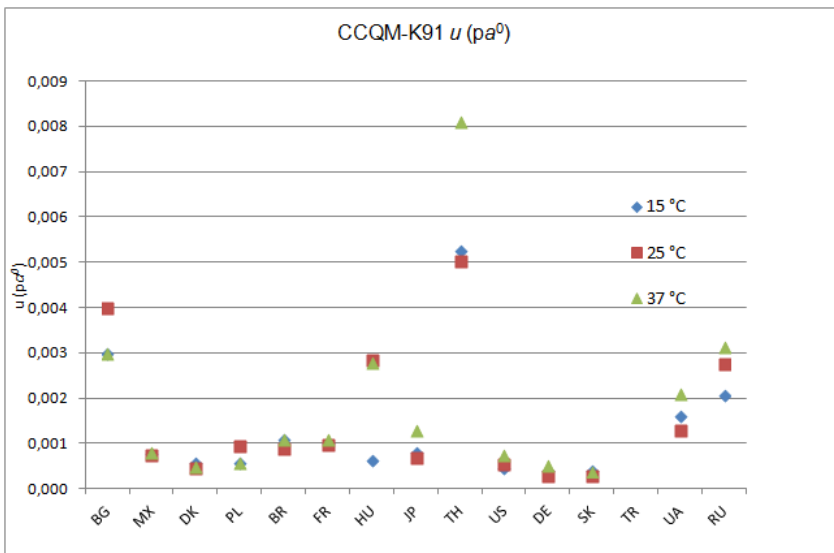


Fig. 12: Standard uncertainty ($k = 1$) of the regression line at 15 °C, 25 °C and 37 °C.

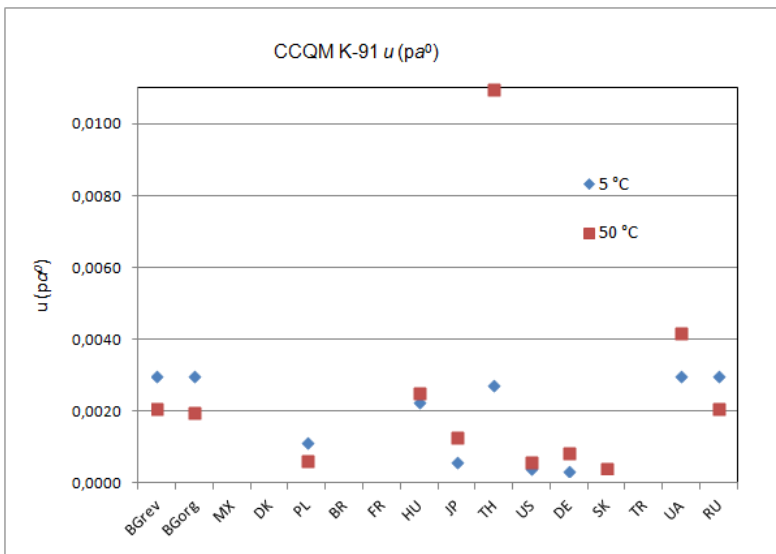


Fig. 13: Standard uncertainty ($k = 1$) of the regression line at 5 °C and 50 °C.

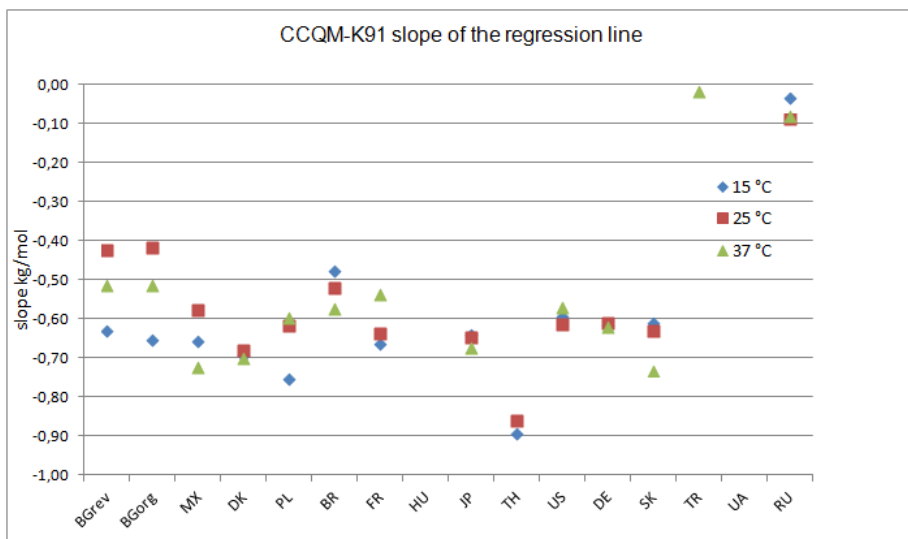


Fig. 14: Slope of the regression line at 15°C, 25 °C and 37 °C.

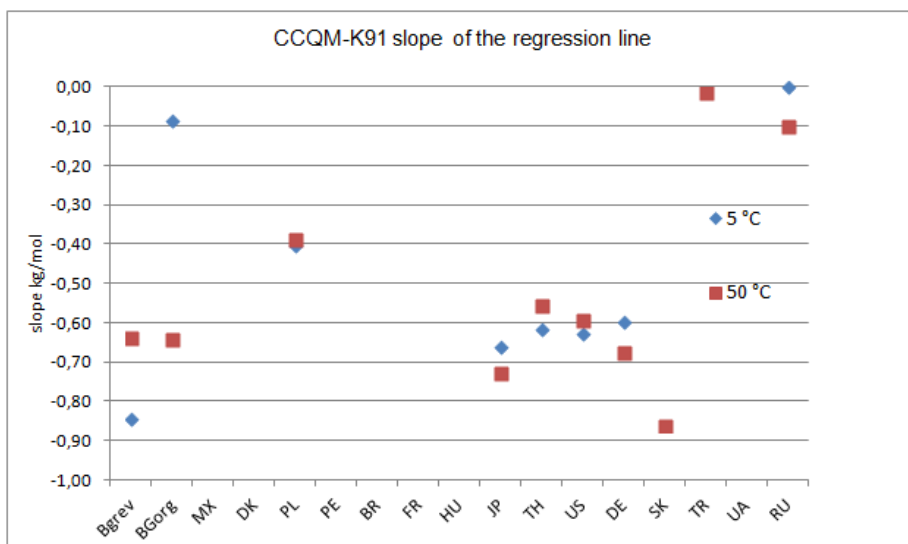
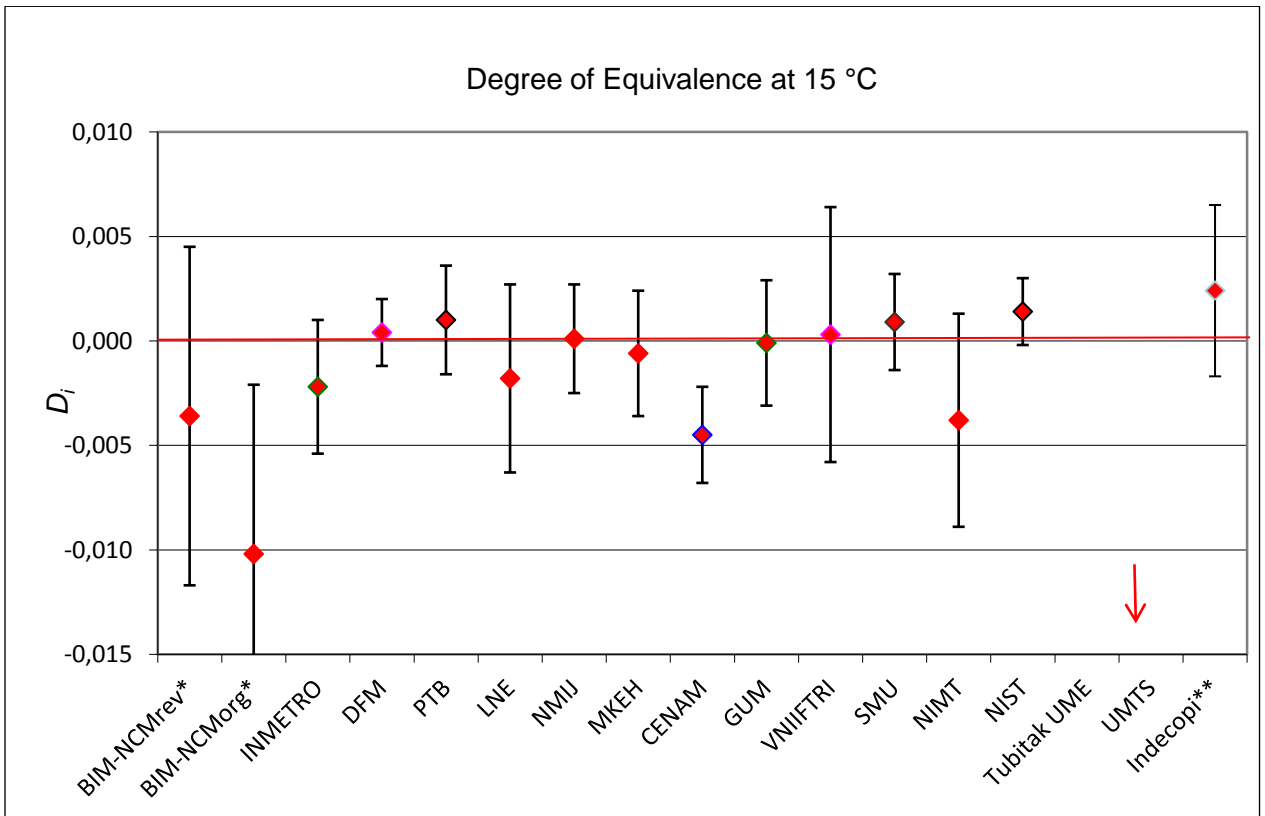
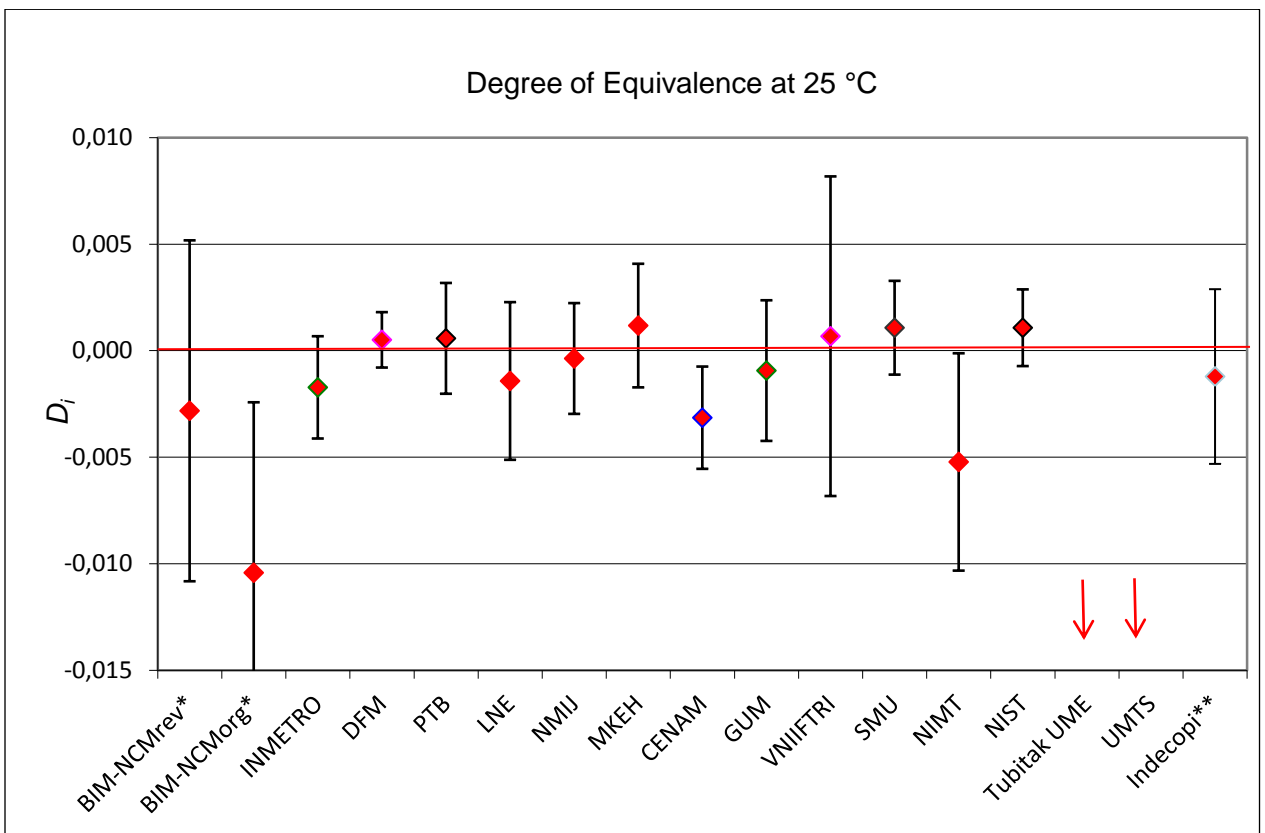


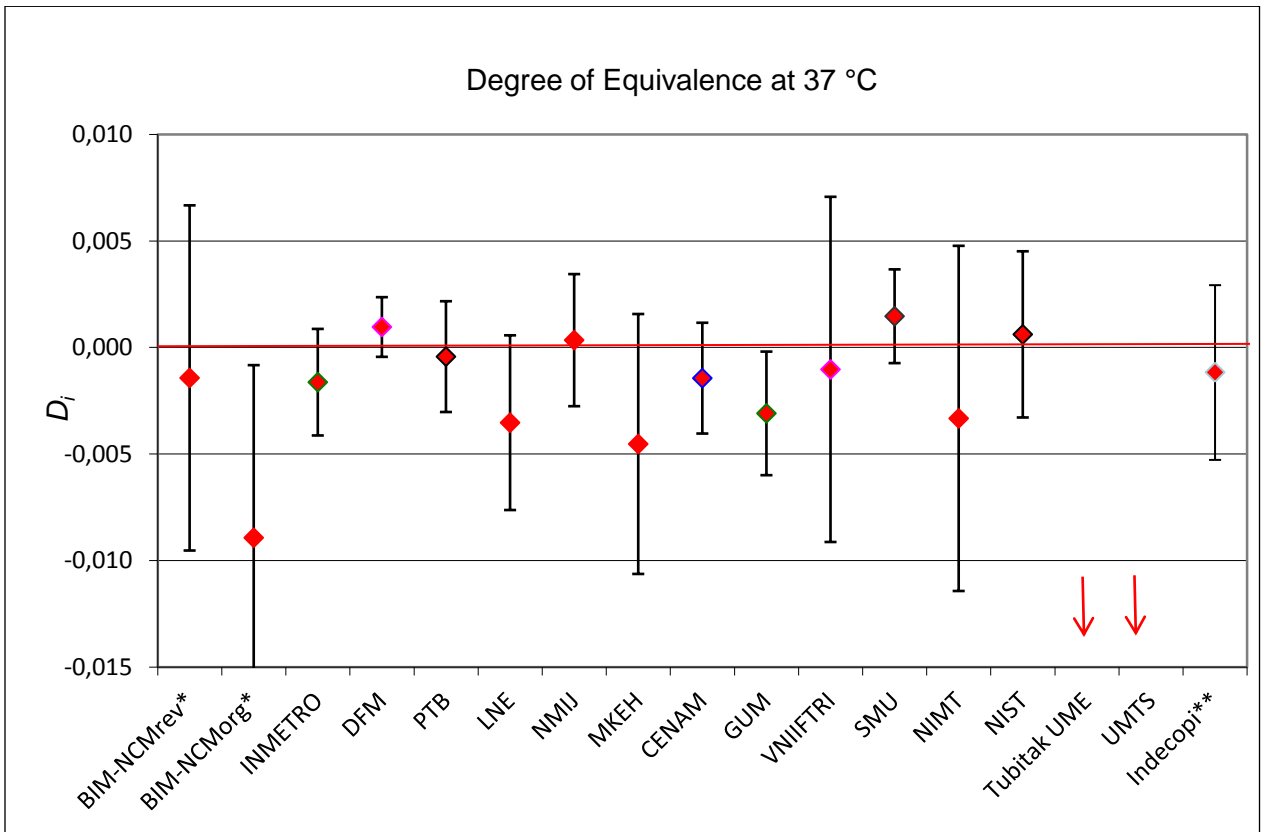
Fig. 15: Slope of the regression line at 5°C and 50 °C.



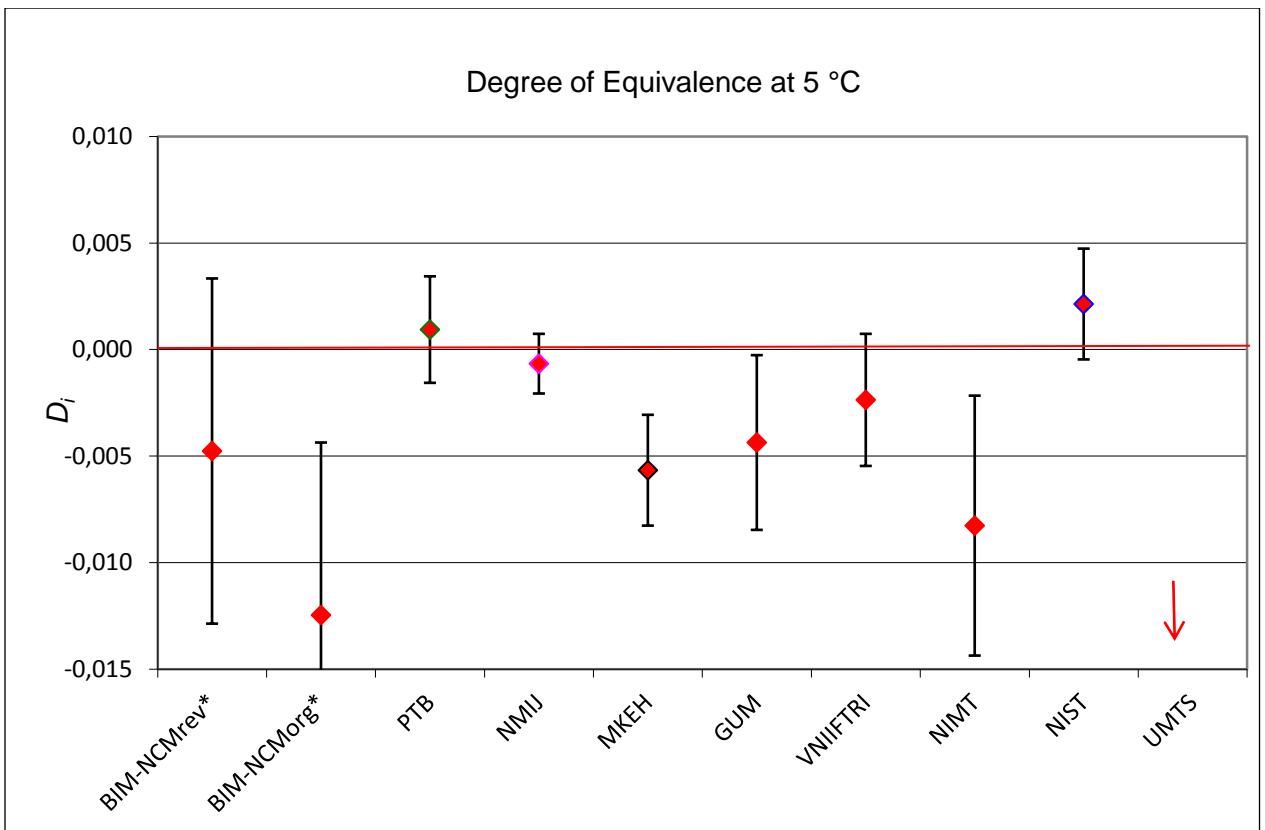
Fig, 16: Degree of Equivalence and its uncertainty ($k = 2$) at 15 °C. The result of UA is out of range.



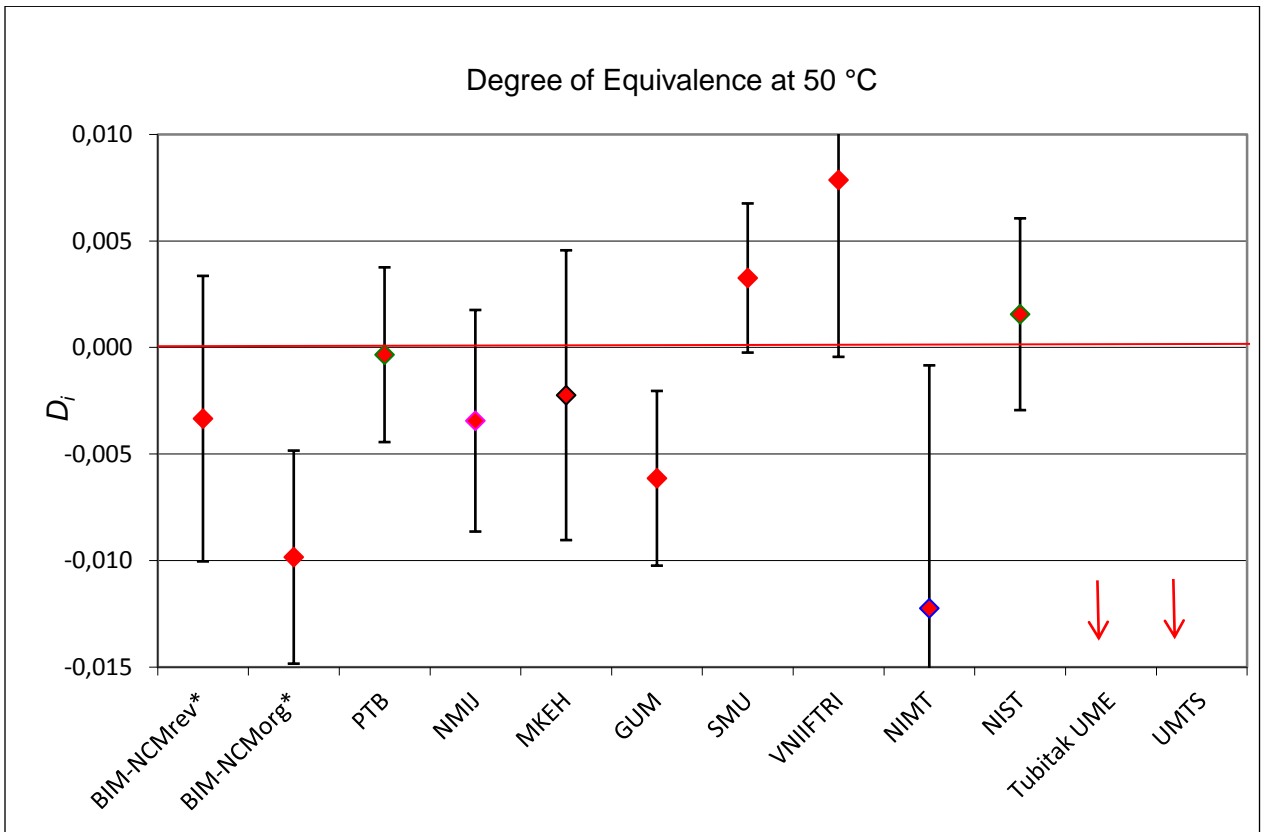
Fig, 17: Degree of Equivalence and its uncertainty ($k = 2$) at 25 °C. The results of TR and UA are out of range.



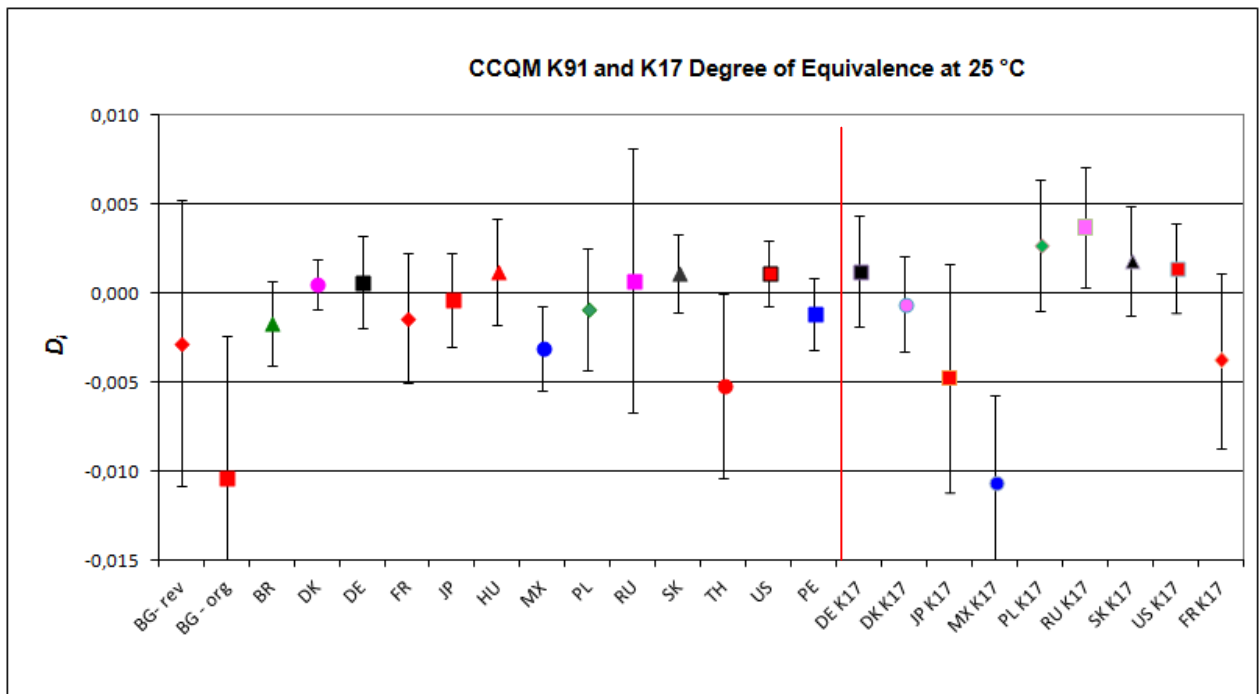
Fig, 18: Degree of Equivalence and its uncertainty ($k = 2$) at 37 °C. The results of TR and UA are out of range.



Fig, 19: Degree of Equivalence and its uncertainty ($k = 2$) at 5 °C. The result of UA is out of range.



Fig, 20: Degree of Equivalence and its uncertainty ($k = 2$) at 50 °C. The results of TR and UA are out of range.



Fig, 21: Degree of Equivalence and its uncertainty ($k = 2$) at 25 °C. Compared are the results for CCQM-K17 and for CCQM-K91.