PTB
Physikalisch-Technische Bundesanstalt
Braunschweig und Berlin

CCQM WG on Electrochemical Analysis

Final report on CCQM – K99
Key comparison on pH of an unknown phosphate buffer
March 2015

F. Bastkowski, P. Spitzer, B. Sander, M. Máriássy, L. Dimitrova, A. Reyes, A. Rodríguez, V. Lara Manzano, A. Vospelova, P. T. Jakobsen, M. Pawlina, M. Korol, W. Kozlowski, M. Delgado, G. Ticona Canaza, J. C. Dias, F. B. Gonzaga, Z. Nagyné Szilágyi, Beáta Jakusovszky, Leoš Vyskočil, T. Nongluck, J. Waters, K. W. Pratt, T. Asakai, I. Maksimov, Z. Hankova, E. Uysal, V. Gavrilkin, S. V. Prokunin, E. Ferreira, S. Fajardo

Abstract

Results of CCQM-K99 key comparison on unknown phosphate buffer pH ~ 7.5 at 5 °C, 15 °C, 25 °C, 37 °C and 50 °C are reported. Good agreement is found between the majority of participants.

Subject field

Amount of substance

Subject

Determination of the acidity functions at zero chloride molality of an unknown phosphate buffer, pH ~7.5 by Harned cell measurements at 5 °C, 15 °C, 25 °C, 37 °C and 50 °C.

Table of Contents

Purpose of the comparison

This key comparison has been performed to evaluate the degree of equivalence of national standard measurement procedures for the determination of the pH of phosphate buffer solutions.
The comparison was restricted to the use of either the primary Harned cell[1] or the secondary differential potentiometric cell[2] 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 designated institute respectively and if the CMCs are based on this method. Only the results obtained by the primary method were used to calculate the KCRV.

Phosphate buffer is widely used to calibrate pH electrodes. A buffer solution of 0.008695 mol/kg KH_2PO_4 and 0.03043 mol/kg Na_2HPO_4 is one of the primary pH reference buffer solutions recommended by IUPAC. Certified reference materials are issued by several NMIs based on primary measurement.

In this comparison measurements of pH has been performed at 15 °C, 25 °C, 37 °C and additionally at 5 °C, and 50 °C.

Time schedule

Dispatch of the samples:	11 February 2014
Deadline for receipt of the report:	23 May 2014
Results distributed	13 June 2014
Draft A report distributed	06 February 2015
Discussion of results and Draft A report	via e-mail, February/March 2015
Draft B report distributed	13 March 2015
EAWG approval of Draft B report	EAWG meeting, 16-17 April 2015
Final report	23 December 2015

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 Sander
Tel: +49 531 592 3132
Fax: +49 531 592 3015
Email: beatrice.sander@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	Bulgaria	Bulgarian Institute of Metrology	BIM, NCM	Lyudmila Dimitrova
2	Mexico	Centro Nacional de Metrologia	CENAM	Adrian Reyes/Aaron Rodríguez
3	Czech Republic	Czech Metrology Institute	CMI	Alena Vospelova
4	Denmark	Danish Fundamental Metrology A/S	DFM	Pia Tønnes Jakobsen
5	Poland	Central Office of Measures	GUM	Wladyslaw Koslowski
6	Bolivia	Instituto Boliviano de Metrología	IBMETRO	Mabel Delgado
7	Peru	Instituto Nacional de Defensa de la Competencia y de la Protección de la Propiedad Intelectual	INDECOPI	Galia Ticona Canaza
8	Brazil	National Institute of Metrology, Quality and Technology	INMETRO	Fabiano Barbieri Gonzaga
9	Israel	The National Physical Laboratory of Israel	INPL	Elena Kardash
10	Uruguay	Laboratorio Tecnológico del Uruguay	LATU	Elizabeth Ferreira Simone Fajardo
11	Hungary	Hungarian Trade Licensing Office	MKEH	Zsófia Nagyné Szilágyi, Beáta Jakusovszky
12	Thailand	National Institute of Metrology (Thailand)	NIMT	Ms. Nongluck Tangpaisarnkul
13	USA	National Institute of Standards and Technology	NIST	Jason Waters Kenneth W. Pratt
14	Japan	National Metrology Institute of Japan	NMIJ	Toshiaki Asakai, Igor Maksimov
15	Germany	Physikalisch-Technische Bundesanstalt	PTB	Frank Bastkowski, Beatrice Sander, Petra Spitzer
16	Slovakia	Slovak Institute of Metrology	SMU	Zuzana Hankova
17	Ukraine	State Enterprise All-Ukrainian State Research and production Center of Standardization Metrology, Certification and Consumers' Rights Protection (Ukrmetrteststandart)	UMTS	Vladimir Gavrilkin
18	Turkey	TÜBİTAK UME	UME	Emrah Uysal
19	Russia	National Scientific and Research Institute for Physical-technical and Radio-technical Measurements	VNIIFTRI	Sergey V. Prokunin

Tab. 1: List of participants in key comparison CCQM-K99

Sample preparation and distribution

The phosphate buffer solution was prepared from deionized water, potassium hydrogen phosphate and sodium hydrogen phosphate both from Merck (CertiPUR®) at the ZMK (Zentrum fuer Messen und Kalibrieren) facilities in Germany by colleagues from PTB. ZMK is a calibration laboratory accreted 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. The sample solution was prepared at 25-Nov-2013 by dissolving 118.41 g of KH_2PO_4 and 432.25 g of Na_2HPO_4 in 100.000 kg of deionized water. The mass fraction of water in the solution was *w*(H2O) = 0.994524. The homogeneity of the material was measured before shipment and the stability of the sample solution was checked by Harned cell measurements. Each participant received three 1 L HDPE numbered bottles filled with the comparison solution and sealed in aluminized plastic bags. Shipment to all participants was performed at the same time. Due to shipment problems the reporting deadline was shifted twice.

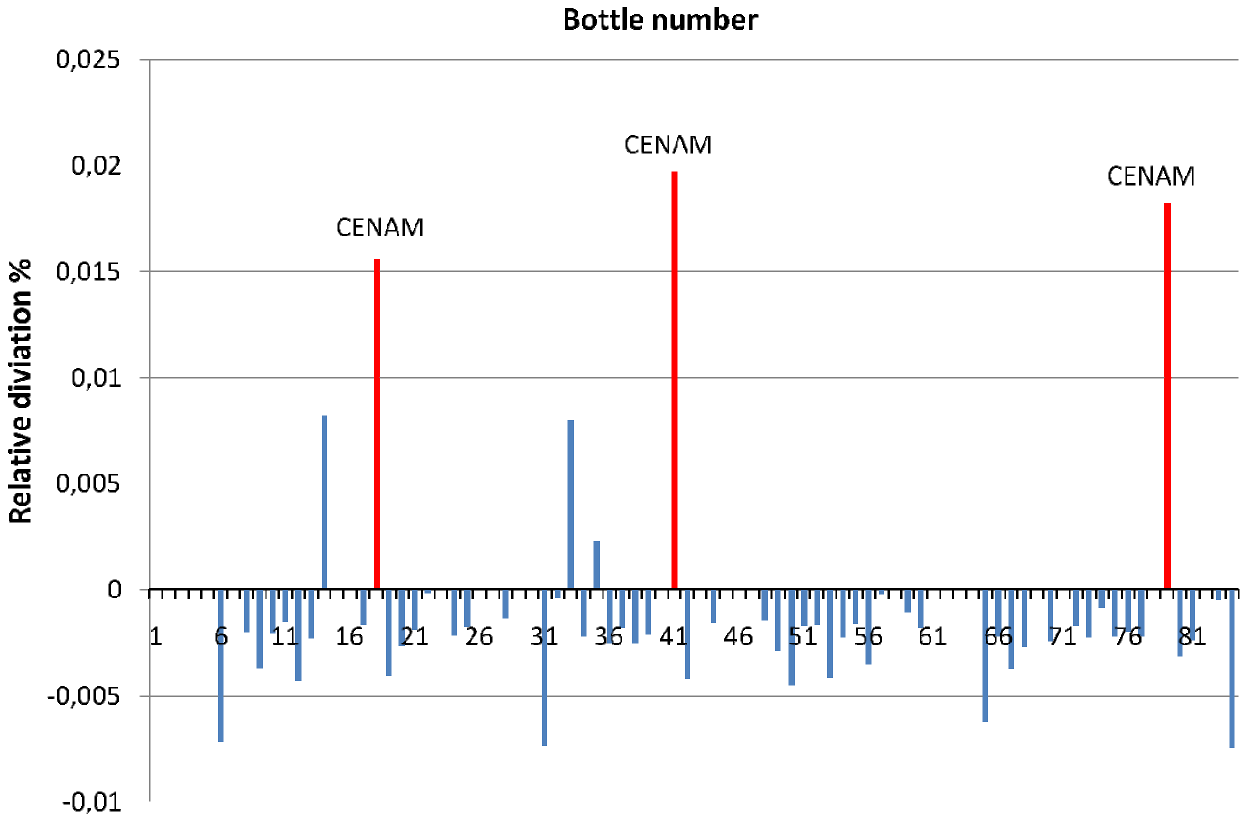

Fig.1: Relative deviation (%) of the bottle mass reported by the participants from the bottle mass calculated at the PTB from balance reading.

Sample homogeneity and stability

Before shipment the homogeneity between the bottles was checked at 25 °C. The stability of the bottled solution was evaluated over the measurement period (08 January – 03 June 2014) at 15 °C, 25 °C and 37 °C. 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 mol kg^{-1}, 0.010 mol kg^{-1} and 0.015 mol kg^{-1}. The samples were measured during a period of fourteen days. The results are summarized in table 2 and shown in figure 2 for pa^0 of the bottled buffer solution at 25 °C.

Sample	Date	Method	Acidity function at zero - 6 -hloride molality at 25 °C
26	8 Jan 2014	Harned cell	7.5237 (u = 0.001)
85	14 Jan 2014	Harned cell	7.5237 (u = 0.001)
2	21 Jan 2014	Harned cell	7.5237 (u = 0.001)

Tab 2: Homogeneity check at 25 °C at coordinating laboratory before shipment

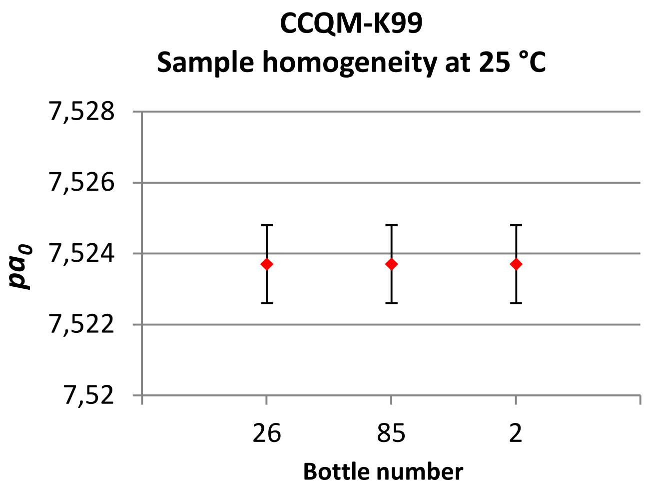

Fig.2: Sample homogeneity at 25 °C. The standard uncertainty (k=1) is given.

To evaluate the stability of the sample solution results of homogeneity testing and of three additional measurement runs were used. To validate the stability of the samples the pa^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 4 to 6 for 15 °C, 25 °C and 37 °C.

	Acidity function at temperature			
Date of measurement	**15 °C**	**25 °C**	**37 °C**	**Uncertainty u (k=1)**
08. Jan 2014	7.5557	7.5237	7.5032	0.0011
14. Jan 2014	7.5560	7.5237	7.5028	0.0011
21. Jan 2014	7.5557	7.5237	7.5031	0.0011
11. Mar 2014	7.5547	7.5235	7.5028	0.0011
09. Apr 2014	7.5553	7.5235	7.5027	0.0011
03. Jun 2014	7.5567	7.5241	7.5030	0.0011

Tab 3: Sample stability over a five months period. The measurement result of KC CCQM-K99 of the coordinating laboratory is shown in the second last row.

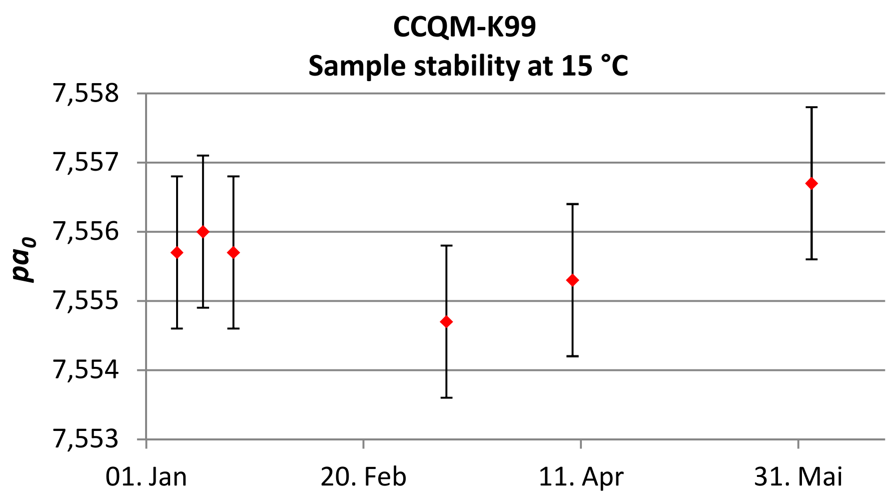

Fig.3: Validation of the sample stability at 15 °C. The standard uncertainty (k=1) is given

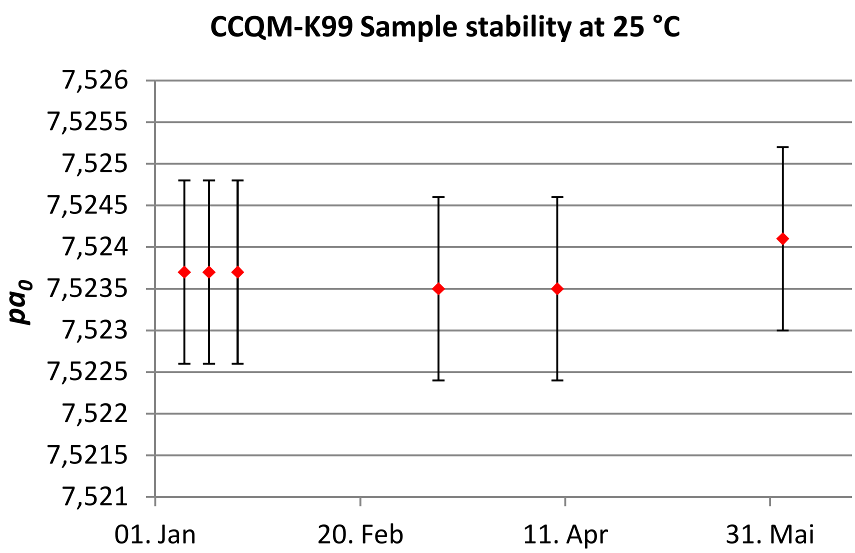

Fig.4: Validation of the sample stability at 25 °C. The standard uncertainty (k=1) is given

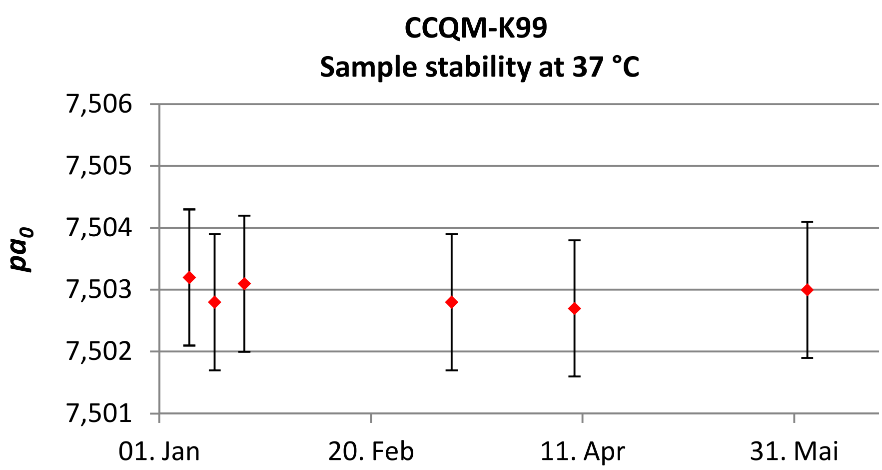

Fig.5: Validation of the sample stability at 37 °C. The standard uncertainty (k=1) is given.

Timetable of measurements and Comments

NMI	Sample received	Measurement Period	Report Date	Revised Report	Comments
IBMETRO	03 Mar	22 May	23 May		IBMETRO reported a mistake in the buoyancy correction and provided revised bottle masses
INMETRO	11 March	14 – 17 Apr	06 May		
BIM/NCM	18 Feb	20 Feb	23 May	04 Dez	more detailed description of the uncertainty budget in the revised report
CMI	13 Feb	20 May – 02 Jun	05 Jun		
DFM	14 Feb	26 – 28 Feb	13 Mar	05 Feb 2015	more detailed description of the uncertainty budget in the revised report
PTB	26 Nov 2013	09 Apr	14 May	06 Jun	Revision of partial H_2 pressure, however no significant effect on the uncertainty budget
NMIJ	04 Mar	06 – 18 Mar	28 Mar		
MKEH	17 Feb	08 May	26 May	10 Dez	Erroneous statement of standard uncertainty (k=1) for the acidity function, corrected in the revised report
INPL			-	-	No results due to staff shortage.
CENAM	03 Mar	12 – 21 Mar	21 May	18 Jun	Erroneous statement of pH instead of the acidity function for 25 °C, corrected in the revised report
INDECOPI	10 Mar	14 Mar – 15 May	24 May		
GUM	14 Feb	14 – 21 Mar	01 Apr		
VNIIFTRI	05 Mar	13 Mar	11 May		
SMU	21 Feb	13 Mar	23 May	09 Feb 2015, 09:31	Erroneous statement of E1 instead of E0, corrected in the revised report
NIMT	04 Mar	24 Mar – 08 Apr	23 May	06 Feb 2015	Erroneous statement of standard uncertainty (k=1) for the acidity function, corrected in the revised report
TÜBITAK UME	11 May	15 – 26 May	03 Jun		
UMTS	24 Feb	14 – 23 Apr	21 May		
LATU	08 Apr	07 – 15 May	23 May		
NIST	07 Mar	10 Mar	04 Apr		

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

Problems reported to the coordinator

- Due to shipment delays, the reporting deadline had to be postponed twice. Shipment to the following institutes took longest: INMETRO (Br), Tübitak UME (Tr), LATU (Uy), the sample bottles had to be shipped to Tübitak UME (Tr) twice. First attempt with "POST" failed, second attempt with "DSV global transport and logistics" was successful
- LATU (Uy) reported that one of the aluminized bag has been opened by the Uruguayan customs, however this hasn´t any effect on the mass integrity
- LATU (Uy) reported that measurement could only be performed at 25 °C and 37 °C, as the provided sample volume was not sufficient
- VNIIFTRI (Ru) reported that measurements could not be performed at 5 °C and 50 °C due to staff shortage
- SMU (Sk) reported that measurements could not be performed at 50 °C due to staff shortage

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 buffer[3]. The primary method for pH is based on the measurement of the potential difference of cell I without liquid junction

Pt | H_2 (g, *p*°) | buffer, Cl^- | AgCl | Ag   Cell I

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:

$$E_1 = E^0 - k\log(a_H/m^0)(m_{Cl}\gamma_{Cl}/m^0) \qquad (1)$$

In Eq. 1, E^0 is the standard potential of the Ag/AgCl reference electrode, m^0 = 1 mol kg^{-1}, m_{Cl} and γ_{Cl} the molality and activity coefficient of the chloride ion. *k* equals *RT* ln10/*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.

Pt | H_2 (g, *p*°) | HCl | AgCl | Ag,   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* HCl = 0.01 mol kg^{-1}. The mean activity coefficient of the HCl at the measurement temperature for this nominal molality is taken from literature[4] .

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

The acidity function p*a* is calculated for each measured cell potential E_1 using Eq. 3.

$$\mathrm{p}a = (E_1 - E^0)/k + \log(m_{Cl}/m^0) \qquad (3)$$

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 p*a* to m_{Cl} = 0. The reported result for the key comparison CCQM-K99 is pa^0 at each measurement temperature.

---

[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

As secondary method for pH the differential potentiometry (Baucke cell) was used by INDECOPI, LATU and IBMETRO[1]. 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.

$$\mathrm{Pt(1)|H_2|\ buffer\ S_1\ ||\ buffer\ S_2\ |H_2|Pt(2).} \qquad \text{Cell III}$$

Cell III consists of two identical Pt|H_2 electrodes, Pt(1) and Pt(2); and two quasi-identical buffers, S_1 and S_2, with pH values, pH(S_1) and pH(S_2). A diaphragm, ||, separates S_1 and S_2. The cell is constructed such that the H_2 pressure, p_{H_2}, at Pt(1) and Pt(2) is identical. pH(S_1) is given by Eq.4.

$$\mathrm{pH(S_2)} = \mathrm{pH(S_1)} - \frac{E_3 - E_\mathrm{j}}{k}, \qquad (4)$$

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, |pH(S2) – pH(S1)| ≤ 0.02, and 3 < pH < 11 $|E_\mathrm{j}|<0.1|E_3$.

Results and discussion

All participants except of INPL delivered results. It was agreed previously that only results from primary measurements are used to calculate the key comparison reference value (KCRV).
INDECOPI (PE), LATU (UY) and IBMETRO (Bo) applied a secondary method. They 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 values reported by these institutes are recalculated as pa^0 by assuming an ionic strength of the buffer of 0.1 mol kg^{-1}. All participants were requested to measure the pa^0 at 15 °C, 25 °C, 37 °C and additionally at 5 °C and 50 °C. Eight institutes provided additional results at 5 °C and 50 °C. The results for the key comparison, pa^0, are given in table 5 to 6 below at each measurement temperature. The uncertainty is the standard uncertainty with k =1.
Tables 7 and 8 summarize the E^0 values at all measurement temperatures. The E^0 values at 25 °C are shown in figure 11. In table 9 and 10 the uncertainty of the intercept and the slope of the regression line obtained from linear extrapolation of the acidity function pa to m_{Cl} = 0 are given. The data are shown in figures 12 to 15. The HCl molality and the method used to standardize the HCl are given in table 11.

[1] Baucke FGK (1994) J Electroanal Chem 368:67–75

Institute	Country	Acidity function at 15°C	***u*** (k=1)	Acidity function at 25°C	***u*** (k=1)	Acidity function at 37°C	***u*** (k=1)
BIM/ NCM	BG	7.5553	0.0020	7.5228	0.0020	7.4951	0.0020
IBMETRO	BO			7.5276	0.0050		
INMETRO	BR	7.5582	0.0013	7.5255	0.0013	7.5006	0.0022
CMI	CZ	7.5585	0.0013	7.5287	0.0013	7.4954	0.0020
DFM	DK	7.5563	0.0008	7.5232	0.0008	7.5021	0.0008
PTB	DE	7.5553	0.0011	7.5235	0.0011	7.5027	0.0011
MKEH	HU	7.5558	0.0030	7.5226	0.0033	7.4973	0.0034
NMIJ	JP	7.5561	0.0010	7.5236	0.0010	7.5025	0.0010
CENAM	MX	7.5561	0.0016	7.5239	0.0027	7.4973	0.0024
INDECOPI	PE	7.5542	0.0020	7.5209	0.0020	7.5013	0.0020
GUM	PL	7.5474	0.0013	7.5178	0.0014	7.4917	0.0016
VNIIFTRI	RU	7.5520	0.0020	7.5190	0.0021	7.4970	0.0023
SMU	SK	7.5554	0.0016	7.5220	0.0015	7.5005	0.0019
NIMT	TH	7.5006	0.0197	7.4679	0.0143	7.4482	0.0110
UME	TR	7.5337	0.0010	7.5291	0.0010	7.4812	0.0010
UMTS	UA	7.5683	0.0028	7.5295	0.0021	7.5055	0.0021
LATU	UY			7.5206	0.0050	7.5028	0.0050
NIST	US	7.5578	0.0008	7.5255	0.0008	7.5036	0.0008

Tab 5: Results at 15 °C, 25 °C and 37 °C. The uncertainty is stated as standard measurement uncertainty (*k* = 1)

Institute	Country	Acidity function at 5°C	***u*** (k=1)	Acidity function at 50°C	***u*** (k=1)
BIM/ NCM	BG			7.4839	0.0022
PTB	DE	7.6062	0.0012	7.4981	0.0011
NMIJ	JP	7.6038	0.0011	7.4983	0.0011
GUM	PL	7.5983	0.0014	7.4756	0.0022
NIMT	TH	7.5724	0.0085	7.4345	0.0043
UME	TR	7.6019	0.0010	7.4551	0.0009
UMTS	UA	7.6108	0.0026	7.4947	0.0034
NIST	US	7.6082	0.0010	7.4990	0.0010

Tab 6: Results at 5 °C and 50 °C. The uncertainty is stated as standard measurement uncertainty (*k* = 1)

Institute	**Country**	***E^0*/V at 15 °C**	***u(E^0)* (k=1)**	***E^0*/V at 25 °C**	***u(E^0)* (k=1)**	***E^0*/V at 37 °C**	***u(E^0)* (k=1)**
BIM/ NCM	BG	0.228565	0.0001	0.222338	0.0001	0.214234	0.0001
INMETRO	BR	0.228604	0.000065	0.222457	0.000066	0.214230	0.000066
CMI	CZ	0.228616	0.00039	0.222463	0.00039	0.214488	0.00058
DFM	DK	0.22871	0.000058	0.22249	0.000059	0.21430	0.000062
PTB	DE	0.228673	0.000056	0.222459	0.000058	0.214235	0.000060
MKEH	HU	0.22769	0.00017	0.22130	0.00017	0.21239	0.0002
NMIJ	JP	0.228618	0.000039	0.222445	0.000043	0.214285	0.000045
CENAM	MX	0.228464	0.000046	0.222209	0.000041	0.214054	0.000055
GUM	PL	0.228530	0.000031	0.222375	0.000024	0.214215	0.000026
VNIIFTRI	RU	0.228728	0.000072	0.222501	0.000074	0.214227	0.000077
SMU	SK	0.228675	0.000045	0.222490	0.000046	0.214217	0.000047
NIMT	TH	0.234846	0.000027	0.229284	0.000027	0.223195	0.000027
UME	TR	0.2287168	0.0000393	0.2225763	0.0000403	0.2145406	0.0000415
UMTS	UA	0.22787	0.00010	0.22189	0.00009	0.21374	0.00009
NIST	US	0.228523	0.000007	0.222339	0.000021	0.214239	0.000020

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

Institute	**Country**	***E^0*/V at 5 °C**	***u(E^0)* (k=1)**	***E^0*/V at 50 °C**	***u(E^0)* (k=1)**
BIM/ NCM	BG			0.20454	0.0002
PTB	DE	0.234111	0.000054	0.204456	0.000062
NMIJ	JP	0.234082	0.000042	0.204494	0.000052
GUM	PL	0.234082	0.000041	0.204525	0.000026
NIMT	TH	0.214921	0.000026	0.203801	0.000028
UME	TR	0.2344227	0.0000383	0.2045240	0.0000429
UMTS	UA	0.23369	0.00010	0.20404	0.00010
NIST	USA	0.234029	0.000012	0.204440	0.000036

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

Institute	Country	*u(intercept)*			Slope (extrapolation)		
		15 °C	25 °C	37 °C	15 °C	25 °C	37 °C
BIM/ NCM	BG	0.001	0.0008	0.0005	-1.488	-1.073	-1.14
INMETRO	BR	0.0010	0.0011	0.0021	-0.8740	-0.9446	-0.7864
CMI	CZ	0.001	0.0011	0.0019	-1.0662	-1.1805	-1.1874
DFM	DK	0.00078	0.0007605	0.0007653	-1.129	-1.052	-1.052
PTB	DE	0.00050	0.00045	0.00039	-0.99	-1.00	-1.00
MKEH	HU	0.00046	0.00152	0.001648	-0.4131	-0.4681	-0.527
NMIJ	JP	0.00033	0.00021	0.00022	-1.1324	-1.1226	-1.1307
CENAM	MX	0.0014	0.0020	0.0021	-1.135512	-1.1028012	-1.386604
GUM	PL	0.000586	0.0007922	0.0011771	-0.5554503	-0.6981866	-0.5829760
VNIIFTRI	RU	0.0006	0.0008	0.001	-0.975	-0.894	-0.765
SMU	SK	0.001	0.001077	0.0015869	-0.6879	-0.6894	-0.8875
NIMT	TH	0.017	0.009922	0.0024868	-1.1174	-0.5221	-0.5283
UME	TR	0.00043	0.00038	0.00049	-1.4668	-1.5334	-0.8702
UMTS	UA	0.0020	0.0013	0.0012	-1.56	-1.15	-1.38
NIST	US	0.00068	0.00058	0.00052	-1.123492	-1.122049	-1.105089

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

Institute	Country	*u(intercept)*		Slope (extrapolation)	
		5 °C	50 °C	5 °C	50 °C
BIM/ NCM	BG		0.0008		-0.780
PTB	DE	0.00055259	0.00040	-0.99	-1.02
NMIJ	JP	0.00033	0.00031	-1.1343	-1.1404
GUM	PL	0.00042	0.00196	-0.929167719	-0.531116
NIMT	TH	0.008	0.0041	-0.3781	-0.7199
UME	TR	0.00042	0.00014	-1.6169	-0.5352
UMTS	UA	0.0016	0.0029	-1.23	-1.07
NIST	USA	0.0008	0.00072	-1.163131	-1.060613

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

NMI	HCl molality m_{Cl} (mol kg^{-1})	Standardization technique for HCl
BIM/ NCM	0.0100	potentiometric titration
CENAM	0.0101	coulometry
CMI	0.0100	coulometry
DFM	0.0099996	Coulometry + gravimetric dilution
GUM	0.0100	coulometry
INMETRO	0.0099968	coulometry
MKEH	0.010005	coulometry
NIMT	0.0101	potentiometric titration
NIST	0.0100	coulometry
NMIJ	0.010000	coulometry
PTB	0.0100	coulometry
SMU	0.0100	coulometry
UMTS	0.01000	coulometry
UME	0.01000	coulometry
VNIIFTRI	0.0100	coulometry

Tab.11: HCl molality and method of standardization

Calculation of the KCRV and its uncertainty

Three possibilities for determination of the KCRV are listed in Table 12 and 13. For all estimators the institutes using a secondary setup INDECOPI, LATU, IBMETRO were omitted from the calculation of the KCRV. A common consistency check was performed based on a CCQM guide (CCQM Guidance note: Estimation of a consensus KCRV and associated Degrees of Equivalence). However based on the procedure shown in this document a consistent subset among the institutes could not be determined. Therefore, results, which differed considerably from the bulk of the results – as can be seen from the figures 6-10 – were considered to be outliers. NIMT results were considered to be outlier at all temperatures and therefore also have been omitted for the calculation of the KCRV. UME results were considered to be outlier at 15 °C, 37 °C and 50 °C and were therefore omitted for the calculation of the KCRV at these temperatures. NIMT and UME agreed on this decision. The standard deviation for the estimators at all temperatures after rejection of the outliers is considerably smaller as for the estimators containing all results.

	15 °C		25 °C		37 °C	
Estimator	Value	*u* (k = 1)	Value	*u* (k = 1)	Value	*u* (k = 1)
Mean	7.5563	0.0013	7.5241	0.0007	7.4993	0.0011
Median	7.5561	0.0003	7.5235	0.0008	7.5005	0.0018
uncertainty weighted mean	7.5561	0.0003	7.5246	0.0003	7.5013	0.0004
Birge ratio	2.54		2.51		2.57	

Tab.12: Values of candidate estimator for the KCRV at 15 °C, 25 °C and 37 °C for CQQM-K99

	5 °C		50 °C	
Estimator	Value	*u* (k = 1)	Value	*u* (k = 1)
Mean	7.6049	0.0018	7.4916	0.0039
Median	7.6050	0.0029	7.4964	0.0076
uncertainty weighted mean	7.6043	0.0005	7.4960	0.0006
Birge ratio	3.16		5.10	

Tab.13: Values of candidate estimator for the KCRV for CQQM-K99 at 5 °C and 50 °C

The uncertainty weighted mean pa^0_R was agreed on at the EAWG meeting in the frame of the CCQM meeting in Paris (16./17.04.2015). For CCQM-K99 it was calculated using Eq4. Where *N* is the number of participants, w_i is the normalized weight for participant *i*, and pa^0_i is the result for participant *i*.

$$\mathrm{p}a_R^0 = \sum_{i=1}^{N} w_i \mathrm{p}a_i^0 \tag{4}$$

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

$$w_i = \frac{C}{u(x_i)^2} \tag{5}$$

$$C = \frac{1}{\sum_{i=1}^{N} \frac{1}{u(x_i)^2}} \tag{6}$$

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). $u_R(pa^0_R)$ is given by Eq 7.

$$u_R(\mathrm{p}a_R^0) = \sqrt{\frac{\sum_{i=1}^{N} w_i \left(\mathrm{p}a_i^0 - \mathrm{p}a_R^0\right)^2}{(N-1)\cdot \sum_{i=1}^{N} w_i}} \tag{7}$$

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.

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

The Birge ratio R = u_R/u_m calculated for the CCQM-K99 is always larger than one as given in tables 12 and 13, 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 $u_R(pa^0_R)$ were taken as the standard uncertainty of the KCRV, *u*(KCRV). The final value of the KCRV and its standard uncertainty (k =1) is listed for each temperature in table 14.

15 °C		25 °C		37 °C		5 °C		50 °C	
KCRV	u(k = 1)	KCRV	u(k = 1)	KCRV	u(k = 1)	KCRV	u(k = 1)	KCRV	u(k = 1)
7.5561	0.0009	7.5246	0.0008	7.5013	0.0009	7.6043	0.0015	7.4960	0.0029

Tab. 14: KCRV and its standard uncertainty, *U(k=1)*, for CCQM-K99

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.

$$D_i = \left(\mathrm{pa}_i^0 - \mathrm{KCRV}\right) \qquad (9)$$

$$u_{corr}(D_i) = \sqrt{u_{corr}^2(\mathrm{KCRV}) + (1 - 2 \cdot w_i) \cdot u^2\left(pa_i^0\right)} \qquad (10)$$

Values for D_i and $u(D_i)$ are given in Table 15 and 16

Institute	**Country**	***D*$_i$ at 15 °C**	***U* (k=2)**	***D*$_i$ at 25 °C**	***U* (k=2)**	***D*$_i$ at 37 °C**	***U* (k=2)**
BIM/ NCM	BG	-0.0008	0.0043	-0.0018	0.0042	-0.0062	0.0043
IBMETRO	BO			0.0030			
INMETRO	BR	0.0021	0.0030	0.0009	0.0029	-0.0007	0.0047
CMI	CZ	0.0024	0.0030	0.0041	0.0028	-0.0059	0.0043
DFM	DK	0.0002	0.0022	-0.0014	0.0020	0.0008	0.0022
PTB	DE	-0.0008	0.0027	-0.0011	0.0026	0.0014	0.0027
MKEH	HU	-0.0003	0.0062	-0.0020	0.0067	-0.0040	0.0070
NMIJ	JP	-0.0000	0.0025	-0.0010	0.0024	0.0012	0.0026
CENAM	MX	-0.0001	0.0035	-0.0007	0.0056	-0.0040	0.0051
INDECOPI	PE	-0.0019	0.0043	-0.0037	0.0042	0.0001	0.0043
GUM	PL	-0.0087	0.0030	-0.0068	0.0031	-0.0096	0.0036
VNIIFTRI	RU	-0.0041	0.0043	-0.0056	0.0044	-0.0043	0.0049
SMU	SK	-0.0007	0.0035	-0.0026	0.0033	-0.0008	0.0041
NIMT	TH	-0.0555	0.0394	-0.0567	0.0286	-0.0531	0.0221
UME	TR	-0.0224	0.0025	0.0045	0.0023	-0.0201	0.0026
UMTS	UA	0.0122	0.0058	0.0049	0.0044	0.0042	0.0045
LATU	UY			-0.0040	0.0101	0.0016	0.0101
NIST	US	0.0017	0.0022	0.0010	0.0021	0.0023	0.0022

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

Institute	Country	D_i at 5 °C	*U* (k=2)	D_i at 50 °C	*U* (k=2)
BIM/ NCM	BG			-0.0121	0.0071
PTB	DE	0.0019	0.0036	0.0021	0.0060
NMIJ	JP	-0.0006	0.0036	0.0023	0.0059
GUM	PL	-0.0060	0.0039	-0.0204	0.0071
NIMT	TH	-0.0319	0.0172	-0.0615	0.0102
UME	TR	-0.0024	0.0034	-0.0409	0.0058
UMTS	UA	0.0065	0.0059	-0.0013	0.0088
NIST	US	0.0039	0.0034	0.0030	0.0059

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

Conclusions

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.

How far the light shines

Phosphate reference buffer solutions are widely used as pH standards in the neutral range. In this comparison the participants have demonstrated their capability to measure the pH value of a phosphate buffer in the range between pH (25 °C) = 6.8 to 7.5. This statement is valid for the temperature range from 5°C to 50°C, however, regarding the assessment of CMCs it must be emphasized that the corresponding measurement uncertainties increase at 5°C and 50°C. Consequently, CMC uncertainties must consider the temperature dependence in case.

Figures

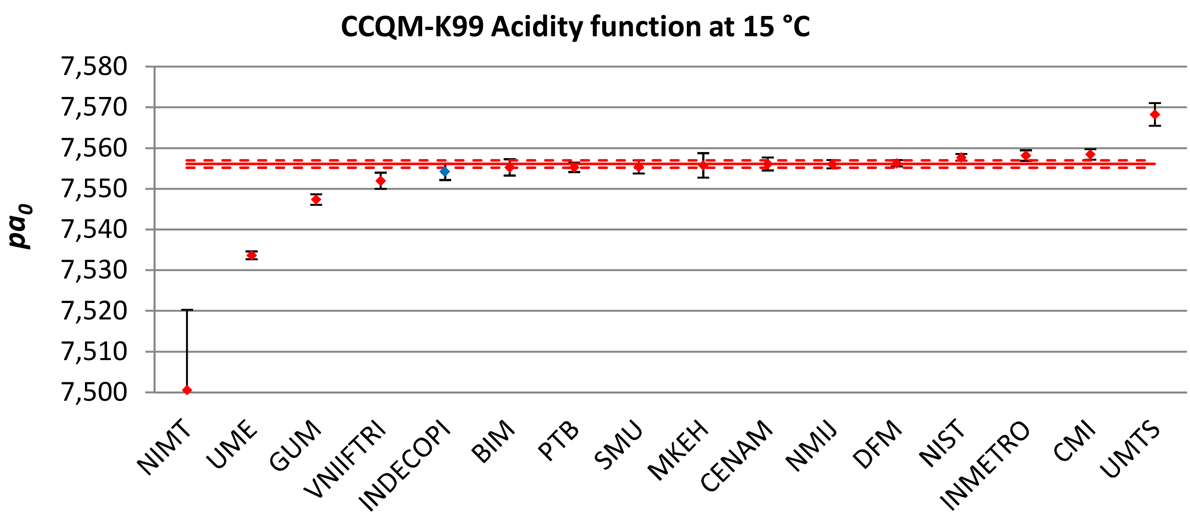

Fig 6: CCQM-K99 pa^0 at 15 °C. The standard uncertainty (k=1) is given.
Red line: KCRV and dotted lines: uncertainty of the KCRV (k = 1).

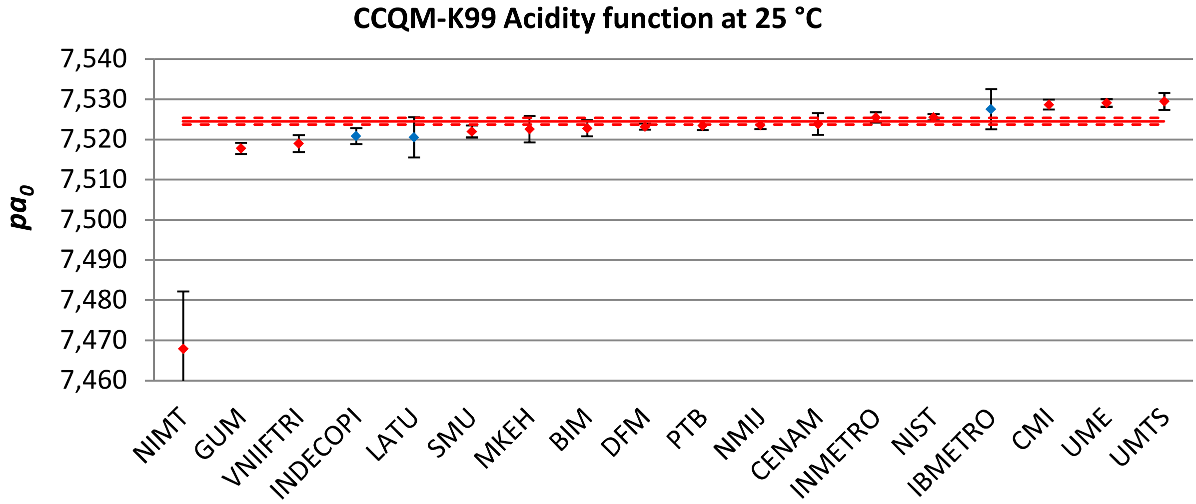

Fig. 7: CCQM-K99 pa^0 at 25 °C. The standard uncertainty (k=1) is given.
Red line: KCRV and dotted lines: uncertainty of the KCRV (k = 1).

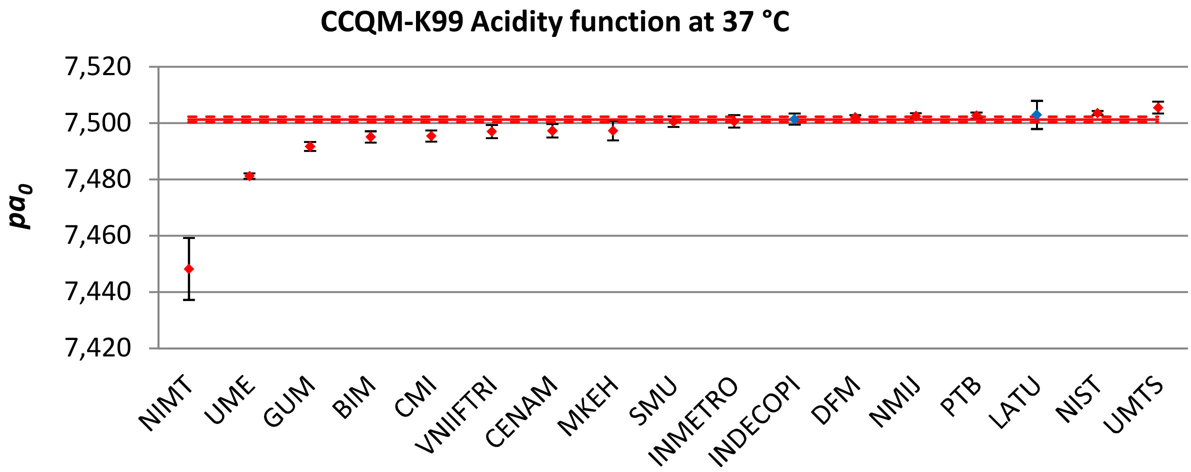

Fig. 8: CCQM-K91 pa^0 at 37 °C. The standard uncertainty (k=1) is given.
Red line: KCRV and dotted lines: uncertainty of the KCRV (k = 1).

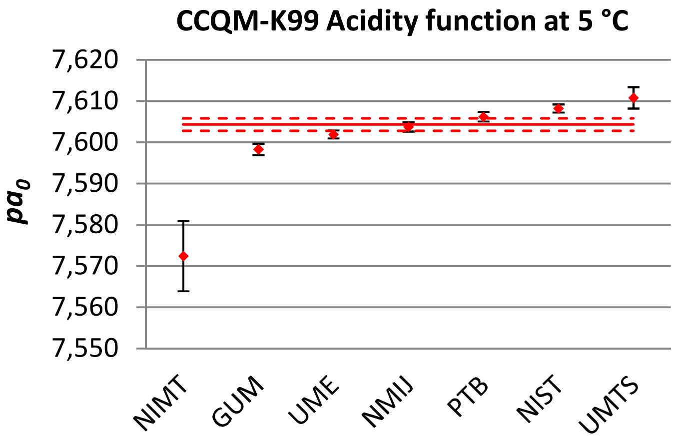

Fig. 9: CCQM-K99 pa^0 at 5 °C. The standard uncertainty (k=1) is given.
Red line: KCRV and dotted lines: uncertainty of the KCRV (k =1).

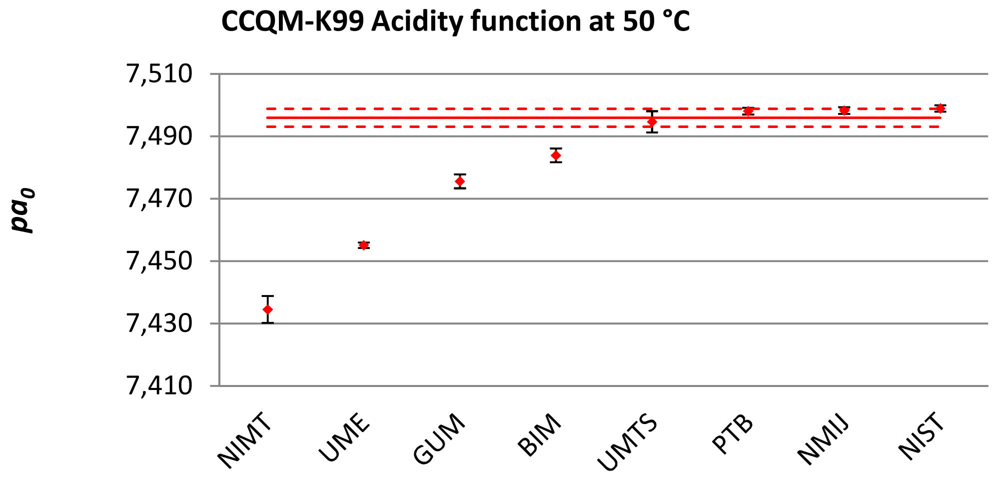

Fig. 10: CCQM-K99 pa^0 at 50 °C. The standard uncertainty (k=1) is given.
Red line: KCRV and dotted lines: uncertainty of the KCRV (k = 1).

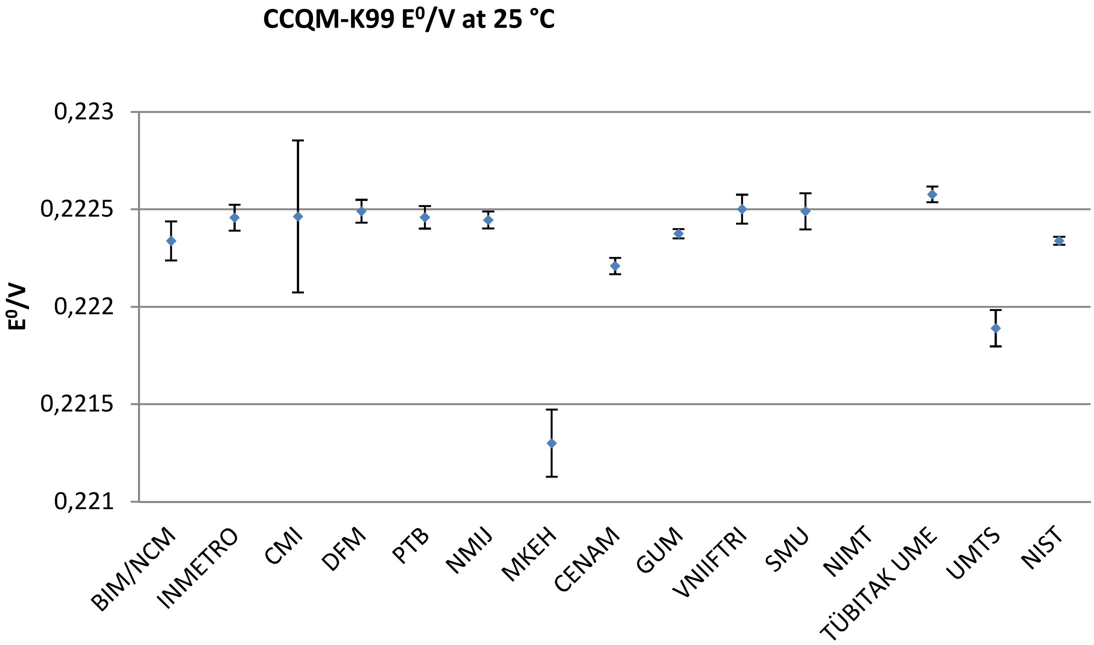

Fig. 11: Standard potential of the Ag/AgCl electrodes at 25 °C. The result of NIMT is out of range.

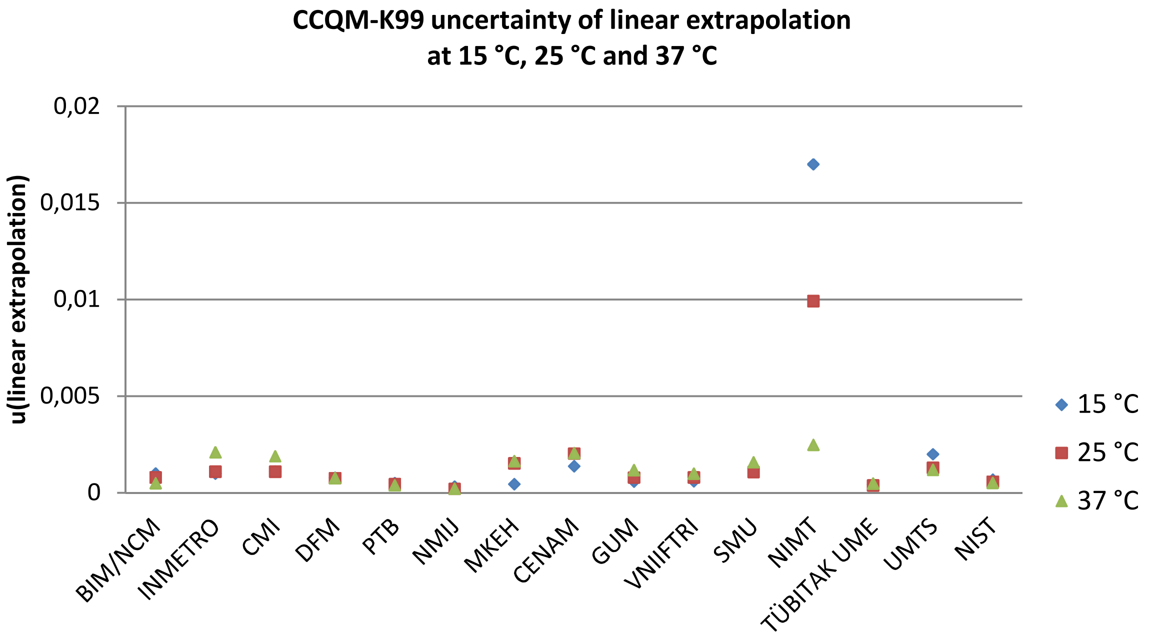

Fig. 12: Standard uncertainty (k = 1) of the regression line at 15 °C, 25 °C and 37 °C

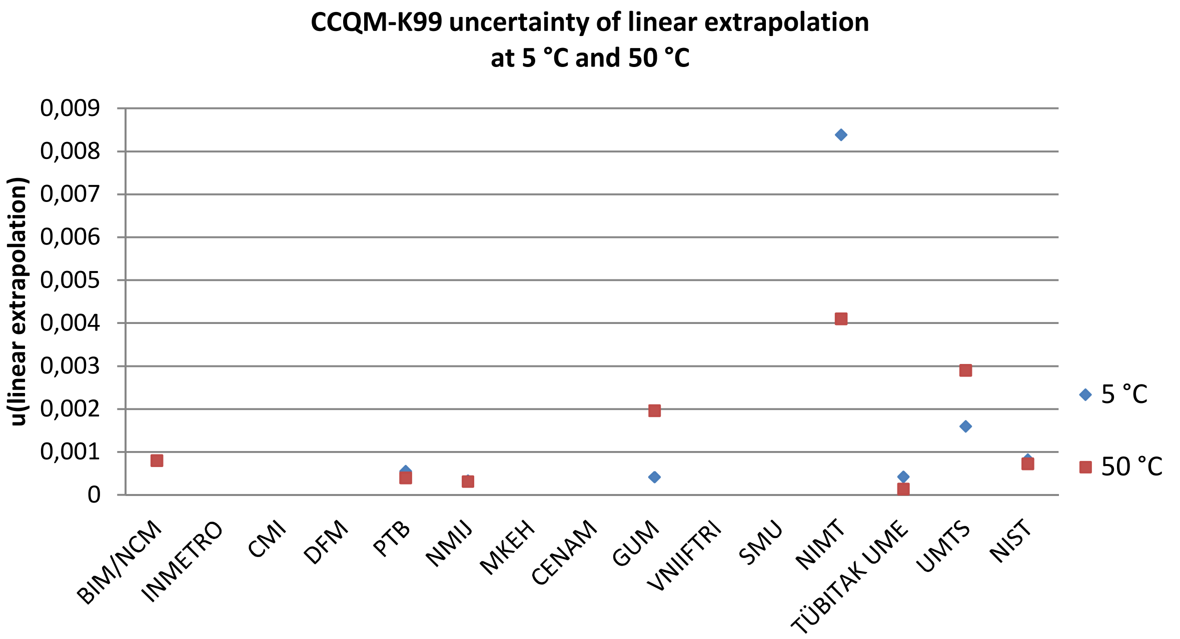

Fig. 13: Standard uncertainty (k = 1) of the regression line at 5 °C and 50 °C

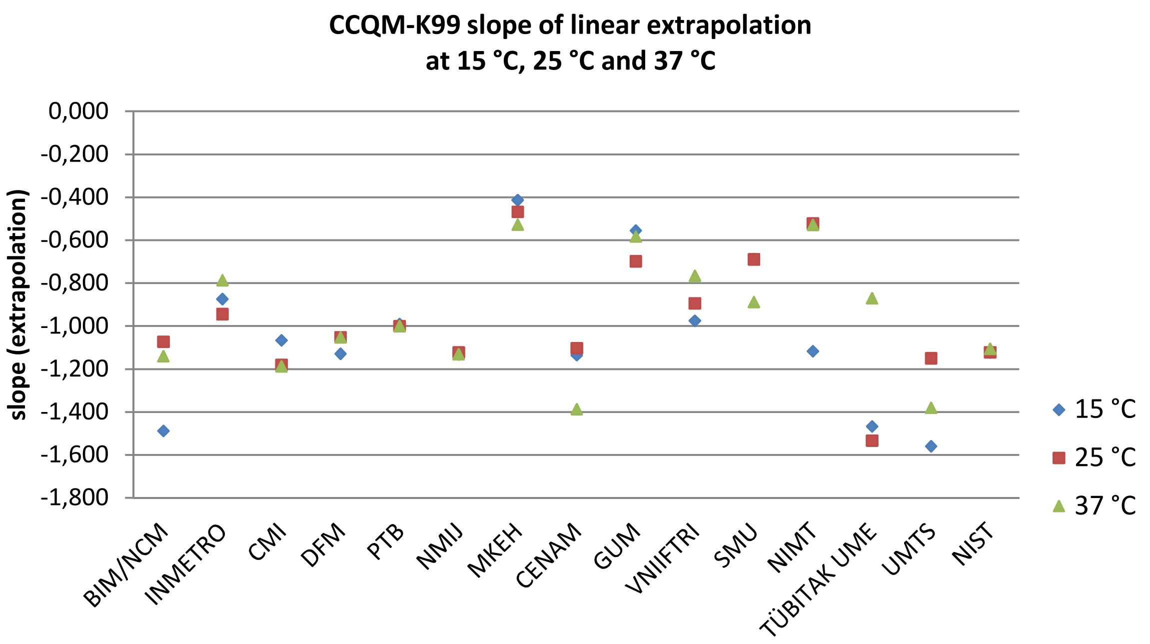

Fig. 14: Slope of the regression line at 15°C, 25 °C and 37 °C

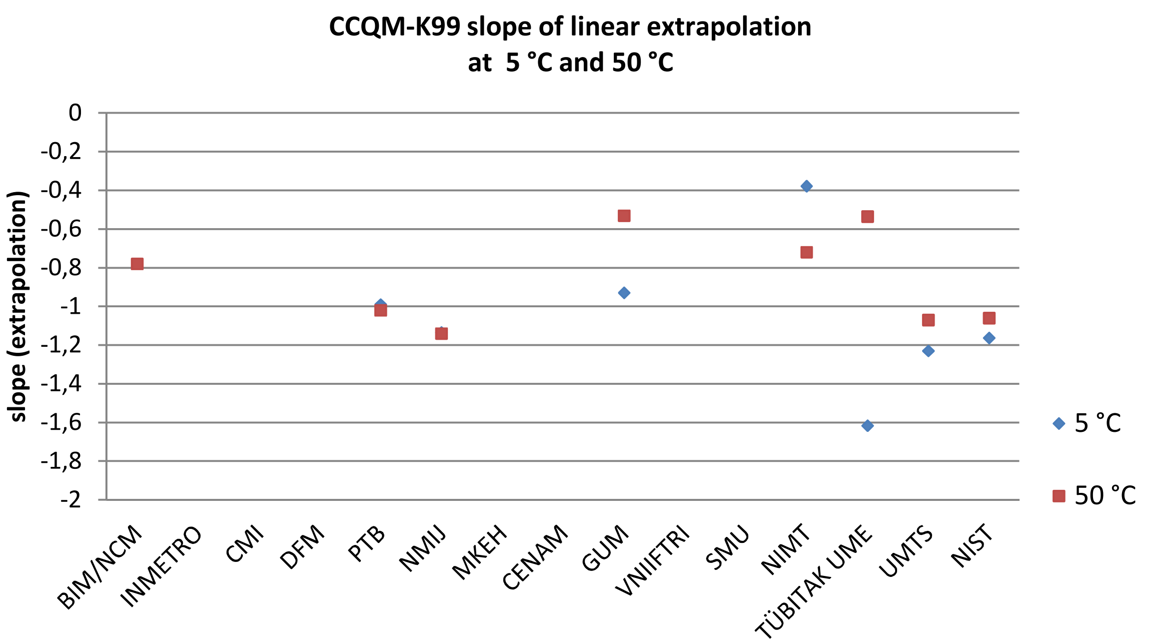

Fig. 15: Slope of the regression line at 5°C and 50 °C

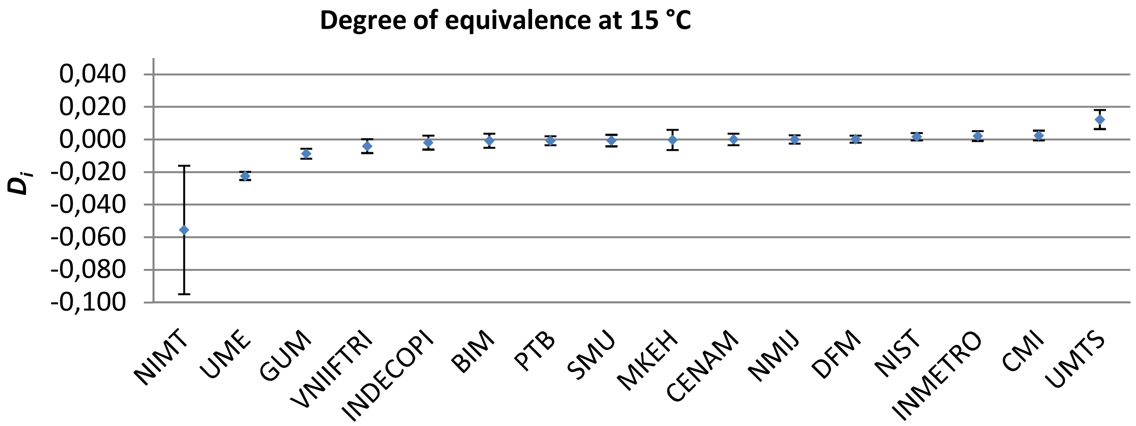

Fig. 16: Degree of Equivalence and its uncertainty (k = 2) at 15 °C.

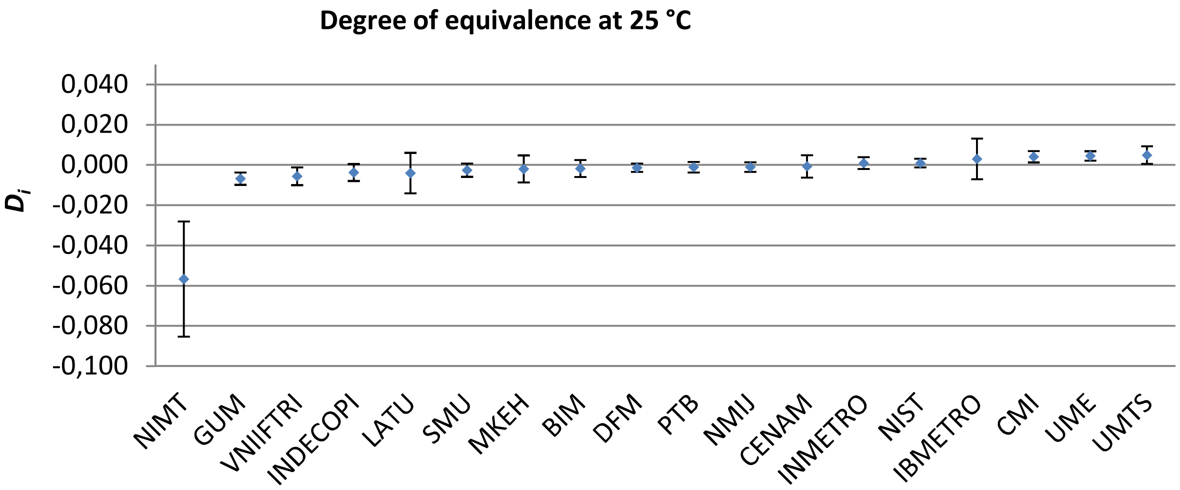

Fig. 17: Degree of Equivalence and its uncertainty (k = 2) at 25 °C.

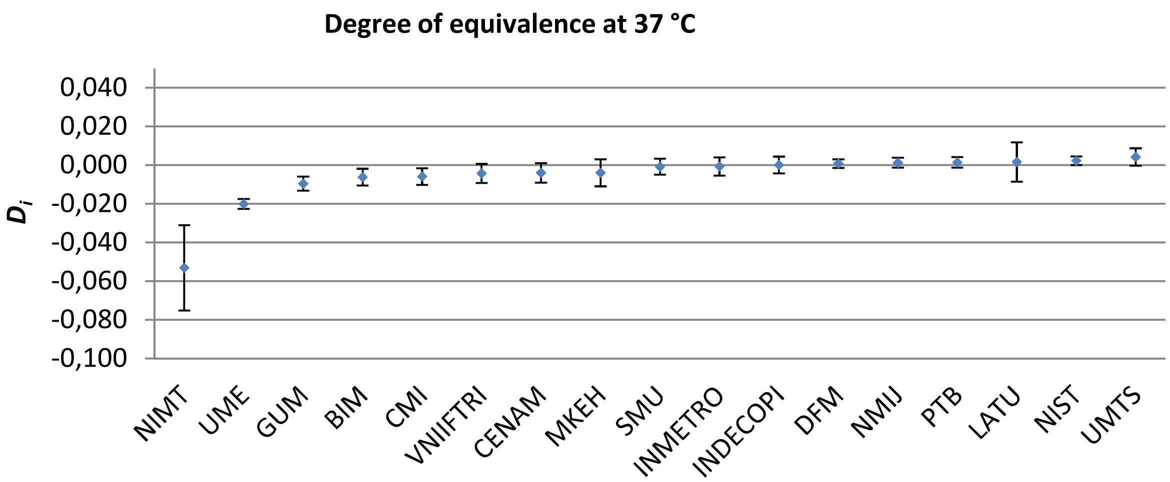

Fig. 18: Degree of Equivalence and its uncertainty (k = 2) at 37 °C.

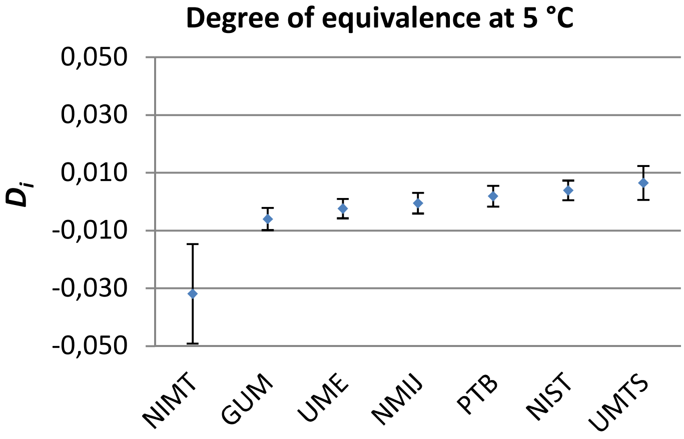

Fig. 19: Degree of Equivalence and its uncertainty (*k* = 2) at 5 °C.

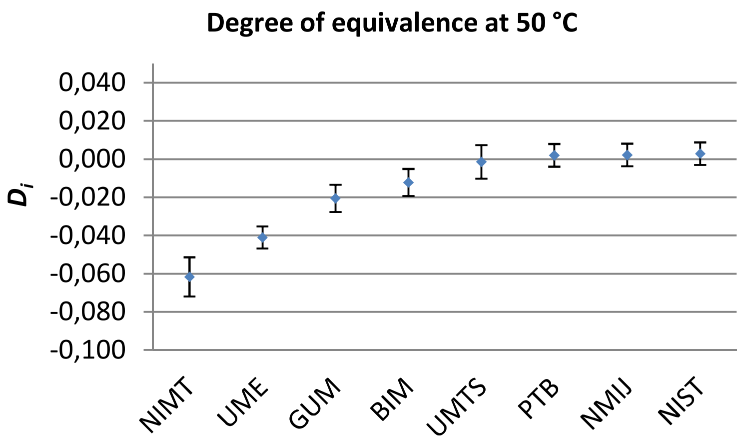

Fig. 20: Degree of Equivalence and its uncertainty (*k* = 2) at 50 °C.