Report of Key Comparison SIM.QM-K91

pH of phthalate buffer (nominal pH ~4.01 at 25 ºC)

Final Report

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Abstract

At the SIM meeting in Buenos Aires, from 30 May to 1 June 2012, it was decided to perform a RMO Key comparison on pH measurement coordinated by INMETRO.

Therefore, this RMO Key comparison, named SIM.QM-K91, aimed to investigate the degree of equivalence of measurement procedures for the pH determination of a phthalate buffer solution (nominal pH around 4.01 at 25 °C). 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, $KHC_8H_4O_4$, is one of the primary pH reference buffer solutions recommended by IUPAC [1].

It was only allowed to participate in this comparison by using a differential cell [2] or a glass electrode, instead of primary cells [1], if the highest metrological standard in the institute or if the CMCs are based on the type of cell to be used. The results obtained by INMETRO and NIST (which have also participated in CCQM-K91 comparison) were used to link the results from the other institutes to the KCRV of CCQM-K91.

In this comparison, pH measurements were performed at 25 °C, and optionally also at 15 °C and 37 °C. Nine institutes took part of the comparison, whose results are presented in this report.

Contents

Introduction

Metrology area

Amount of Substance

Branch

Electrochemistry

Subject

Determination of the acidity function at zero chloride molality (pa^0) of an unknown phthalate buffer (nominal pH ~4.01 at 25 °C) at 25 °C, and optionally at 15 °C and 37 °C, by using Harned cell, differential potentiometric cell, or glass electrode measurements.

Time schedule

Dispatch of the samples	01 October 2014
Deadline for receipt of the measurement report	30 November 2014
Draft A Report	22 January 2015
Draft B Report	02 April 2015

Coordinating laboratory

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Participants

Nine institutes, including INMETRO, have participated in the SIM.QM-K91 comparison. Information about these institutes are shown in Table 1.

Table 1. Participants in the SIM.QM-K91 comparison.

Nº	Country	Institute	Acronym	Contact Person
1	BG	Bulgarian Institute of Metrology	BIM	L. Dimitrova
2	BO	Instituto Boliviano de Metrología	IBMETRO	M. Delgado
3	BR	Instituto Nacional de Metrologia, Qualidade e Tecnologia	INMETRO	F.B. Gonzaga

4	CO	Instituto Nacional de Metrología de Colombia	INM	R.O. Cristancho
5	PE	Instituto Nacional de Defensa de la Competencia y de la Proteccion de la Propiedad Intelectual	INDECOPI	G.T. Canaza
6	TH	National Institute of Metrology	NIMT	N. Tangpaisarnkul
7	UA	Ukrmetrteststandart	UMTS	V. Gavrilkin
8	US	National Institute of Standards and Technology	NIST	K.W. Pratt
9	UY	Laboratorio Tecnológico del Uruguay	LATU	S. Fajardo

Sample description

Sample preparation and distribution

On 21 March 2014 one batch of phthalate buffer solution was prepared from deionized water and potassium hydrogen phthalate and transferred to 120 HDPE bottles (250 mL each). The bottles were properly closed, labeled and numbered (according to the order filling), sealed using paraffin tape and put into plastic bags. The mass fraction of water in the solution was w(H2O) = 0.989881 g g^{-1}.
Each participant received from four to eight HDPE bottles, selected randomly. Shipment to all participants was performed on 1 October 2014 by courier company FedEx and the tracking number was reported by e-mail. Except IBMETRO, all participants received the samples up to 13 October 2014. IBMETRO has only received the samples on 11 November 2014.

Check of bottles integrity

The participants were requested to inspect the received bottles for visible damage (bottle broken or with leakage) and to weigh them in order to verify if they keep unchanged during the transport. No visible damage was reported for all bottles.
Figure 1 shows the relative deviation for the bottles, taken into account the mass at origin (measured at INMETRO) and the mass at destination (reported by the other institutes). Although IBMETRO has received eight bottles, the masses of only three bottles (used in the measurements) were reported. As can be seen, all bottle masses reported agreed within 0.01% with the bottle masses measured at INMETRO.

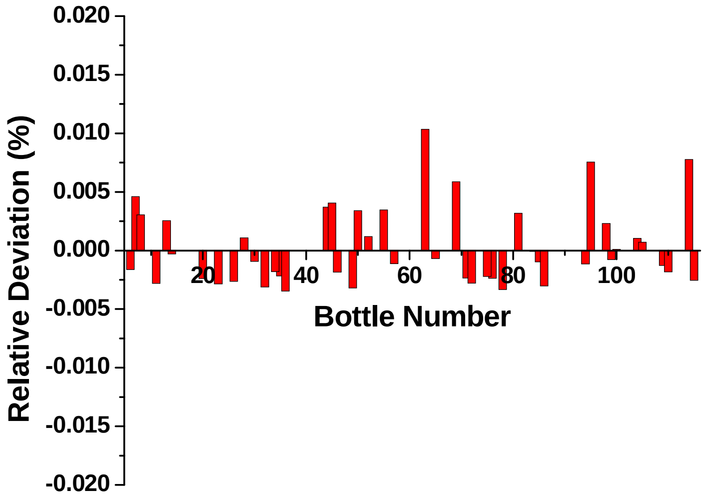

Figure 1. Relative deviation between the masses at origin (INMETRO) and destination.

Check of homogeneity and short term stability

Before shipment, the homogeneity and the short term stability of the samples were checked by differential potentiometric measurements, at 25 °C, using a Baucke-based cell [2]. For the homogeneity, one bottle from the beginning of the batch (considering the filling order) was measured against four other bottles along the batch. The data are shown in Table 2. As can be seen, all potential differences measured are related to pH deviations (between the reference and testing bottles) lower than 0.0004, indicating that there was no significant pH differences between the bottles.

Table 2. Results obtained for the homogeneity study.

Reference Bottle	Testing Bottle	ΔE (µV)	|ΔpH|
3	5	−6.12	0.0001
	40	−10.16	0.0002
	80	8.73	0.0001
	119	15.25	0.0003

For the short term stability, two reference bottles stored at room temperature (22 °C) were measured against four other bottles stored at 4 and 50 °C for 15 and 30 days. The bottles were selected randomly. The data are shown in Table 3. As can be seen, although the potential differences measured were slightly higher than those obtained in the homogeneity study, the values are still related to negligible pH deviations (between the reference and testing bottles), indicating that there was no significant pH variations when the samples were stored at 4 or 50 °C for up to 30 days.

Table 3. Results obtained for the short term stability study.

Reference Bottle	Temp. Reference (°C)	Testing Bottle	Temp. Testing (°C)	Storage Time (days)	ΔE (µV)	|ΔpH|
41	22	17	4	15	22.50	0.0004
		38	50		25.72	0.0004
66		116	4	30	22.21	0.0004
		61	50		13.68	0.0002

Check of long term stability

In order to check the stability of the sample, primary pH measurements were taken at 25 °C for some bottles, selected randomly, in irregular intervals along about four months (from 16 September 2014 to 15 January 2015). The measurement results are given in Figure 2. For these results, the linear regression statistical test (using the least-squares method), for 95% confidence level, gave a *p*-value (for the time) of 0.979, showing that the acidity function variation over time was statistically not significant (*p*-value > 0.05). In addition, the chi-square statistical test, also for 95% confidence level, gave a calculated chi-square of 2.546, which is lower than the tabled chi-square (9.488), showing that the acidity function results over time were statistically similar, taking into account their uncertainties.

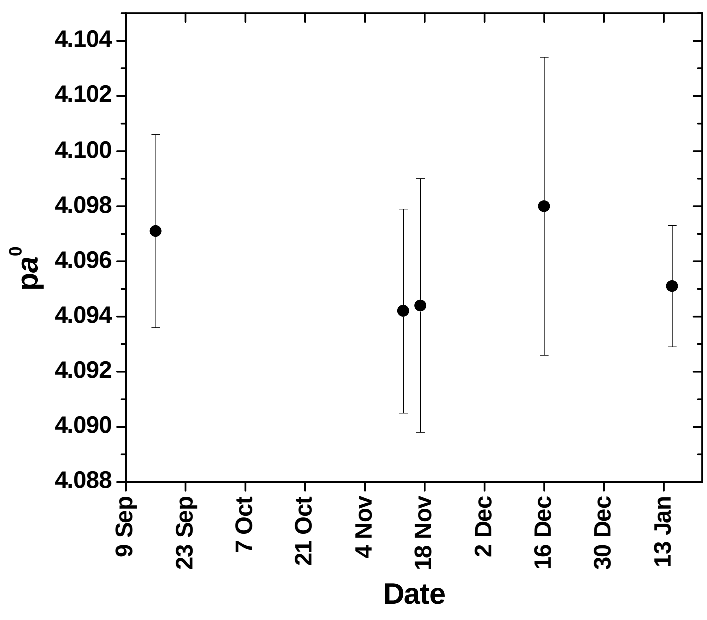

Figure 2. Measurement results for checking the stability of the samples, with expanded uncertainties (k=2).

Results and discussion

Reported results

All institutes have sent their measurement reports. The timetable and some measurement details used by the institutes are given in Table 4. IBMETRO and INDECOPI did not inform in their measurement reports the time periods of when their measurements were taken. The results reported by the institutes are shown in Tables 5 to 7 and Figures 3 to 5. The pH values reported by those institutes that used a differential potentiometric cell were recalculated as pa^0 by using a buffer ionic strength of 0.0535 mol kg^{-1} and Debye–Hückel temperature-dependent constants cited in the literature [1].

Table 4. Timetable and some measurement details.

Country	Sample Received	Measurement Period	Report Date	Measurement Cell	Measurement Temperatures
BG	9 Oct	21 to 25 Nov	30 Nov	Primary	15, 25, 37 °C
BO	11 Nov	—	28 Nov	Differential (INMETRO CRM)	25 °C
BR	—	13 to 26 Nov	28 Nov	Primary	15, 25, 37 °C
CO	6 Oct	16 to 23 Oct	18 Nov	Differential (BIM CRM)	25 °C
PE	13 Oct	—	1 Dec	Differential (NIST and PTB CRMs)	15, 25, 37 °C
TH	6 Oct	8 Dec	19 Dec	Primary	15, 25, 37 °C
UA	9 Oct	13 to 18 Nov	29 Nov	Primary	15, 25, 37 °C
US	3 Oct	6 to 11 Nov	28 Nov	Primary	15, 25, 37 °C
UY	9 Oct	18 to 25 Nov	28 Nov	Differential (NIST CRM)	15, 25, 37 °C

Table 5. Results reported by the institutes, at 15 °C, with standard uncertainties (u).

Country	pH	pa^0	u (k=1)
BG	—	4.0850	0.0019
BR	—	4.0831	0.0020
PE	4.0011	4.0873	0.0015
TH	—	4.0759	0.0033
UA	—	4.0549	0.0027
US	—	4.0900	0.0018
UY	4.001	4.087	0.005

Table 6. Results reported by the institutes, at 25 °C, with standard uncertainties (u).

Country	**pH**	**p*a*^{0}**	**u (*k*=1)**
BG	—	4.0945	0.0021
BO	4.004	4.092	0.002
BR	—	4.0944	0.0023
CO	4.0097	4.0973	0.0026
PE	4.0068	4.0944	0.0015
TH	—	4.0845	0.0018
UA	—	4.0617	0.0019
US	—	4.0979	0.0015
UY	4.008	4.096	0.005

Table 7. Results reported by the institutes, at 37 °C, with standard uncertainties (u).

Country	**pH**	**p*a*^{0}**	**u (*k*=1)**
BG	—	4.1146	0.0019
BR	—	4.1177	0.0020
PE	4.0252	4.1147	0.0015
TH	—	4.1420	0.0038
UA	—	4.0724	0.0019
US	—	4.1184	0.0018
UY	4.027	4.117	0.005

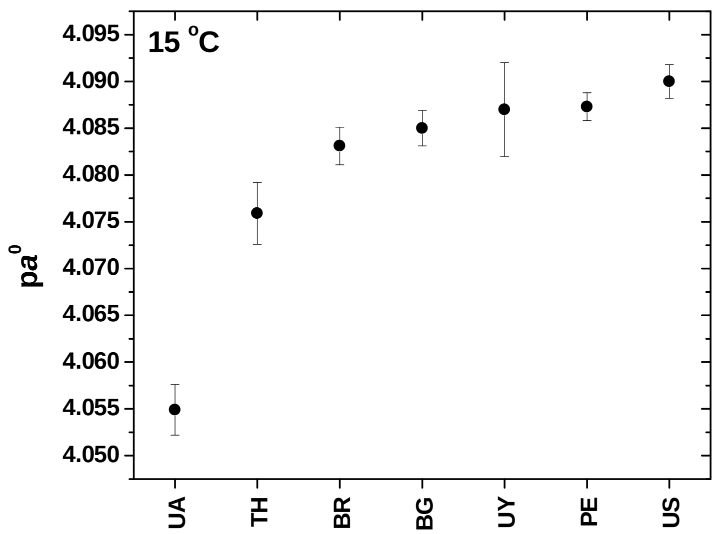

Figure 3. Acidity function results, at 15 °C, with standard uncertainties (*k*=1).

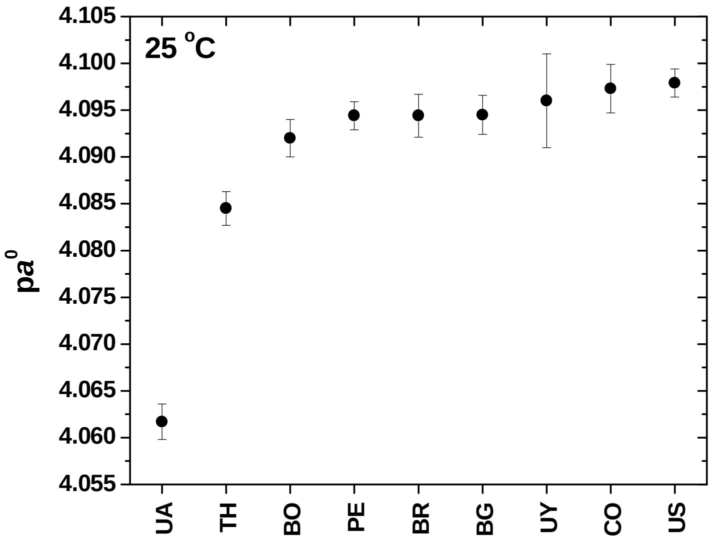

Figure 4. Acidity function results, at 25 °C, with standard uncertainties (*k*=1).

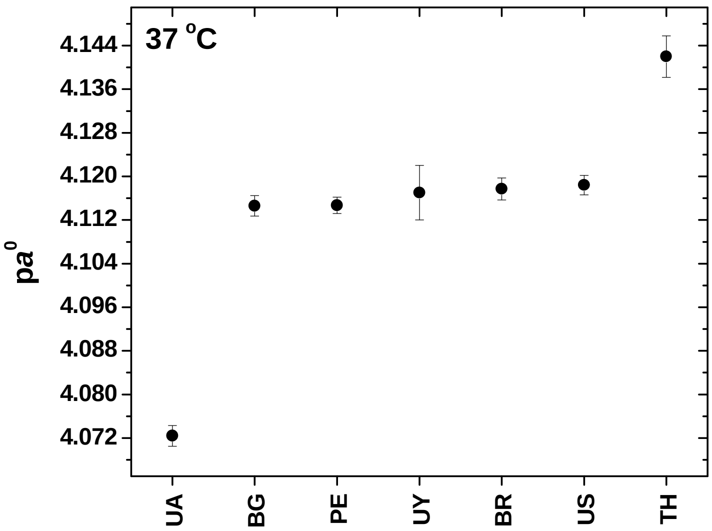

Figure 5. Acidity function results, at 37 °C, with standard uncertainties (*k*=1).

Degrees of equivalence and link to CCQM-K91

In order to link the results of the present key comparison to those of the original comparison CCQM-K91 [3], the results of INMETRO and NIST (linking laboratories) in both comparisons were taken into account in the calculation of the degrees of equivalence (D_i) for the other institutes in the present comparison, as shown previously [4,5]. For that, the average degree of equivalence of INMETRO and NIST in the original comparison ($D_{avg\text{-}CCQM}$) was calculated according to Equation 1.

$$D_{avg\text{-}CCQM} = AF_{avg\text{-}CCQM} - KCRV_{CCQM} \qquad (1)$$

Where $AF_{avg\text{-}CCQM}$ is the average result from INMETRO and NIST in the original comparison and $KCRV_{CCQM}$ is the reference value of the original comparison. Therefore, the $D_{avg\text{-}CCQM}$

value was used in the calculation of the degrees of equivalence for the other institutes in the present comparison (D_i), as shown in Equation 2.

$$D_i = AF_i - AF_{avg\text{-}SIM} + D_{avg\text{-}CCQM} \qquad (2)$$

Where AF_i is the result of a given institute in the present comparison and $AF_{avg\text{-}SIM}$ is the average result from INMETRO and NIST also in the present comparison. For the calculation of the degree of equivalence uncertainties for the other institutes in the present comparison (U_{D_i}), the standard uncertainty of the KCRV value of the original comparison ($u_{KCRV_{CCQM}}$) was also taken into account, as shown in Equation 3.

$$U_{D_i} = 2\sqrt{u_{AF_i}^2 + u_{AF_{avg\text{-}SIM}}^2 + u_{KCRV_{CCQM}}^2} \qquad (3)$$

Where u_{AF_i} is the standard uncertainty of a given institute in the present comparison and $u_{AF_{avg\text{-}SIM}}$ is the standard uncertainty of the average result between INMETRO and NIST also in the present comparison. The $u_{AF_{avg\text{-}SIM}}$ was calculated according to Equation 4.

$$u_{AF_{avg\text{-}SIM}} = \sqrt{\frac{s^2}{N}} \qquad (4)$$

Where s is the standard deviation between the results of INMETRO and NIST in the present comparison and N is the number of results (equals to 2 in this case). The D_i and U_{D_i} results are given in Table 8. Figures 6 to 8 show plots of these results in comparison to those of the original comparison.

Table 8. Degrees of equivalence linked to CCQM-K91, with expanded uncertainties (U).

Country	**15 °C**		**25 °C**		**37 °C**	
	D_i	**U (*k*=2)**	**D_i**	**U (*k*=2)**	**D_i**	**U (*k*=2)**
BG	−0.0019	0.0079	−0.0019	0.0055	−0.0039	0.0040
BO	—	—	−0.0045	0.0054	—	—
CO	—	—	0.0008	0.0063	—	—
PE	0.0004	0.0076	−0.0020	0.0047	−0.0038	0.0032
TH	−0.0111	0.0096	−0.0119	0.0051	0.0235	0.0077
UA	−0.0320	0.0088	−0.0347	0.0052	−0.0461	0.0040
UY	0.0000	0.0122	−0.0004	0.0106	−0.0015	0.0101

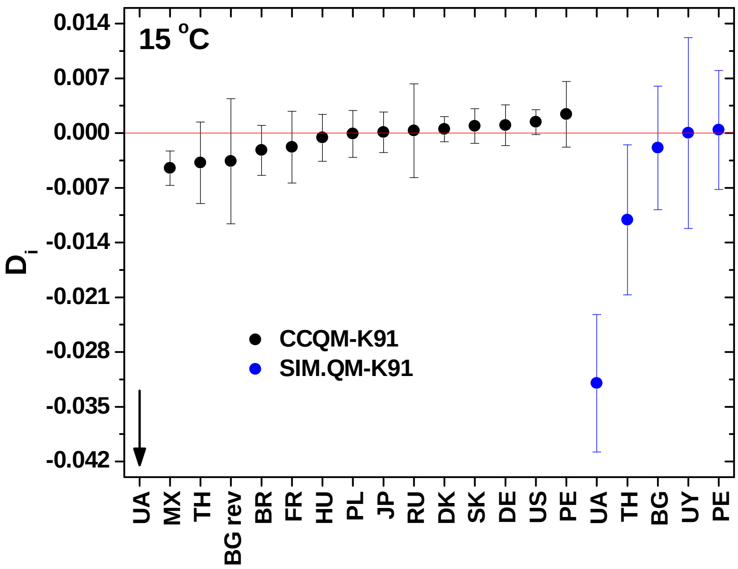

Figure 6. Degrees of equivalence linked to CCQM-K91, with expanded uncertainties (*k*=2), for results at 15 °C.

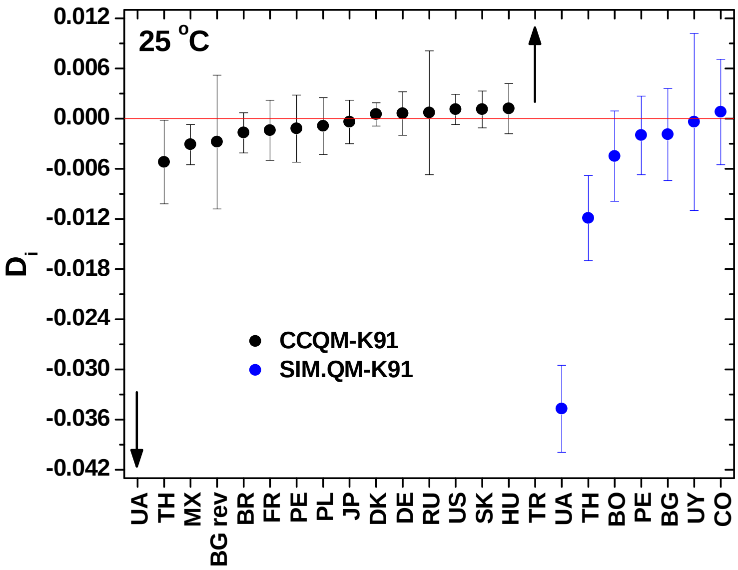

Figure 7. Degrees of equivalence linked to CCQM-K91, with expanded uncertainties (*k*=2), for results at 25 °C.

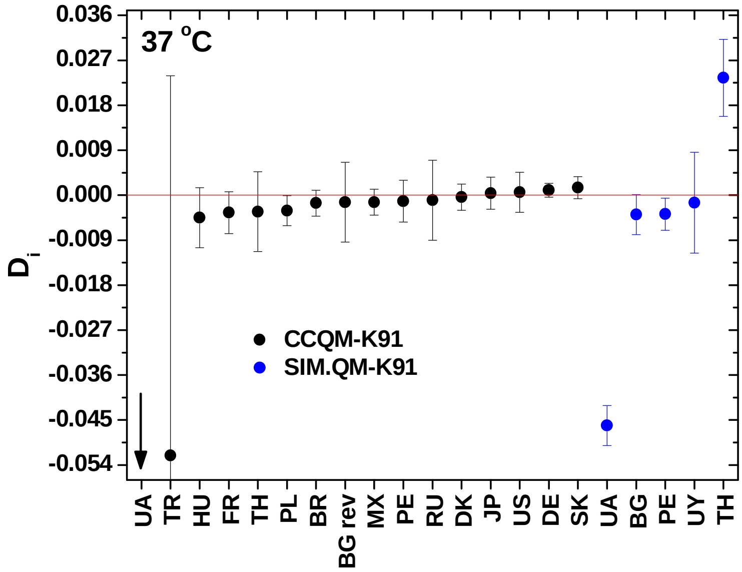

Figure 8. Degrees of equivalence linked to CCQM-K91, with expanded uncertainties (*k*=2), for results at 37 °C.

How far the light shines

The results can be considered to be representative for measurement capabilities in the range from pH 4.0 to 4.2 (at 25 °C).

Acknowledgments

INMETRO gratefully acknowledges the contributions of all participants and of the members of the CCQM Working Group on Electrochemical Analysis for their valuable suggestions concerning the measurement protocol and the evaluation process.

References

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