

# Key Comparison CCQM–K20 pH of Tetroxalate Buffer

**Final report: September 2008**

## **Abstract**

The key comparison (KC) CCQM-K20 was performed to demonstrate the capability of the participating National Metrology Institutes (NMIs) to measure the pH value of an unknown potassium tetroxalate buffer by the primary method. The buffer of nominal pH ~ 1.7 was measured at three temperatures: 15 °C, 25 °C, and 37 °C. The comparison was an activity of the Electrochemical Working Group (EAWG) of the CCQM and was coordinated by NIST (USA).

All participants applied the primary method for pH. The result for the unknown buffer solution is the acidity function at zero chloride molality,  $p\alpha^0$ . Values for the Key Comparison Reference Value (KCRV) and its uncertainty, and the Degrees of Equivalence ( $D_i$ ) are reported. Good agreement of the results was observed for the majority of participants.

## **Metrology Area**

Amount of Substance

## **Branch**

Electrochemistry

## **Subject**

Determination of the acidity functions at zero chloride molality of an unknown tetroxalate buffer, pH ~1.7, by Harned cell measurements at 15 °C, 25 °C, and 37 °C.

## **Time schedule**

Dispatch of the samples:	13 September 2007
Deadline for receipt of the report:	31 December 2007
Discussion of results:	EAWG meeting, 31 March 2008
Draft A Report	July 2008

## **Participants**

The list of participants is given in Table 1. All participants except VNIIFTRI indicated their intention to participate by the deadline, 31 August 2007. Owing to e-mail problems, VNIIFTRI indicated its intention to participate at the EAWG meeting in Charleston, 2 October 2007.

Table 1. Table of participants, Key Comparison CCQM-K20.

Acronym	Participant (NMI)	Country	ISO 3166-1	Analyst(s)
CENAM	Centro Nacional de Metrología	Mexico	MX	M. Monroy, A. Reyes
ČMI	Český metrologický institut	Czech Republic	CZ	A. Vospelova
DFM	Dansk fundamental metrology	Denmark	DK	P. Jakobsen
GUM	Główny urząd miar	Poland	PL	A. Mateuszuk, M. Pawlina, W. Kozłowski
INPL	The National Physical Laboratory of Israel	Israel	IL	E. Kardash
INMETRO	Instituto Nacional de Metrologia, Normalização e Qualidade Industrial	Brasil	BR	P. Borges, I. Fraga, J. Dias, B. Rossini, S. Sobral
NCM-BIM	National Center of Metrology	Bulgaria	BG	L. Dimitrova
NIST	National Institute of Standards and Technology	USA	US	K. Pratt
NMIJ	National Metrology Institute of Japan	Japan	JP	M. Ohata, I. Maksimov, A. Hioki
SMU	Slovenský metrologický ústav	Slovak Republic	SK	A. Mathiasová, L. Vyskočil
UMTS	Ukrainian State Research and Production Center of Standardization Metrology, Certification, and Consumers' Rights Protection	Ukraine	UA	V. Gavrilkin S. Nagibin
VNIIFTRI	All-Russian Scientific Institute for Physical-Technical and Radiological Measurements	Russia	RU	V. Kutovoy, V. Zvezdina

## Coordinating Laboratory

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## Sample preparation and bottling

The tetroxalate buffer solution was prepared from deionised water and potassium tetroxalate dihydrate (stated compound) as the starting material. Subsequent experiments (see below) indicated that as supplied, the compound contained excess water, but that the composition of the salt itself conformed to the stoichiometric ratio of  $\text{H}_2\text{C}_2\text{O}_4:\text{HC}_2\text{O}_4^-$ , equal to 1:1. The presence of excess water did not impair the use of the compound in the Key Comparison.

Potassium tetroxalate dissolves rather slowly in water. To avoid the possibility of having undissolved salt present when the 1 L bottles were filled for distribution to the participants, the following procedure was followed. The total volume of solution, ca. 50 L, was prepared by mixing five 10 L (nominal) aliquots of buffer solution, each prepared gravimetrically in a 10 L bottle to an indicated relative accuracy of 0.007 % or less. Each aliquot was shaken until the solid potassium tetroxalate salt had dissolved, as verified by visual inspection. The aliquots were then transferred successively to a 50 L bottle, and the total batch was shaken for 1 h to homogenize the entire batch.

The entire batch solution was transferred to fifty-one new 1 L high-density polyethylene (HDPE) bottles, which were labelled in filling order. The HDPE bottles had been cleaned at NIST by filling each bottle with deionized water, letting it soak overnight, rinsing it three times with ~50 mL portions of deionized water, and emptying it after each rinsing. This set of steps was performed three times for each bottle. After the final rinse, the bottles were dried in a forced-flow oven at ~60 °C. Each cap was hand-tightened and subsequently re-tightened twice, after which plastic shrink tubing was applied to the cap and neck of each bottle. After labelling and weighing, the bottles were sealed in aluminized polyethylene terephthalate (PET) bags, which served as a diffusion barrier.

The mass fraction of water,  $w_{\text{H}_2\text{O}}$ , of the final solution, based on the theoretical salt composition,  $\text{KH}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ , was  $w_{\text{H}_2\text{O}} = 0.989204 \text{ g g}^{-1}$ , including the contribution of the water of crystallization.

### Solution homogeneity and stability

The homogeneity of the bottles was checked by measuring the  $p\text{a}^0$  of the bottled solution from the first (1) and last (51) bottles filled from the batch of CCQM-K20 solution. The primary measurement method was used. Owing to the limited volume per bottle, a single solution was prepared from each bottle at each added molality of NaCl, (0.005, 0.010, and 0.015) mol kg<sup>-1</sup>, used in the primary method. This preparation yielded six total solutions, one pair derived from each source bottle (1 and 51) at each added molality of NaCl. The results are shown in Table 2, along with the CCQM-K20 result of the coordinating laboratory and the dates of the respective measurements.

Table 2. Measurements of Homogeneity and Stability at Coordinating Laboratory (25 °C).

Bottle(s)	Date	$p\text{a}^0$	$U(k = 2)$
1 = initial	11-13 Sep 07	1.7939	0.0013
51 = final	11-13 Sep 07	1.7931	0.0031
K20 (6, 24, 47)	13-17 Dec 07	1.7928	0.0010

No significant differences were noted between the  $p\text{a}^0$  results derived from the two bottles. No uniform trend (e.g., bottle 1 always higher) was noted between the values of the acidity function for the respective solutions at each added molality of NaCl. Values of the acidity function for each pair at the same added molality of NaCl agreed to within 0.0008. This data indicates further that the samples from the two bottles were indistinguishable from each other.

The results of the preliminary homogeneity test also were used to evaluate the stability of the CCQM-K20 buffer over the measurement period (11 September – 17 December 2007). The

results in Table 2 also demonstrate that the  $pa^0$  of the CCQM-K20 solution, as determined at the coordinating laboratory, remained stable over the specified measurement period.

### **Sample delivery and verification of mass stability of shipped bottles**

The sample bottles were weighed on 31 August 2007 and were sealed in the aluminized PET bags immediately after weighing. The sample bottles were shipped on 13 September 2007<sup>1</sup>. Each participant received three 1 L HDPE numbered bottles, packaged as described above. The receipt dates of the samples are given in Table 4 below. Participants were requested to provide the balance reading,  $m_W$ ; the ambient pressure,  $p$ , and temperature,  $T$ , at the time of weighing; and the calculated mass of each bottle as received,  $m_{\text{received}}$ . These participant-supplied values of  $m_{\text{received}}$  had been corrected for air buoyancy using the formula used at the given NMI. Independently, the coordinating laboratory also calculated separate values of  $m_{\text{received}}$  from the participant-supplied values of  $m_W$ ,  $p$ , and  $T$ , using the same formula for buoyancy correction that had been used to calculate the initial masses,  $m_0$ . The relative change in mass (referred to  $m_0$ ) was calculated for each bottle using each of the two calculated values for  $m_{\text{received}}$ . The results are shown in Table 3:

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<sup>1</sup> The bottles to VNIIFTRI were shipped on 3 October 2007.

Table 3. Masses of Sample Bottles and Relative Changes in Mass on Shipping.

Sample information		31-Aug-07 mass, $m_0$ /g	Weighing Date (NMI)	Relative change in mass, $\Delta m/m_0$	
NMI	Bottle			NMI calc'n	Coord. Lab calc'n
CENAM	8	1110.694	29-Sep-07	-0.002 %	-0.001 %
	32	1102.217	29-Sep-07	-0.003 %	-0.002 %
	41	1097.221	8-Nov-07	-0.002 %	0.000 %
ČMI	2	1097.199	3-Nov-07	-0.001 %	-0.001 %
	22	1090.249	3-Nov-07	-0.002 %	-0.002 %
	42	1122.945	3-Nov-07	-0.002 %	-0.002 %
DFM	5	1105.796	26-Oct-07	-0.002 %	-0.003 %
	28	1103.239	26-Oct-07	-0.003 %	-0.003 %
	37	1110.390	26-Oct-07	-0.003 %	-0.003 %
GUM	15	1093.307	19-Oct-07	-0.002 %	-0.003 %
	20	1096.294	19-Oct-07	-0.003 %	-0.004 %
	43	1120.926	19-Oct-07	-0.001 %	-0.002 %
INMETRO	11	1109.215	26-Dec-07	-0.003 %	-0.003 %
	27	1096.243	18-Dec-07	-0.003 %	-0.003 %
	45	1110.246	20-Dec-07	-0.007 %	-0.007 %
INPL	17	1106.814	27-Nov-07	-0.002 %	-0.002 %
	25	1087.951	27-Nov-07	-0.002 %	-0.002 %
	50	1143.250	27-Nov-07	-0.002 %	-0.002 %
NCM-BIM	7	1101.155	19-Sep-07	0.004 %	0.003 %
	31	1105.892	19-Sep-07	0.003 %	0.003 %
	38	1089.489	19-Sep-07	0.004 %	0.004 %
NIST	6	1089.987	12-Dec-07	-0.002 %	-0.002 %
	24	1095.578	12-Dec-07	-0.002 %	-0.002 %
	47	1106.713	12-Dec-07	-0.002 %	-0.002 %
NMIJ	10	1088.699	27-Sep-07	-0.002 %	-0.002 %
	21	1113.177	27-Sep-07	-0.002 %	-0.002 %
	35	1103.862	27-Sep-07	-0.002 %	-0.002 %
SMU	9	1089.523	18-Sep-07	-0.001 %	0.000 %
	19	1071.542	18-Sep-07	-0.002 %	0.000 %
	49	1108.238	18-Sep-07	-0.001 %	0.001 %
UMTS	16	1090.596	16-Oct-07	0.002 %	-0.002 %
	26	1101.494	16-Oct-07	0.001 %	-0.002 %
	44	1085.713	16-Oct-07	0.002 %	-0.003 %
VNIIFTRI	4	1106.597	19-Dec-07	-0.003 %	-0.004 %
	18	1100.386	19-Dec-07	-0.003 %	-0.004 %
	39	1098.988	19-Dec-07	0.001 %	0.001 %
Coordinating Lab - test	1	1092.660	10-Sep-07	0.000 %	0.000 %
	51	1132.695	10-Sep-07	0.000 %	0.000 %

The data in Table 3 demonstrate that except for one bottle sent to INMETRO, all bottles remained constant in mass to within 0.004 %, relative, between the initial bagging in the aluminized PET bags on 31 August and the date of measurement. The larger deviation in bottle 45, sent to INMETRO, was traced to compromise of the bag seal in Brazilian customs inspection, prior to receipt of the shipment by INMETRO. Even in this case, the relative change in mass was only -0.007 %. Based on the dilution value [1] for tetroxalate buffer [2], this change in mass corresponds to a pH change of only 0.000 27, insignificant in terms of this Key Comparison.

The data also demonstrate that the buoyancy correction agrees to better than 0.001 % with that used by the coordinating laboratory, with the exception of UMTS, where the relative

difference is ca. 0.005 %. The slight apparent difference in the SMU (Slovak Republic) buoyancy correction is explained by the inclusion by SMU of a correction factor to the balance reading into their buoyancy correction.

### Timetable of Measurements and Submission of Reports

The dates of receipt of the samples, the dates of measurements, and reporting dates are given in Table 4. All dates are 2007, except as noted.

Table 4. Dates of Sample Receipt, Measurement Period, and Report Date.

NMI	Sample Received	Measurement Period	Report Date	Revised report	Comments
CENAM	24 Sep	29 Oct - 8 Nov	20 Dec		
ČMI	17 Sep	1 Nov - 7 Dec	19 Dec		
DFM	17 Sep	31 Oct - 2 Nov	20 Dec		
GUM	17 Sep	19 Oct - 11 Nov	31 Dec		
INMETRO	2 Oct	18 - 27 Dec	2 Jan 2008		e-mail problem
INPL	20 Sep	9 - 26 Dec	31 Dec		
NCM-BIM	17 Sep	13 - 23 Nov	28 Dec	11 Mar 2008	
NIST	12 Sep	13 - 17 Dec	18 Dec		
NMIJ	25 Sep	16 - 21 Nov	27 Dec		
SMU	17 Sep	24 - 28 Sep	1 Oct		
UMTS	27 Sep	15 - 23 Oct	21 Dec		
VNIIFTRI	23 Oct	19 Dec	31 Dec		no uncertainties

All reports were received by the deadline, 31 December 2007, with three exceptions:

INMETRO had e-mail problems and informed the coordinating laboratory of this fact in advance. The e-mail was received on 2 January 2008 and the report was accepted.

The VNIIFTRI report, received on 31 December 2007, contained no uncertainty information and no assigned uncertainties. The associated e-mail from VNIIFTRI stated that they hoped to complete the graphs and uncertainty analysis in January, but no subsequent e-mail was received. A follow-up request was e-mailed in April 2008 to both e-mail addresses used by VNIIFTRI. No further reply was received. In the absence of the required uncertainty data, the VNIIFTRI data cannot be used in the calculation of the KC Reference Value (KCRV).

NCM-BIM submitted their original report on 28 December 2007. This report used an incorrect method for performing the extrapolation of the acidity function to zero molality of added chloride to obtain  $p_a^0$ . After the preliminary results were distributed to all participants, NCM-BIM corrected this error in a revised report, submitted on 11 March 2008. According to the KC protocol, the original reported value is used to calculate the degrees of equivalence for NCM-BIM, while the corrected value is used in the calculation of the KCRV.

### Measurement Technique

Participants were requested to use the primary measurement technique (Harned Cell) for pH. The primary measurement [3] consists of measurements of the potential,  $E_I$ , for cell I,



where  $b_{\text{Cl}}$  is the molality of NaCl or KCl added to the buffer. Measurements of the potential,  $E_{\text{II}}$ , for cell II,



are simultaneously performed in an HCl solution of molality,  $b_{\text{HCl}} = 0.01 \text{ mol kg}^{-1}$ . The standard potential,  $E^\circ$ , of the Ag|AgCl reference electrodes is calculated from each  $E_{\text{II}}$  according to Eq 1:

$$E^\circ = E_{\text{II}} + 2k \log \frac{b_{\text{HCl}} \gamma_{\pm\text{HCl}}}{b^\circ}. \quad (1)$$

In Eq 1,  $\gamma_{\pm\text{HCl}}$  is the mean activity coefficient of HCl at a molality of  $b_{\text{HCl}}$ , and  $b^\circ = 1 \text{ mol kg}^{-1}$ . The quantity  $k$  equals  $RT \ln 10 / F$ , where  $R$ ,  $T$ , and  $F$  are the gas constant, the thermodynamic temperature, and the Faraday constant, respectively.

Values for the acidity function,  $pa$ , are calculated for each measured  $E_{\text{I}}$  value using Eq 2, where the operator  $p$  represents  $-\log_{10}$ :

$$pa = \frac{(E_{\text{I}} - E^\circ)}{k} + \log \frac{b_{\text{Cl}}}{b^\circ}. \quad (2)$$

The acidity function at  $b_{\text{Cl}} = 0$ ,  $pa^0$ , for the given temperature is obtained from the linear extrapolation of the set of values for  $pa$  to  $b_{\text{Cl}} = 0$ . The reported result for the Key Comparison is  $pa^0$ .

## Results and Discussion

The CCQM-K20 measurements were performed at three temperatures: 15 °C, 25 °C, and 37 °C. Results from all participants are given in Table 5 and (excluding INPL) in Figures 1a through 1c.

The INPL used an electrochemical cell in which the Pt|H<sub>2</sub> and Ag|AgCl half cells are separated by a high-resistance connection, similar to that used in commercial sleeve-junction reference electrodes. In the discussion of the CCQM-K20 results, the EAWG decided to exclude the results of the INPL, based on their use of this high-resistance connection between the Pt|H<sub>2</sub> and Ag|AgCl half-cells.

Table 5. Results of Key Comparison CCQM-K20.

NMI	15 °C		25 °C		37 °C	
	$pa^0$	$U$	$pa^0$	$U$	$pa^0$	$U$
CENAM	1.7808	0.0058	1.7918	0.0051	1.8050	0.0024
ČMI	1.7827	0.0041	1.7933	0.0045	1.8074	0.0039
DFM	1.7816	0.0029	1.7911	0.0028	1.8078	0.0043
GUM	1.7889	0.0038	1.7990	0.0038	1.8133	0.0044
INMETRO	1.7718	0.0029	1.7867	0.0056	1.7995	0.0061
INPL	1.8141	0.0082	1.8222	0.0078	1.8345	0.0079
NCM-BIM	---	---	1.7788	0.0044	1.8001	0.0046
NCM-BIM (revised)	---	---	1.7825	0.0044	1.8035	0.0046
NIST	1.78423	0.00077	1.7928	0.0010	1.8061	0.0014
NMIJ	1.7844	0.0022	1.7934	0.0022	1.8077	0.0022
SMU	1.7818	0.0020	1.7917	0.0020	1.8068	0.0020
UMTS	1.7828	0.0038	1.7897	0.0028	1.8035	0.0032
VNIIFTRI	1.7838	---	1.7915	---	1.8057	---

Figure 1a. Results of Key Comparison CCQM-K20, 15 °C, Excluding INPL. Error Bars Correspond to Expanded ( $k = 2$ ) Uncertainties.

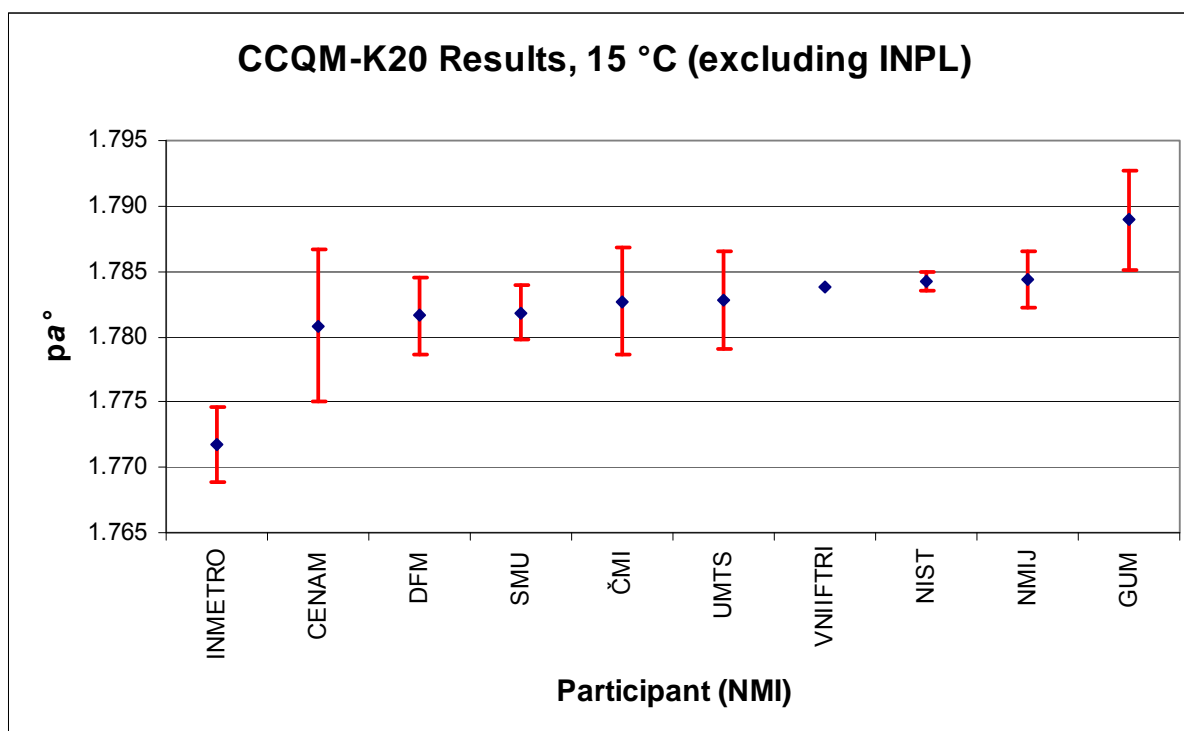




Figure 1b. Results of Key Comparison CCQM-K20, 25 °C, Excluding INPL. Error Bars Correspond to Expanded ( $k = 2$ ) Uncertainties.

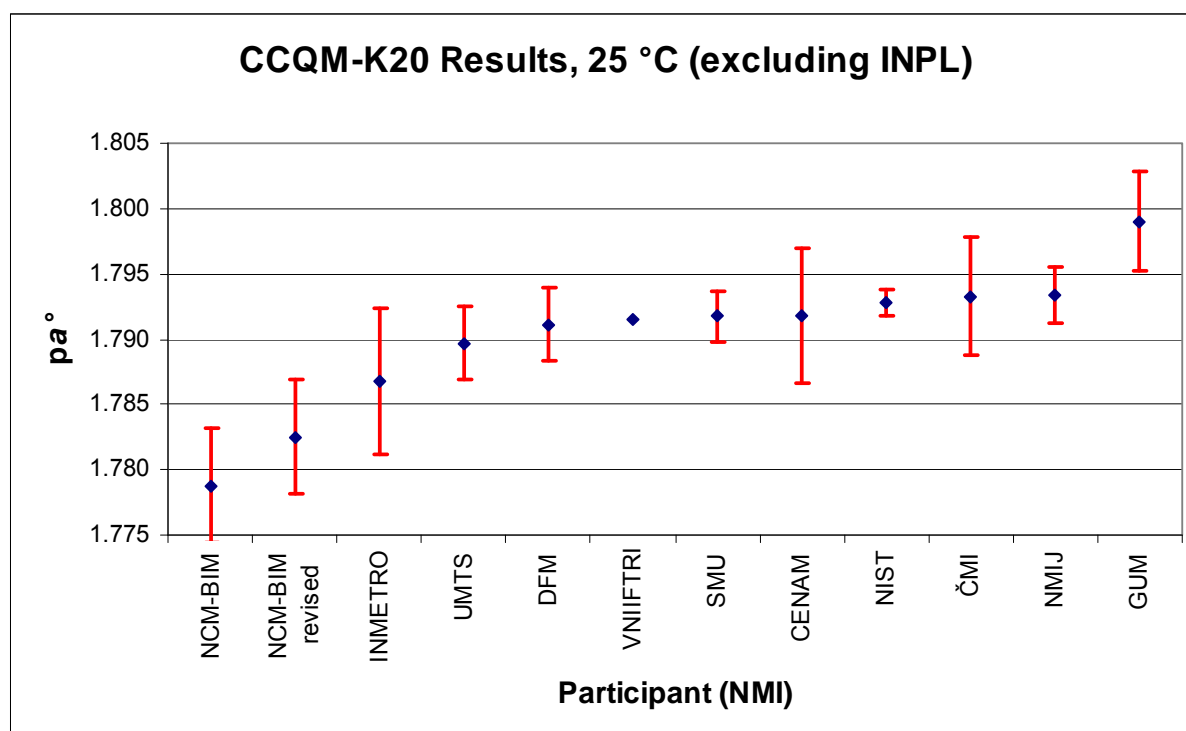
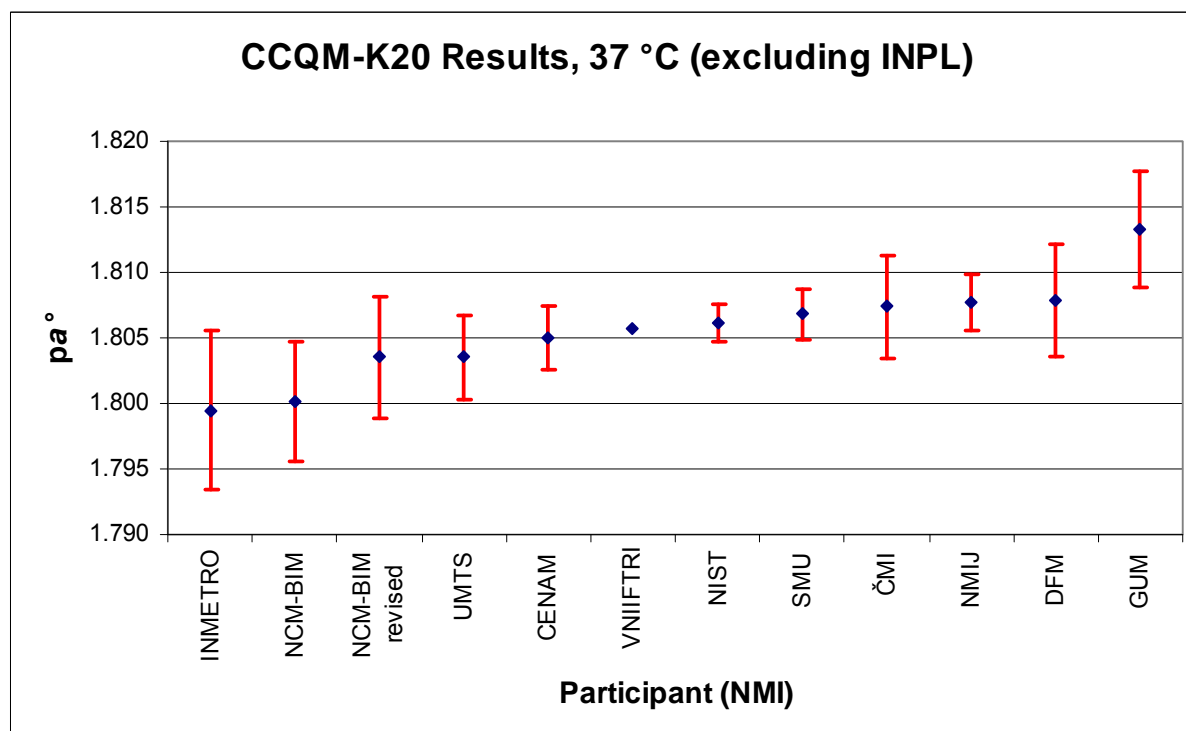


Figure 1c. Results of Key Comparison CCQM-K20, 37 °C, Excluding INPL. Error Bars Correspond to Expanded ( $k = 2$ ) Uncertainties.



Other information reported by the participants is given in Table 6, including the HCl molality and method of standardization; the standard potential,  $E^\circ$ , and its combined standard uncertainty,  $u_c(E^\circ)$ ; and the uncertainty of the extrapolation to obtain  $pa^0$ .

Table 6. Other Information Reported by the Participants.

NMI	HCl molality, $b_{\text{HCl}}/(\text{mol kg}^{-1})$	Standardization Technique for HCl <sup>a</sup>	Ag AgCl std. potential, $E^0/V$ (25 °C)	$u_c(E^0)/V$ (25 °C)	$u(\text{extrapolation})$ at 25 °C
CENAM	0.010002	gravimetric pot. titration	0.222342	0.000031	0.0019
ČMI	0.010000	coulometry (SMU)	0.22259	0.000053	0.0020
DFM	0.010002	coulometry + grav. dilution	0.22242	0.000039	0.0015
GUM	0.010001	pot. titration (AgCl)	0.222165	0.000089	0.0011
INMETRO	0.009985	gravimetric pot. titration	0.222758	0.000059	0.0026
INPL	0.010000	acid/base titration	0.22175	0.00023	0.0005
NCM-BIM	0.01030	titrimetry (NaOH, Me red)	0.22228	0.000052	0.0033
NIST	0.010004	coulometry (H <sup>+</sup> )	0.222419	0.000020	0.0004
NMIJ	0.009996	coulometry (H <sup>+</sup> )	0.22260	0.000051	0.0003
SMU	0.010007	coulometry + conductimetry	0.222390	0.000047	0.0002
UMTS	0.010001	coulometry	0.222495	0.000076	0.0004
VNIIFTRI	0.009920	not stated	0.22237	not reported	not reported

<sup>a</sup> Abbreviations: pot. = potentiometric, grav. = gravimetric, Me = methyl.

### Calculation of the KCRV and Its Uncertainty

There are several possibilities for determination of the KCRV. These possibilities are listed in Table 7. For each estimator, the INPL and VNIIFTRI results are omitted from the calculation, and the revised NCM-BIM results are used.

Table 7. Values of Candidate Estimators<sup>a</sup> for the KCRV for CCQM-K20.

Estimator	15 °C		25 °C		37 °C	
	Value	$u(k=1)$	Value	$u(k=1)$	Value	$u(k=1)$
Arithmetic Mean	1.7821	0.0015	1.7912	0.0014	1.8061	0.0011
<b>Weighted Mean</b>	<b>1.7833</b>	<b>0.0010</b>	<b>1.79223</b>	<b>0.00078</b>	<b>1.80634</b>	<b>0.00067</b>
Median	1.7827	0.0010	1.79176	0.00097	1.80647	0.00086
MM-Median	1.7828	0.0027	1.7918	0.0030	1.8062	0.0009

<sup>a</sup> Estimator used to determine KCRV is in **bold** type. Symbols:  $u$  = standard uncertainty;  $k$  = coverage factor.

The differences between the estimators are insignificant. Based on the decision of the EAWG at its meeting on 31 March 2008, the weighted mean and its uncertainty were selected as the estimators for the KCRV in CCQM-K20. This approach is the same as that used to calculate the KCRV in the preceding CCQM-K9 (phosphate buffer) [4] and CCQM-K17 (phthalate buffer) [5]. It differs from the approach used in the preceding CCQM-K18 (carbonate buffer) [6] and CCQM-K19 (borate buffer) [7], both of which used the median and its uncertainty to determine the KCRV and its uncertainty.

The weighted mean of the participants' results,  $pa_R^0$ , for CCQM-K20 was calculated using Eq 3:

$$pa_R^0 = \sum_{i=1}^n w_i pa_i^0 . \quad (3)$$

In Eq 3,  $n$  is the number of participants,  $w_i$  is the normalized weight for participant  $i$ , and  $pa_i^0$  is the reported result for participant  $i$ .

The  $w_i$  are given by Eq 4, where  $u(x_i)$  is the reported standard uncertainty for participant  $i$ :

$$w_i = \frac{1}{\frac{u^2(x_i)}{\sum_{i=1}^n \frac{1}{u^2(x_i)}}} . \quad (4)$$

The uncertainty of the weighted mean for CCQM- K20 determined by the external consistency method,  $u_E(pa_R^0)$ , was calculated for each temperature using Eq 5:

$$u_E(pa_R^0) = \sqrt{\frac{\sum_{i=1}^n w_i (pa_i^0 - pa_R^0)^2}{n-1}} . \quad (5)$$

The uncertainty of the weighted mean for CCQM- K20 determined by the internal consistency method,  $u_m(pa_R^0)$ , was also calculated. The value for  $u_m(pa_R^0)$  is given by Eq 6:

$$u_m(pa_R^0) = \sqrt{\frac{1}{\sum_{i=1}^n \frac{1}{u^2(x_i)}}} . \quad (6)$$

The Birge ratio,  $R = u_E/u_m$ , was then calculated at each temperature. The results were  $R = 3.249$  for the data at 15 °C,  $R = 2.181$  for the data at 25 °C, and  $R = 1.619$  for the data at 37 °C. These  $R$  values, which are in the same range as those obtained for CCQM-K9 [4] and CCQM-K17 [5], indicate that the external consistency method yields a better estimate of the true uncertainty of the results than does the internal consistency method. From this analysis, the calculated values of  $u_E(pa_R^0)$  were taken as the standard uncertainty of the KCRV,  $u(\text{KCRV})$ .

The final value of the KCRV and its expanded uncertainty ( $k = 2$ ) at each temperature are listed in Table 8:

Table 8. KCRV and Its Expanded Uncertainty,  $U$ , for CCQM-K20.

15 °C		25 °C		37 °C	
KCRV	$U(k = 2)$	KCRV	$U(k = 2)$	KCRV	$U(k = 2)$
1.7833	0.0020	1.7922	0.0016	1.8063	0.0013

### Calculation of the Degrees of Equivalence

The degrees of equivalence for each participant,  $D_i$ , and its standard uncertainty,  $u(D_i)$ , are given by Eq 7 and Eq 8, respectively:

$$D_i = pa_i^0 - \text{KCRV}, \quad (7)$$

$$u(D_i) = \sqrt{u^2(pa_i^0) + u^2(\text{KCRV})}. \quad (8)$$

Values for  $D_i$  and  $u(D_i)$  are given in Table 9 for each participant. For NCM-BIM,  $D_i$  and  $u(D_i)$  are calculated using the originally-submitted values. For VNIIFTRI, no value is calculated for  $D_i$ , as no value for  $u_i$  was reported.

Table 9. Degrees of Equivalence,  $D_i$ , and Standard Uncertainty,  $u(D_i)$ , for CCQM-K20.

Participant (NMI)	15 °C		25 °C		37 °C	
	$D_i$	$u(k=1)$	$D_i$	$u(k=1)$	$D_i$	$u(k=1)$
KCRV <sup>a</sup>	1.7833	0.0010	1.7922	0.0008	1.8063	0.0007
CENAM	-0.0025	0.0031	-0.0004	0.0027	-0.0013	0.0014
ČMI	-0.0006	0.0023	0.0011	0.0024	0.0010	0.0021
DFM	-0.0017	0.0018	-0.0011	0.0016	0.0015	0.0023
GUM	0.0056	0.0021	0.0068	0.0021	0.0070	0.0023
INMETRO	-0.0116	0.0018	-0.0055	0.0029	-0.0069	0.0031
INPL	0.0308	0.0042	0.0300	0.0040	0.0282	0.0040
NCM-BIM	---	---	-0.0097	0.0023	-0.0028	0.0024
NIST	0.0009	0.0011	0.0005	0.0009	-0.0002	0.0010
NMIJ	0.0010	0.0015	0.0012	0.0013	0.0014	0.0013
SMU	-0.0015	0.0014	-0.0005	0.0013	0.0005	0.0012
UMTS	-0.0005	0.0021	-0.0025	0.0016	-0.0028	0.0017
VNIIFTRI	---	---	---	---	---	---

<sup>a</sup> KCRV at each temperature is listed in the corresponding  $D_i$  column of the table.

### Comparison of CCQM-K20 with Previous pH KCs

Table 10 summarizes the dispersion of results of those pH KCs completed to date [4-8]. The standard deviation and range (total spread) of each set of results at 25 °C (excluding those results not used in calculating the respective KCRV) are listed. The standard deviation and range for CCQM-K20 are smaller, respectively, than in most other pH KCs, reflecting the absence of complicating factors in the tetroxalate buffer.

Table 10. Dispersion Metrics for pH Key Comparisons at 25 °C.

CCQM KC	nominal pH	St dev	( $pa_{\max}^0 - pa_{\min}^0$ )
K9	6.9	0.0053	0.0189
K9.2	6.9	0.0068	0.0193
K17	4.0	0.0051	0.0143
K18	10.0	0.0087	0.0292
K19	9.2	0.0041	0.0142
K20	1.7	0.0044	0.0165

### How Far the Light Shines

CCQM-K20 completes the original set of pH KCs covering the whole set<sup>2</sup> of buffers that are measured using the primary measurement method for pH. The tetroxalate buffer is the buffer with the lowest pH value, ~1.7, normally certified using the primary pH method. The whole set of pH KCs covers the pH range 1.7 – 10.0 for which the primary measurement is normally used. With specific respect to CCQM-K20, the participants in CCQM-K20 (excepting INPL and VNIIFTRI) have demonstrated their capability to measure the pH of tetroxalate buffer solutions.

### Conclusion

Twelve NMIs participated in the Key Comparison of tetroxalate buffer using the primary method of measurement (Harned cell). Good agreement was found for the majority of participants. The spread of reported values was smaller than in most previous Key Comparisons in the area of pH.

### Acknowledgment

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<sup>2</sup> The saturated calcium hydroxide buffer, pH ~12.4, is certified using the primary method but has insufficient long-term stability to be used in a CCQM pH KC.

6. Final Report for Key Comparison CCQM-K18, available at [http://kcdb.bipm.org/AppendixB/appbresults/ccqm-k18/ccqm-k18\\_final\\_report.pdf](http://kcdb.bipm.org/AppendixB/appbresults/ccqm-k18/ccqm-k18_final_report.pdf)
7. Final Report for Key Comparison CCQM-K19, available at [http://www.bipm.org/utis/common/pdf/final\\_reports/QM/K19/CCQM-K19.pdf](http://www.bipm.org/utis/common/pdf/final_reports/QM/K19/CCQM-K19.pdf)
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