Key Comparison CCQM-K73
Amount Content of H^+ in Hydrochloric Acid ($0.1\ mol\cdot kg^{-1}$)

Final Report: 26 October 2012

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Abstract

This key comparison (KC), CCQM-K73, was performed to demonstrate the capability of the participating National Metrology Institutes (NMIs) to measure the amount content of H^+, ν_{H^+}, in an HCl solution with a nominal ν_{H^+} of $0.1\ mol\cdot kg^{-1}$. A parallel Pilot Study, CCQM-P19.2, was performed for NMIs that did not desire to participate in the KC. The comparison was a joint activity of the Electrochemical Working Group (EAWG) and Inorganic Analysis Working Group (IAWG) of the CCQM and was coordinated by NIST (USA) and CENAM (México).

The method of determination of ν_{H^+} was left to the individual participant. All participants used either coulometry or titrimetry with potentiometric determination of the endpoint.

The agreement of the results was not commensurate with the claimed uncertainties of the subset of participants that claimed small uncertainties for this determination. A workshop on technical issues relating to the CCQM-K73 measurements was conducted at the joint IAWG-EAWG meeting at the Bureau International des Poids et Mesures (BIPM), Paris (Sèvres) in April 2010. Several possible sources of bias were investigated, but none could explain the observed dispersion among the participants' results.

In the absence of a specific cause for the dispersion, the IAWG and EAWG decided to assign a Key Comparison Reference Value, KCRV, and standard uncertainty of the KCRV, u_{KCRV}, based on the DerSimonian-Laird statistical estimator. The u_{KCRV} is dominated by the between-laboratory scatter of results in CCQM-K73. The uncertainty estimates from the participants with the lowest reported uncertainties remain unsupported by this KC.

Metrology Area
Amount of Substance

Branches
Electrochemistry, Inorganic Analysis

Subject
Determination of the amount content of H^+ in hydrochloric acid solutions.

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[1] Study Coordinator

[2] Organizational affiliations of all authors listed in Table 1.

Time schedule

Dispatch of the samples:	26 June 2009
Deadline for receipt of the report:	30 September 2009
Discussion of results:	EAWG/IAWG Joint meeting, 4 November 2009
Draft A Report	December 2009

All dates in this Report are 2009, unless noted otherwise.

Participants

The list of participants is given in Table 1 for CCQM-K73. VNIIFTRI originally registered for CCQM-K73 but withdrew after it proved impossible to ship the samples to them. DFM originally registered for CCQM-K73 and received samples, but withdrew owing to equipment difficulties.

Table 1. Table of participants, Key Comparison CCQM-K73.

Acronym	Participant (NMI)	Country	Analyst(s)
CENAM	Centro Nacional de Metrología	México	Jose Luis Ortiz-Aparicio, Francisco Javier Matehuala-Sanchez
DFM	Dansk fundamental metrology	Denmark	Pia Tønnes Jakobsen
GUM	Główny urząd miar	Poland	Monika Pawlina, Władysław Kozłowski
INMETRO	Instituto Nacional de Metrologia, Normalização e Qualidade Industrial	Brazil	Paulo P. Borges, Wiler B. da Silva Junior
INTI	Instituto Nacional de Tecnología Industrial	Argentina	Mónica B. Borinsky-Ana Hernandez-Mabel Puelles-Nadia Hatamleh-Osvaldo Acosta
IPQ	IPQ/UMCA-LCM, Instituto Português da Qualidade - Scientific and Applied Metrology Unit	Portugal	M. João Nunes, M.J. Guiomar Lito, M. Filomena Camões, Eduarda Filipe
KRISS	Korea Research Institute of Standards and Science	Korea	Euijin Hwang, Youngran Lim
NIM	National Institute of Metrology of P. R. China	China	Wu Bing; Wang Qian; Wei Chao
NIST	National Institute of Standards and Technology	USA	Kenneth W. Pratt
NMIJ	National Metrology Institute of Japan	Japan	Akiharu Hioki, Toshiaki Asakai
SMU	Slovenský metrologický ústav	Slovak Republic	Michal Máriássy, Zuzana Hanková
UMTS	Ukrainian State Research and Production Center of Standardization Metrology, Certification, and Consumers’ Rights Protection	Ukraine	Sergey Nagibin, Olexandra Manska, Vladimir Gavrilkin
VNIIFTRI	All-Russian Scientific Institute for Physical-Technical and Radiological Measurements	Russia	Viatcheslav Kutovoy

Coordinating Laboratories

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A copy of the Technical Protocol distributed to all participants is attached as an Appendix to this Report.

Sample preparation and bottling

The CCQM-K73/P19.2 solution was prepared from concentrated reagent-grade hydrochloric acid (Mallinckrodt AR[3], Lot H611 T13A01) and high-purity deionized water. The water had an indicated electrolytic conductivity of 18.2 MΩ·cm at delivery. A 150 mL portion of this acid was added to ≈18 L H_2O and the solution was mixed by agitating and subsequently by bubbling house N_2 (mass fraction of CO_2 < 1 μmol·mol^{-1}) through the solution for > 1 h. Preliminary titration of this solution yielded $\nu_{H+} \approx 0.9958$ mol·kg^{-1}. To permit a larger number of bottles to be filled, a 2 L additional portion of solution was prepared from ≈ 2 L H_2O and 17 mL of the same reagent grade hydrochloric acid. This second portion was added to the original batch to yield the final batch. The composite solution was thoroughly mixed by agitation and bubbling with house N_2 for 2 h. This final batch (the "CCQM-K73 solution") had a volume of ≈ 20 L, with a nominal ν_{H+} of 0.1 mol·kg^{-1}.

Sixty-four 250 mL high-density polyethylene (HDPE) bottles were cleaned by rinsing three times in water and soaking in water for 3 h or longer. This cycle was performed a total of three times. The bottles then were rinsed a final three times with water and were dried at 50 °C to 70 °C in an oven. The clean, dry bottles were filled with the CCQM-K73 solution and numbered/labeled consecutively in filling order on 23 June. The caps of the filled bottles were hand-torqued and allowed to sit overnight. They were re-torqued the following morning and re-weighed. All masses remained constant within 0.010 g. Heat-shrink seals were then applied to the necks of the re-torqued bottles. The sealed bottles were labeled, weighed, and bagged in transparent polyethylene (PE) bags. Then, the PE-bagged, labeled bottles were sealed in aluminized polyethylene terephthalate (PET) bags, which were numbered and labeled identically to the bottles. Finally, the PET-bagged bottles were weighed. The PET-bagged bottles were delivered to the NIST Shipping Department on 26 June, and were shipped to participants from 26 June through 1 July. The first (1) and last (64) bottles were retained at NIST for verification of homogeneity of the CCQM-K73 solution.

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[3] Certain commercial equipment, instruments, or materials are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Solution homogeneity and stability

Coulometric titrations of samples from bottles 1 and 64 were performed to verify the homogeneity of the CCQM-K73 solution with respect to the set of bottles. Coulometric titrations of solution directly taken from the carboy were also performed immediately before and following this bottling step. Results of these titrations are shown in Table 2.

The sample was not deaerated after the main titration [1] in the preliminary titrations. However, as the preliminary titrations were performed from deaerated solution (see details of preparation, above), the solution may be assumed to be largely free from dissolved CO_2. This assumption was verified by noting that the maximum slope of the titration curve in the final titration was only about 8 % lower than the maximum slope of the titration curve in the initial titration (both slopes normalized to 1 L, to account for the increase in volume on addition of the sample).

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

Source	Date of titration	$\nu_{H^+}/(\mathrm{mol \cdot kg^{-1}})$
carboy (**before** filling bottles)	22-Jun	0.100 922 9
carboy (**before** filling bottles)	22-Jun	0.100 922 2
carboy (**before** filling bottles)	23-Jun	0.100 923 9
carboy (**before** filling bottles) [a]	23-Jun	0.100 916 6
carboy (**after** filling bottles)	23-Jun	0.100 916 8
CCQM-K73 Bottle 64	24-Jun	0.100 918 3
CCQM-K73 Bottle 1	24-Jun	0.100 917 6
CCQM-K73 Bottle 64	24-Jun	0.100 913 7
CCQM-K73 Bottle 1	24-Jun	0.100 914 4
Mean		0.100 918 5
Standard Deviation (SD)		0.000 003 7
SD of Mean		0.000 001 2

[a] Carboy was vigorously swirled prior to this titration to assure homogeneity of contents.

The data in Table 2 provide an evaluation of homogeneity and stability of the CCQM-K73 solution to the precision of the coulometric method as implemented at the preparing laboratory (NIST). The agreement between the preliminary titrations of Bottles 1 and 64 indicates that the CCQM-K73 solution as bottled was homogeneous. The ≈ 0.007 % decrease noted in the preliminary titrations of the carboy solution (prior to bottling) in Table 2 likely resulted from the incorporation of condensate water in the carboy neck into the bulk solution at the time of mixing. The agreement between the results of the titrations of Bottles 1 and 64 and the results of the carboy titrations indicate that no significant change in ν_{H^+} resulted from the bottling procedure. Finally, the agreement between all these preliminary titrations (performed in June) and the NIST CCQM-K73 titrations (performed at the end of September) indicate that any drift that occurred over the entire designated period [2] of the CCQM-K73 measurements was < 0.007 % (cf. the reported mass changes documented in Table 3).

Although the lack of sample deaeration in the preliminary titrations compromises this assessment of drift to some extent, the fact that the preliminary titrations were performed on substantially deaerated solution reduced the component of uncertainty for dissolved CO_2 from ca. 0.011 % (calculated for non-deaerated solution in equilibrium with atmospheric CO_2) to ≈ 0.005 % for these preliminary titrations.

Sample delivery

The sample bottles were shipped from NIST on 26 June through 1 July. Each participant received two or three 0.25 L HDPE numbered bottles, packaged as described above, according to the quantity requested.

Following the initial shipment, VNIIFTRI reported that delivery of the CCQM-K73 samples required two special licenses, as Russian regulations classify hydrochloric acid (of any concentration) a precursor for narcotics. VNIIFTRI was not able to obtain these licenses in the required time frame and requested to withdraw from CCQM-K73 on 3 August.

Verification of mass stability of shipped bottles

Participants were requested to measure the mass of the PET-bagged bottles soon after receipt (storing at least overnight to assure temperature equilibrium with the weighing laboratory). These masses are listed in Table 3 as m_{bag}, along with the weighing dates[4].

Immediately before performing the measurement of $\nu_{\mathrm{H^+}}$, participants were requested to measure the mass of the bottle outside the bags (removed from the external PET and internal PE bags). These masses are listed in Table 3 as m_{bottle}, along with the weighing dates.

Participants also reported the balance reading, m_{W}; the ambient pressure, p, and temperature, T, at the time of each weighing. If the relative change in mass using the submitted m_{bag} or m_{bottle} differed by > 0.02 % from the initial pre-shipment masses, $m_{0,\mathrm{bag}}$ and $m_{0,\mathrm{bottle}}$, the coordinating laboratory independently calculated separate values of m_{bag} and m_{bottle} from the participant-supplied values of m_{W}, p, and T using the formula used to calculate $m_{0,\mathrm{bag}}$ and $m_{0,\mathrm{bottle}}$. The coordinating laboratory then contacted the participant to verify the weighing and calculation for buoyancy.

The data in Table 3 demonstrate that except for one value of m_{bag} reported by IPQ, the bagged bottles remained constant in mass to within 0.015%, relative, between the initial sealing in the aluminized PET bags on 25 June and the respective date of measurement. The values of m_{bottle} outside the bags also remained constant to within 0.013 %, relative, although a small loss in mass was evident in almost all cases.

The relative changes in m_{bag} and m_{bottle} listed in Table 3 are referenced to $m_{0,\mathrm{bag}}$ and $m_{0,\mathrm{bottle}}$, respectively. If the relative changes are referenced instead to the mass of solution, the values of $\Delta m_{\mathrm{bag}}/m_{0,\mathrm{bag}}$ and $\Delta m_{\mathrm{bottle}}/m_{0,\mathrm{bottle}}$ in Table 3 should be multiplied by 1.11 and 1.12, respectively.

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[4] Masses of the PET-bagged bottles for NIST in Table 3 were measured immediately prior to opening the PET bags.

Table 3. Mass Changes on Shipping: PET-Bagged Bottles and Sample Bottles.

Sample information		Data Pertaining to Bagged Bottle				Data Pertaining to Bottle outside Bags			
NMI	Bottle No.	25-Jun pre-ship mass, $m_{0,\mathrm{bag}}$/g	Weighing Date at NMI	m_{bag}/g (NMI)	Relative change in mass $\Delta m_{\mathrm{bag}}/m_{0,\mathrm{bag}}$	24-Jun pre-ship mass, $m_{0,\mathrm{bottle}}$/g	Weighing Date for m_{bottle} (NMI)	m_{bottle}/g (NMI)	Relative change in mass $\Delta m_{\mathrm{bottle}}/m_{0,\mathrm{bottle}}$
CENAM	4	314.553	3-Aug	314.552	-0.0003%	300.944	1-Sep	300.926	-0.0060%
	44	308.011	3-Aug	307.997	-0.0044%	294.485	1-Sep	294.456	-0.0097%
	49	309.536	3-Aug	309.531	-0.0015%	296.170	1-Sep	296.152	-0.0059%
DFM	20	313.624	2-Jul	313.635	0.0034%	300.158	---	---	---
	31	311.777	2-Jul	311.783	0.0018%	298.196	---	---	---
GUM	25	312.708	14-Jul	312.710	0.0005%	299.083	8-Sep	299.071	-0.0040%
	39	309.474	14-Jul	309.460	-0.0045%	295.896	15-Sep	295.886	-0.0033%
	60	312.755	14-Jul	312.760	0.0015%	298.170	16-Sep	298.155	-0.0050%
INMETRO	21	311.778	27-Jul	311.775	-0.0011%	298.598	6-Aug	298.583	-0.0052%
	56	307.128	27-Jul	307.119	-0.0027%	293.662	6-Aug	293.631	-0.0107%
INTI	19	312.102	6-Jul	312.120	0.0059%	298.342	5-Aug	298.340	-0.0007%
	42	309.613	6-Jul	309.620	0.0022%	296.300	---	---	---
	53	312.035	6-Jul	312.050	0.0049%	298.325	20-Aug	298.310	-0.0051%
IPQ	8	304.238	3-Jul	304.380	0.0468%	290.943	29-Jul	290.938	-0.0015%
	36	309.285	3-Jul	309.250	-0.0113%	295.654	14-Aug	295.634	-0.0069%
	45	309.393	3-Jul	309.340	-0.0171%	295.835	17-Aug	295.815	-0.0065%
KRISS	10	312.968	7-Jul	312.986	0.0059%	299.435	15-Sep	299.408	-0.0090%
	33	310.722	7-Jul	310.740	0.0056%	296.987	29-Sep	296.949	-0.0127%
NIM	9	309.891	6-Jul	309.894	0.0008%	296.477	23-Sep	296.461	-0.0055%
	40	307.165	6-Jul	307.172	0.0024%	293.480	23-Sep	293.470	-0.0035%
NIST	3	309.554	24-Sep	309.562	0.0025%	295.818	25-Sep	295.809	-0.0027%
	28	312.398	24-Sep	312.406	0.0025%	299.184	24-Sep	299.174	-0.0033%
	57	310.558	24-Sep	310.569	0.0034%	296.981	28-Sep	296.969	-0.0040%
NMIJ	7	312.014	30-Jun	312.015	0.0003%	298.317	11-Aug	298.308	-0.0029%
	27	314.019	30-Jun	314.020	0.0003%	300.207	---	---	---
	52	308.259	30-Jun	308.264	0.0016%	294.547	---	---	---
SMÚ	6	306.600	7-Jul	306.606	0.0019%	293.054	23-Sep	293.042	-0.0040%
	59	306.273	7-Jul	306.277	0.0015%	292.457	23-Sep	292.446	-0.0038%
UMTS	14	309.970	21-Jul	309.954	-0.0050%	296.607	25-Aug	296.583	-0.0082%
	62	310.056	21-Jul	310.042	-0.0044%	296.026	25-Aug	295.999	-0.0090%

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.

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

NMI	Study	Sample Received	Measurement Period	Report Received
CENAM	K73	20-Jul	1-6 Sep	30-Sep
DFM	K73	1-Jul	---	---
GUM	K73	14-Jul	8, 16 Sep	30-Sep
INMETRO	K73	24-Jul	24 Aug-18 Sep	24-Sep
INTI	K73	1-Jul	5, 19 Aug	7-Oct
IPQ	K73	2-Jul	29 Jul-25 Aug	30-Sep
KRISS	K73	29-Jun	28-30 Sep	1-Oct
NIM	K73	6-Jul	2-17 Sep	27-Sep
NIST	K73	25-Jun	24-28 Sep	1-Oct
NMIJ	K73	29-Jun	12-13 Sep	30-Sep
SMU	K73	30-Jun	23-25 Sep	29-Sep
UMTS	K73	9-Jul	26-27 Sep	30-Sep
VNIIFTRI	K73	---	---	---

All CCQM-K73 reports were received by the deadline, excepting INTI, who requested (and was granted) an extension within the allotted timeframe. The results were distributed to all participants on 20 October.

Correspondence with Participants

Each participant was contacted as the weighing and reported results were received by the coordinator. One participant also received specific correspondence from the coordinator prior to the report deadline as noted below.

CENAM requested advice regarding the correct procedure to follow if analysis is performed using more than one method. On being advised that the selection of method(s) and whether to combine results is left solely to the participant, CENAM elected to submit the coulometric result as their CCQM-K73 result and to submit the separate titrimetric result as an information value. CENAM was also advised to recheck the weighings of their bottles and did so. The results in Table 3 reflect the revised mass values.

In none of the above cases was any information released or implied in any correspondence regarding the value of ν_{H^+} for the CCQM-K73 solution, prior to the release of the summary of results to all participants on 20 October.

Results and Discussion

The results are summarized in Table 5 for CCQM-K73. In addition to the official results, several participants also reported “information only” values for the CCQM-K73 solution based on other determinations. The information only results are listed in Table 6 for comparison with the official results.

Table 5. Results of Key Comparison CCQM-K73 Sorted by Value.

NMI	**Amount Content of H^+**	
	ν_{H^+}/(mol·kg^{-1})	U/(mol·kg^{-1})
IPQ	0.100 143	0.000 092
UMTS	0.100 42	0.000 48
INTI	0.100 87	0.000 30
CENAM	0.100 894	0.000 013
KRISS	0.100 906	0.000 018
NIM	0.100 917	0.000 080
NIST	0.100 922 4	0.000 004 5
SMÚ	0.100 936 7	0.000 007 8
NMIJ	0.100 941 5	0.000 005 8
INMETRO	0.100 974 1	0.000 004 9
GUM	0.101 04	0.000 26

Table 6. Results of “Information Only” Values for CCQM-K73 Solution Sorted by Value.

NMI	**Measurand *j***	**Amount Content**	
		ν_j/(mol·kg^{-1})	U_j/(mol·kg^{-1})
CENAM	H^+	0.100 884	0.000 038
NIM	Cl^-	0.100 922	0.000 102
NIM	H^+	0.101 070	0.000 114

The above-tabulated values are presented in graphical form in Figures 1a and 1b, with the results sorted by value within the given study. The Key Comparison Reference Value (KCRV), calculated as described below, is shown in Figure 1a as a reference. Figure 1b is identical to Figure 1a except that the *y*-axis is expanded by a factor of 10 around the KCRV.

Figure 1a. Results of Key Comparison CCQM-K73 and Submitted “Information-Only” Values. Error Bars Correspond to Standard Uncertainties (k = 1).

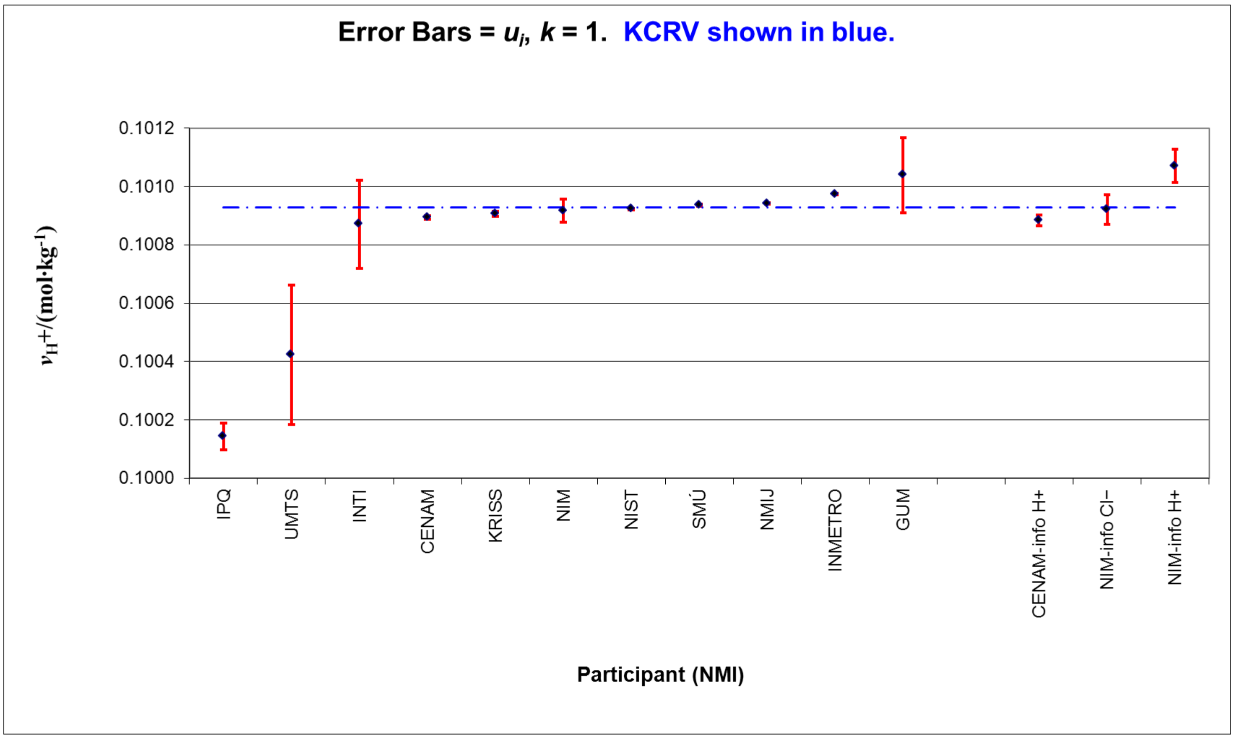
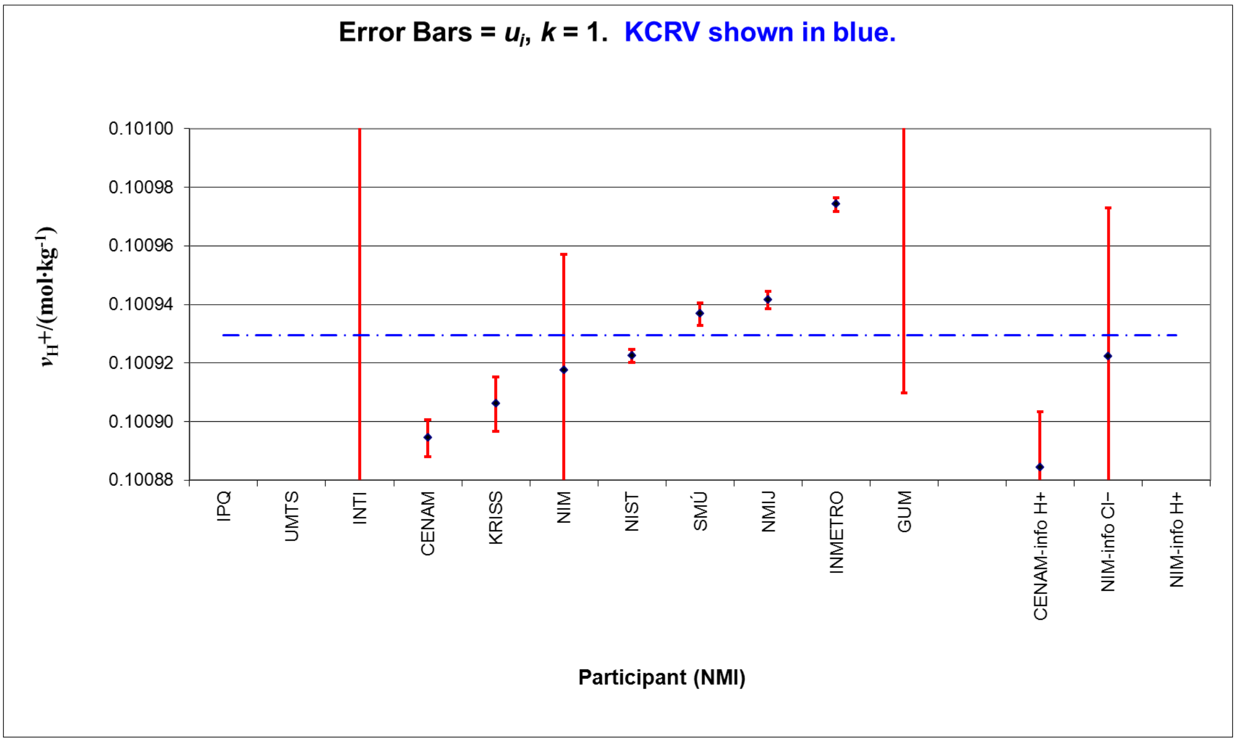


Figure 1b. 10-Fold Expansion of Figure 1a around KCRV.



Measurement Techniques

Table 7 lists the methods used by the participants. Participants are listed in alphabetical order within each set of results.

Table 7. Participant Methods.

Set of Results	NMI	Method (for titrimetry – reference compound)	CRM[a] (for titrimetry), Comments (coulometry)
K73	CENAM	coulometry – vertical	
	GUM	titrimetry (Tris[b])	SMÚ A0701509
	INMETRO	coulometry – vertical	
	INTI	titrimetry (KHP[c])	NIST 84j
	IPQ	titrimetry Cl^- (KCl)	NIST 999b
	KRISS	coulometry – horizontal, 2 IC	
	NIM	coulometry – horizontal, 2 IC	
	NIST	coulometry – horizontal, 2 IC	
	NMIJ	coulometry – horizontal, 2 IC	
	SMÚ	coulometry – vertical	
	UMTS	coulometry – agar membrane, 1 IC	
Info values	CENAM – H^+	titrimetry (Tris)	NIST 723d
	NIM – Cl^-	coulometry Cl – horizontal, 2 IC	Result uncorrected for Br
	NIM – H^+	titrimetry (Na_2CO_3)	NIM GBW06101A

[a] Certified reference material
[b] Tris(hydroxymethyl)aminomethane
[c] Potassium hydrogen phthalate

For participants who used coulometry, Table 7 notes the configuration of the coulometric cell and the number of intermediate compartments (IC) used. Coulometric cells use two general configurations: vertical and horizontal [3]. Vertical cells have the counter-electrode half-cell (anode for titrations of H^+) situated vertically along the center axis of the sample half-cell (cathode for titrations of H^+). An intermediate compartment (IC) along this same axis connects the two half-cells. To avoid losses of sample or titrant, the IC usually is filled with solution withdrawn from the sample cell prior to sample introduction and returned during the course of the main titration. Horizontal cells have the counter-electrode half-cell and the sample half-cell situated parallel (side-by-side), with one or (generally) two ICs connecting the two half-cells near their bottoms. In both configurations, any sample or titrant that diffuses into the IC(s) is returned to the sample cell by emptying and filling the IC(s) pneumatically (piston burette or gas pressure/vacuum).

All participants that used coulometry used a silver anode in the coulometric cell. Anode geometries varied. A silver anode has the advantage that the pH of the anolyte (electrolyte in the anode compartment) remains virtually constant during the electrolysis, owing to the absence of H^+ in the anodic half-reaction:

$$\mathrm{Ag} + \mathrm{Cl}^- \rightarrow \mathrm{AgCl(s)} + e^-.$$

Participants that used titrimetry generally used gravimetric delivery of the major fraction of the titrant, with volumetric additions near the end point.

IPQ performed an argentimetric titration of Cl^{-} in the CCQM-K73 sample. No correction was performed for Br^{-}. The reported value of ν_{H^+} was obtained via the assumption of equality between the reported ν_{H^+} and the amount content of total halide (result of the Ag^+ titration) in the HCl sample.

Traceability of Titrimetric Results

Titrimetric methods are (in principle) primary ratio methods [4]. A titrimetric method compares an amount of analyte to a standard of the same quantity. Therefore, each titrimetric result must be traceable to a reference compound. For each participant that used titrimetry, Table 7 notes the reference compound that was used and the specific certified reference material (CRM) that served as the acidimetric standard. Two exceptions are noted. The IPQ result was not traceable to an acidimetric standard, but rather to a KCl standard.

Each CRM noted in Table 7 (other than the pH CRM with no certified assay) was certified by coulometry. The Tris CRMs were certified using HCl as the excess added substance in a coulometric back-titration. Hence, the issues discussed below with respect to the CCQM-K73 coulometric results apply indirectly to those participants that used Tris as the reference CRM. Although an existing KC is available for KHP [5], certain problems associated with the coulometric determination of ν_{H^+} in the CCQM-K73 solution apply also in the case of KHP. The NIM Na_2CO_3 CRM was certified by coulometry with electrogenerated H^+ [6] and does not involve the coulometric standardization of HCl in its certification.

Statistical Evaluation of the Results

A Birge analysis [7] of the CCQM-K73 results was performed. The weighted mean of the participants' results, $\nu_{\mathrm{R}}(\mathrm{H}^+)$, for CCQM-K73 was calculated using Eq 1:

$$\nu_{\mathrm{R}}(\mathrm{H}^+) = \sum_{i=1}^{n} w_i \nu_i(\mathrm{H}^+) . \tag{1}$$

The w_i are given by Eq 2, where $u(x_i)$ is the reported standard uncertainty for participant i:

$$w_i = \frac{\dfrac{1}{u^2[\nu_i(\mathrm{H}^+)]}}{\displaystyle\sum_{i=1}^{n} \frac{1}{u^2[\nu_i(\mathrm{H}^+)]}} . \tag{2}$$

The uncertainty of the weighted mean for CCQM-K73 determined by the external consistency method, $u_{\mathrm{E}}[\nu_{\mathrm{R}}(\mathrm{H}^+)]$, was calculated at each temperature using Eq 3:

$$u_{\mathrm{E}}[\nu_{\mathrm{R}}(\mathrm{H}^+)] = \sqrt{\frac{\displaystyle\sum_{i=1}^{n} w_i \left(\nu_i(\mathrm{H}^+) - \nu_{\mathrm{R}}(\mathrm{H}^+)\right)^2}{n-1}} . \tag{3}$$

In Eq 3, n is the number of participants, w_i is the normalized weight for participant i, and $\nu_i(\mathrm{H}^+)$ is the reported result for participant i.

The uncertainty of the weighted mean for CCQM- K73 determined by the internal consistency method, $u_\mathrm{m}[\nu_\mathrm{R}(\mathrm{H}^+)]$, was also calculated. The value for $u_\mathrm{m}[\nu_\mathrm{R}(\mathrm{H}^+)]$ is given by Eq 4:

$$u_\mathrm{m}[\nu_\mathrm{R}(\mathrm{H}^+)] = \sqrt{\frac{1}{\sum_{i=1}^{n} \frac{1}{u^2[\nu_i(\mathrm{H}^+)]}}} . \qquad (4)$$

The Birge ratio, $R = u_\mathrm{E}/u_\mathrm{m}$, was then calculated at each temperature. The result including all CCQM-K73 participants was R = 7.923. The Birge ratio including all CCQM-K73 participants except IPQ was 6.024. Each of these R values indicate that in each case (including or excluding IPQ), the external (between-participant) uncertainty greatly dominates over the claimed uncertainties of the participants. The value compares to R values between 1.6 and 3.6 for pH KCs [10-15], in which the claimed uncertainties were far more consistent with the between-participant scatter.

The CCQM-K73 results were subsequently submitted for statistical evaluation by S. Ellison, LGC. His analysis (slightly rephrased from [8]) is as follows.

> The χ^2 on all the CCQM-K73 participants came out over 600. This value is far too large. Usually, the problem goes away after eliminating the obvious outliers (in this case, IPQ). Omitting IPQ, the χ^2 is still ≈300. To accept the hypothesis of mutual consistency, the χ^2 would have to be not greater than about 20.
>
> Other explorations make it clear that this is not down to any one or two labs. IPQ aside, it is mostly a matter of substantive disagreement among the labs with the smallest uncertainties.
>
> With such marked disagreement among those labs, there is no real point in seeking a KCRV at all, unless the differences turn out to be attributable to test material inhomogeneity. Otherwise, the participants with large uncertainties can mostly take some comfort from it – they mostly agree with each other and with the participants with small uncertainties. On this evidence, the participants with large uncertainties have no additional work to do. The participants in the middle, particularly those with the four smallest uncertainties, need to work to find out what is going on. In other words, about half the data set are in disagreement and the other half mostly have such large uncertainties that they all agree with everyone.
>
> [Ellison's] recommendation is not to put a KCRV on CCQM-K73, and it is even more difficult to assign an uncertainty to the KCRV. If an uncertainty is assigned to the KCRV, it would be large.
>
> [Ellison's] current favorite estimator for this kind of situation (an MM-estimate, which is uncertainty-respecting, very robust, and uses a Birge-like scale expansion) comes in at 0.100 928 2 $\mathrm{mol \cdot kg^{-1}}$ with a standard deviation of the mean of 0.000 005 8 $\mathrm{mol \cdot kg^{-1}}$. The only CCQM-K73 participants that are heavily downweighted in this calculation are IPQ and INMETRO.
>
> Even if the MM-estimate model is used, [Ellison is] still not at all sure what should be used for the uncertainties of the degrees of equivalence.

Calculation of the KCRV and Its Uncertainty

Calculations of candidate KCRVs, x, and corresponding combined standard uncertainties of the candidate KCRVs, u_KCRV, were performed using two data sets: (1), the set of nine CCQM-K73 results (excluding IPQ and UMTS), n = 9; and (2), the central set of seven coulometric results from CENAM through INMETRO (see Table 5, Figures 1a and 1b), $n = 7$. The $n = 9$ set contains titrimetric results from two participants: INTI and GUM. The $n = 7$ set includes only the coulometric results.

Calculations were performed for each data set using the following statistical estimators: mean (unweighted), median, Graybill-Deal, and DerSimonian-Laird. The results are shown in Table 8 for the $n = 9$ set and Table 9 for the $n = 7$ set.

Table 8. Statistical Estimators for CCQM-K73 Results. IPQ and UMTS Excluded ($n = 9$).

Estimator	Candidate Value, $x/(\mathrm{mol\cdot kg^{-1}})$	$u(\mathrm{Value})/(\mathrm{mol\cdot kg^{-1}})$
Mean	0.100 933 6	0.000 016 4
Median	0.100 922 4	0.000 011 8
Graybill-Deal	0.100 941 1	0.000 001 4
DerSimonian-Laird	0.100 929 6	0.000 010 8

Table 9. Statistical Estimators for CCQM-K73 Results. Coulometric Results Only, Excluding UMTS ($n = 7$).

Estimator	$\mathrm{Value}/(\mathrm{mol\cdot kg^{-1}})$	$u(\mathrm{Value})/(\mathrm{mol\cdot kg^{-1}})$
Mean	0.100 927 5	0.000 009 9
Median	0.100 922 4	0.000 011 2
Graybill-Deal	0.100 940 9	0.000 001 4
DerSimonian-Laird	0.100 929 2	0.000 010 9

The best estimator for the present data should consider the degree of confidence in the reported uncertainties of the participants. The mean and median each neglect the reported uncertainties in obtaining the final value. The Graybill-Deal estimator overestimates the effect of results with low uncertainties and is inappropriate for the present set of data.

Preliminary results were presented to the April 2011 joint IAWG-EAWG meeting of the CCQM. At this meeting, it was felt that the uncertainties reflect the differences in the procedures, yet many of the reported uncertainty intervals do not overlap. Accordingly, it was decided to use the DerSimonian-Laird estimator for the KCRV and u_{KCRV} for CCQM-K73.

Based on the above analysis, the Degrees of Equivalence, d_i, and uncertainties of the Degrees of Equivalence, $u(d_i)$, were calculated for each participant. Values of d_i were calculated using Eq 5, where the KCRV is given by the DerSimonian-Laird mean, x_{DL}, and x_i is the reported result of participant i:

$$d_i = x_i - x_{\mathrm{DL}}. \qquad (5)$$

For the nine participants for which the results were used in calculating the KCRV, the $u(d_i)$ were calculated using Eq 6, where u_i is the standard uncertainty reported by participant i, λ is the interlaboratory variation, and $u(x_{\mathrm{DL}})$ is the standard uncertainty of x_{DL}:

$$u(d_i) = \sqrt{u_i^2 + \lambda - u^2(x_{\mathrm{DL}})}. \qquad (6)$$

For the two participants (IPQ and UMTS) whose results were not used in calculating the KCRV, the $u(d_i)$ were calculated using Eq 7:

$$u(d_i) = \sqrt{u_i^2 + \lambda + u^2(x_{\mathrm{DL}})}. \qquad (7)$$

Table 10 gives the $x_{\mathrm{KCRV}} = x_{\mathrm{DL}}$, x_i, u_{KCRV}, d_i, $u(d_i)$; and the corresponding relative quantities, d_i/x_{KCRV}, $u(d_i)/x_{\mathrm{KCRV}}$, for CCQM-K73. The $u(d_i)$ for CCQM-K73 have a minimum value, equal to $\sqrt{\lambda - u^2(x_{\mathrm{DL}})}$ = 0.000 024 mol·kg^{-1}, that is set by the between-laboratory scatter of results. This circumstance limits the utility of the results of this KC to support claimed uncertainties that are smaller than this value.

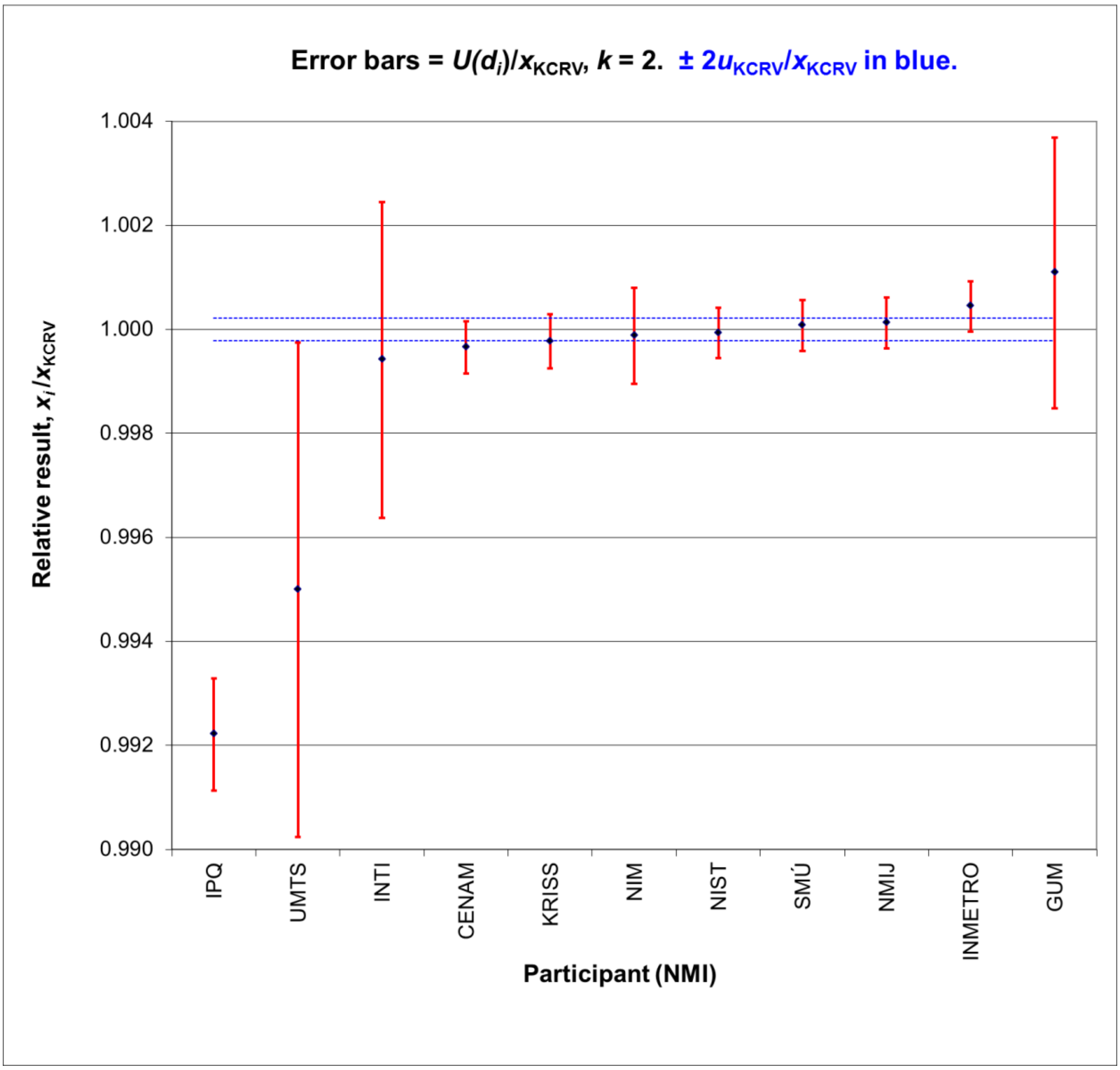
Table 10. Key Comparison Reference Value[a] for CCQM-K73, x_{KCRV}; its Standard Uncertainty, u_{KCRV}; Degrees of Equivalence, d_i; Standard Uncertainties of the d_i, $u(d_i)$; and Relative Values of these Quantities Referred to x_{KCRV}.

Participant (NMI)	Value, x_i/(mol·kg^{-1})	d_i/(mol·kg^{-1})	$u(d_i)$/(mol·kg^{-1})	Relative value, x_i/x_{KCRV}	d_i/x_{KCRV}	$u(d_i)/x_{\mathrm{KCRV}}$
KCRV	0.100 930	---	0.000 011	1.000 00	---	0.000 11
IPQ	0.100 143	-0.000 786	0.000 054	0.992 21	-0.007 79	0.000 54
UMTS	0.100 424	-0.000 506	0.000 240	0.994 99	-0.005 01	0.002 38
INTI	0.100 871	-0.000 059	0.000 153	0.999 41	-0.000 59	0.001 52
CENAM	0.100 894	-0.000 035	0.000 025	0.999 65	-0.000 35	0.000 25
KRISS	0.100 906	-0.000 024	0.000 026	0.999 77	-0.000 23	0.000 26
NIM	0.100 917	-0.000 012	0.000 047	0.999 88	-0.000 12	0.000 46
NIST	0.100 922	-0.000 007	0.000 025	0.999 93	-0.000 07	0.000 24
SMÚ	0.100 937	0.000 007	0.000 025	1.000 07	0.000 07	0.000 25
NMIJ	0.100 942	0.000 012	0.000 025	1.000 12	0.000 12	0.000 24
INMETRO	0.100 974	0.000 044	0.000 025	1.000 44	0.000 44	0.000 24
GUM	0.101 039	0.000 109	0.000 131	1.001 08	0.001 08	0.001 30

[a] First line of table presents x_{KCRV}, u_{KCRV}, and $u_{\mathrm{KCRV}}/x_{\mathrm{KCRV}}$.

The above-tabulated relative values are presented in graphical form in Figure 2, with the results sorted in order of increasing x_i/x_{KCRV}.

Figure 2. Relative Degrees of Equivalence, d_i/x_{KCRV}, for CCQM-K73. Error Bars Denote Expanded Uncertainty of d_i, $U(d_i)/x_{KCRV}$, with $k = 2$.



Determination of Impurities

CENAM and NIM determined impurities in the CCQM-K73 solution. The reported determinations, in terms of mass fraction of the given element, are listed in Table 11. Inductively coupled plasma – mass spectrometry (ICP-MS) was used in all determinations.

Table 11. Reported Impurities in CCQM-K73 Solution.

NMI	**Impurity *i***	**Mass Fraction**		**Comments**
		w_i/(μg·kg^{-1})	U_i/(μg·kg^{-1})	
CENAM	Na K	27.3, 27.5, 14.08 16.9, 22.2, 10.6	1.0, 2.2, 0.79 1.5, 1.0. 1.5	w_i and U_i values listed for bottles 4, 44, 49, in that order
NIM	Br	336	17	Agilent 7500CE, standard addition

How Far the Light Shines

Key Comparison CCQM-K73 directly covers the dissemination of the direct measurement of ν_{H^+} at those NMIs that provide this service to customers. The value of ν_{H^+} typically measured in such instances is on the order of 0.1 mol·kg^{-1}. However, standardization of strong acids via the determination of the anion of the strong acid (e.g., ν_{Cl^-} by argentimetry in HCl solutions) is not covered by CCQM-K73. In addition, the measurement of significantly smaller ν_{H^+} values (e.g., acid rain samples) is not covered, unless the larger uncertainties for the measurement in dilute solutions are taken into account.

In addition to the direct dissemination of the measurement of ν_{H^+}, CCQM-K73 also provides information on two other major uses of standard HCl solutions at NMIs.

The first use is in the certification of those base CRMs in which an HCl solution with ν_{H^+} on the order of 0.1 mol·kg^{-1} is used as the titrant (or as the excess added substance in a coulometric back-titration) for the acidimetric certification of the CRM. In such cases, CCQM-K73 informs only regarding the attainable uncertainty for the standardization of the titrant (or the excess added substance), not as to the overall certification of the base CRM itself. In most such cases, the uncertainty of the CRM titration (or coulometric back-titration) significantly exceeds that of the standardization of the HCl.

The second use of standard HCl solutions at NMIs is in the determination of the standard electrode potential, $E°$, for Ag|AgCl electrodes used in the primary measurement of pH [3,9]. For this application, the value of ν_{H^+} is usually fixed at 0.01 mol·kg^{-1}. The relevant uncertainty for the disseminated pH measurement is given by the pH KC for the corresponding buffer [10-15]. However, CCQM-K73 can inform as to the expected uncertainty for the standardization of the HCl solution itself. The claimed uncertainty must take into account any increase in the uncertainty associated either with the titration of a solution with $\nu_{\mathrm{H}^+} = 0.01$ mol·kg^{-1} or with the gravimetric dilution of a solution with $\nu_{\mathrm{H}^+} \approx 0.1$ mol·kg^{-1} to $\nu_{\mathrm{H}^+} = 0.01$ mol·kg^{-1}.

Conclusion

Eleven NMIs participated in Key Comparison CCQM-K73, Amount Content of H^+ in Hydrochloric Acid. The agreement among participants with the lowest uncertainties was not as good as would be expected, although agreement among participants with large reported uncertainties was acceptable. Candidate values for the KCRV and u_{KCRV} were calculated using several statistical estimators.

In an effort to resolve the observed discrepancy in the results, a Coulometric Workshop was conducted in April 2010 at the joint meeting of the EAWG and IAWG. Although several

NMIs reported detailed investigations of possible sources of bias at that Workshop and in subsequent work, no specific cause for the dispersion of results was evident.

A part of the excess variation originates from the change in mass of the bottles during shipment. However, this source of uncertainty was evaluated by a controlled protocol of mass checks of the bottles on receipt. The results of these mass checks indicate that the change in mass associated with shipment (see Table 3) only accounts for a small fraction of the observed excess variation of the results among those participants with the lowest reported uncertainties.

In the absence of a specific cause for the dispersion, the IAWG and EAWG decided to assign a KCRV and u_{KCRV} based on the DerSimonian-Laird statistical estimator. The uncertainty u_{KCRV} is dominated by the between-laboratory scatter of results in CCQM-K73. Owing to the high between-laboratory scatter, the claims of the participants with the lowest reported uncertainties cannot be supported by this comparison.

Acknowledgment
The coordinating laboratory gratefully acknowledges the contributions of all participants and of the members of the CCQM Working Groups on Inorganic Analysis and Electrochemical Analysis for their valuable suggestions concerning the measurement protocol and the evaluation process. The contributions of David Duewer (NIST), Hugo Gasca-Aragón (NIST and CENAM), and Steve Ellison (LGC) in the statistical evaluation are also gratefully acknowledged.

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Appendix

Technical Protocol

CCQM-K73/CCQM-P19.2 Amount Content of H^+ in Hydrochloric Acid

Introduction

Key Comparison CCQM-K73 and the parallel Pilot Study CCQM-P19.2 are being performed to evaluate the degree of equivalence of national measurement procedures for the assay of hydrochloric acid. The measurand is amount content of hydrogen ion, $\nu_{\mathrm{H^+}}$. The nominal value of $\nu_{\mathrm{H^+}}$ is 0.1 $\mathrm{mol \cdot kg^{-1}}$.

The measurement procedure is left to the participant. Any method or combination of methods is acceptable. It is anticipated that the majority of participants will use coulometry or titrimetry.

Information on impurities, particularly bromide, is also of interest. This information will be provided as an annex to the Key Comparison and Pilot Study results.

Time schedule

Dispatch of the samples:	30 June 2009
Deadline for receipt of the Data Reporting Form	30 September 2009
Draft A report distributed	1 November 2009
Discussion of results and Draft A report	EAWG/IAWG joint meeting, Nov. 2009
Draft B report	1 March 2010
Approval of Draft B report	EAWG/IAWG joint meeting, April 2010

Description of the sample and details of shipment

The HCl comparison solution is prepared from deionized water and reagent-grade hydrochloric acid. This solution is bottled in separately-numbered, 250 mL high-density polyethylene (HDPE) bottles. The cap of each bottle is sealed with a transparent, heat-shrink plastic seal that extends to the neck of the bottle. Each bottle is sealed inside two bags: a transparent, interior polyethylene bag and an exterior aluminized polyethylene terephthalate (PET) bag. Each bottle and its exterior PET bag are labeled with the number of the bottle and a description of the contents.

Each participant will receive two (three, if requested) separately-numbered bottles filled with the comparison solution. The bottles will be shipped in a cardboard box or other container by air courier. The coordinating laboratory will send the tracking number by email to the contact person of the corresponding receiving laboratory. The contents will be marked “aqueous solution” with value 1 USD per bottle. Please be attentive to possible customs delays, etc. Shipment to all participants will be performed at the same time.

The Coordinating Laboratory will verify the homogeneity of the material before shipment and will perform a stability check in the course of the comparison.

Two spreadsheets are being distributed simultaneously with this Technical Protocol. The file K73_P19.2_bottle_masses.xls is for reporting the masses of the bottles and related information, for verification of integrity of the shipment. The second file, K73_P19.2_Data_Reporting_Form.xls, is used to report the results of the measurements of ν_{H^+} and measurements of impurities.

Actions at receipt of samples

1. Inspect the bagged bottles for visible damage or leakage.
2. Confirm the sample receipt (by e-mail), report any damage, and send the weighing data for the bagged bottles to the Coordinating Laboratory using the worksheet "(1) Bagged Bottles". Please send this information as soon as it is available, to permit timely reshipment of a new bottle if necessary.
3. Store the bottles at room temperature in their original PET bags. Refrigeration of the bottles is not necessary.

Instructions for participants

1. Weigh each bagged bottle with a resolution of 0.01 g or less to verify its integrity during shipping. Allow the bagged bottle to equilibrate in the weighing laboratory overnight before performing the weighing. Report both the weighing result (balance reading) and the bottle mass (corrected for air buoyancy) on the worksheet "(1) Bagged Bottles". Use an assumed aggregate density of 1000 $kg \cdot m^{-3}$ for the bagged bottle in correcting for air buoyancy. Also report on this worksheet the ambient atmospheric pressure and temperature at the time the bottle was weighed.
2. Store the bottles in their original exterior bags until you are ready to perform the measurements of ν_{H^+}.
3. When you are ready to start the measurements of ν_{H^+}, open the exterior bag by cutting it between or above the red lines on the outside the bag. These red lines correspond approximately to the upper edge of the interior polyethylene bag.
4. Remove the bottle with its transparent, interior bag from the exterior bag. Verify that no drops of liquid are present on the inside surface of the interior bag. If drops are noted, leakage has occurred. In this case, please contact the Coordinating Laboratory immediately to obtain a replacement bottle.
5. Remove the bottle from the interior bag.
6. Weigh the bottle, removed from the interior bag, including its label and heat-shrink plastic seal. Repeat the procedure in Step 1 of this section for the bottle removed from both bags. Record these data on the worksheet "(2) bottles" and send the data to the Coordinating Laboratory. Use an assumed aggregate density of 1000 $kg \cdot m^{-3}$ for the unbagged bottle.
7. Remove the heat-shrink plastic seal before opening the bottle. Make a small cut (1 mm to 2 mm) in the top portion of the seal with a scissors or knife. Then, peel the remaining seal off the bottle.
8. Please send the file K73_P19.2_bottle_masses.xls to the Coordinating Laboratory a second time with the masses of the unbagged bottles entered in the second worksheet.
9. Perform the assay measurements of ν_{H^+} using your selected procedure. To the extent possible, your selected procedure should conform with that which you use to disseminate this measurement capability at your institute.

Reporting

The Data Reporting Form should be sent to the Coordinating Laboratory before 30 September 2009, preferentially by e-mail. The Coordinating Laboratory will confirm the receipt of each Data Reporting Form. If the confirmation does not arrive within 1 week, please contact the Coordinating Laboratory to identify the problem.

The Data Reporting Form has three worksheets, Summary, H+ results, and Method+Example. The requested data should be entered into the corresponding boxes on each sheet. Certain items are automatically copied from one sheet to another. These items only have to be entered once. If you cannot enter your data into the cells as supplied, please change the format as necessary or submit the data in another form. A separate text report in place of the description “Analytical method - detailed description” is equally acceptable.

Please be sure to indicate in the Summary sheet the comparison in which you are participating, by entering an “X” in the applicable box of the Summary worksheet. This X will automatically cause the corresponding comparison to be entered into the worksheets and graph titles.

The uncertainty calculations should conform to the ISO document *Guide to the Expression of Uncertainty in Measurement*, 1st ed., ISO, Geneva, Switzerland, 1995. Both Type A and Type B components of uncertainty and a summary of how they are calculated must be included. Use the coverage factor, $k = 2$, to calculate the expanded uncertainty of your result.

Information requested:

1. Report the results as amount content of H^+, accompanied by a full uncertainty budget, on the worksheet “H+ results”.
2. Give a detailed description of the measurement procedure. For coulometry, this should include the following: description of the coulometric cell, volume of electrolyte in the working chamber, endpoint evaluation procedure, and the equipment used.
3. Give the complete measurement equation in the designated space in the worksheet “Method+Example”. Include in the space below the values of the input quantities (raw data) for a representative measurement. The data should enable the Coordinating Laboratory to recalculate of the result of that measurement.
4. In the worksheet “H+ results”, report all the individual results, not only the final mean value.
5. Provide a complete uncertainty budget for your measurement. This uncertainty budget must include instrumental sources of uncertainty (mass, time, voltage, volume, ...) as well as chemical ones (endpoint estimation, CO_2 interference, side-reactions, purity of calibration standards, ...)
6. In order to facilitate comparisons of your measured masses (for assay measurements), please also provide either (1) the air density used for each buoyancy correction, or (2) the air temperature, humidity and pressure in your laboratory at the time of each mass measurement.
7. Report the details of the procedure used (a separate text file can be used).
8. Information on impurities is welcome, especially for Br^-, owing to the influence of trace Br^- on the standard potential of the Ag|AgCl electrode in pH metrology.

Reference value

The reference value will be agreed upon on the joint meeting of the EAWG and IAWG in November 2009.

Participation

Participation in CCQM-K73 is open to all institutes eligible for a key comparison in this field. Participation in CCQM-P19.2 is additionally open to other designated laboratories. National Metrology Institutes that desire to use the results of the present comparison to support Claims of Measurement Capability (CMCs) should participate in CCQM-K73, not in CCQM-P19.2.

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