

Report of the key comparison APMP.QM-K19

APMP comparison on pH measurement of borate buffer

(Final Report)

Participants:

Akiharu Hioki, Toshiaki Asakai, Igor Maksimov, Toshihiro Suzuki and Tsutomu Miura (NMIJ); Krairerk Obromsook, Nongluck Tangpaisarnkul and Patumporn Rodruangthum (NIMT); Siu-Kay Wong and Wai-Hing Lam (GLHK); Osman Zakaria and Khirul Anuar Mohd. Amin (NML-SIRIM); Ngo Huy Thanh (VMI); Michal Máriássy, Leos Vyskocil and Zuzana Hankova (SMU); Paola Fisicaro and Daniela Stoica (LNE); Nahar Singh and Daya Soni (NPLI); Galia Ticona Canaza (INDECOPi); Viatcheslav Kutovoy (VNIIFTRI); Fabiano Barbieri Gonzaga and Júlio Cesar Dias (INMETRO); Alena Vospelova (CMI); Nickolay Bakovets (BelGIM); Bibinur Zhanasbayeva (KazInMetr).

Coordinated by

**Akiharu Hioki, Toshiaki Asakai, Igor Maksimov, Toshihiro Suzuki and
Tsutomu Miura (NMIJ),
Krairerk Obromsook and Nongluck Tangpaisarnkul (NIMT)**

September 2014

Abstract

The APMP.QM-K19 was organised by TCQM of APMP to test the abilities of the national metrology institutes in the APMP region to measure a pH value of a borate buffer. This APMP comparison on pH measurement was proposed by the National Metrology Institute of Japan (NMIJ) and the National Institute of Metrology (Thailand) (NIMT) at the APMP-TCQM meeting held November 26-27, 2012. After approval by TCQM, the comparison has been conducted by NMIJ and NIMT. The comparison is a key comparison following CCQM-K19 and CCQM-K19.1. The comparison material was a borate buffer of pH around 9.2 and the measurement temperatures were 15 °C, 25 °C and 37 °C. This is the second APMP key comparison on pH measurement and the fourth APMP comparison on pH measurement following APMP.QM-P06 (two phosphate buffers) in 2004, APMP.QM-P09 (a phthalate buffer) in 2006 and APMP.QM-K9/APMP.QM-P16 (a phosphate buffer) in 2010-2011.

The results can be used further by any participant to support its CMC claim at least for a borate buffer. That claim will concern the pH method employed by the participant during this comparison and will cover the used temperature(s) or the full temperature range between 15°C and 37 °C for the participant which measured pH values at the three temperatures.

1. Introduction

Measurement of pH is fundamental in many fields including environmental analysis and its accurate measurement is very important.

Following the pilot studies APMP.QM-P06 (two phosphate buffers) in 2004 and APMP.QM-P09 (a phthalate buffer) in 2006 conducted by NMIJ, and the key comparison APMP.QM-K9 (a phosphate buffer) and the parallel pilot study APMP.QM-P16 in 2010-2011 conducted by NMIJ and NIMT, the two institutes NMIJ and NIMT jointly proposed a key comparison of "pH measurement of borate buffer" at the APMP-TCQM meeting held November 26-27, 2012. Since the proposal was approved as APMP.QM-K19, NMIJ and NIMT have acted as coordinating laboratories. The pH values of a borate buffer were measured at the three temperatures (15 °C, 25 °C and 37 °C). Each participant could use any suitable method of measurement, not only a primary pH method with a Harned cell. Each participant using a secondary pH method was required to identify the traceability source. The homogeneity of the material used in this comparison had been investigated prior to the comparison. This is the second key comparison within APMP in the field of pH determination. NMI's or officially designated institutes (DI's), even outside APMP, were invited to participate in this comparison. SMU participated from the outside of APMP for more reliable linkage of APMP.QM-K19 to CCQM-K19.

It was decided to conduct a parallel pilot study designated APMP.QM-P25, for which the same samples measured by the APMP.QM-K19 participants were also used.

2. List of Participants

Table 1 contains the abbreviated and full names of all participating NMI's and DI's.

Table 1 List of participating NMI's and DI's

No.	Participant	Country/Economy
1	NMIJ National Metrology Institute of Japan	Japan
2	NIMT National Institute of Metrology (Thailand)	Thailand
3	GLHK Government Laboratory	Hong Kong
4	NML-SIRIM National Metrology Laboratory, SIRIM Berhad	Malaysia
5	VMI Vietnam Metrology Institute	Vietnam
6	SMU Slovak Institute of Metrology	Slovakia
7	LNE Laboratoire National de Metrologie et d'Essais	France
8	NPLI National Physical Laboratory of India	India
9	INDECOPI Instituto Nacional de Defensa de la Competencia y de la Protección de la Propiedad Intelectual	Peru
10	VNIIFTRI All-Russian Scientific Research Institute for Physical Technical and Radiotechnical Measurements, Rosstandart	Russia
11	INMETRO Instituto Nacional de Metrologia, Qualidade e Tecnologia	Brazil
12	CMI Czech Metrology Institut	Czech Republic
13	BelGIM Belarussian State Institute of Metrology	Belarus
14	KazInMetr Kazakhstan Institute of Metrology	Kazakhstan

3. Sample

The comparison material was a borate buffer of pH around 9.2 whose composition was slightly changed from the typical one for borate buffers. Each participant was provided with a 1000 mL bottle of the buffer; the participant employing a Harned cell method could be provided with two bottles (if requested). The result by a Harned cell method was reported as an acidity function; pH values were calculated afterwards by the coordinating institutes using the Bates–Guggenheim convention. The pH values were compared with those obtained by secondary pH methods, mainly by a glass-electrode. The link to CCQM-K19 was considered on the basis of the results (by a Harned cell method) from the NMI's which have successfully participated in the related CCQM comparisons.

The comparison sample was a borate buffer of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (molality 0.009872 mol/kg) prepared at NMIJ in April, 2013. The total volume of batch was 50 L, subsequently divided into 47 subsamples of 1000 mL polyethylene bottles. The pH value of the borate buffer is around 9.2 and the mass fraction of water in the buffer is 0.996 25; this information was given to the participants before measurements. The ionic strength I (as molality) calculated from the buffer composition is 0.019 745 mol/kg. The Debye-Huckel constants A in the equation used for the Bates-Guggenheim convention [Eq(1)] are 0.5026 at 15 °C, 0.5108 at 25 °C and 0.5215 at 37 °C.

$$\log \gamma_{Cl}^o = -A \sqrt{I} / (1 + 1.5 \sqrt{I}) \quad \text{Eq(1)}$$

Therefore, the values of $\log \gamma_{Cl}^o$ to be added to the acidity function obtained by a Harned cell method were equal to -0.0583 at 15 °C, -0.0593 at 25 °C and -0.0605 at 37 °C. The composition of the sample was a little different from that of the typical borate buffer. However, since the pH value of the sample for the APMP comparison is close to that for CCQM-K19, it is possible to link APMP.QM-K19 to CCQM-K19.

The homogeneity of the material was tested before shipping the samples; the pH values at 25 °C had experimental standard deviation 0.0003 for six subsamples by a glass-electrode method and experimental standard deviation 0.0008 for four subsamples by a Harned cell method.

The stability of the material was tested by four measurements with a Harned cell method from April to September 2013. The acidity function values obtained at 25 °C were 9.2395, 9.2397, 9.2382 and 9.2388 on April 18, May 1, September 12 and September 24, respectively: all the results were within ± 0.001 range.

The samples were sent to the participants from NMIJ by EMS mail on May 20, 2013 except for KazInMetr on May 23, 2013. All samples reached their destinations safely. The contact persons are given in Table 2.

Table 2 List of contact persons of NMI's

Participant	Contact person
NMIJ	Akiharu Hioki
NIMT	Nongluck Tangpaisarnkul
GLHK	Siu-kay Wong
NML-SIRIM	Osman Zakaria
VMI	Ngo Huy Thanh
SMU	Leos Vyskocil
LNE	Paola Fisicaro
NPLI	Nahar Singh
INDECOPI	Galia Ticono Canaza
VNIIFTRI	Viatcheslav Kutovoy
INMETRO	Fabiano Barbieri Gonzaga
CMi	Alena Vospelova
BelGIM	Nickolay Bakovets
KazInMetr	Bibinur Zhanasbayeva

4. Technical Protocol

The technical protocol attached as Annex A instructed participants about samples, methods of measurement, reporting and time schedule. The deadline for the reporting of results was September 30, 2013.

5. Methods of Measurement

Each participant could use a Harned cell method as employed in CCQM-K19 and CCQM-K19.1 or any suitable method of pH measurement (usually a glass-electrode method). The measurements had to be carried out by using standards with metrological traceability.

The methods are summarised in Table 3.

Table 3 The measurement methods used in APMP.QM-K19

	Participants
Harned cell method	NMIJ, NIMT, SMU, LNE, INMETRO, CMI, KazInMetr
Glass-electrode method	GLHK, NML-SIRIM, VMI, NPLI
Differential potentiometric cell method	INDECOPI, BelGIM

6. Results

The relative changes of bottle masses after shipping are presented in Figure 1. Each of NIMT, SMU, LNE, VNIIFTRI, INMETRO, CMI, and KazInMetr reported the changes on two bottles. Each change was very small and it substantially did not affect the pH value.

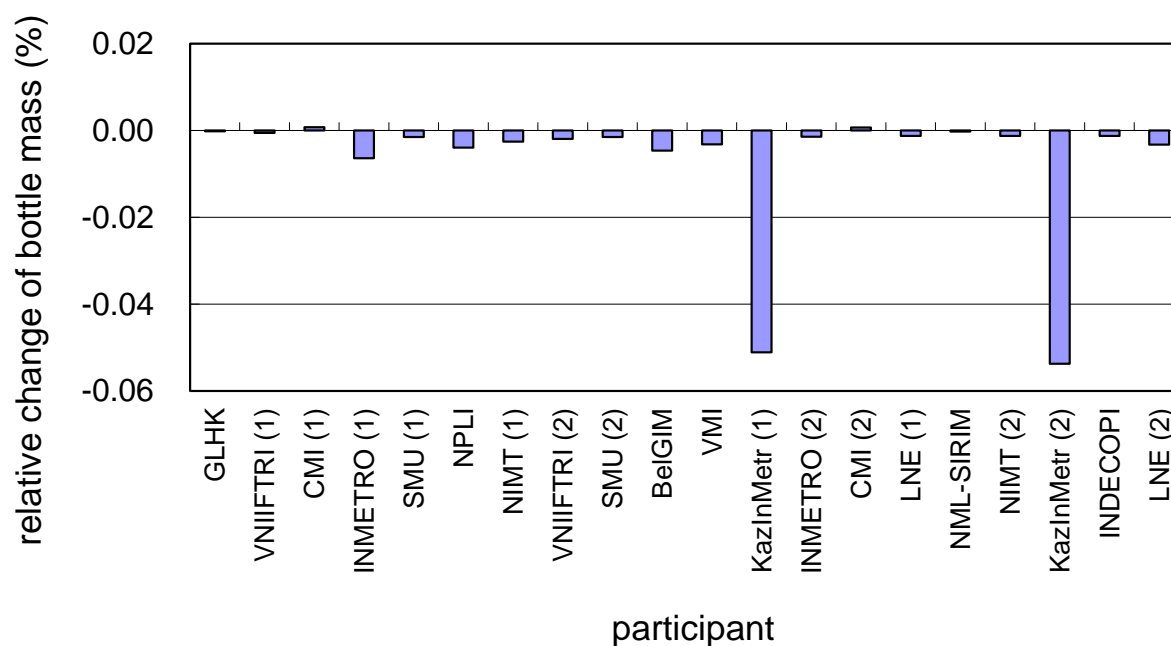


Fig. 1 Relative change of bottle mass after shipping

The person (Dr. V. Kutovoy) in charge of primary pH measurements at VNIIFTRI passed away after receiving the sample; therefore, VNIIFTRI could not submit their results of pH measurements.

The results of pH measurements are given in Tables 4-6 and illustrated in Figures 2-4. The bars in the Figures indicate the reported combined standard uncertainty (coverage factor $k = 1$). The result by a

Final Report of APMP.QM-K19 (September 2, 2014)

Harned cell method was reported as an acidity function; the pH value was calculated using the Bates–Guggenheim convention. In such way pH values can be compared with the pH values obtained by a glass-electrode method or a differential potentiometric cell method. For each temperature, both the arithmetic mean and the median of the results of all participants are shown. The horizontal line in each Figure indicates the arithmetic mean of the results of SMU and NMIJ.

Table 4 Results of APMP.QM-K19 at 15 °C

Participant	Calibration standards	Reported acidity function	$\log \gamma_{\text{Cl}}$	Reported (or calculated) pH	Combined standard uncertainty
NMIJ	---	9.3309	-0.0583	9.2726	0.0012
NIMT	---	9.3488	-0.0583	9.2905	0.0045
GLHK	NIST CRMs			9.280	0.0073
NML-SIRIM	NMIJ CRMs			9.2919	0.0035
VMI	pH buffer from NIMT			9.270	0.0065
SMU	---	9.3322	-0.0583	9.2739	0.0014
LNE	---	9.3318	-0.0583	9.2735	0.0014
NPLI					
INDECOPI	NIST CRM			9.274	0.002
INMETRO	---	9.3265	-0.0583	9.2682	0.0010
CMI	---	9.3342	-0.0583	9.2759	0.0011
BeIGIM	VNIIFTRI CRMs			9.297	0.0032
KazInMetr					

Table 5 Results of APMP.QM-K19 at 25 °C

Participant	Calibration standards	Reported acidity function	$\log \gamma_{\text{Cl}}$	Reported (or calculated) pH	Combined standard uncertainty
NMIJ	---	9.2395	-0.0593	9.1802	0.0011
NIMT	---	9.2703	-0.0593	9.2110	0.0034
GLHK	NIST CRMs			9.188	0.0061
NML-SIRIM	NMIJ CRMs			9.2030	0.0035
VMI	pH buffer from NIMT			9.208	0.0053
SMU	---	9.2392	-0.0593	9.1799	0.0010
LNE	---	9.2397	-0.0593	9.1804	0.0014
NPLI	Merck,* traceable to NIST/PTB			8.9775	0.0343
INDECOPI	NIST CRM			9.182	0.002
INMETRO	---	9.2352	-0.0593	9.1759	0.0011
CMI	---	9.2380	-0.0593	9.1787	0.0018
BeIGIM	VNIIFTRI CRMs			9.1977	0.0022
KazInMetr	---	9.2407	-0.0593	9.1814	0.0015

* The calibration solutions were commercial ones.

Table 6 Results of APMP.QM-K19 at 37 °C

Participant	Calibration standards	Reported acidity function	$\log \gamma_{\text{Cl}}^{\circ}$	Reported (or calculated) pH	Combined standard uncertainty
NMIJ	---	9.1517	-0.0605	9.0912	0.0011
NIMT	---	9.1761	-0.0605	9.1156	0.0041
GLHK	NIST CRMs			9.100	0.0062
NML-SIRIM	NMIJ CRMs			9.1125	0.0035
VMI	pH buffer from NIMT			9.131	0.0052
SMU	---	9.1503	-0.0605	9.0898	0.0018
LNE	---	9.1512	-0.0605	9.0907	0.0014
NPLI	Merck,* traceable to NIST/PTB			8.845	0.0572
INDECOPI	NIST CRM			9.093	0.002
INMETRO	---	9.1458	-0.0605	9.0853	0.0017
CMI	---	9.1480	-0.0605	9.0875	0.0011
BelGIM	VNIIFTRI CRMs			9.1073	0.0031
KazInMetr					

* The calibration solutions were commercial ones.

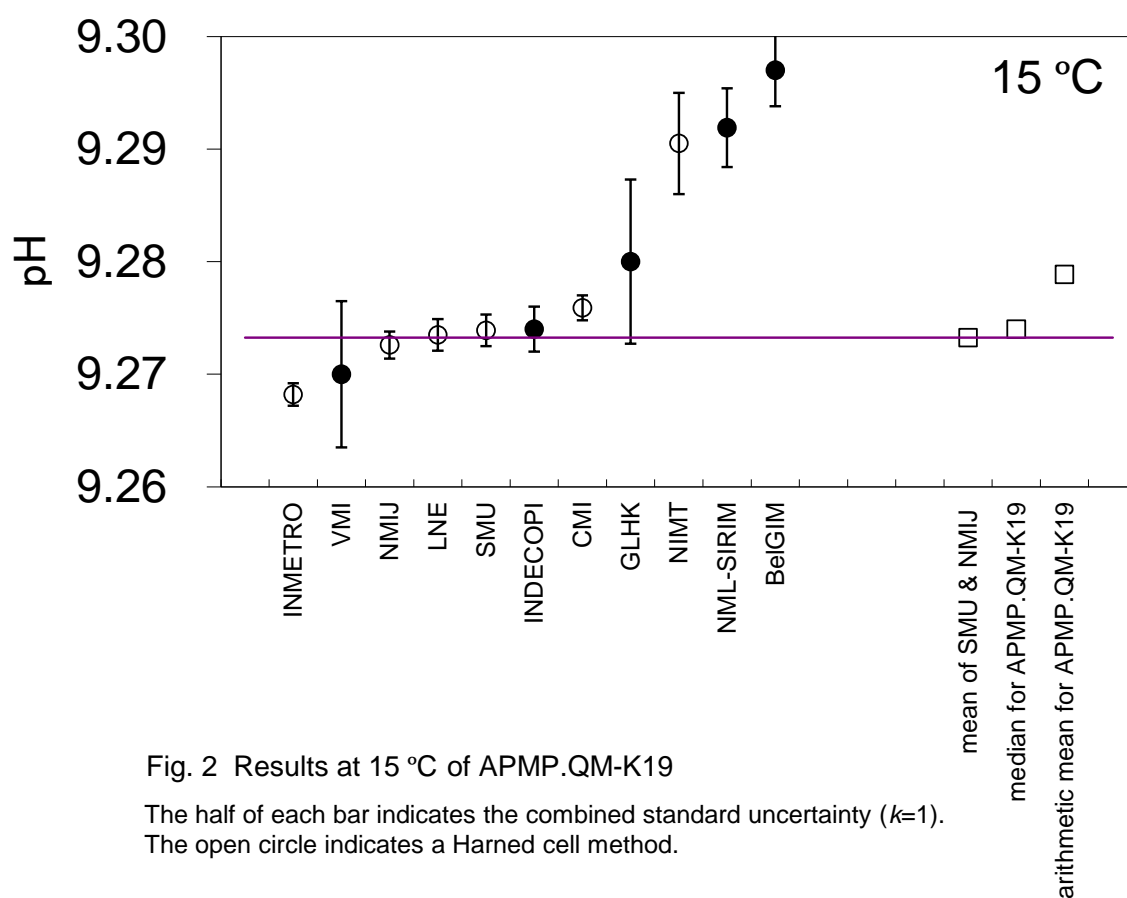


Fig. 2 Results at 15 °C of APMP.QM-K19

The half of each bar indicates the combined standard uncertainty ($k=1$).
The open circle indicates a Harned cell method.

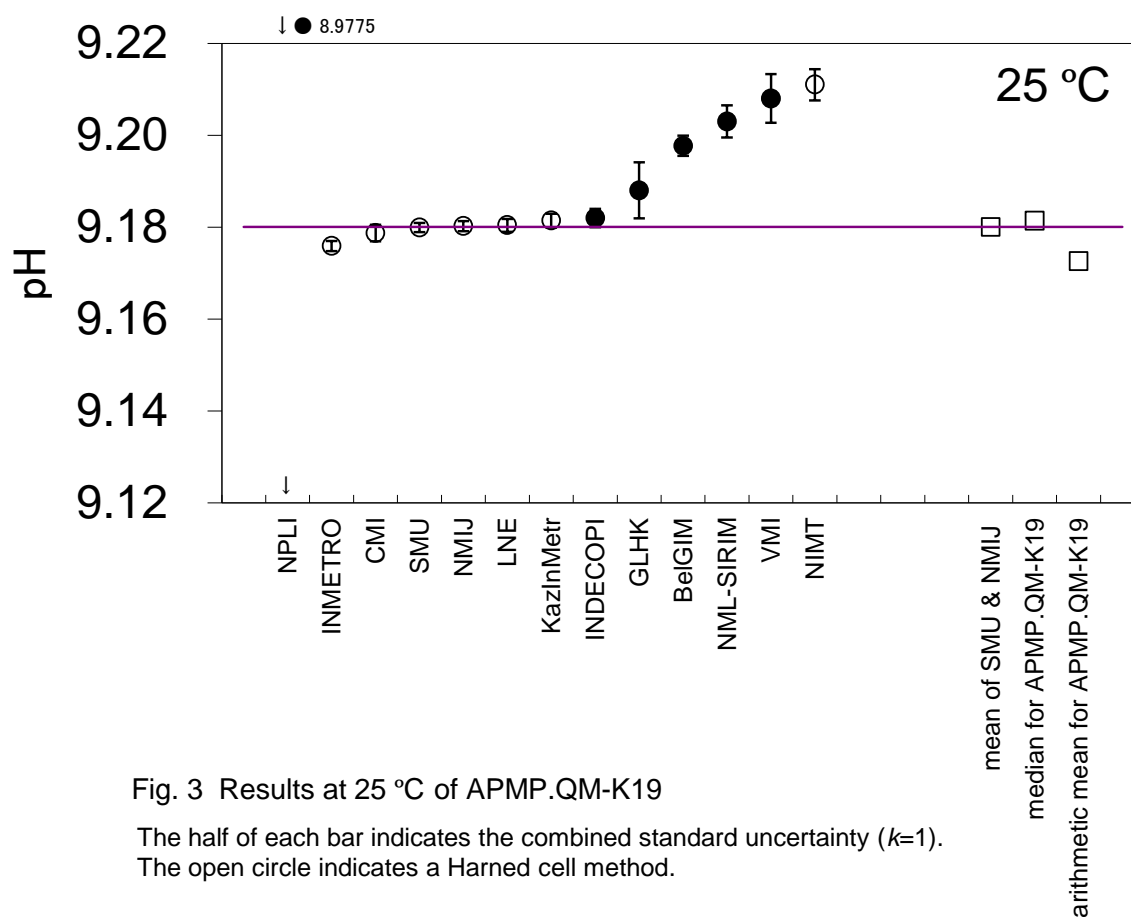


Fig. 3 Results at 25 °C of APMP.QM-K19

The half of each bar indicates the combined standard uncertainty ($k=1$).
The open circle indicates a Harned cell method.

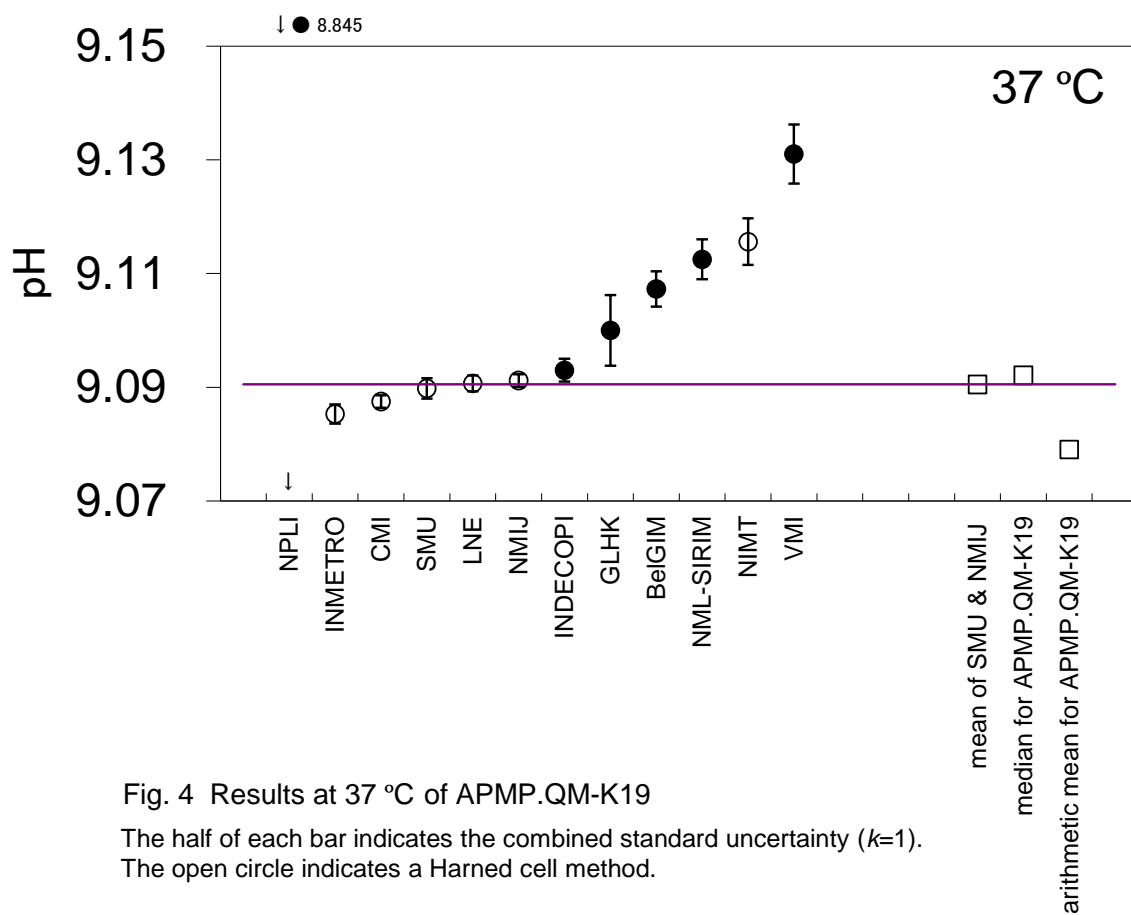


Fig. 4 Results at 37 °C of APMP.QM-K19

The half of each bar indicates the combined standard uncertainty ($k=1$).
The open circle indicates a Harned cell method.

7. Discussion

Judging from the results, there are some participants which should improve their abilities or examine some missing uncertainty sources. Regarding VMI, the difference between the result at 15 °C and those at the other temperatures was not natural. The other participants showed a good agreement with each other within their expanded uncertainties ($k = 2$), regardless of whether or not the method was a Harned cell method.

8. Equivalence statements

NMIJ and SMU participated in CCQM-K19; therefore, the two participants in APMP.QM-K19 (NMIJ and SMU) could have links to CCQM-K19. As shown in the technical protocol of APMP.QM-K19, the two NMI's were used as the anchor points to link the present RMO key comparison to CCQM-K19. As shown below, the results of the two NMI's for APMP.QM-K19 were consistent with those for CCQM-K19.

The results of CCQM key comparison can be obtained from the BIPM KCDB (http://kcdb.bipm.org/AppendixB/KCDB_ApB_search.asp). Table 7 shows degrees of equivalence (DoE) for NMIJ and SMU, as reported in CCQM-K19. Table 8 shows the summarised results of APMP.QM-K19. Table 9 shows each DoE and its standard uncertainty for APMP.QM-K19 which was linked to CCQM-K19.

Table 7 DoE estimated from CCQM-K19

NMI	15 °C		25 °C		37 °C	
	D_i	$U(D_i)$	D_i	$U(D_i)$	D_i	$U(D_i)$
NMIJ (i = NMIJ)	0.0002	0.0029	0.0003	0.0031	0.0005	0.0029
SMU (i = SMU)	-0.0012	0.0026	-0.0011	0.0024	-0.0006	0.0026
mean($D_{\text{NMIJ}} + D_{\text{SMU}}$:K19)	-0.0005		-0.0004		-0.00005	

	15 °C	25 °C	37 °C
KCRV(K19)	9.3222	9.2300	9.1421
as acidity function (AF)			
$u(KCRV(K19))$	0.0007	0.00065	0.0012

NMI	15 °C	25 °C	37 °C
	$u(D_i)^*$	$u(D_i)^*$	$u(D_i)^*$
NMIJ (i = NMIJ)	0.0013	0.0014	0.0008
SMU (i = SMU)	0.0011	0.0010	0.0005
$u(\text{mean}(D_{\text{NMIJ}} + D_{\text{SMU}}):K19)$	0.0011	0.0011	0.0013

D_i : each result of DoE (i indicates each participant). If necessary, such expressions as DoE(i:K19), DoE(i:APMP) are also used. The D_i and $U(D_i)$ values for CCQM-K19 are available from the BIPM KCDB.

AF_i : each result (acidity function) of a comparison (i indicates each participant). If necessary, such an expression as $AF_i(K19)$ is also used.

$D_{\text{NMIJ}} = \text{DoE}(\text{NMIJ}:K19) = AF_{\text{NMIJ}}(K19) - \text{KCRV}(K19)$ from CCQM-K19.

$D_{\text{SMU}} = \text{DoE}(\text{SMU}:K19) = AF_{\text{SMU}}(K19) - \text{KCRV}(K19)$ from CCQM-K19.

$u^2(D_i)^* = (U(D_i)/2)^2 - u^2(\text{KCRV}(K19))$.

$D_{\text{mean}(\text{NMIJ} + \text{SMU}:K19)} = \text{mean}(D_{\text{NMIJ}} + D_{\text{SMU}}:K19) = (D_{\text{NMIJ}} + D_{\text{SMU}})/2$.

$u^2(D_{\text{mean}(\text{NMIJ} + \text{SMU}:K19)}) = u^2(\text{mean}(D_{\text{NMIJ}} + D_{\text{SMU}}:K19))$
 $= [u^2(D_{\text{NMIJ}})^* + u^2(D_{\text{SMU}})^*]/4 + u^2(\text{KCRV}:K19)$.

KCRV(K19): KCRV for CCQM-K19.

$u(\text{KCRV}(K19))$: combined standard uncertainty of KCRV(K19).

Table 8 Summarised results of APMP.QM-K19*

NMI	15 °C		25 °C		37 °C	
	pH _i	$u(pH_i)$	pH _i	$u(pH_i)$	pH _i	$u(pH_i)$
NIMT	9.2905	0.0045	9.211	0.0034	9.1156	0.0041
GLHK	9.280	0.0073	9.188	0.0061	9.100	0.0062
NML-SIRIM	9.2919	0.0035	9.2030	0.0035	9.1125	0.0035
VMI	9.27	0.0065	9.2080	0.0053	9.131	0.0052
LNE	9.2735	0.0014	9.1804	0.0014	9.0907	0.0014
NPLI			8.9775	0.0343	8.845	0.0572
INDECOPI	9.274	0.002	9.1820	0.0020	9.093	0.002
INMETRO	9.2682	0.001	9.1759	0.0011	9.0853	0.0017
CMI	9.2759	0.0011	9.1787	0.0018	9.0875	0.0011
BelGIM	9.297	0.0032	9.20	0.0022	9.1073	0.0031
KazInMetr			9.181	0.0015		
NMIJ	9.2726	0.0012	9.1802	0.0011	9.0912	0.0011
SMU	9.2739	0.0014	9.1799	0.0010	9.0898	0.0018
mean(NMIJ+SMU:APMP)	9.27325		9.18005		9.0905	
$u[\text{mean(NMIJ+SMU:APMP)}]$		0.0009		0.0007		0.0011

* Summarised from Tables 4, 5 and 6.

pH_i: each result of a comparison (i indicates each participant). If necessary, such expressions as pH_i(K19), pH_i(APMP) are also used.

$u(pH_i)$: combined standard uncertainty of pH_i in the corresponding key comparison.

$\text{mean(NMIJ+SMU:APMP)} = [pH_{\text{NMIJ}}(\text{APMP}) + pH_{\text{SMU}}(\text{APMP})]/2$.

$u^2(\text{mean(NMIJ+SMU:APMP)}) = [u^2(pH_{\text{NMIJ}}(\text{APMP})) + u^2(pH_{\text{SMU}}(\text{APMP}))]/4$.

Table 9 DoE for APMP.QM-K19 (linked to CCQM-K19)

NMI	15 °C		25 °C		37 °C	
	D_i	$u(D_i)$	D_i	$u(D_i)$	D_i	$u(D_i)$
NIMT	0.0167	0.0047	0.0305	0.0036	0.0251	0.0044
GLHK	0.0062	0.0074	0.0076	0.0062	0.0095	0.0064
NML-SIRIM	0.0181	0.0038	0.0225	0.0037	0.0220	0.0039
VMI	-0.0038	0.0067	0.0275	0.0055	0.0405	0.0055
LNE	-0.0003	0.0020	0.0000	0.0019	0.0002	0.0022
NPLI			-0.2030	0.0343	-0.2455	0.0572
INDECOPI	0.0002	0.0025	0.0015	0.0024	0.0025	0.0026
INMETRO	-0.0056	0.0017	-0.0046	0.0017	-0.0052	0.0024
CMI	0.0021	0.0018	-0.0018	0.0022	-0.0030	0.0020
BelGIM	0.0232	0.0035	0.0172	0.0026	0.0168	0.0035
KazInMetr			0.0009	0.0020		

$D_i = \text{DoE}(i: \text{APMP})$

$= \text{pH}_i(\text{APMP}) - \text{mean}(\text{NMIJ} + \text{SMU}: \text{APMP}) + \text{DoE}(\text{mean}(\text{NMIJ} + \text{SMU}: \text{K19}))$.

$u^2(D_i) = u^2(\text{pH}_i(\text{APMP})) + u^2[\text{mean}(\text{NMIJ} + \text{SMU}: \text{APMP})] + u^2(D_{\text{mean}(\text{NMIJ} + \text{SMU}: \text{K19})})$.

It should be understood that each DoE for NMIJ and SMU is shown in Table 7 for CCQM-K19.

Each result of the two NMI's for CCQM-K19 is consistent with the reference value and the mean value of DoE's of the two NMI's for CCQM-K19 suite is also consistent with the reference value. The pH values of the two NMI's for APMP.QM-K19 were in a good agreement with each other. Thus, regarding the two NMI's, it is recognised that there is good consistency between CCQM-K19 and APMP.QM-K19.

The DoE linked to CCQM-K19 for each participant in APMP.QM-K19 is shown in Table 9 and Figure 5. Unfortunately, the results of some participants are not consistent with the reference value $\text{mean}(\text{NMIJ} + \text{SMU}: \text{APMP})$, though those of the other participants are consistent with it.

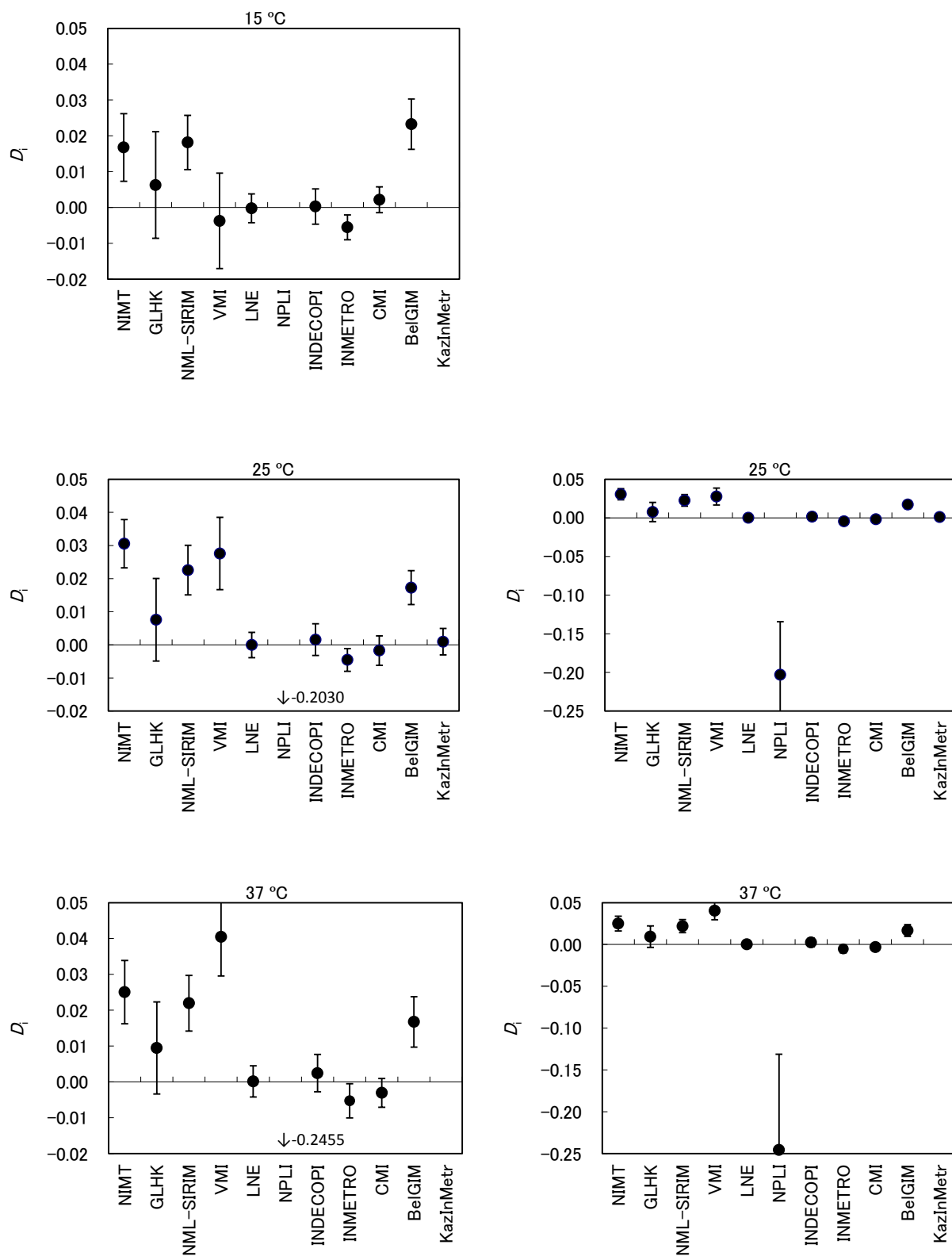


Fig. 5 Degree of equivalence D_i and expanded uncertainty U_i
The half of each bar indicates the expanded uncertainty ($k = 2$) of D_i .

9. Conclusion

The APMP key comparison APMP.QM-K19 could suitably be linked to CCQM-K19. Comparability of measurement results was successfully demonstrated by many participating NMI's for the measurement of pH of a borate buffer within related expanded uncertainties. It is expected that the performance of each participant in the present key comparison is representative for measurement of pH of a borate buffer with the same technique as used in the present comparison.

The results can be used further by any participant to support its CMC claim at least for a borate buffer. That claim will concern the pH method employed by the participant during this comparison and will cover the used temperature(s) or the full temperature range between 15°C and 37 °C for the participant which measured pH values at the three temperatures.

This comparison showed that some participants in APMP.QM-K19 should improve their abilities or examine some missing uncertainty sources. The value D_i should be considered when the ability of such a participant on pH measurement of a borate buffer is evaluated.

10. Acknowledgement

The work of the key comparison was done by the contributions from many scientists or analysts as well as the contact persons: Toshiaki Asakai, Igor Maksimov, Yoshiyasu Yamauchi, Sachiko Ohnuma, Toshihiro Suzuki and Tsutomu Miura (NMIJ); Patumporn Rodruangthum (NIMT); Wai-Hing Lam (GLHK); Khirul Anuar Mohd. Amin (NML-SIRIM); Zuzana Hankova (SMU); Daniela Stoica (LNE); Daya Soni (NPLI); Júlio Cesar Dias (INMETRO). AH thanks Dr. Michal Máriássy (SMU) for his useful suggestion about the frame of this comparison and the present report.

Annex A - Technical protocol

APMP.QM-K19 and APMP.QM-P25

APMP comparison on pH measurement of a borate buffer Call and technical protocol (January 24, 2013)

1.Introduction

The National Metrology Institute of Japan (NMIJ) and the National Institute of Metrology in Thailand (NIMT) would like to initiate an APMP comparison on pH measurement to support CMC claim for pH. The comparison is a key comparison following CCQM-K19 and CCQM-K19.1. The objective of the key comparison is to give an opportunity to NMIs or officially designated institutes in APMP which did not participate in the CCQM comparisons, especially to those which usually employ the glass-electrode method for pH measurement. The comparison material is a borate buffer of pH around 9.2 and the measurement temperatures is at 15 °C, 25 °C and 37 °C. NMIJ and NIMT proposed the present key comparison at the APMP-TCQM meeting held November 26-27, 2012 and the proposal was agreed as APMP.QM-K19. This is the second APMP key comparison on pH measurement and the forth APMP comparison on pH measurement following APMP.QM-K9/P16 (a phosphate buffer). In parallel with the key comparison APMP.QM-K19, a pilot study is carried out, in which the same sample measured by the APMP.QM-K19 participants is also used.

Sample

The comparison material is a borate buffer of pH around 9.2 whose composition is slightly changed from the typical composition. Each participant will be provided with a 1000 mL bottle of the buffer; the participant employing a Harned cell method can be provided with two bottles (if requested). The link to CCQM-K19 (including CCQM-K19.1) will be considered on the basis of the results (by a Harned cell method) from the NMIs who have successfully participated in the related CCQM comparisons.

The result by a Harned cell method should be reported as an acidity function; pH values will be calculated using the Bates–Guggenheim convention. Those pH values will be compared with the pH values obtained by other methods as a glass-electrode method.

Methods of measurement

Each participant can use a Harned cell method as employed in the CCQM-K19 suite or any suitable method of pH measurement (usually a glass-electrode method). NMIs or officially designated laboratories are welcome to participate in this comparison. The measurements should be carried out by using standards with metrological traceability. A pilot study is carried out in parallel with the key comparison; some expert calibration laboratories can participate in the pilot study. Because of the limited number of sample units, the number per economy might have to be restricted.

Reporting

The results at 15 °C, 25 °C and 37 °C should be reported to NMIJ (Akiharu Hioki; aki-hioki@aist.go.jp) and NIMT (Nongluck Tangpaisarnkul; nongluck@nimt.or.th), accompanied by

a full uncertainty budget. Reporting the details of the procedure, traceability links, and the instrument(s) used is very desirable.

Time schedule

Formal call for participation: January, 2013
Deadline of registration of participation: February 28, 2013
Dispatch of the samples (from NMII): May, 2013
Deadline for submitting the results: September 30, 2013

Participants

Participation is open to all interested NMIs or officially designated laboratories that can perform the determination. An NMI or an officially designated laboratory may nominate other institutes or laboratories to participate in the pilot study. Please inform NMII (Akiharu Hioki) of the contact person, the shipping address, and so on using the attached registration form. Though the principal purpose of the present comparison is to support the institutes in the APMP region, participation is open to all interested NMIs or officially designated laboratories in the other RMOs.

We would like to ask NMIs or officially designated laboratories to coordinate participation within their economies including inviting participants in the pilot study, shipping samples, and receiving the reports. The coordinating laboratories might invite some NMIs outside APMP to participate in the key comparison or some expert laboratories directly to participate in the pilot study.

Coordinating laboratories

Dr. Akiharu Hioki, Dr. Toshiaki Asakai, Dr. Igor Maksimov, Dr. Toshihiro Suzuki and Dr. Tsutomu Miura
National Metrology Institute of Japan (NMII)

Dr. Krairerk Obromsook and Ms. Nongluck Tangpaisarnkul
National Institute of Metrology in Thailand (NIMT)

Contact: Dr. Akiharu Hioki (E-mail: aki-hioki@aist.go.jp)