Report of the key comparison APMP.QM-K9

APMP comparison on pH measurement of phosphate buffer

(Final Report)

Participants:
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Coordinated by
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Chainarong Cherdchu and Nongluck Tangpaisarnkul (NIMT)

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Abstract

The APMP.QM-K9 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 phosphate 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) in August, 2009. After approval by TCQM, the comparison has been conducted by NMIJ and NIMT. The comparison is a key comparison following CCQM-K9, CCQM-K9.1 and CCQM-K9.2. The comparison material was a phosphate buffer of pH around 6.86 and the measurement temperatures were 15 ºC, 25 ºC and 37 ºC. This is the first APMP key comparison on pH measurement and the third APMP comparison on pH measurement following APMP.QM-P06 (two phosphate buffers) in 2004 and APMP.QM-P09 (a phthalate buffer) in 2006.

The results can be used further by any participant to support its CMC claim for a phosphate 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 enviromental analysis and its accurate measurement is very important.

Following the pilot studies APMP.QM-P06 (two phosphate buffers) and APMP.QM-P09 (a phthalate buffer) conducted by NMIJ, the two institutes NMIJ and NIMT jointly proposed a key comparison of "pH measurement of phosphate buffer" to TCQM of APMP. Since the proposal was approved as APMP.QM-K9, NMIJ and NIMT have acted as coordinating laboratories. The pH values of a phosphate buffer were measured at the three temperatures (15 ºC, 25 ºC and 37 ºC). 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 first key comparison in the field of pH determination within APMP. NMI's or officially designated laboratories were invited to participate in this comparison. SMU participated from the outside of APMP for more reliable linkage of APMP.QM-K9 to CCQM-K9.

It was decided to conduct a parallel pilot study designated APMP.QM-P16, for which the same samples measured by the APMP.QM-K9 participants were also used.

2. List of Participants

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

Table 1 List of participating NMI'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	**MSL** Measurement Standards Laboratory of New Zealand	New Zealand
5	**NIM** National Institute of Metrology	China
6	**RCC-LIPI** Research Center for Chemistry	Indonesia
7	**SIRIM BERHAD** National Metrology Laboratory, SIRIM BERHAD	Malaysia
8	**SMU** Slovak Institute of Metrology	Slovakia
9	**ITDI** Industrial Technology Development Institute	Philippines
10	**VMI** Vietnam Metrology Institute	Vietnam

3. Sample

The comparison material was a phosphate buffer of pH around 6.86 whose composition was slightly changed from the typical one for equimolal standard phosphate. 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-K9 (including CCQM-K9.1 and CCQM-K9.2) 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 phosphate buffer of Na_2HPO_4 (molality 0.0219 mol/kg) and KH_2PO_4 (molality 0.0217 mol/kg) prepared at NMIJ in October, 2009. The total volume of batch was 30 L, subsequently divided into 29 subsamples of 1000 mL polyethylene bottles. The pH value of the phosphate buffer is around 6.86 and the mass fraction of water in the buffer is 0.99397; this information was given to the participants before measurements. The ionic strength (as molality) calculated from the buffer composition is 0.0874 mol/kg. The Debye-Huckel constants *A* in the equation used for the Bates-Guggenheim convention [Eq(1)] are 0.5026 at 15 ºC, 0.5108 at 25 ºC and 0.5215 at 37 ºC.

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

Therefore, the values of log γ^{o}_{Cl} to be added to the acidity function obtained by a Harned cell method were equal to -0.1029 at 15 ºC, -0.1046 at 25 ºC and -0.1068 at 37 ºC. The composition of the sample was a little different from that of the equimolal standard phosphate buffer. However, since the pH value of the sample for the APMP comparison is close to that for CCQM-K9, it is possible to link APMP.QM-K9 to CCQM-K9.

The homogeneity of the material was tested before shipping the samples; the pH values at 25 ºC were within $\pm$0.001 range for three subsamples by a glass-electrode method and within $\pm$0.0008 range for two subsamples by a Harned cell method.

The stability of the material was tested by three measurements with a Harned cell method from October to December 2009. The pH values obtained at 25 ºC were 6.9871, 6.9884 and 6.9864 on October 19, November 12 and December 14, respectively: all the results were within ±0.001 range.

The samples were sent to the participants from NMIJ by EMS mail on October 22, 2009. 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; Masaki Ohata
NIMT	Chainarong Cherdchu; Nongluck Tangpaisarnkul
GLHK	Siu-Kay Wong
MSL	Andrew Tromans
NIM	Hongyu Xiu
RCC-LIPI	Nuryatini
SIRIM BERHAD	Osman Bin Zakaria
SMU	Leos Vyskocil
ITDI	Hermelina H. Bion
VMI	Ngo Huy Thanh

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 December 31, 2009.

5. Methods of Measurement

Each participant could use a Harned cell method as employed in CCQM-K9, CCQM-K9.1 and CCQM-K9.2 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 methods for APMP.QM-K9

	Participants
Harned cell method	NMIJ, NIMT, MSL, NIM, SMU
Glass-electrode method	GLHK, RCC-LIPI, SIRIM BERHAD, ITDI, VMI

6. Results

The relative changes of bottle masses after shipping are presented in Fig. 1. NIM reported the changes on two bottles. Each change was very small and it substantially did not affect the pH value.

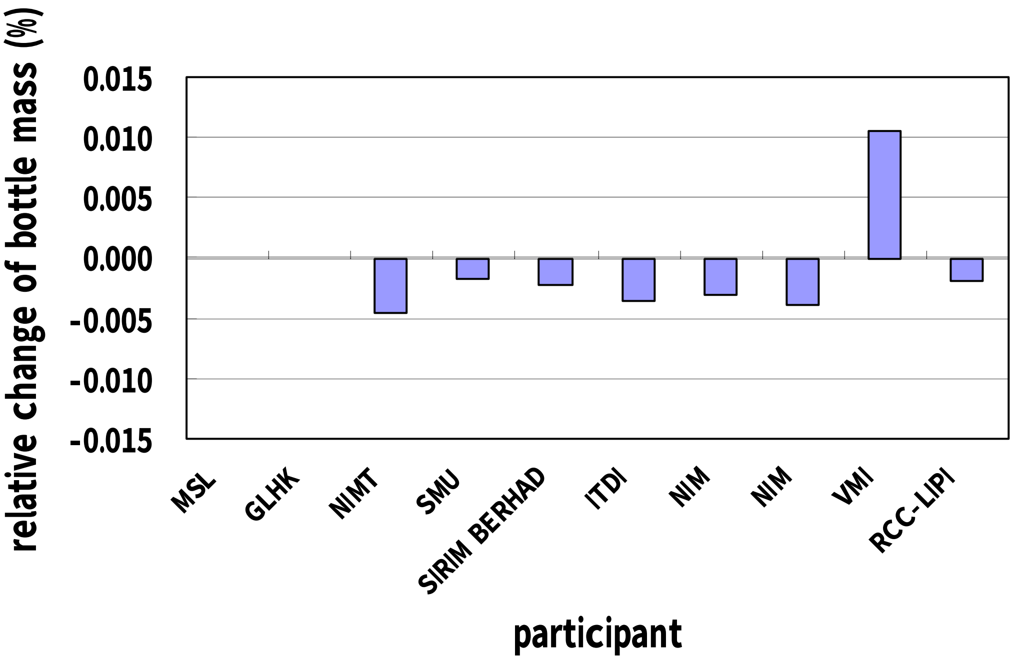

Fig. 1 Relative change of bottle mass after shipping

The 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 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. 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, NIM and NMIJ.

Table 4 Results of APMP.QM-K9 at 15 ºC

Participant	Calibration standards	Reported acidity function	log γ^0_{Cl}	Reported (or calculated) pH	Combined standard uncertainty
NMIJ	---	7.0198	-0.1029	6.9169	0.0012
NIMT	---	7.0145	-0.1029	6.9116	0.00445
GLHK	NIST CRM			6.919	0.0055
MSL					---
NIM	---	7.0210	-0.1029	6.9181	0.00175
RCC-LIPI					---
SIRIM BERHAD	NMIJ CRMs			6.9218	0.0014
SMU	---	7.0200	-0.1029	6.9171	0.00185
ITDI	Ajax Fine Chem*			6.88	0.025
VMI					---

* The calibration solutions were commercial ones.

Table 5 Results of APMP.QM-K9 at 25 ºC

Participant	Calibration standards	Reported acidity function	log γ^0_{Cl}	Reported (or calculated) pH	Combined standard uncertainty
NMIJ	---	6.9871	-0.1046	6.8825	0.0012
NIMT	---	6.9847	-0.1046	6.8801	0.00325
GLHK	NIST CRM			6.883	0.0057
MSL	---	7.0160	-0.1046	6.9114	0.0015
NIM	---	6.9881	-0.1046	6.8835	0.00175
RCC-LIPI	NIST CRM			6.8650	0.0066
SIRIM BERHAD	NMIJ CRMs			6.8797	0.0014
SMU	---	6.9891	-0.1046	6.8845	0.00115
ITDI	Ajax Fine Chem*			6.82	0.0265
VMI	KRISS CRM			6.880	0.042

* The calibration solutions were commercial ones.

Table 6 Results of APMP.QM-K9 at 37 ºC

Participant	Calibration standards	Reported acidity function	log γ^0_{Cl}	Reported (or calculated) pH	Combined standard uncertainty
NMIJ	---	6.9662	-0.1068	6.8594	0.0013
NIMT	---	6.9643	-0.1068	6.8575	0.0044
GLHK	NIST CRM			6.859	0.0056
MSL					---
NIM	---	6.9650	-0.1068	6.8582	0.00175
RCC-LIPI					---
SIRIM BERHAD	NMIJ CRMs			6.8541	0.00155
SMU	---	6.9672	-0.1068	6.8604	0.00125
ITDI	Ajax Fine Chem*			6.78	0.02685
VMI					---

* The calibration solutions were commercial ones.

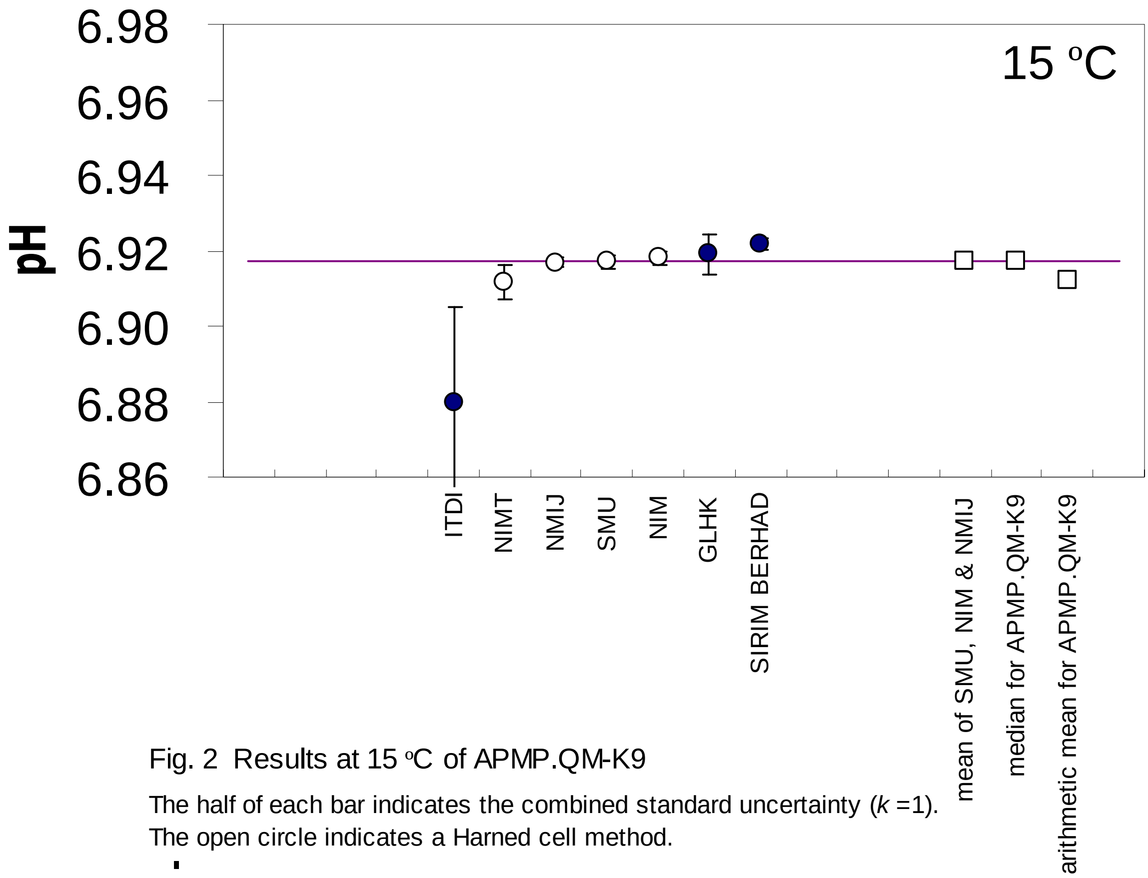

Fig. 2 Results at 15 °C of APMP.QM-K9

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

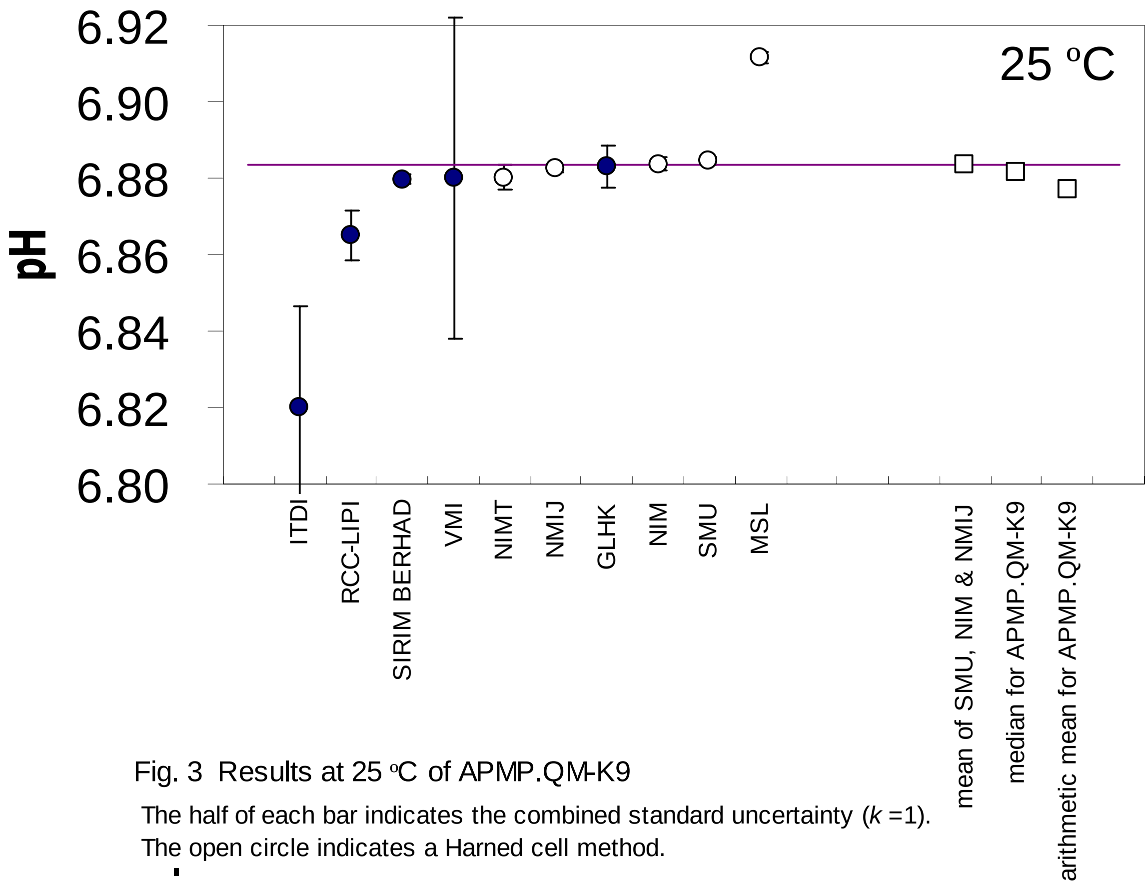

Fig. 3 Results at 25 °C of APMP.QM-K9

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

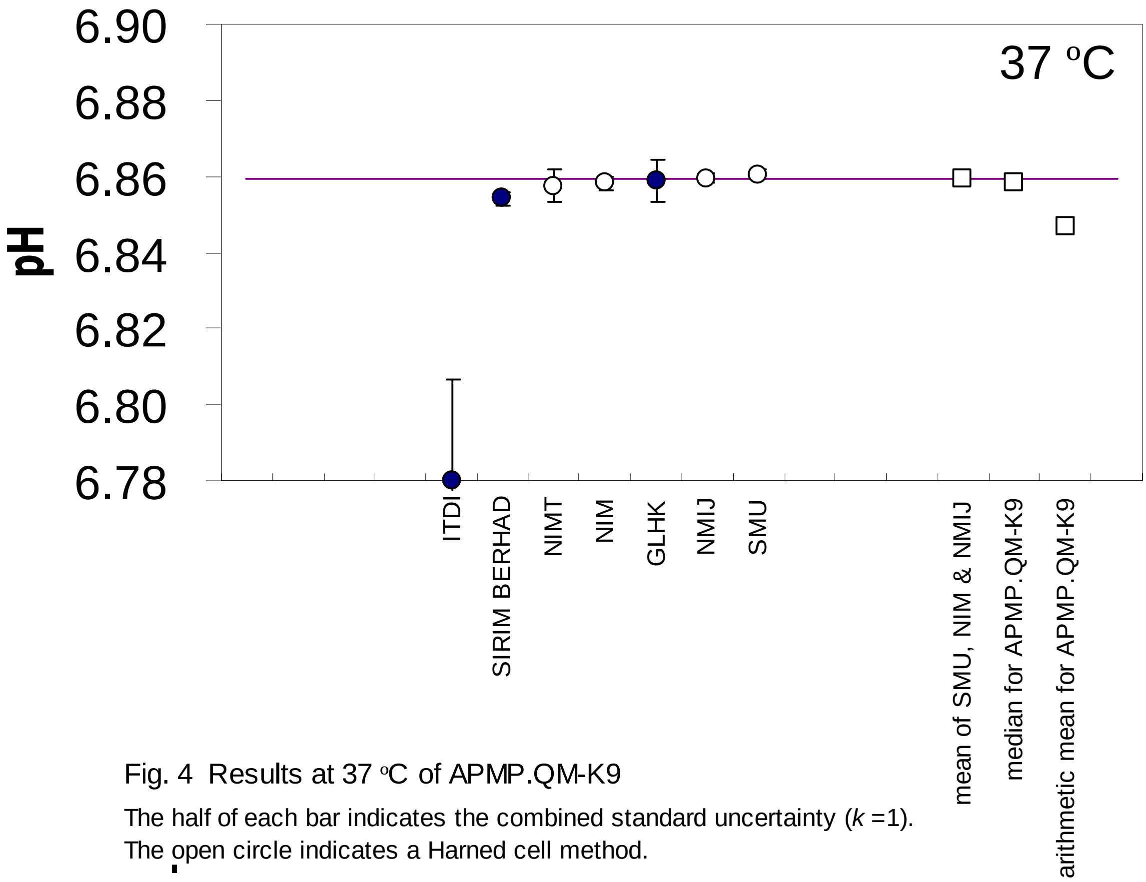

Fig. 4 Results at 37 °C of APMP.QM-K9

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. 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

NIM participated in CCQM-K9. SMU also participated in CCQM-K9, but their originally reported results had errors. Though SMU submitted their corrected results, those are not recognised as the official results of CCQM-K9. SMU participated in CCQM-K9.1; the result was linked to CCQM-K9 through PTB (Germany). NMIJ participated in CCQM-K9.2; the result was linked to CCQM-K9 through VNIIFTRI (Russia) and PTB. Consequently, the three participants in APMP.QM-K9 (NIM, SMU and NMIJ) have links to CCQM-K9. As shown in the technical protocol of APMP.QM-K9, the three NMI's were used as the anchor points to link the present RMO key comparison to CCQM-K9. As shown below, the results of the three NMI's for APMP.QM-K9 were consistent with those for CCQM-K9 (including CCQM-K9.1 and CCQM-K9.2).

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 NIM, SMU and NMIJ, as reported in CCQM-K9, K9.1 and K9.2. Table 8 shows the summarised results of APMP.QM-K9. Table 9 shows each DoE and its standard uncertainty for APMP.QM-K9 which was linked to CCQM-K9.

Table 7 DoE estimated from CCQM-K9, K9.1 and K9.2

NMI	15 °C		25 °C		37 °C	
	D_i	$U(D_i)$	D_i	$U(D_i)$	D_i	$U(D_i)$
NIM (i = NIM)	-0.0025	0.0061	-0.0033	0.0042	-0.0024	0.0042
SMU (s) (i = SMU (s))	0.0027	0.0031	0.0021	0.0033	0.0029	0.0036
NMIJ (s) (i = NMIJ (s))	-0.0013	0.0032	-0.0009	0.0029	-0.0008	0.0032
mean(D_{NIM}+$D_{SMU(s)}$+$D_{NMIJ(s)}$:K9)	-0.0004		-0.0007		-0.0001	

	15 °C	25 °C	37 °C
KCRV(K9)	6.8975	6.8633	6.8394
u(KCRV(K9))	0.0005	0.0006	0.0006

NMI	15 °C	25 °C	37 °C
	$u(D_i)'$	$u(D_i)'$	$u(D_i)'$
NIM (i = NIM)	0.0030	0.0020	0.0020
SMU (s) (i = SMU (s))	0.0015	0.0015	0.0017
NMIJ (s) (i = NMIJ (s))	0.0015	0.0013	0.0015
u(mean(D_{NIM}+$D_{SMU(s)}$+$D_{NMIJ(s)}$:K9))	0.0013	0.0011	0.0012

D_i: each result of DoE (i indicates each NMI). If necessary, such expressions as DoE(i:K9), DoE(i:APMP) are also used. The D_i and $U(D_i)$ values are available from the BIPM KCDB.
pH_i: each result of a comparison (i indicates each NMI). If necessary, such expressions as pH_i(K9), pH_i(K9.2), pH_i(APMP) are also used.
D_{NIM}=DoE(NIM:K9)=pH_{NIM}(K9)-KCRV(K9) from CCQM-K9.
$D_{SMU(s)}$=[$pH_{SMU(s)}$(K9.1)-pH_{PTB}(K9.1)]+DoE(PTB:K9) from CCQM-K9.1.
$D_{NMIJ(s)}$=[$pH_{NMIJ(s)}$(K9.2)-mean(VNIIFTRI+PTB:K9.2)]+[mean(VNIIFTRI+PTB:K9)-KCRV(K9)] from CCQM-K9.2.
$u^2(D_i)'=(U(D_i)/2)^2 - u^2(\text{KCRV(K9)})$.
$D_{mean(NIM+SMU(s)+NMIJ(s):K9)}$=mean($D_{NIM}$+$D_{SMU(s)}$+$D_{NMIJ(s)}$:K9)= ($D_{NIM}$+$D_{SMU(s)}$+$D_{NMIJ(s)}$)/3.
$u^2(D_{mean(NIM+SMU(s)+NMIJ(s):K9)})=u^2(\text{mean}(D_{NIM}+D_{SMU(s)}+D_{NMIJ(s)}\text{:K9}))$
$=[u^2(D_{NIM})'+u^2(D_{SMU(s)})'+u^2(D_{NMIJ(s)})']/9+u^2(\text{KCRV:K9})$.
KCRV(K9): KCRV for CCQM-K9.
u(KCRV(K9)): combined standard uncertainty of KCRV(K9).

Table 8 Summarised results of APMP.QM-K9*

NMI	15 °C		25 °C		37 °C	
	pH_i	$u(pH_i)$	pH_i	$u(pH_i)$	pH_i	$u(pH_i)$
NIMT	6.9116	0.00445	6.8801	0.0033	6.8575	0.0044
GLHK	6.919	0.0055	6.883	0.0057	6.859	0.0056
MSL			6.9114	0.0015		
RCC-LIPI			6.8650	0.0066		
SIRIM BERHAD	6.9218	0.0014	6.8797	0.0014	6.8541	0.00155
ITDI	6.88	0.025	6.82	0.0265	6.78	0.02685
VMI			6.880	0.042		
NIM	6.9181	0.00175	6.8835	0.00175	6.8582	0.00175
SMU	6.9171	0.00185	6.8845	0.00115	6.8604	0.00125
NMIJ	6.9169	0.0012	6.8825	0.0012	6.8594	0.0013
mean(NIM+SMU+NMIJ:APMP)	6.9174		6.8835		6.8593	
u[mean(NIM+SMU+NMIJ:APMP)]		0.0009		0.0008		0.0008

* Summarised from Tables 4, 5 and 6.
pH_i: each result of a comparison (i indicates each NMI). If necessary, such expressions as pH_i(K9), pH_i(K9.2), pH_i(APMP) are also used.
$u(pH_i)$: combined standard uncertainty of pH_i in the corresponding key comparison.
mean(NIM+SMU+NMIJ:APMP)= $[pH_{NIM}(APMP) + pH_{SMU}(APMP) + pH_{NMIJ}(APMP)]/3$.
u^2(mean(NIM+SMU+NMIJ:APMP)) $=[u^2(pH_{NIM}(APMP))+u^2(pH_{SMU(s)}(APMP))+u^2(pH_{NMIJ}(APMP))]/9$.

Table 9 DoE for APMP.QM-K9 (linked to CCQM-K9 suite)

NMI	15 °C		25 °C		37 °C	
	D_i	$u(D_i)$	D_i	$u(D_i)$	D_i	$u(D_i)$
NIMT	-0.0061	0.0047	-0.0041	0.0035	-0.0019	0.0046
GLHK	0.0013	0.0057	-0.0012	0.0059	-0.0004	0.0058
MSL			0.0272	0.0020		
RCC-LIPI			-0.0192	0.0067		
SIRIM BERHAD	0.0041	0.0021	-0.0045	0.0020	-0.0053	0.0021
ITDI	-0.0377	0.0251	-0.0642	0.0265	-0.0794	0.0269
VMI			-0.0042	0.0420		

D_i=DoE(i:APMP)
=pH_i(APMP)-mean(NIM+SMU+NMIJ:APMP)+DoE(mean(NIM+SMU(s)+NMIJ(s):K9)).
$u^2(D_i)=u^2(pH_i(APMP)) + u^2[mean(NIM+SMU+NMIJ:APMP)] + u^2(D_{mean(NIM+SMU(s)+NMIJ(s):K9)})$.

It should be understood that each DoE for NIM, SMU and NMIJ is shown in Table 7 for CCQM-K9.

Each result of the three NMI's for CCQM-K9 suite is consistent with the reference value and the mean value of DoE's of the three NMI's for CCQM-K9 suite is also consistent with the reference value. The pH values of the three NMI's for APMP.QM-K9 were in a good agreement with each other. Thus, regarding the three NMI's, it is recognised that there is good consistency between CCQM-K9 and APMP.QM-K9.

The DoE linked to CCQM-K9 for each participant in APMP.QM-K9 is shown in Table 9 and Fig. 5. Unfortunately, the results of some participants are not consistent with the reference value mean(NIM+SMU+NMIJ:APMP), though those of the other participants are consistent with it.

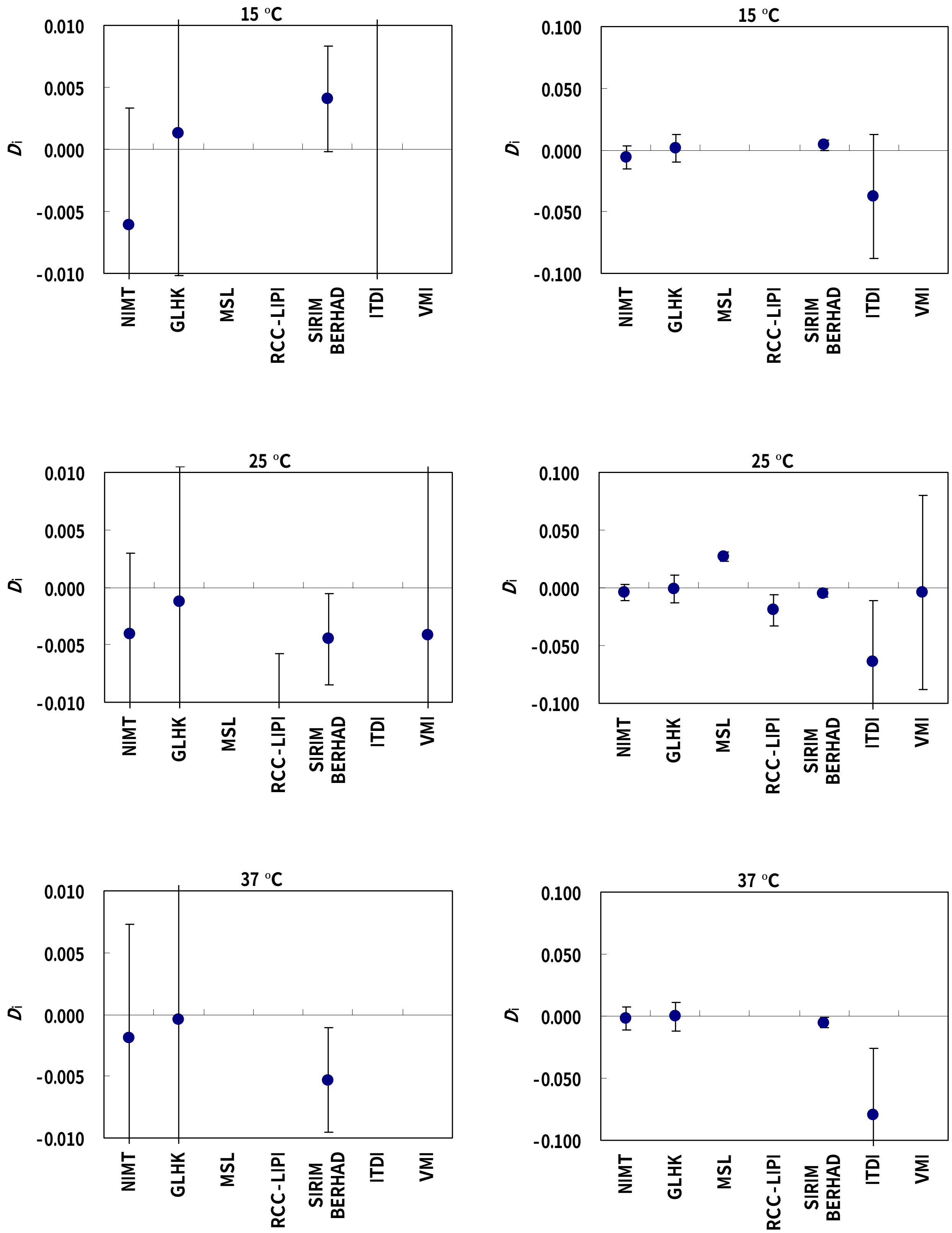

Fig. 5 Degree of equivalence D_i and expanded uncertainty U_i
The half of each bar indicates the expanded uncertainty (k = 2) of D_i.

9. Conclusion

The APMP key comparison APMP.QM-K9 could suitably be linked to CCQM-K9. Comparability of measurement results was successfully demonstrated by many participating NMI’s for the measurement of pH of a phosphate 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 phosphate buffer with the same technique as used in the present comparison.

This comparison showed that some participants in APMP.QM-K9 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 phosphate buffer is evaluated.

10. Acknowledgement

The work of the key comparison was done by the contributions from many scientists as well as the contact persons: Igor Maksimov and Yoshiyasu Yamauchi (NMIJ); Patumporn Manam (NIMT); Bing Wu (NIM); Andreas (RCC-LIPI); Khirul Anuar Mohd. Amin (SIRIM BERHAD); Anna Mathiasova (SMU); Emma D. Tayag (ITDI). 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-K9 and APMP.QM-P16: APMP comparison on pH measurement

Call for participants and technical protocol

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. The comparison is a key comparison following CCQM-K9.2. The comparison material will be a phosphate buffer of pH around 6.86 and the measurement temperatures will be at 15 ºC, 25 ºC and 37 ºC. This will be the first APMP key comparison on pH measurement and the third APMP comparison on pH measurement following APMP.QM-P06 (two phosphate buffers) and APMP.QM-P09 (a phthalate buffer).

Sample

The comparison material will be a phosphate buffer of pH around 6.86 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-K9 (including CCQM-K9.1 and CCQM-K9.2) 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 CCQM-K9.2 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 will be carried out in parallel with the key comparison; some expert 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 ºC, 25 ºC and 37 ºC should be reported to NMIJ (Akiharu Hioki), accompanied by a full uncertainty budget. Reporting the details of the procedure, traceability links, and the instrument(s) used is very desirable.

Time schedule

Deadline of registration of participation: September 30, 2009
Dispatch of the samples: middle in October, 2009
Deadline for submitting the results: December 31, 2009

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 NMIJ (Akiharu Hioki) of the contact person, the shipping address, and so on using the attached registration form. Even if you do not wish to participate, please inform NMIJ of it.

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 and Dr. Masaki Ohata
National Metrology Institute of Japan (NMIJ)

Dr. Chainarong Cherdchu and Ms. Nongluck Tangpaisarnkul
National Institute of Metrology in Thailand (NIMT)

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