

# **Report of the key comparison APMP.QM-K91**

## **APMP comparison on pH measurement of phthalate buffer**

**(Final Report)**

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## **Abstract**

The APMP.QM-K91 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 phthalate buffer. This APMP comparison on pH measurement was proposed by the National Metrology Institute of Japan (NMIJ) at the APMP-TCQM meeting held September 22-23, 2014. After approval by TCQM, the comparison has been conducted by NMIJ. The comparison is a key comparison following CCQM-K91. The comparison material was a phthalate buffer of pH around 4.0 and the measurement temperatures were 15 °C, 25 °C and 37 °C. This is the third APMP key comparison on pH measurement and the fifth APMP comparison on pH measurement following APMP.QM-P06 (two phosphate buffers) in 2004, APMP.QM-P09 (a phthalate buffer) in 2006, APMP.QM-K9/APMP.QM-P16 (a phosphate buffer) in 2010-2011 and APMP.QM-K19/APMP.QM-P25 (a borate buffer) in 2013-2014.

The results can be used further by any participant to support its CMC claim at least for a phthalate 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, 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, and the key comparison APMP.QM-K19 (a borate buffer) and the parallel pilot study APMP.QM-P25 in 2013-2014 conducted by NMIJ and NIMT, NMIJ proposed a key comparison of "pH measurement of phthalate buffer" at the APMP-TCQM meeting held September 22-23, 2014. Since the proposal was approved as APMP.QM-K91, NMIJ has acted as a coordinating laboratory. The pH values of a phthalate 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 third 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.

It was decided to conduct a parallel pilot study designated APMP.QM-P29, for which the same samples measured by the APMP.QM-K91 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	<b>NMIJ</b> National Metrology Institute of Japan	Japan
2	<b>RCChem-LIPI</b> Research Center for Chemistry - LIPI	Indonesia
3	<b>VMI</b> Vietnam Metrology Institute	Vietnam
4	<b>CMI</b> Czech Metrology Institute	Czech Republic
5	<b>PTB</b> Physikalisch-Technische Bundesanstalt	Germany
6	<b>VNIIFTRI</b> All-Russian Scientific Research Institute for Physical Technical and Radiotechnical Measurements, Rosstandart	Russia
7	<b>Tübitak Ume</b> Tübitak Ume	Turkey
8	<b>CENAM</b> Centro Nacional de Metrologia	Mexico
9	<b>INACAL (formerly INDECOPI)</b> National Institute for Quality	Peru
10	<b>NML-SIRIM</b> National Metrology Laboratory, SIRIM Berhad	Malaysia
11	<b>BeIGIM</b> Belarussian State Institute of Metrology	Belarus
12	<b>GLHK</b> Government Laboratory	Hong Kong

## 3. Sample

The comparison material was a phthalate buffer of pH around 4.0 whose composition was little changed from the typical one for phthalate 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 institute using the Bates–Guggenheim convention. The pH values were compared with those obtained by secondary pH methods, mainly by a glass-electrode or a differential potentiometric cell. The link to CCQM-K91 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 phthalate buffer (molality 0.050000 mol/kg) prepared at NMIJ in January, 2015. The total volume of batch was 50 L, subsequently divided into 47 subsamples of 1000 mL polyethylene bottles. The pH value of the phthalate buffer is around 4.0 and the mass fraction of water in the buffer is 0.989 89; this information was given to the participants before measurements. The ionic strength  $I$  (as molality) calculated from the buffer composition is 0.0535 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.

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

Therefore, the values of  $\log \gamma_{Cl}^{\circ}$  to be added to the acidity function obtained by a Harned cell method were equal to -0.0863 at 15 °C, -0.0877 at 25 °C and -0.0896 at 37 °C. The composition of the sample was little different from that of the typical phthalate buffer. Therefore, since the pH value of the sample for the APMP comparison is close to that for CCQM-K91, it is possible to link APMP.QM-K91 to CCQM-K91.

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The homogeneity of the material was tested before shipping the samples; the pH values at 25 °C had experimental standard deviation 0.0009 for six subsamples by a glass-electrode method and experimental standard deviation 0.0006 for five subsamples by a Harned cell method.

The stability of the material was tested by five measurements with a Harned cell method from January to June 2015. The acidity function values obtained at 25 °C were 4.0944, 4.0948, 4.0955, 4.0938 and 4.0947 on January 23, January 27, February 27, June 23 and June 25, respectively: all the results were within  $\pm 0.001$  range.

The samples were sent to the participants from NMIJ by EMS mail on March 12, 2015. All samples reached their destinations safely. The contact persons are given in Table 2.

Table 2 List of contact persons of NMIJ's

Participant	Contact person
<b>NMIJ</b>	Akiharu Hioki
<b>RCCChem-LIPI</b>	Rosi Ketrin
<b>VMI</b>	Ngo Huy Thanh
<b>CMI</b>	Alena Vospelova
<b>PTB</b>	Frank Bastkowski
<b>VNIIFTRI</b>	Sergey Prokunin, Vladimir Dobrovolskiy
<b>Tübitak Ume</b>	Emrah Uysal
<b>CENAM</b>	Judith Velina Lara-Manzano
<b>INACAL</b>	Galia Ticona Canaza
<b>NML-SIRIM</b>	Khirul Anuar Mohd. Amin, Haslina Abd. Kadir
<b>BelGIM</b>	Nickolay Bakovets
<b>GLHK</b>	Siu-kay Wong

## 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 August 31, 2015. As a matter of fact, the last result was submitted on September 23, 2015.

## 5. Methods of Measurement

Each participant could use a Harned cell method as employed in CCQM-K91 or any suitable method of pH measurement (usually a glass-electrode method or a differential potentiometric cell one). 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-K91

	Participants
Harned cell method	NMIJ, CMI, PTB, VNIIFTRI, Tübitak Ume, CENAM
Glass-electrode method	VMI, NML-SIRIM, GLHK
Differential potentiometric cell method	RCChem-LIPI, INACAL, BelGIM

## 6. Results

The relative changes of bottle masses after shipping are presented in Figure 1. Each of CMI, PTB, VNIIFTRI, Tübitak Ume, CENAM and INACAL reported the changes on two bottles. Each change was very small and it substantially did not affect the pH value.

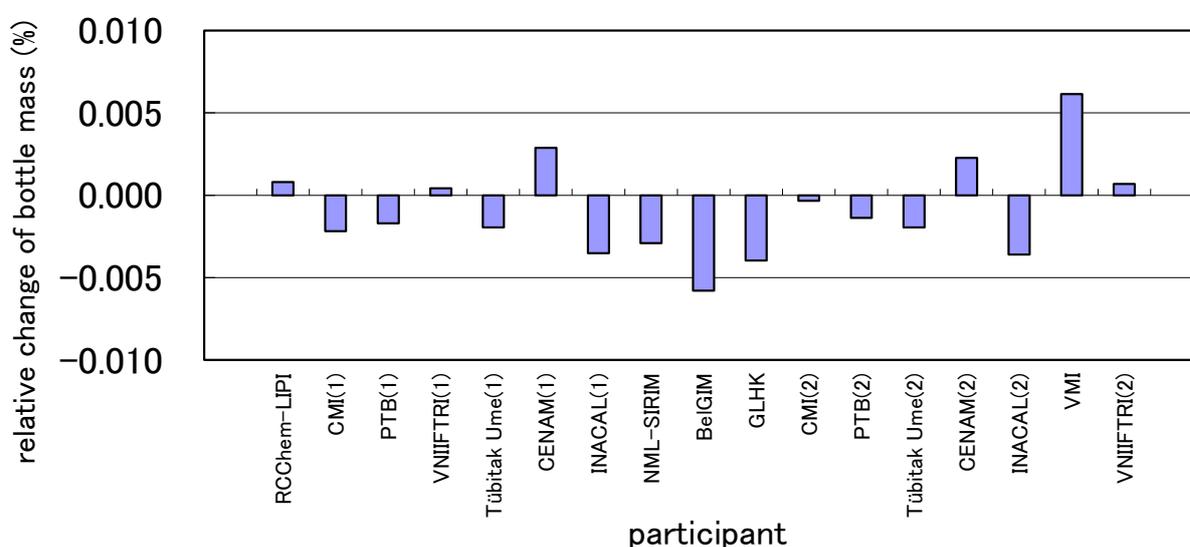


Fig. 1 Relative change of bottle mass after shipping

The results of pH measurements are given in Tables 4 to 6 and illustrated in Figures 2 to 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 a way pH values can be compared with the pH values obtained by a glass-electrode method or a differential potentiometric cell one. 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 PTB and NMIJ.

The comparison results were discussed at the APMP-TCQM meeting held November 2-3, 2015 and circulated to the participants on December 3, 2015. After the disclosure of the results, Tübitak Ume found a mistake in their newly used software which caused a systematic error due to a computational error. Their corrected acidity function values reported on December 11, 2015 were  $4.0899 \pm 0.0028$  at 15 °C,  $4.0956 \pm 0.00165$  at 25 °C and  $4.1141 \pm 0.0034$  at 37 °C, where each value following  $\pm$  indicates the combined standard uncertainty. According to the rule, the originally submitted results are used for all Tables and Figures in the present report.

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Table 4 Results of APMP.QM-K91 at 15 °C

Participant	Calibration standards	Reported acidity function	$\log \gamma_{\text{Cl}^-}$	Reported (or calculated) pH	Combined standard uncertainty
<b>NMIJ</b>	---	4.0859	-0.0863	3.9996	0.0011
<b>RCChem-LIPI</b>	NIST CRM			4.000	0.0009
<b>VMI</b>	Reagecon,* traceable to NIST			4.013	0.0051
<b>CMI</b>	---	4.0853	-0.0863	3.9990	0.0017
<b>PTB</b>	---	4.0883	-0.0863	4.0020	0.0012
<b>VNIIFTRI</b>	---	4.0841	-0.0863	3.9978	0.0019
<b>Tübitak Ume</b>	---	4.1084	-0.0863	4.0221	0.0027
<b>CENAM</b>	---	4.0821	-0.0863	3.9958	0.0070
<b>INACAL</b>	NIST CRM			3.9998	0.0015
<b>NML-SIRIM</b>	NMIJ CRMs			3.9983	0.0029
<b>BelGIM</b>	VNIIFTRI CRM			3.9900	0.0031
<b>GLHK</b>	NIST CRMs			4.000	0.0071

\* The calibration solutions were commercial ones.

Table 5 Results of APMP.QM-K91 at 25 °C

Participant	Calibration standards	Reported acidity function	$\log \gamma_{\text{Cl}^-}$	Reported (or calculated) pH	Combined standard uncertainty
<b>NMIJ</b>	---	4.0945	-0.0877	4.0068	0.0011
<b>RCChem-LIPI</b>	NIST CRM			4.006	0.0009
<b>VMI</b>	Reagecon,* traceable to NIST			4.028	0.0051
<b>CMI</b>	---	4.0973	-0.0877	4.0096	0.0036
<b>PTB</b>	---	4.0962	-0.0877	4.0085	0.0012
<b>VNIIFTRI</b>	---	4.0953	-0.0877	4.0076	0.0019
<b>Tübitak Ume</b>	---	4.1169	-0.0877	4.0292	0.0015
<b>CENAM</b>	---	4.0858	-0.0877	3.9981	0.0047
<b>INACAL</b>	NIST CRM			4.0056	0.0015
<b>NML-SIRIM</b>	NMIJ CRMs			4.0085	0.0032
<b>BelGIM</b>	VNIIFTRI CRM			4.0002	0.0021
<b>GLHK</b>	NIST CRMs			4.006	0.0065

\* The calibration solutions were commercial ones.

Table 6 Results of APMP.QM-K91 at 37 °C

Participant	Calibration standards	Reported acidity function	$\log \gamma_{\text{Cl}^-}$	Reported (or calculated) pH	Combined standard uncertainty
<b>NMIJ</b>	---	4.1154	-0.0896	4.0258	0.0011
<b>RCChem-LIPI</b>	NIST CRM			4.026	0.0009
<b>VMI</b>	Reagecon,* traceable to NIST			4.112	0.0050
<b>CMI</b>	---	4.1133	-0.0896	4.0237	0.0019
<b>PTB</b>	---	4.1162	-0.0896	4.0266	0.0012
<b>VNIIFTRI</b>	---	4.1171	-0.0896	4.0275	0.0018
<b>Tübitak Ume</b>	---	4.1356	-0.0896	4.0460	0.00275
<b>CENAM</b>	---	4.1206	-0.0896	4.0310	0.0084
<b>INACAL</b>	NIST CRM			4.0262	0.0020
<b>NML-SIRIM</b>	NMIJ CRMs			4.0108	0.0028
<b>BelGIM</b>	VNIIFTRI CRM			4.0153	0.0032
<b>GLHK</b>	NIST CRMs			4.024	0.0057

\* The calibration solutions were commercial ones.

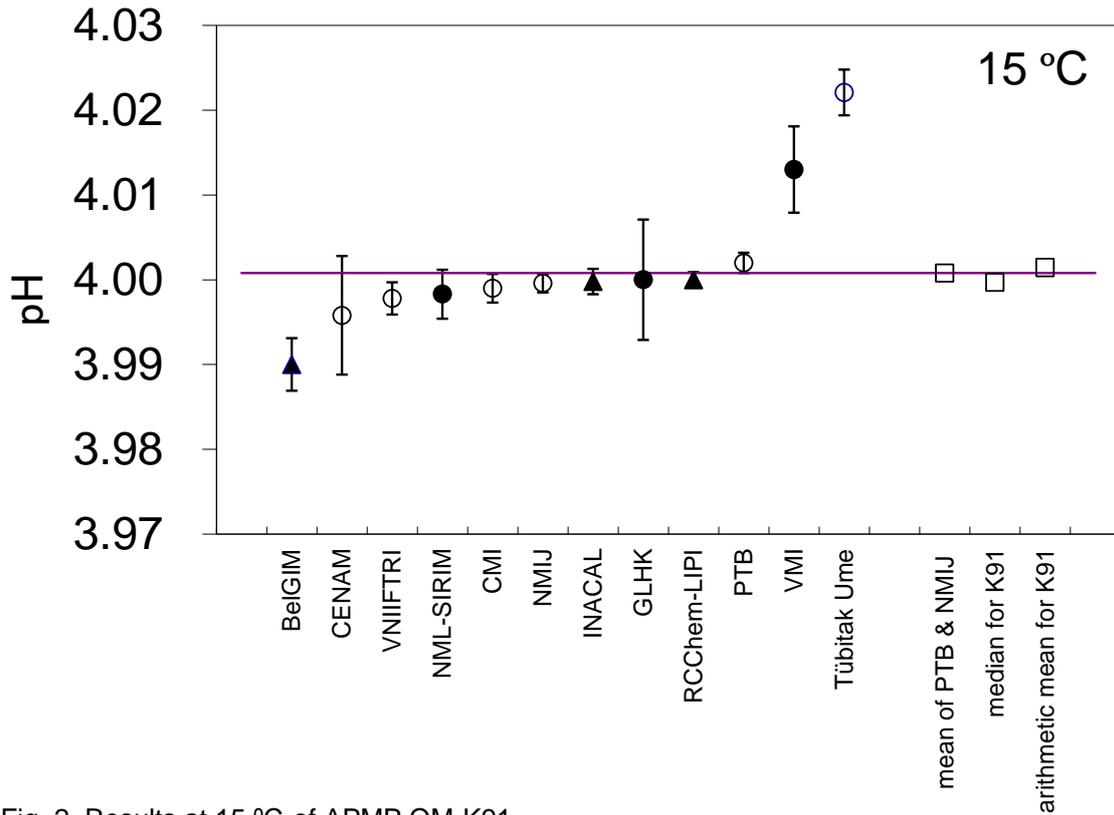


Fig. 2 Results at 15 °C of APMP.QM-K91

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

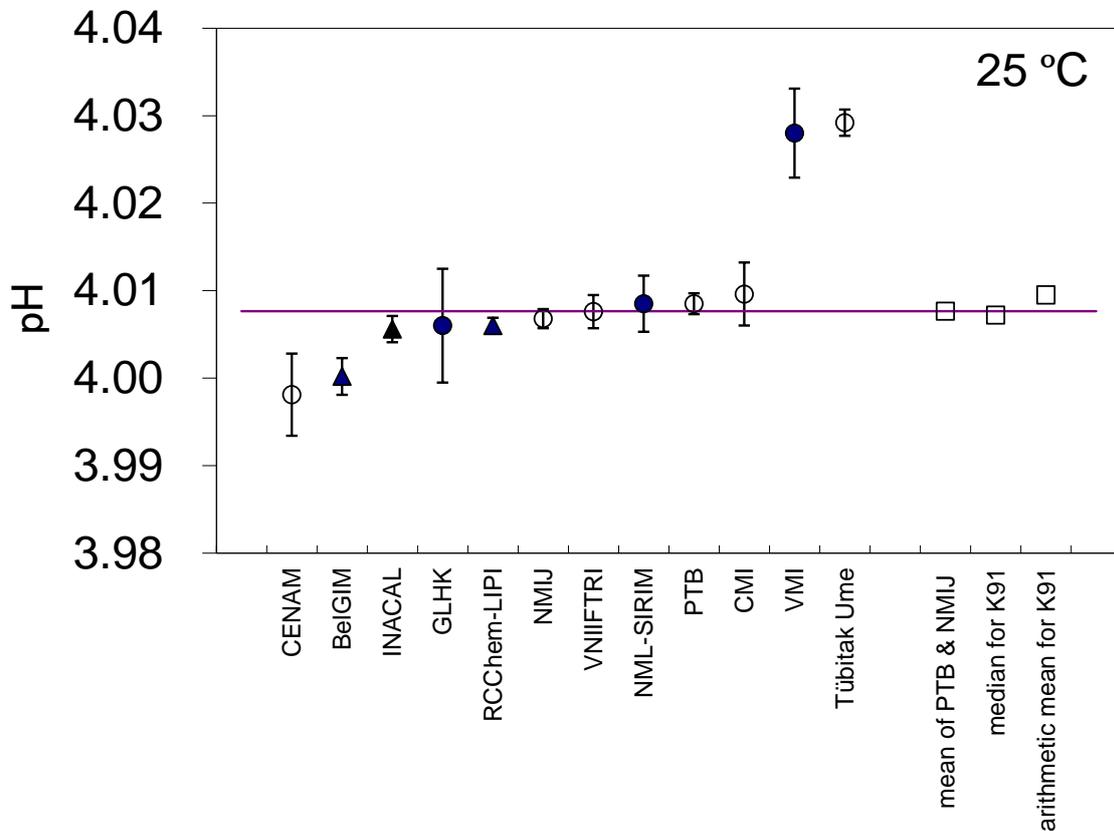


Fig. 3 Results at 25 °C of APMP.QM-K91

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

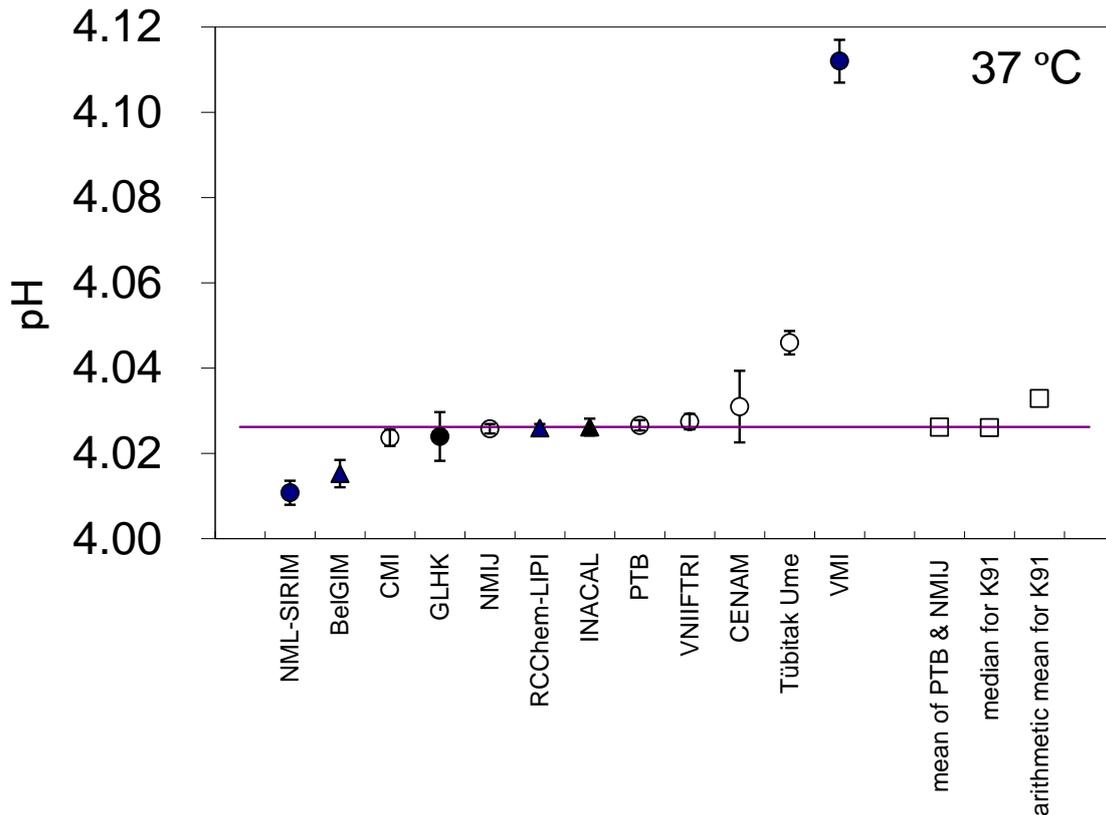


Fig. 4 Results at 37 °C of APMP.QM-K91

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

NMIJ and PTB participated in CCQM-K91; therefore, the two participants in APMP.QM-K91 (NMIJ and PTB) could have links to CCQM-K91. As shown in the technical protocol of APMP.QM-K91, the two NMI's were used as the anchor points to link the present RMO key comparison to CCQM-K91. As shown below, the results of the two NMI's for APMP.QM-K91 were consistent with those for CCQM-K91.

The results of CCQM key comparison can be obtained from the BIPM KCDB ([http://kcdb.bipm.org/AppendixB/KCDB\\_ApB\\_search.asp](http://kcdb.bipm.org/AppendixB/KCDB_ApB_search.asp)). Table 7 shows degrees of equivalence (DoE) for NMIJ and PTB, as reported in CCQM-K91. Table 8 shows the summarised results of APMP.QM-K91. Table 9 shows each DoE and its standard uncertainty for APMP.QM-K91 which was linked to CCQM-K91.

Table 7 DoE estimated from CCQM-K91

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)	0.0001	0.0026	-0.0004	0.0025	0.0004	0.0031
PTB (i = PTB)	0.0010	0.0026	0.0006	0.0025	-0.0004	0.0026
mean( $D_{\text{NMIJ}}+D_{\text{PTB}}$ :K91)	0.00055		0.0001		0.0000	

	15 °C	25 °C	37 °C
KCRV(K91) as acidity function ( $AF$ ) $u(\text{KCRV(K91)})$	4.0853 0.00055	4.0935 0.000415	4.1147 0.00046

NMI	15 °C	25 °C	37 °C
	$u(D_i)'$	$u(D_i)'$	$u(D_i)'$
NMIJ (i = NMIJ)	0.0012	0.0012	0.0015
PTB (i = PTB)	0.0012	0.0012	0.0012
$u(\text{mean}(D_{\text{NMIJ}}+D_{\text{PTB}}):K91)$	0.0010	0.0009	0.0011

$D_i$ : each result of DoE (i indicates each participant). If necessary, such expressions as DoE(i:K91), DoE(i:APMP) are also used. The  $D_i$  and  $U(D_i)$  values for CCQM-K91 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  $AF_i(\text{K91})$  is also used.

$D_{\text{NMIJ}} = \text{DoE}(\text{NMIJ:K91}) = AF_{\text{NMIJ}}(\text{K91}) - \text{KCRV}(\text{K91})$  from CCQM-K91.

$D_{\text{PTB}} = \text{DoE}(\text{PTB:K91}) = AF_{\text{PTB}}(\text{K91}) - \text{KCRV}(\text{K91})$  from CCQM-K91.

$u^2(D_i)' = (U(D_i)/2)^2 - u^2(\text{KCRV}(\text{K91}))$ .

$D_{\text{mean}(\text{NMIJ} + \text{PTB}:K91)} = \text{mean}(D_{\text{NMIJ}} + D_{\text{PTB}}:K91) = (D_{\text{NMIJ}} + D_{\text{PTB}})/2$ .

$u^2(D_{\text{mean}(\text{NMIJ} + \text{PTB}:K91)}) = u^2(\text{mean}(D_{\text{NMIJ}} + D_{\text{PTB}}:K91))$   
 $= [u^2(D_{\text{NMIJ}})' + u^2(D_{\text{PTB}})'] / 4 + u^2(\text{KCRV:K91})$ .

KCRV(K91): KCRV for CCQM-K91.

$u(\text{KCRV}(\text{K91}))$ : combined standard uncertainty of KCRV(K91).

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Table 8 Summarised results of APMP.QM-K91\*

NMI	15 °C		25 °C		37 °C	
	pH <sub>i</sub>	u(pH <sub>i</sub> )	pH <sub>i</sub>	u(pH <sub>i</sub> )	pH <sub>i</sub>	u(pH <sub>i</sub> )
RCChem-LIPI	4.000	0.0009	4.006	0.0009	4.026	0.0009
VMI	4.013	0.0051	4.028	0.0051	4.112	0.0050
CMI	3.9990	0.0017	4.0096	0.0036	4.0237	0.0019
VNIFTRI	3.9978	0.0019	4.0076	0.0019	4.0275	0.0018
Tübitak Ume	4.0221	0.0027	4.0292	0.0015	4.0460	0.00275
CENAM	3.9958	0.0070	3.9981	0.0047	4.0310	0.0084
INACAL	3.9998	0.0015	4.0056	0.0015	4.0262	0.0020
NML-SIRIM	3.9983	0.0029	4.0085	0.0032	4.0108	0.0028
BelGIM	3.9900	0.0031	4.0002	0.0021	4.0153	0.0032
GLHK	4.000	0.0071	4.006	0.0065	4.024	0.0057
NMIJ	3.9996	0.0011	4.0068	0.0011	4.0258	0.0011
PTB	4.0020	0.0012	4.0085	0.0012	4.0266	0.0012
mean(NMIJ+PTB:APMP)	4.0008		4.00765		4.0262	
u[mean(NMIJ+PTB:APMP)]		0.0008		0.0008		0.0008

\* Summarised from Tables 4, 5 and 6.

pH<sub>i</sub>: each result of a comparison (i indicates each participant). If necessary, such expressions as pH<sub>i</sub>(K91), pH<sub>i</sub>(APMP) are also used.

u(pH<sub>i</sub>): combined standard uncertainty of pH<sub>i</sub> in the corresponding key comparison.

mean(NMIJ+PTB:APMP) = [pH<sub>NMIJ</sub>(APMP) + pH<sub>PTB</sub>(APMP)]/2.

u<sup>2</sup>(mean(NMIJ+PTB:APMP)) = [u<sup>2</sup>(pH<sub>NMIJ</sub>(APMP)) + u<sup>2</sup>(pH<sub>PTB</sub>(APMP))]/4.

Table 9 DoE for APMP.QM-K91 (linked to CCQM-K91)

NMI	15 °C		25 °C		37 °C	
	$D_i$	$u(D_i)$	$D_i$	$u(D_i)$	$D_i$	$u(D_i)$
RCChem-LIPI	-0.0003	0.0016	-0.0015	0.0015	-0.0002	0.0016
VMI	0.0127	0.0053	0.0204	0.0052	0.0858	0.0052
CMI	-0.0013	0.0021	0.0021	0.0038	-0.0025	0.0023
VNIFTRI	-0.0025	0.0023	0.0001	0.0023	0.0013	0.0022
Tübitak Ume	0.0218	0.0030	0.0217	0.0019	0.0198	0.0031
CENAM	-0.0045	0.0071	-0.0094	0.0049	0.0048	0.0085
INACAL	-0.0005	0.0020	-0.0019	0.0019	0.0000	0.0024
NML-SIRIM	-0.0020	0.0032	0.0009	0.0034	-0.0154	0.0031
BelGIM	-0.0103	0.0034	-0.0073	0.0024	-0.0109	0.0035
GLHK	-0.0003	0.0072	-0.0015	0.0066	-0.0022	0.0059

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

$= \text{pH}_i(\text{APMP}) - \text{mean}(\text{NMIJ} + \text{PTB}: \text{APMP}) + \text{DoE}(\text{mean}(\text{NMIJ} + \text{PTB}: \text{K91}))$ .

$u^2(D_i) = u^2(\text{pH}_i(\text{APMP})) + u^2[\text{mean}(\text{NMIJ} + \text{PTB}: \text{APMP})] + u^2(D_{\text{mean}(\text{NMIJ} + \text{PTB}: \text{K91})})$ .

It should be understood that each DoE for NMIJ and PTB is shown in Table 7 for CCQM-K91.

Each result of the two NMI's for CCQM-K91 is consistent with the reference value and the mean value of DoE's of the two NMI's for CCQM-K91 suite is also consistent with the reference value. The pH values of the two NMI's for APMP.QM-K91 were in a good agreement with each other. Thus, regarding the two NMI's, it is recognised that there is good consistency between CCQM-K91 and APMP.QM-K91.

The DoE linked to CCQM-K91 for each participant in APMP.QM-K91 is shown in Table 9 and Figure 5. Unfortunately, the results of some participants are not consistent with the reference value mean(NMIJ+PTB:APMP), though those of the other participants are consistent with it.

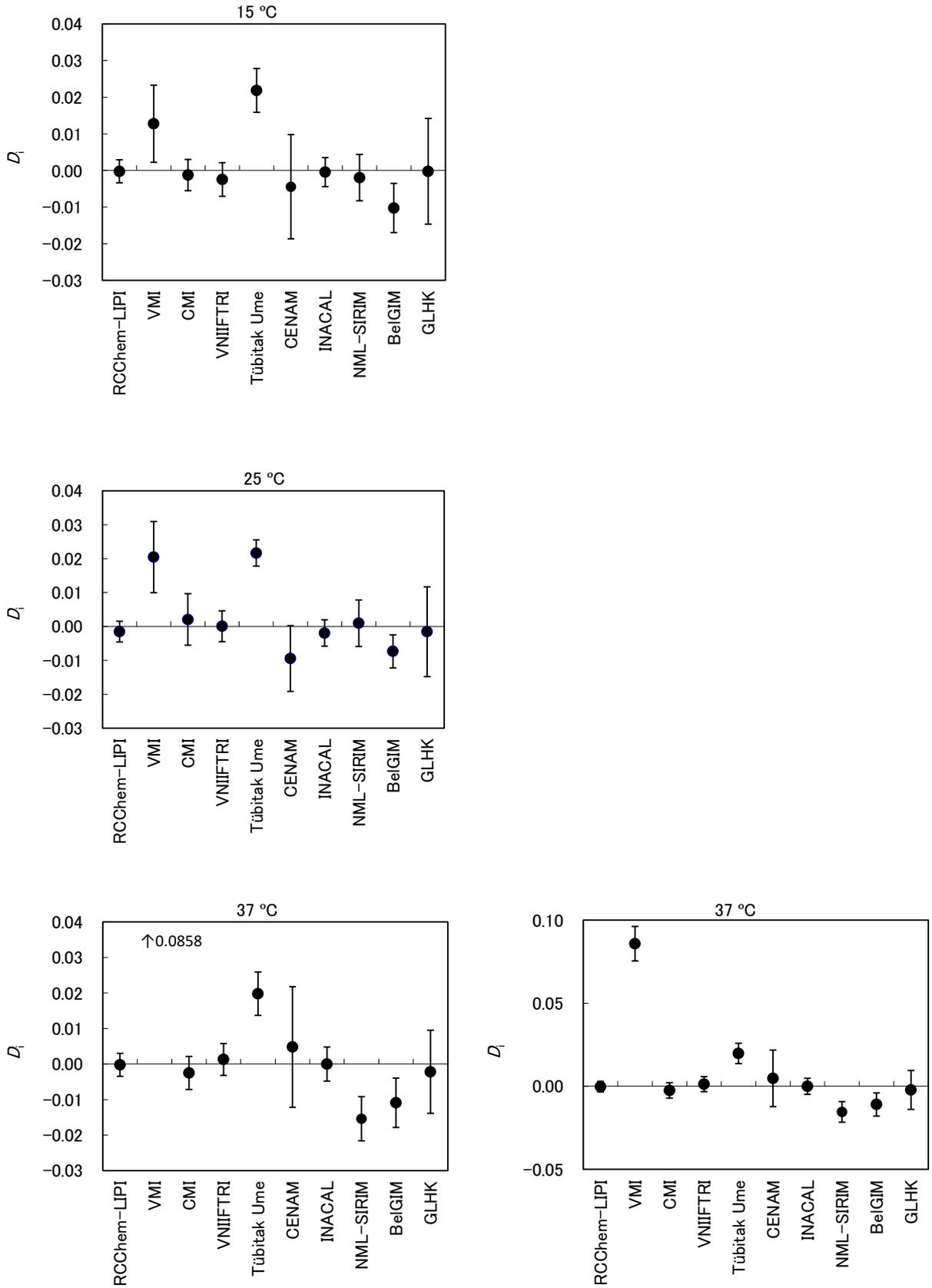


Fig. 5 Degree of equivalence  $D_i$  and expanded uncertainty  $U_i$   
 The half of each bar indicates the expanded uncertainty ( $k = 2$ ) of  $D_i$ .

## 9. Conclusion

The APMP key comparison APMP.QM-K91 could suitably be linked to CCQM-K91. Comparability of measurement results was successfully demonstrated by many participating NMI's for the measurement of pH of a phthalate 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 phthalate 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 phthalate 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 suitably measured pH values at the three temperatures.

This comparison showed that some participants in APMP.QM-K91 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 phthalate buffer is evaluated.

## 10. Acknowledgement

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## **Annex A - Technical protocol**

### **APMP.QM-K91 and APMP.QM-P29**

#### **APMP comparison on pH measurement of a phthalate buffer Call and technical protocol (November 4, 2014)**

##### **Introduction**

The National Metrology Institute of Japan (NMIJ) would like to initiate an APMP comparison on pH measurement to support CMC claim for pH. The comparison is a key comparison following CCQM-K91. 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 phthalate buffer of pH around 4.0 and the measurement temperatures are 15 °C, 25 °C and 37 °C. NMIJ proposed the present key comparison at the APMP-TCQM meeting held September 22-23, 2014 and the proposal was agreed as APMP.QM-K91. This is the third APMP key comparison on pH measurement and the fifth APMP comparison on pH measurement following APMP.QM-K19/P25 (a borate buffer). In parallel with the key comparison APMP.QM-K91, a pilot study APMP.QM-P29 is carried out, in which the same sample measured by the APMP.QM-K91 participants is also used.

##### **Sample**

The comparison material is a phthalate buffer of pH around 4.0 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-K91 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 comparison.

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-K91 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; akihioki@aist.go.jp), 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: November, 2014  
Deadline of registration of participation: December 31, 2014  
Dispatch of the samples: March or April, 2015  
Deadline for submitting the results: August 31, 2015

### **Participants**

Participation is open to all interested NMIs or officially designated laboratories that can perform the determination. APMP members can 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. 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. The coordinating laboratory might invite some NMIs outside APMP to participate in the key comparison or some expert calibration laboratories directly to participate in the pilot study.

### **Coordinating laboratory**

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

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