# CCQM-K9

## pH determination on two phosphate buffers by Harned cell measurements

## Follow-up bilateral comparison SMU – PTB

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## 1. Introduction

The first key comparison for the quantity pH, CCQM-K9, was carried out to assess the degree of equivalence of the national primary measurement procedures used to determine the pH of primary standard buffer solutions.
One participant, the SMU (Slovenský metrologický ústav), discovered a calculation error which influenced the measurement result. This observation was stated after the results of the key comparison K9 had been disclosed. It was decided to use the uncorrected result for appendix B of the MRA and the corrected result for evaluating the key comparison reference value (KCRV).
A follow-up bilateral comparison was agreed by the SMU and the PTB (Physikalisch-Technische Bundesanstalt), Germany , the pilot laboratory for CCQM-K9.
The measurement protocol for the follow-up comparison was similar to the K9 key comparison. The value obtained for the acidity function at zero chloride molality, $pa_0$ of the sample as reported by SMU and PTB is taken as the final result of the bilateral comparison.

## 2. Participants

Table 1. Participants in the CCQM-K9 subsequent bilateral comparison

| **Institute** | **Country** |
|---|---|
| PTB<br>Physikalisch-Technische Bundesanstalt | Germany |
| SMU<br>Slovenský metrologický ústav | Slovakia |

## 3. Samples

The sample was a two-component phosphate buffer containing potassium dihydrogen phosphate ($KH_2PO_4$) and disodium hydrogen phosphate ($Na_2HPO_4$). The sample was prepared from the same NIST Standard Reference Material as the samples for CCQM-K9. A batch of 8 kg solution from NIST SRM 186If and NIST SRM 186IIf at the molality of 0.025 each was prepared and distributed in 1kg bottles by PTB. The composition of the sample was very similar to that of sample (1) in CCQM-K9.
The homogeneity of the batch was tested by PTB in measuring the pH of three randomly-selected bottles. The electrolytic conductivity of the water used for preparation was 0,5 µS $cm^{-1}$. SMU received three bottles together with a description how to store the sample. Only the total mass of the sample and the amount of water in the sample were given to the SMU. The hydrochloric acid and the sodium chloride needed for the measurements was not provided but individual laboratory material of stated high quality was used in the comparison.

## 4. Principle of measurement

The principle of measurement has been described in the report of CCQM-K9. The measurement uncertainty has been calculated by both participants also according to the same procedure as for CCQM-K9.

The measurements are carried out at 15 °C, 25 °C and 37 °C.

## 5. Results

The pH values given in table 2 to 4 and illustrated in figure 1 to 3 are calculated by the pilot laboratory for an ionic strength of the buffer $I = 0.100$ mol $kg^{-1}$.

Table 2. Results at a measurement temperature of 15 °C

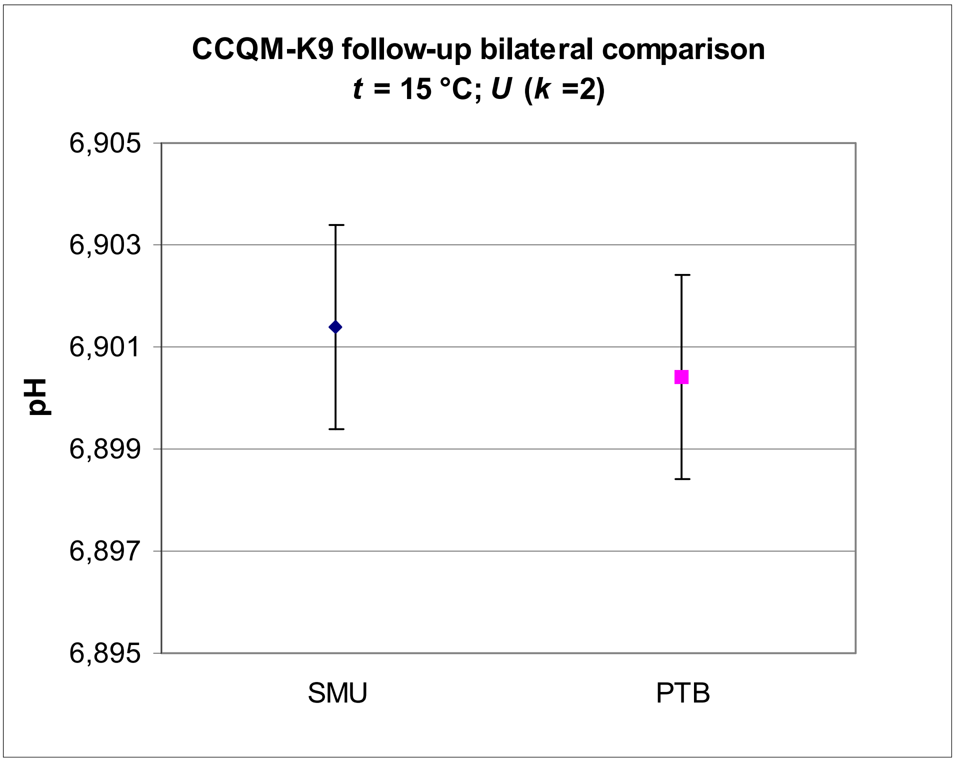
| Participant | Reported value Acidity function $pa_0$ | pH | Uncertainty $u$ ($k$ = 1) | Uncertainty $U$ ($k$ =2) |
|---|---|---|---|---|
| **SMU** | 7.0092 | 6.9014 | 0.00100 | 0.0020 |
| **PTB** | 7.0082 | 6.9004 | 0.00105 | 0.0021 |

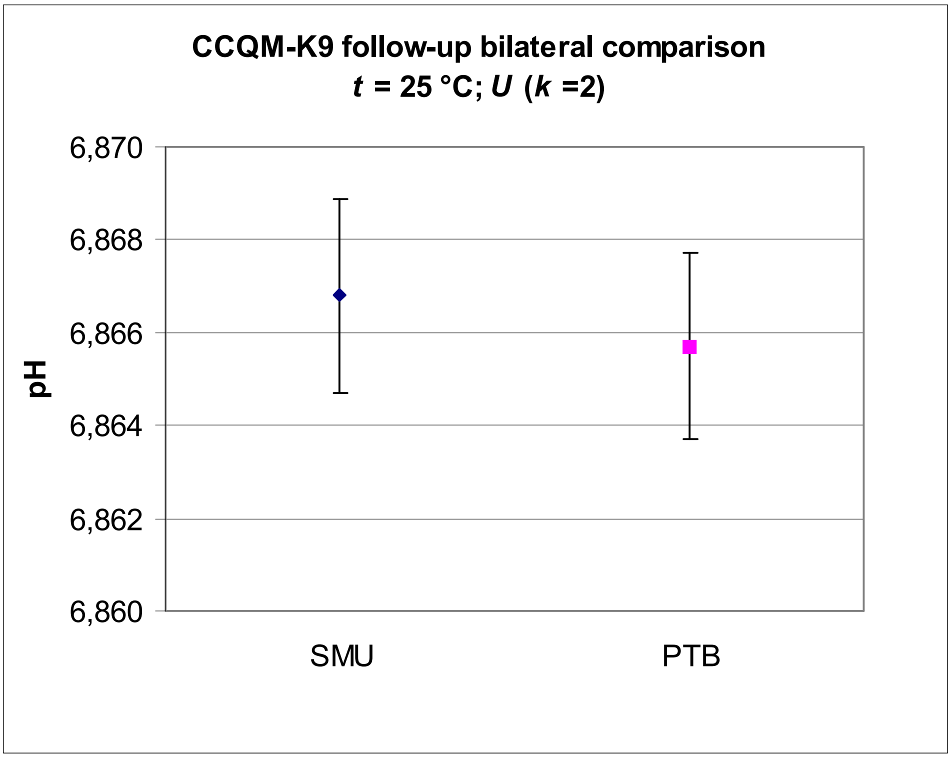
Table 3. Results at a measurement temperature of 25 °C

| Participant | Reported value Acidity function $pa_0$ | pH | Uncertainty $u$ ($k$ = 1) | Uncertainty $U$ ($k$ =2) |
|---|---|---|---|---|
| **SMU** | 6.9764 | 6.8668 | 0.00105 | 0.0021 |
| **PTB** | 6.9753 | 6.8657 | 0.00105 | 0.0021 |

Table 4. Results at a measurement temperature of 37 °C

| Participant | Reported value Acidity function $pa_0$ | pH | Uncertainty $u$ ($k$ = 1) | Uncertainty $U$ ($k$ =2) |
|---|---|---|---|---|
| **SMU** | 6.9558 | 6.8439 | 0.00125 | 0.0025 |
| **PTB** | 6.9541 | 6.8422 | 0.00105 | 0.0021 |





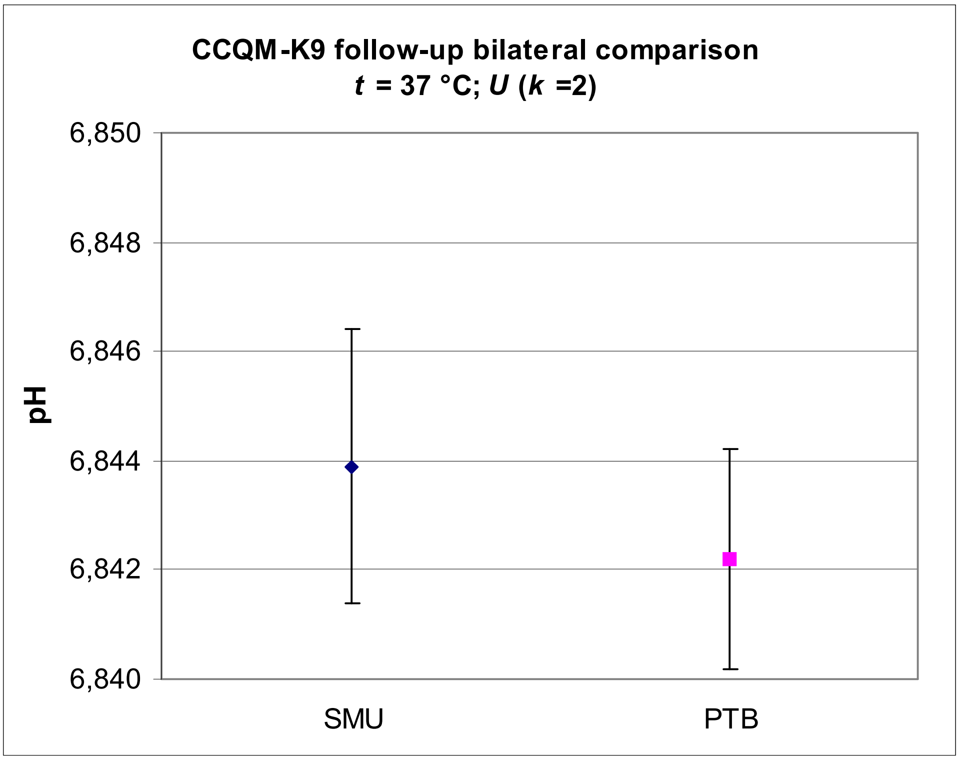




Figure 2 to 4. pH values at measurement temperatures of 15 °C, 25°C and 37°C..
The uncertainty represented is the expanded uncertainty with the coverage factor $k$ =2

## 6. Link to CCQM-K9

The results of the bilateral comparison allow a new line of data to be included for SMU in the table of matrices of equivalence and graphs of CCQM-K9.The result of PTB in CCQM-K9 (sample1) acts in that case as a link between the subsequent bilateral and the original key comparison. The performance of PTB within its uncertainty is assumed to be similar in both cases therefore it is assumed that the bias between the PTB result and the KCRV remains constant over the two comparisons. The new degree of equivalence for SMU, $D_{\mathrm{i\ (SMU(s))}}$ is calculated from the degree of equivalence of the PTB in K9, $D_{\mathrm{i(PTB(K9))}}$ and from the degree of equivalence between PTB and SMU in the subsequent bilateral comparison, $\mathrm{D_{ij}}$ according to equations (1) and (2):

$$D_{i(\mathrm{SMU(s)})} = D_{i(\mathrm{PTB(K9)})} + D_{ij(\mathrm{PTB(s);SMU(s)})} \tag{1}$$

$$D_{ij(\mathrm{PTB(s);SMU(s)})} = \mathrm{pH}_{(\mathrm{SMU(s)})} - \mathrm{pH}_{(\mathrm{PTB(s)})} \tag{2}$$

The uncertainty of the new degree of equivalence of SMU ($D_{\mathrm{i}}$ ) taking into account the uncertainty contribution considered by the PTB due to the reproducibility of its two results. This additional uncertainty contribution is assumed to be equal to the uncertainty associated with the result of PTB of the bilateral comparison, .$u_{\mathrm{i(pH\ (PTB(s))}}$. The expanded uncertainty ($k$ = 2) is calculated from equation (3) and (4)

$$U_{i(SMU(s))} = \sqrt{2^2\left(u^2_{i(\mathrm{SMUB(s')})} + u^2_{\mathrm{R(K9)}}\right)} \tag{3}$$

$$u_{i(\mathrm{SMU(s')})} = \sqrt{u^2_{i(\mathrm{PTB(s)})} + u^2_{i(\mathrm{SMUB(s)})}} \tag{4}$$

where $u_{\mathrm{R(K9)}}$ is the uncertainty estimated for the key comparison reference value for CCQM-K9 (sample1).
The degree of equivalence between SMU(s) and the other laboratories is given by a pair of numbers,

$$D_{i(SMU(s))j} = D_{i(\mathrm{SMU(s)})} - D_j \tag{5}$$

and $U_{\mathrm{i(SMU(s))j}}$, the expanded uncertainty of $D_{i(SMU(s))j}$ ,($k$ = 2), which is calculated according to equation (6)

$$U_{i(SMU(s))_j} = 2\sqrt{u_{i(SMU(s'))}{}^2 + u_j{}^2}\ . \tag{6}$$