

Final report for CCQM-K17

pH determination on a phthalate buffer by Harned cell measurements

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Abstract

The second key comparison for the quantity pH, CCQM-K17, 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.

The CCQM-K17 comparison allows estimations of the capability of ten national metrology institutes (NMIs) to determine the pH of a phthalate buffer of unknown concentration at different temperatures. The key comparison was co-ordinated by the CCQM Working Group on Electrochemical Analysis and piloted by the Physikalisch-Technische Bundesanstalt (PTB) with assistance from the National Institute of Standards and Technology (NIST) and the Slovak Institute of Metrology (SMU).

The measurement results of the NMIs agreed not at the same level as for the first key comparison on pH CCQM-K9. The results obtained by seven of the eleven participants agree very well within the uncertainty stated by the participants. Four participants obtained results somewhat lower. The two groups of results are most obviously at a measurement temperature of 37°C.

Summary of the measurement results

Temperature in °C	15		25		37	
KCRV	pH _R	<i>u_R</i>	pH _R	<i>u_R</i>	pH _R	<i>u_R</i>
	4.0093	0.00089	4.0156	0.00109	4.0343	0.00125
Single results Lab <i>i</i>	pH _{<i>i</i>}	<i>u_i</i>	pH _{<i>i</i>}	<i>u_i</i>	pH _{<i>i</i>}	<i>u_i</i>
NRCCRM	4,0070	0,00200	4,0150	0,00200	4,0370	0,00200
PTB	4,0100	0,00110	4,0168	0,00110	4,0360	0,00150
DPL	4,0074	0,00080	4,0150	0,00080	4,0351	0,00080
KRISS	4,0033	0,00150	4,0104	0,00170	4,0296	0,00170
AIST	4,0024	0,00318	4,0108	0,00303	4,0261	0,00393
CENAM	4,0020	0,00240	4,0050	0,00220	4,0290	0,00200
GUM	4,0123	0,00150	4,0183	0,00150	4,0355	0,00150
VNIIFTRI	4,0130	0,00130	4,0193	0,00130	4,0380	0,00130
SMU	4,0095	0,00105	4,0174	0,00110	4,0397	0,00145
CMI	4,0014	0,00170	4,0050	0,00170	4,0272	0,00105
NIST	4,0108	0,00047	4,0170	0,00062	4,0371	0,00130

Table A2. Summary of results of CCQM-K17.

1 Introduction

The primary measurement procedure for pH is based on the measurement of the potential difference between a platinum hydrogen electrode and a silver/silver chloride reference electrode of an electrochemical cell filled with a selected buffer solution, often called the Harned cell. A conventional procedure makes it possible to relate the operation of the Harned cell to the definition of pH, very closely. This conventional procedure suggested by Bates [1] and now recommended by IUPAC [2] is used at present in most of the national metrology institutes involved in pH measurement for the assignment of pH values to primary pH standard buffer solutions at the national standards level.

During its meeting in November 2000 the CCQM Working Group on Electrochemical Analysis, initiated this second key comparison on pH, CCQM-K17, on a phthalate buffers in order to evaluate the degree of equivalence of the national primary measurement procedures for pH.

Eleven national metrology institutes participated. The comparison started in May 2001 and the results were reported until 30 September 2001. The comparison was restricted to the use of Harned cells.

The potassium hydrogen phthalate buffer solution, $m = 0.05$ mol/kg is the reference value pH standard (RVS) of the pH scale of the British Standard Organisation (BSI). According to the 1985 IUPAC recommendation the user has the choice between the NIST based multipoint pH scale and the British one point approach. For the one-point pH scale the phthalate buffer is the reference point for all other so-called operational pH (OS). The pH(OS) are measured in comparison with the phthalate buffer in a cell with free liquid junction [19]

In order to minimise reduction of phthalate the platinum electrodes must be coated by palladium black instead of platinum black.

2 Participation in CCQM-K17

In table 1 the names of all National Metrology Institutes (NMIs) are listed that participated in CCQM-K17.

Participant	Acronym	Country
National Research Centre for Certified Reference Materials	NRCCRM	CN
Physikalisch-Technische Bundesanstalt (Pilot laboratory)	PTB	DE
Danish Primary Laboratory for pH measurements c/o Radiometer Medical A/S	DPL for pH	DK
National Institute of Advanced Industrial Science and Technology	AIST	JP
Korea Research Institute of Standards and Science	KRISS	KR
Centro Nacional de Metrología	CENAM	MX
Central Office of Measures	GUM	PL
National Scientific and Research Institute for Physical–Technical and Radiotechnical Measurements	VNIIFTRI	RU
Slovak Institute of Metrology	SMU	SK
Czech Metrology Institute	CMI	TCH
National Institute of Standards and Technology	NIST	US

Table1. CCQM-K17 key comparison participants

3 Description of the samples

A phthalate buffer, containing potassium hydrogen phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$) at a molality of $0.05 \text{ mol}\cdot\text{kg}^{-1}$ was chosen as transfer standard. The molality ($\text{mol}\cdot\text{kg}^{-1}$) was not known to the participants.

The samples were prepared from the NIST Standard Reference Material SRM 84k and pure water with an electrolytic conductivity of less than $1 \mu\text{S}\cdot\text{cm}^{-1}$. The SRM 84k potassium hydrogen phthalate (KHP) is intended for use as a primary acidimetric standard. The material was not certified as a primary pH reference buffer material. A total of 45 bottles of sample solution was prepared containing each $1 \text{ kg } 0.05 \text{ mol}\cdot\text{kg}^{-1}$ SRM 84k. The sample was prepared and shipped by the pilot laboratory with the assistance of the Zentrum für Messen und Kalibrieren GmbH Sachsen-Anhalt (Germany). The homogeneity of the batch was tested by the pilot laboratory in determining the pH of three randomly-selected bottles. The participants were given the total mass of the sample, the amount of water in the sample and the ionic strengths of the buffer solution, $I = 0.0535 \text{ mol}\cdot\text{kg}^{-1}$.

Each participant received three bottles together with a description how to store the sample. The amount of materials was sufficient to repeat the pH determination for at least three times. The hydrochloric acid and the sodium or potassium 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 pH measurement is carried out by measuring the potential difference of the electrochemical cell (Cell I, Harned cell) at several chloride molalities necessary in order to stabilize the potential of the silver-silver chloride electrode. The determination of the pH value of the buffer solution involves an extrapolation of the measured potential difference to zero chloride molality.



The potential difference E of this cell (corrected to 101.325 kPa partial pressure of hydrogen) depends on the hydrogen ion activity a_{H} , the quantity to be measured, in the following way:

$$E = E^0 - \left[\frac{RT}{F} \ln 10 \right] \lg(a_{\text{H}} / m^0) (m_{\text{Cl}} \gamma_{\text{Cl}} / m^0) \quad (1)$$

This is the measurement equation.

E^0 is the standard potential difference of the cell i.e. at $a_{\text{H}} = a_{\text{Cl}} = 1 \text{ mol}\cdot\text{kg}^{-1}$, m^0 is the standard molality: 1 mol kg^{-1} , γ_{H} and γ_{Cl} are the activity coefficients of the hydrogen and the chloride ion, R is the molar gas constant, F the Faraday constant and T the thermodynamic temperature.

A pH measurement of a buffer solution using cell I usually consists of the following steps .

1. The standard potential difference E^0 is determined from a Harned cell filled with hydrochloric acid of fixed molality, according to equation (2). The mean activity coefficient of HCl, $\gamma_{\pm\text{HCl}}$, at various temperatures is best known at the molality 0.01 mol kg^{-1} [7]

$$E^0 = E + [(2RT/F) \ln 10] [\lg(m_{\text{HCl}} / m^0) (\gamma_{\pm\text{HCl}})] \quad (2)$$

E is corrected to 101.325 kPa partial pressure of hydrogen.

2. Equation (1) can be rearranged to give the acidity function $p\alpha$ so that there are only measurable quantities on the right hand side of equation (3) $p\alpha$ is measured as a function of m_{Cl^-} .

$$p\alpha = -\lg(a_{\text{H}^+} \gamma_{\text{Cl}^-} / m^0) = (E - E^0) / [(RT/F) \ln 10] + \lg(m_{\text{Cl}^-} / m^0), \quad (3)$$

3. Extrapolation of the acidity function to zero chloride molality.

The acidity function

$$p\alpha_0 = -\lg(a_{\text{H}^+} \gamma_{\text{Cl}^-} / m^0)_{m_{\text{Cl}^-} \rightarrow 0} \quad (4)$$

corresponding to zero chloride molality is determined by linear extrapolation according to equation (5) of $p\alpha$ as a function of the chloride molality, using measurements at least three values of m_{Cl^-} in the range from 0.005 to 0.02 mol·kg⁻¹. It is assumed that a linear extrapolation is appropriate if the change in ionic strength produced by the addition of chloride is restricted to less than 20%.

$$p\alpha = p\alpha_0 + b m_{\text{Cl}^-} \quad (5)$$

where b is an empirical, temperature-dependent constant.

4. The activity coefficient γ_{Cl^-} at the ionic strength I of the buffer is obtained by adopting the Bates-Guggenheim convention [1]. Here, the activity coefficient γ_{Cl^-} is given by the expression (6).

$$\lg \gamma_{\text{Cl}^-} = -A(I / m^0)^{1/2} / (1 + 1.5(I / m^0)^{1/2}) \quad (6)$$

A is the Debye-Hückel temperature-dependent limiting slope [9] and I the ionic strength of the buffer solution. According to the Bates-Guggenheim convention the ion size parameter of the Debye-Hückel theory at low ionic strength ($I < 0.1$ mol kg⁻¹) is set equal to the numerical value 1.5 at all measurement temperatures.

5. Calculation of the pH value:

From equations (3), (4), (6) and the definition of the pH, $\text{pH} = -\lg a_{\text{H}^+}$, the pH value is obtained according to equation (7).

$$\text{pH} = p\alpha_0 + \lg \gamma_{\text{Cl}^-} \quad (7)$$

The flowchart in Figure 1 summarizes the steps of the primary measurement procedure of pH.

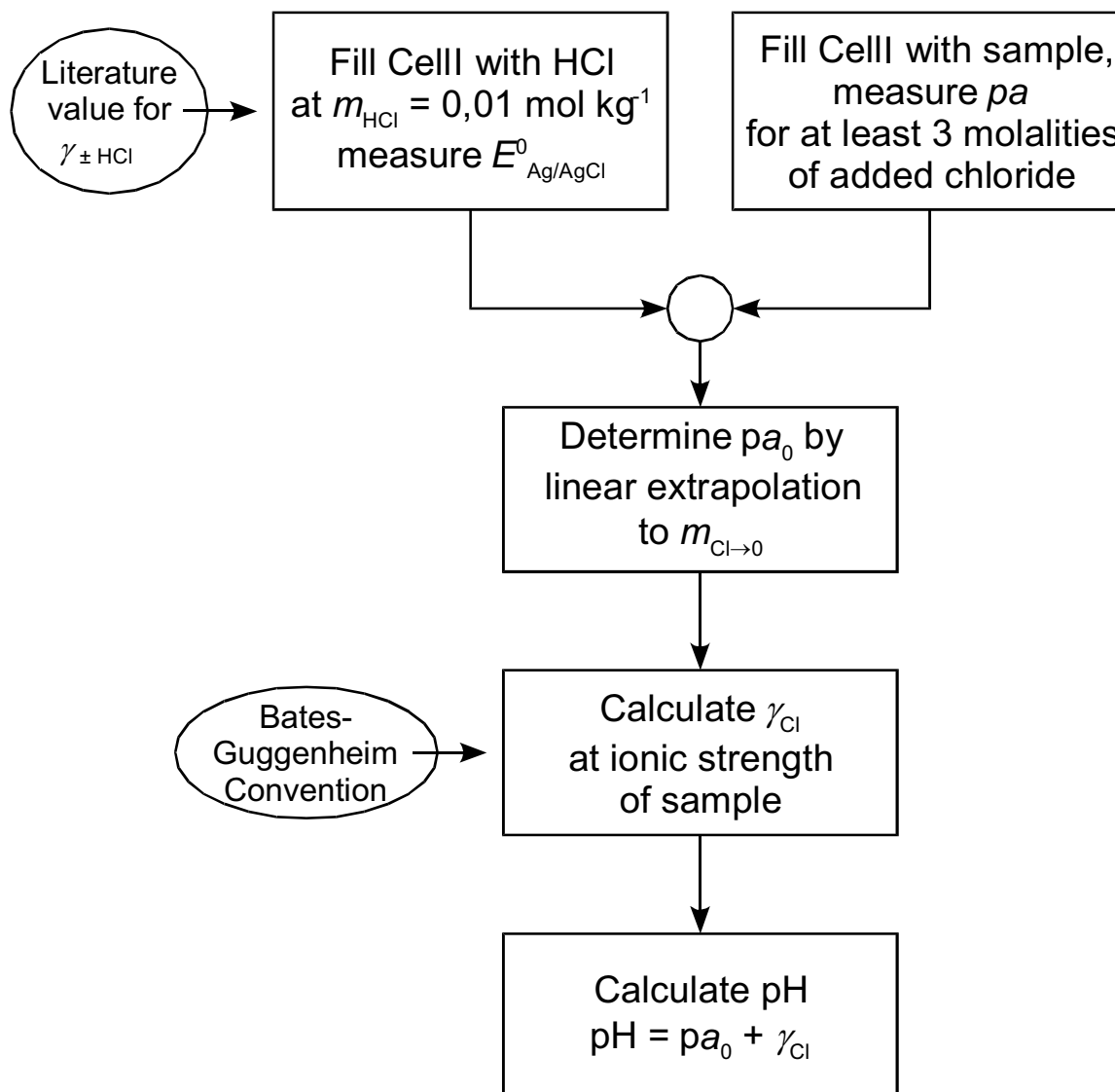


Figure 1. Primary measurement procedure of pH

5 Brief description of the measurement protocol

The samples for CCQM-K17 were sent to the participants together with an instruction package including a result reporting form and an uncertainty budget form.

A working paper on pH measurement was agreed upon by the WG members in 1999, in which the primary procedure for pH measurement was described, including the evaluation of uncertainty [6]. Therefore the protocol only provided the participants with additional experimental details such as measurement temperatures and the range of chloride to be added to the samples.

It was recommended to the participants of CCQM-K17 to carry out the measurements at 15 °C, 25 °C and 37 °C.

As the method of choice for the determination of the molality of HCl coulometric titration was recommended as a primary method. The decision was left to the participants whether to use potassium or sodium chloride. Alkali chloride at least three molalities in the range from

0.005 to 0.02 mol kg⁻¹ were to be added to the buffer solution in step two of the measurement procedure.

The results to be reported were the pH value at every measurement temperature for the sample and the measurement uncertainty belonging to them.

In order to allow a complete evaluation of the key comparison, each participant was requested to report the deviations from CCQM-K9 in experimental details of the sample preparation and equipment used in all steps of the measurement procedure.

6 The measurement equation and the principal components of the uncertainty budget

The measurement equation to determine the pH of the sample is equation (1).

$$E = E^0 - [(RT/F) \ln 10] \lg(m_{\text{H}} \gamma_{\text{H}} / m^0)(m_{\text{Cl}} \gamma_{\text{Cl}} / m^0) \quad (1)$$

It was agreed within the CCQM WG on Electrochemical Analysis not to take the uncertainties associated with the Bates-Guggenheim convention into account. The small uncertainty of the ionic strength I is regarded as insignificant, i.e.:

$$u(\lg(\gamma_{\text{Cl}^-})) \equiv 0. \quad (8)$$

Therefore :

$$u(\text{pH}) = u(\text{p}a_0)$$

A good estimate for the uncertainty of the pH value of the sample is equation (9).

$$u(\text{p}a_0) = \sqrt{u^2(\text{p}a_{m=0.005}) + u^2(\text{intercept})} \quad (9)$$

The standard uncertainty $u(\text{intercept})$ of the extrapolation of the acidity function, $\text{p}a$, to zero chloride molality by a linear least squares fit at the $\text{p}a$ values obtained at the different chloride molalities is obtained according to equation (10)

$$u(\text{intercept}) = s \sqrt{\frac{1}{N} + \frac{\bar{m}_{\text{Cl}}^2}{\sum_{i=1}^N (m_{\text{Cl}} - \bar{m}_{\text{Cl}})^2}}, \quad s^2 = \frac{\sum_{i=1}^N [\text{p}a_{m_{\text{Cl}}} - (\text{p}a_0 + b \cdot m_{\text{Cl}})]^2}{N - 2} \quad (10)$$

s is the residual standard deviation, N the number of measurements used to get $\text{p}a$ at different molalities of chloride, b is the slope of the regression line.

The DPL used an approach slightly different from (10), by replacing the residual standard deviation s by $u(\text{p}a_{m=0.005})$. As far as the scatter around the regression line is small, both approaches give very similar results. The NIST and the SMU reported the uncertainty in a slightly different way combining the uncertainty of the acidity function and the intercept in one table.

The uncertainty of the acidity function at the smallest amount of added chloride, $m_{\text{Cl}} = 0.005 \text{ mol kg}^{-1}$, $u(\text{p}a_{m=0.005})$, is in most cases the largest contribution to the overall

uncertainty. If the scatter around the regression line is large, the uncertainty of the intercept can become the major contribution to the overall uncertainty as it is obvious from table 4 in Annex A.

Estimation of the uncertainty of the acidity function requires the knowledge of the uncertainty contributions from the determination of the standard potential E^0 according to equation (2). The uncertainty in the molality of HCl has been identified as one of the main components contributing to the uncertainty of E^0 . The small uncertainties of F and R do not contribute significantly to the budget and are omitted.

A complete uncertainty budget taking into account all known components which affect the measurement result is given in Table A2 of Annex A for a representative sample at a measurement temperature of 25 °C. The standard uncertainties $u(m_{\text{HCl}})$, $u(E^0)$, $u(p_a)$, $u(\text{intercept})$ and $u(p_{a_0})$ are also summarized in the Annex for this example.

7 Results and uncertainties of the measurements of the individual laboratories

The results obtained for the sample 0.05 mol kg⁻¹ Potassium hydrogen phthalate, KHC₈H₄O₄ at different temperatures together with the associated uncertainties ($k = 2$), as reported to the pilot laboratory, are given in Tables 2 to 4. The graphs showing the results are numbered correspondingly.

8 Discussion of the results

The evaluation of CCQM-K17 mostly confirms the results obtained in the first key comparison on pH CCQM-K9.

The uniformity of the results obtained in CCQM-K9 was better than the uniformity the pH obtained for the phthalate buffer in CCQM-K17. The results obtained by seven of the eleven participants agree very well within the uncertainty stated by the laboratories. Four participants obtained results somewhat lower. The two groups of results are most obviously at a measurement temperature of 37 °C. The degree of equivalence is not significantly influenced by the measurement temperature

The sample sequence has no influence on the reported pH values. This is demonstrated in figure 5 to 7 there the pH as reported by the laboratories are displayed following the sample order.

The preparation of the palladium hydrogen electrodes for measuring the potential of cell (I) requires some skill. The palladium coating is not so stable as the platinum coating normally used for Harned cell measurements.

A possible explanation for the very low pH values obtained by CMI is a evaporation of sample solution while flushing with argon in a preparation step.

All participants carried out the measurements at 15 °C, 25 °C and 37 °C. Nearly all of the participants determined the amount content of HCl by coulometric titration. A high-precision gravimetric method was used by GUM. The magnitudes of the uncertainties stated by the participants and shown in Annex A are similar for both methods.

11 Evaluation of the KCRV

It was agreed upon the CCQM Working Group on Electrochemical Analysis to use the same approach as in CCQM-K9 to assign the key comparison reference value KCRV and the uncertainty associated with it. There is no reason to doubt the uncertainties of the results estimated by the participants, so these can be regarded as credible.

The pH value provided by each laboratory is considered as an unbiased estimate of the quantity of concern [11]. The maximum-likelihood estimator yields the KCRV, pH_R , as the variance based weighted mean [12], [13] according to equations (11), (12) and (13).

$$\text{pH}_R = \frac{\sum_{i=1}^N w_i \text{pH}_i}{\sum_{i=1}^N w_i} \quad (11)$$

where pH_i represent the individual results and w_i : the individual weights.

$$w_i = \frac{C}{u_i^2} \quad (12)$$

$$C = \frac{1}{\sum_{i=1}^N \frac{1}{u_i^2}} \quad (13)$$

The values of u_i are the individual uncertainties and C is the variance.

One method for testing whether measurements of the same quantity are compatible with each other is the so called Birge or Z ratio method [15],[16]. When applying this test, the uncertainty of the KCRV as determined from the individual uncertainties stated by the participants (the internal consistency of the data, equation (14)) is compared to the external consistency taking into account how much each result deviates from the KCRV in relation to its uncertainty. The Birge ratio R_{Birge} calculated for the CCQM-K17 results according to equation (15) is always larger than one, indicating that there is the possibility that some or all of the individual uncertainties have been underestimated. The Birge ratio is higher than calculated for the CCQM-K9 comparison.

$$u(\text{pH}_R)^2 = C \quad (14)$$

A problem with the estimation of the uncertainty according to equation (14) is that a laboratory that quotes an optimistically small uncertainty has a strong influence on the KCRV and makes the uncertainty of the latter unreasonably small [14].

$$R_{\text{Birge}}^2 = \frac{\sum_{i=1}^N \frac{(\text{pH}_i - \text{pH}_R)^2}{u_i^2}}{(N-1)} \quad (15)$$

A reasonable estimate of the uncertainty for the KCRV is therefore that of the external consistency concept [12], [13] taking into account the individual uncertainties and the spread of the results according to equation (16).

$$u_R^2 = \frac{\sum_{i=1}^N (w_i (\text{pH}_i - \text{pH}_R)^2)}{(N-1) \cdot \sum_{i=1}^N w_i} \quad (16)$$

The variance-based weighted mean is stated as the KCRV. The uncertainty of the KCRV, u_R ($k=1$), is calculated according to the external consistency concept, equation (16).

In order to investigate the reasons leading to increased interlaboratory spread even though the experimental designs used are very similar, it was agreed to perform a study. The study CCQM-P37 on fundamental investigations of the primary measurement procedure for pH is designed to reveal these hidden sources of uncertainty.

Further key comparisons will be performed on widely used buffer solutions to continue to investigate the degree of equivalence of the conventional procedure used by the NMIs at the top of the traceability chain for pH.

The spread of results of the key comparison CCQM-K17 give reason for some doubts on the concept of choosing the pH value of the phthalate buffer (pH(RVS)) as reference point for the single pH scale as recommended by the IUPAC in 1985 [17].

12 Acknowledgements. The pilot laboratory gratefully acknowledges the contributions of all participants and of the members of the CCQM Working Group on Electrochemical Analysis and their valuable suggestions concerning the measurement protocol and the evaluation process.

Moreover, special thanks is owed to the NIST for providing the primary pH buffer materials and to B. Werner and M. Mühlbach from the Zentrum für Messen und Kalibrieren GmbH Sachsen-Anhalt (Germany) for the production of the sample.

13 References

1. Bates R. G., Guggenheim E., *Pure and Applied Chem.*, 1960, **1**, 163-168
2. Buck R.P., Rondinini S., Baucke F.G.K., Camoes M.F., Covington A.K, Milton M.J.T., Mussini T., Naumann R., Pratt K.W., Spitzer P., Wilson G.S.
The Measurement of pH - Definition, Standards and Procedures, Report of the Working Party on pH, *Pure and Applied Chem.*, 2001,
<http://www.iupac.org/reports/provisional/archives.html>
3. *Metrologia*, 1996, **33**, 95-96
4. *Metrologia*, 1996, **34**, 375-376
5. *Metrologia*, 2000, **37**, 85-86
6. *Working Documents of the 6th CCQM Meeting*, BIPM, Paris, April 2000
7. Bates R. G., Robinson R. A., *Solution Chemistry*, 1980, **9**, 455
9. Bates R. G., *Determination of pH*, Wiley, New York, 1973, Appendix, Table 4
10. *Guide to the Expression of Uncertainty (GUM)*, ISO, Geneva, 1993
11. Pauwels, J., Lamberty, A., Schimmel, H., *Accred. Qual. Assur.*, 1993, **3**, 180-184
12. DIN 1319-4, *Grundlagen der Messtechnik, Teil 4: Auswertung von Messungen; Messunsicherheit*, Beuth Verlag, Berlin, 1999
13. Dietrich, C.F., *Uncertainty, Calibration and Probability. The Statistics of Scientific and Industrial Measurement, sc. edition*, Adam Hilger, 1991, p. 39-49, p.295-298
14. Cox, M. G., *A Discussion of Approaches for Determining a Reference Value in the Analysis of Key-Comparison Data*, NPL Report CISE 42/99, 1999

- 15 Gränicher, W. H. H., *Messung beendet-was nun?*, Teubner, 1994, p.6-2 – 6-9
- 16 Taylor, B.N., Parker, W. H., Langenberg, D.N., *The Fundamental Constants and Quantum Electrodynamics*, Academic Press, 1969, p.153 – 154
- 17 AK Covington, RG Bates, RA Durst, *Definition of pH scales, standard reference values, measurement of pH and related terminology*. *Pure and Appl. Chem.* (1985) 57: 531
- 18 <http://kcdb.bipm.org/>
- 19 Covington, A. K., *Anal. Chim. Acta* (1981) 127:1

Tables and Figures

Sample: 0.05 mol·kg⁻¹ Potassium hydrogen phthalate

Table 2. pH values at 15 °C

	Temperature	
	15°C	
Laboratory	pH	$U (k = 2)$
NRCCRM	4,0070	0,0040
PTB	4,0100	0,0022
DPL	4,0074	0,0016
KRISS	4,0033	0,0030
AIST	4,0024	0,0064
CENAM	4,0020	0,0048
GUM	4,0123	0,0030
VNIIFTRI	4,0130	0,0026
SMU	4,0095	0,0021
CMI	4,0014	0,0034
NIST	4,0108	0,0010

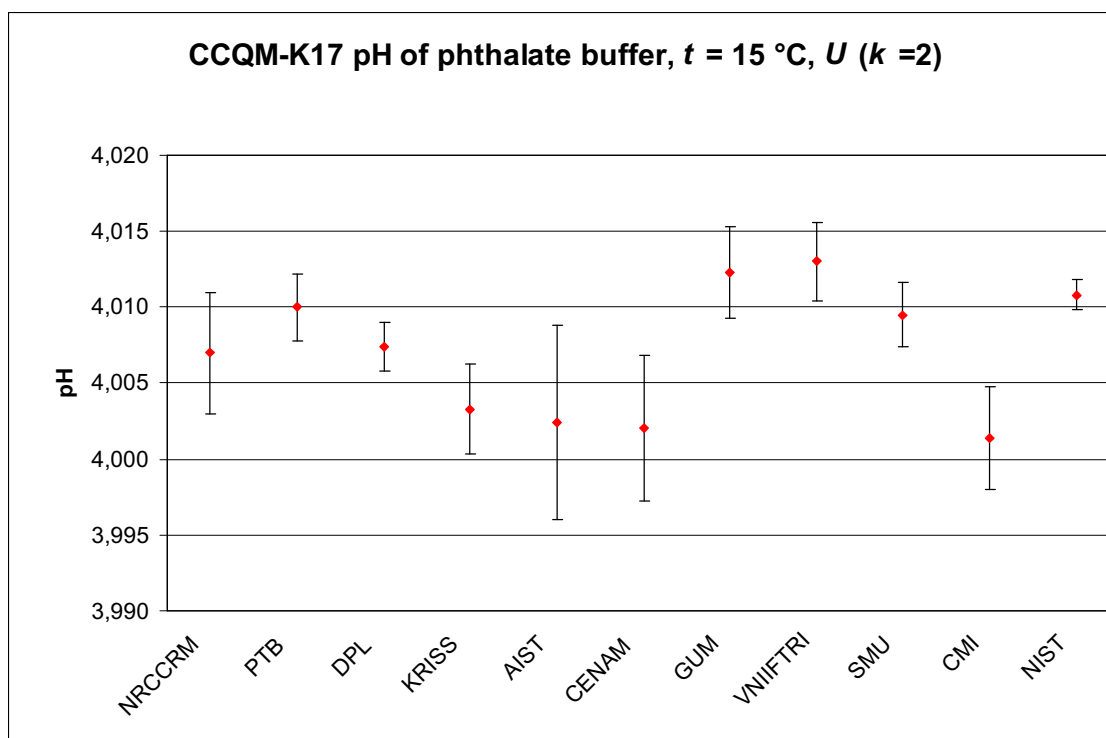


Table 3. pH values at 25 °C

	Temperature	
	25°C	
Laboratory	pH	$U(k = 2)$
NRCCRM	4,0150	0,0040
PTB	4,0168	0,0022
DPL	4,0150	0,0016
KRISS	4,0104	0,0034
AIST	4,0108	0,0061
CENAM	4,0050	0,0044
GUM	4,0183	0,0030
VNIIFTRI	4,0193	0,0026
SMU	4,0174	0,0022
CMI	4,0050	0,0034
NIST	4,0170	0,0014

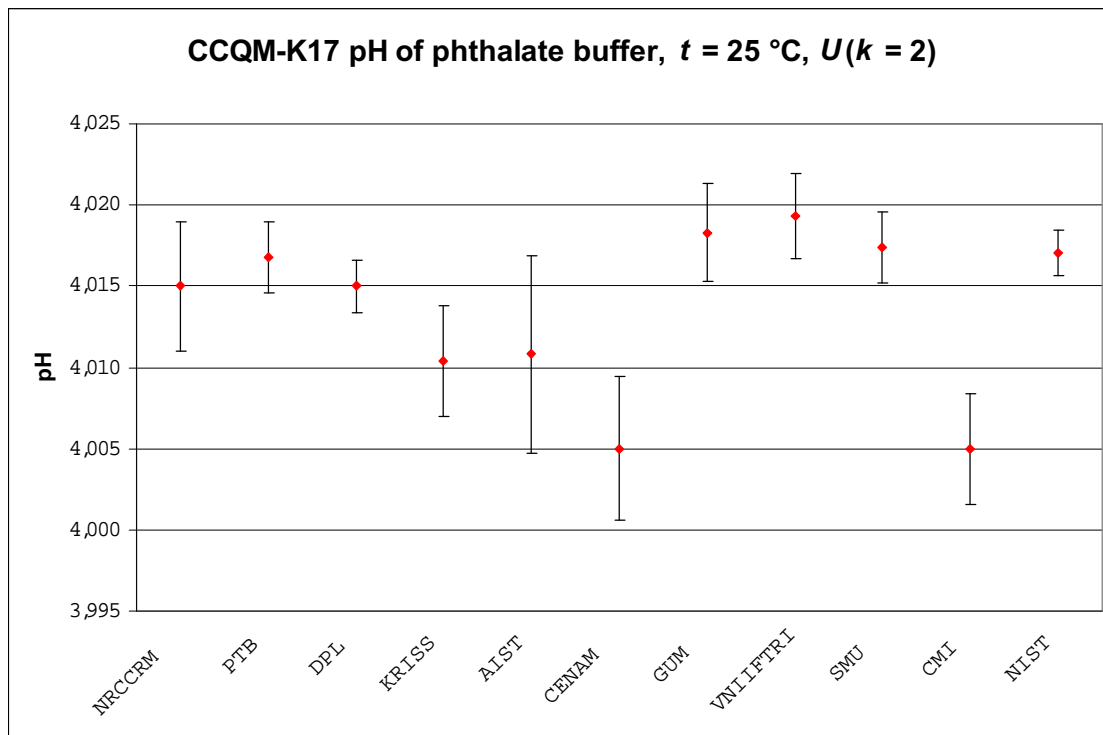


Table 4. pH values at 37 °C

Laboratory	Temperature	
	37°C	
	pH	$U(k = 2)$
NRCCRM	4,0370	0,0040
PTB	4,0360	0,0030
DPL	4,0351	0,0016
KRISS	4,0296	0,0034
AIST	4,0261	0,0079
CENAM	4,0290	0,0040
GUM	4,0355	0,0030
VNIIFTRI	4,0380	0,0026
SMU	4,0397	0,0029
CMI	4,0272	0,0021
NIST	4,0371	0,0026

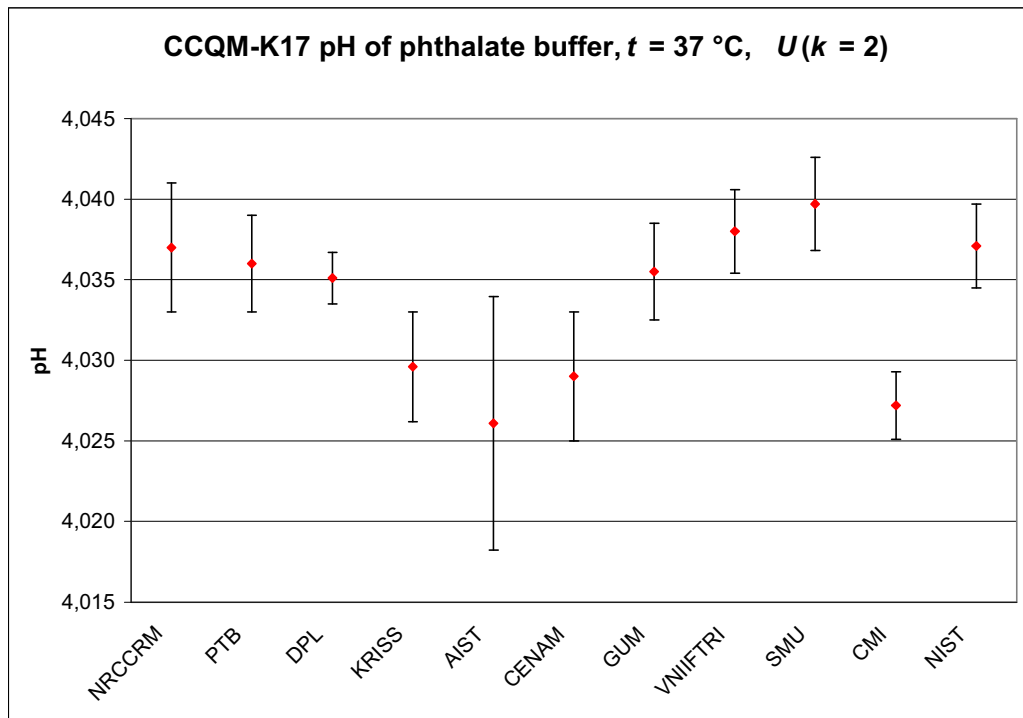


Figure 5. pH values at 25 °C regrouped according to the sample identity

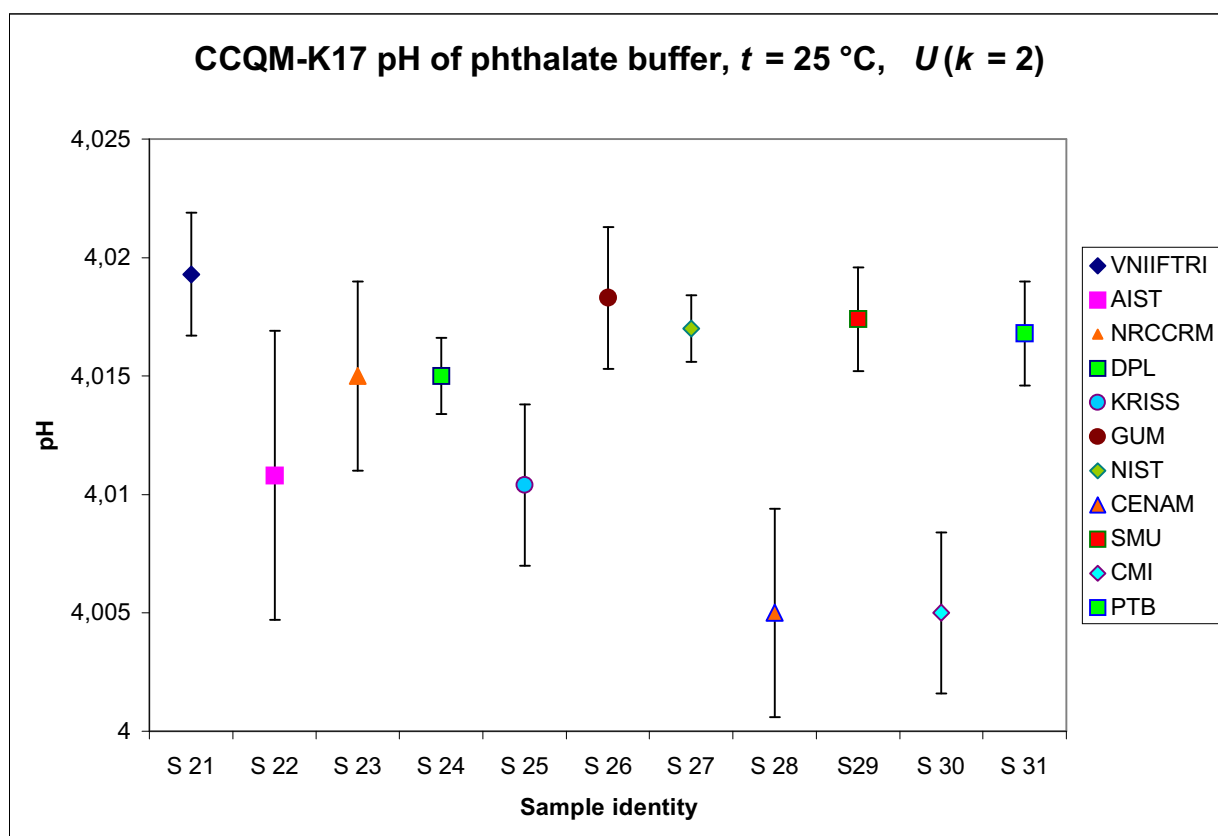


Figure 6. pH values at 15 °C regrouped according to the sample identity

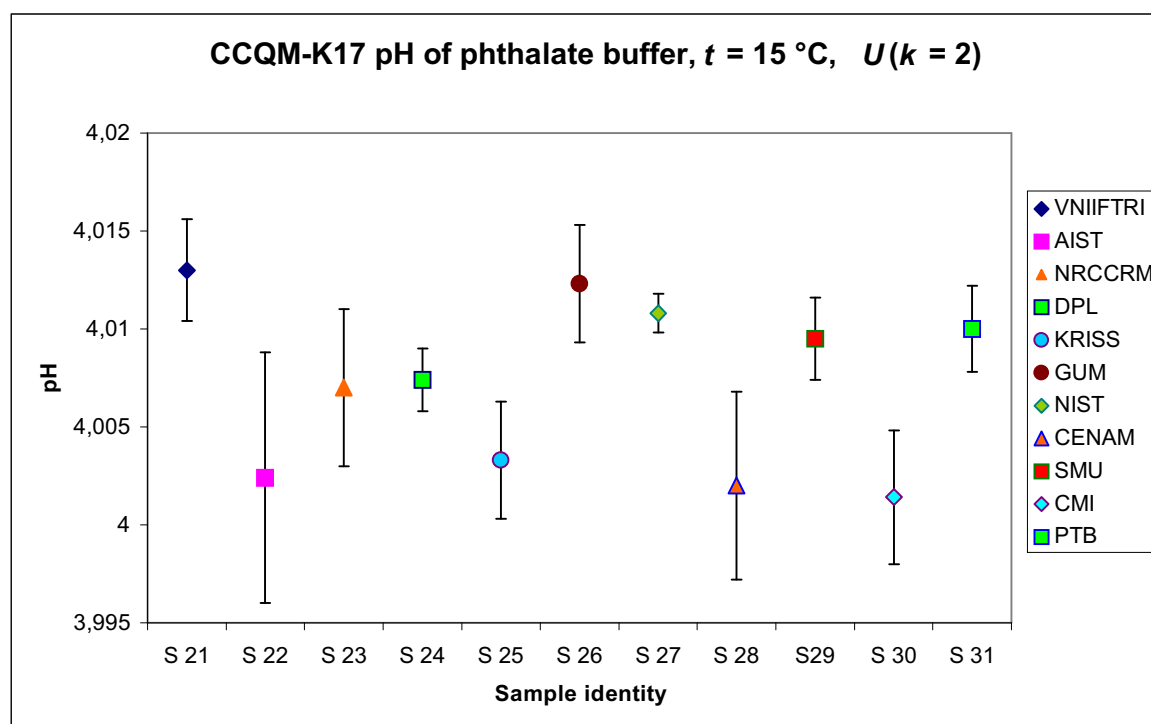
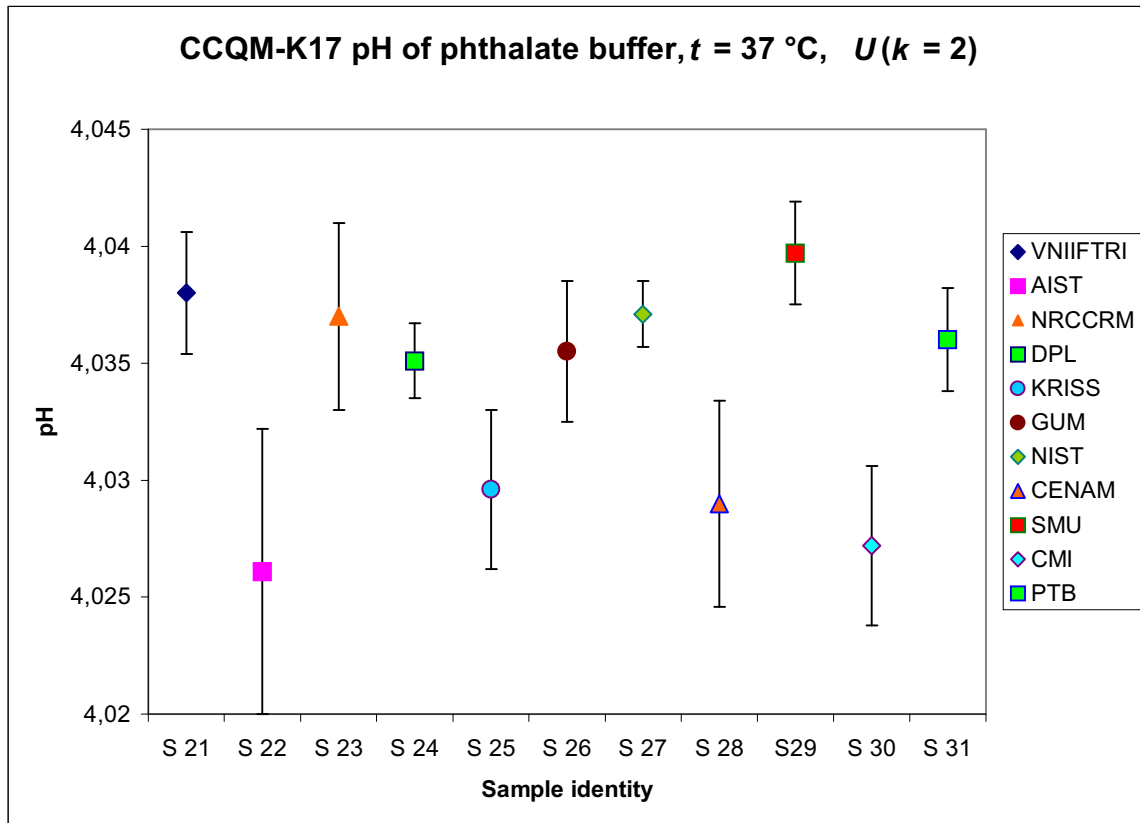


Figure 7 . pH values at 37 °C regrouped according to the sample identity



Final Report for CCQM-K17

pH determination on a phthalate buffer by Harned cell measurements

Annex A

1 Schedule

Key comparison agreed	April 2000 (6 th CCQM)
Starting date:	15 May 2001
Deadline for the receipt of the individual reports	30 September 2001
Draft A report	22 October 2001
Draft B report/ KCRV agreed	April 02 (7 th CCQM)
Final report	October 2002 (WG meeting)

2 Date of Measurement

The acronyms of the participants in CCQM-K17 are listed together with the date of measurement and the sample identification number in table A1.

Participant	Date of Measurement	Sample
NRCCRM	August 2001	23 a, b, c
PTB (pilot)	13 July 2001 – 27 July 2001	31 a, b, c
DPL for pH	11 July 2001 – 16 July 2001	24 a, b, c
AIST	04 July 2001 – 05 September 2001	25 a, b, c
KRISS	18 July 2001 – 28 July 2001	22 a, b, c
CENAM	18 July 2001 – 20 July 2001	28 a, b, c
GUM	09 July 2001 – 24 July 2001	26 a, b, c
VNIIFTRI	10 July 2001 – 25 July 2001	21 a, b, c
SMU	22 September 2001	29 a, b, c
CMI	20 August 2001– 23 September 2001	30 a, b, c
NIST	30 July 2001 – 01 August 2001	27 a, b, c

Table A1. Sample identification and date of measurement for CCQM-K17

3 Measurement results

The results reported for the sample, phthalate buffer with a nominal value $\text{pH} = 4.0$ (25°C) by the laboratories are summarized in table A2 below together with the respective key comparison reference value (KCRV), pH_R , and its uncertainty, u_R ($k = 1$), according to equation (15). u_i is the combined standard uncertainty ($k = 1$) of the result pH_i reported by the participant .

Temperature in $^\circ\text{C}$	15		25		37	
KCRV	pH_R	u_R	pH_R	u_R	pH_R	u_R
	4.0093	0.00089	4.0156	0.00109	4.0343	0.00125
Single results Lab i	pH_i	u_i	pH_i	u_i	pH_i	u_i
NRCCRM	4,0070	0,00200	4,0150	0,00200	4,0370	0,00200
PTB	4,0100	0,00110	4,0168	0,00110	4,0360	0,00150
DPL	4,0074	0,00080	4,0150	0,00080	4,0351	0,00080
KRISS	4,0033	0,00150	4,0104	0,00170	4,0296	0,00170
AIST	4,0024	0,00318	4,0108	0,00303	4,0261	0,00393
CENAM	4,0020	0,00240	4,0050	0,00220	4,0290	0,00200
GUM	4,0123	0,00150	4,0183	0,00150	4,0355	0,00150
VNIIFTRI	4,0130	0,00130	4,0193	0,00130	4,0380	0,00130
SMU	4,0095	0,00105	4,0174	0,00110	4,0397	0,00145
CMI	4,0014	0,00170	4,0050	0,00170	4,0272	0,00105
NIST	4,0108	0,00047	4,0170	0,00062	4,0371	0,00130

Table A2. Summary of results of CCQM-K17.

4 Uncertainty budget

Neglecting the uncertainties associated with the Bates-Guggenheim convention [1] and regarding the small uncertainty of the ionic strength I as insignificant, the uncertainty of the pH value is stated as the uncertainty for the acidity function, $\text{p}a_0$, at zero molality of chloride:

$$u(\text{pH}) = u(\text{p}a_0)$$

The complete uncertainty budget taking into account all known components which affect the measurement result is given in Tables A3 to A5 for a representative example similar to CCQM-K9 [18] according to [6], at a measurement temperature of 25°C .

Quantity	Estimate x_i	Standard uncertainty $u(x_i)$	Sensitivity coefficient $ c_i $	Uncertainty contribution u_i (pa)	Uncertainty contribution u_i (pa) in %
E	0.6 V	$1 \cdot 10^{-5}$ V	16.9 V^{-1}	$1.7 \cdot 10^{-4}$	9.55
E^0 (see table)	0.2 V	$5.2 \cdot 10^{-5}$ V	16.9 V^{-1}	$9 \cdot 10^{-4}$	50.53
T	298 K	$8 \cdot 10^{-3}$ K	0.022 K^{-1}	$1.8 \cdot 10^{-4}$	10.11
m_{Cl}	$0.005 \text{ mol kg}^{-1}$	$2.2 \cdot 10^{-6} \text{ mol kg}^{-1}$	$86.9 \text{ mol}^{-1} \text{ kg}$	$1.9 \cdot 10^{-4}$	10.67
Electrode variation (Ag/AgCl)		$2 \cdot 10^{-5}$ V	16.9 V^{-1}	$3.4 \cdot 10^{-4}$	19.09
P_{H_2}	$1.01 \cdot 10^5$ Pa	3 Pa	$2.2 \cdot 10^{-6} \text{ Pa}^{-1}$	$7 \cdot 10^{-6}$	0.06
u (pa) = 0.0011					

Table A3. Standard uncertainty of the acidity function at $m_{\text{Cl}} = 0.005 \text{ mol kg}^{-1}$

Quantity	Estimate x_i	Standard uncertainty $u(x_i)$	Sensitivity coefficient $ c_i $	Uncertainty contribution u_i (E^0)	Uncertainty contribution u_i (E^0) in %
E	0.464 V	$2 \cdot 10^{-5}$ V	1	$2 \cdot 10^{-5}$ V	23.04
T	298 K	$8 \cdot 10^{-3}$ K	$8 \cdot 10^{-4} \text{ V} \cdot \text{K}^{-1}$	$6.4 \cdot 10^{-6}$ V	7,37
m_{HCl}	0.01 mol kg^{-1}	$1 \cdot 10^{-5} \text{ mol kg}^{-1}$	$5.1 \text{ V} \cdot \text{mol}^{-1} \text{ kg}$	$5.1 \cdot 10^{-5}$ V	57.59
Electrode variation (Ag/AgCl)		$1 \cdot 10^{-5}$ V	1	$1 \cdot 10^{-5}$ V	11.52
P_{H_2}	$1.01 \cdot 10^5$ Pa	3 Pa	$1.3 \cdot 10^{-7} \text{ V} \cdot \text{Pa}^{-1}$	$4.2 \cdot 10^{-7}$ V	0.48
u (E^0) = $5.2 \cdot 10^{-5}$ V					

Table A4. Standard uncertainty of the standard potential of the silver-silver chloride electrode (E^0) from measurements in $m_{\text{HCl}} = 0.01 \text{ mol kg}^{-1}$.

$$u(pa_0) = \sqrt{u^2(pa_{m_{\text{Cl}}=0.005}) + u^2(\text{intercept})}^* \quad (9)$$

(* variance of the ordinate intercept as obtained by the linear regression of the pa values at (mol kg^{-1}): 0,005; 0,010; 0,015)

$$u(\text{intercept}) = s \sqrt{\left[\frac{1}{N} + \frac{\bar{m}_{\text{Cl}}^2}{\sum_{i=1}^N (m_{\text{Cl}} - \bar{m}_{\text{Cl}})^2} \right]}; \quad (10)$$

N (number of measurements) = 9

$$s = \sqrt{\left[\frac{\sum_{i=1}^N (pa_i - (b + pa_0 m_{\text{Cl}}))^2}{(N - 2)} \right]}; \quad b = \text{slope of the regression line}; u(\text{intercept}) = 3.7 \cdot 10^{-4}$$

$$u(pa_0) = \sqrt{0.0011^2 + 0.00037^2} = 0.0011$$

Table A5. Standard uncertainty of the acidity function at zero chloride molality pa_0

The figures A1 and A2 show the relative contributions to the total uncertainty of E^0 and p_a .

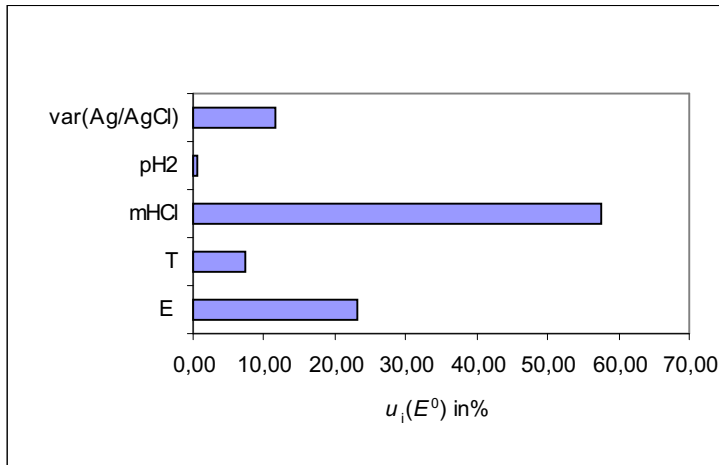


Figure A1. Relative contributions to the uncertainty of the standard potential E^0

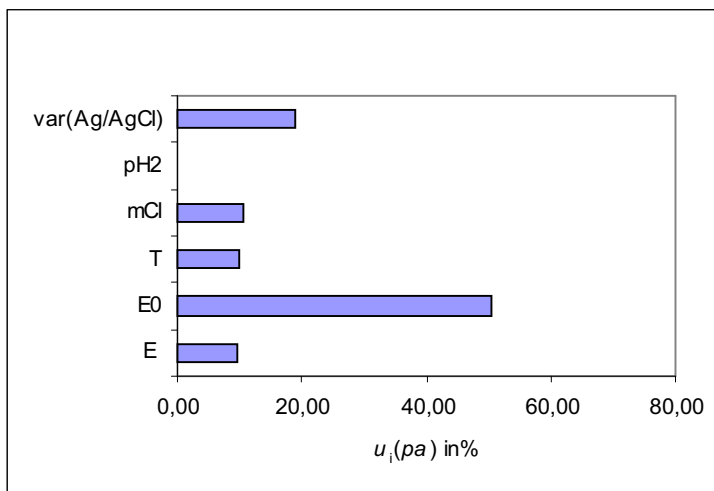


Figure A2. Relative contributions to the uncertainty of the acidity function p_a

4 Individual uncertainties

The standard uncertainties reported by the laboratories for the acidity function, $u(p_a)$, for the standard potential difference, $u(E^0)$, the standard uncertainties $u(m_{\text{HCl}})$ and for the acidity function at zero molality of chloride, $u(p_{a0})$ are summarized in table A6. The values at 25°C are selected as typical examples.

Participant	$u(m_{\text{HCl}})$ mol kg ⁻¹	$u(E^0)$ in V	$u(pa)$ reported by participant	u (intercept) calculated by pilot lab (equ.10)	u (pH) reported by participant
NRCCRM	$1.0 \cdot 10^{-5}$	$6.6 \cdot 10^{-5}$	0.0013	0.00053	0.0020
PTB	$1.0 \cdot 10^{-5}$	$5.2 \cdot 10^{-5}$	0.0011	0.00037	0.0011
DPL	$4.5 \cdot 10^{-6}$	$2.7 \cdot 10^{-5}$	0.00064	0.00061	0.0008
AIST	$1.4 \cdot 10^{-5}$	$1.1 \cdot 10^{-4}$	0.0032	0.0028	0.0030
KRISS	$2.4 \cdot 10^{-6}$	$4.0 \cdot 10^{-5}$	0.0011	0.0011	0.0017
CENAM	$5.0 \cdot 10^{-6}$	$9.4 \cdot 10^{-5}$	0.0016	0.0014	0.0022
GUM	$3.9 \cdot 10^{-6}$	$2.3 \cdot 10^{-5}$	0.00078	0.0012	0.0015
VNIIFTRI	$1.2 \cdot 10^{-5}$	$6.5 \cdot 10^{-5}$	0.0013	0.00087	0.0013
SMU	$2.9 \cdot 10^{-6}$	$3.1 \cdot 10^{-5}$	*	0.00064	0.0011
CMI	$1.0 \cdot 10^{-5}$	$8.2 \cdot 10^{-5}$	0.0017	0.000036	0.0017
NIST	$2.4 \cdot 10^{-7}$	$1.9 \cdot 10^{-5}$	*	0.00048	0,00062

* SMU and NIST reported $u(pa_0)$ at $m_{\text{Cl}}=0$ mol kg⁻¹

Table A6. Uncertainties reported by the laboratories at 25°C.

5 Experimental details

Experimental details of the preparation of the measuring buffer solution from the samples as reported by the participants are summarized in Table A7 .

Participant	Source Preparation	Amount of content determination HCl	Molality reported mol kg ⁻¹	Source drying conditions	Alkali Chloride Addition to the buffer mol kg ⁻¹
NRCCRM		Coulometry	0.00979	KCl 100±0.01% 500°C /2h	0.005 0.01 0.02
PTB	Merck Titrisol	Coulometry	0.01004	NaCl Merck Suprapur 500°C/4h	0.005 0.01 0.015
DPL	stock solution from Merck Suprapur 0.08808 mol kg ⁻¹	Coulometry	0.009998	NaCl Merck Urtiter 500°C/4h	0.005 0.01 0.015
AIST	Cica-Merck Ultrapur grade product	Coulometry	0.009865	KCl Merck Supur 110°C/2h	0.01 0.014 0.017
KRISS	0.1 mol kg ⁻¹ stock solution Alldrich 99,999 %	Coulometry	0.010008	KCl Aldrich 99.999 % 110°C/2h	0.005 0.01 0.015
CENAM		Coulometry	0.00992	NaCl Baker ULTREX; Ultrapure reagent	0.005 0.01 0.015
GUM	analytical grade twice distilled	AgCl precipitation titration	0.009732	KCl analytical grade; add. purification 500°C/4h	0.005 0.01 0.015
VNIIFTRI	HCl 34% Impurities: 10 ⁻⁴ %	Coulometry	0.01003	NaCl, 99.999% inorg impu. 10 ⁻⁴ %	0.005 0.01

				110°C/2h	0.015 0.02
SMU	analytical grade purified by isothermal distillation	Coulometry	0.0099987	NaCl Merck Suprapur 450°C/4h	0.005,0.008 0.01, 0.015 0.019, 0.012
CMI		Coulometry	0.009994		0.005 0.01 0.02
NIST	Mallinckroft 19 L batch; 0.01 mol·L ⁻¹	Coulometry	0.0100023	NaCl Merck Suprapur 110°C/2h	0.005 0.01 0.015

Table A7. Experimental details

6 The key comparison reference value and its uncertainty

The maximum-likelihood estimator yields the KCRV as the variance based weighted mean [13] according to the equations (11), (12) and (13),

$$pH_R = \frac{\sum_{i=1}^N w_i pH_i}{\sum_{i=1}^N w_i} \quad (11)$$

where $x_{i..N}$ are the individual results and $w_{i..N}$ are the individual weights, u_i are the individual standard uncertainties and C is the variance of the weighted mean.

$$w_i = \frac{C}{u_i^2} \quad (12)$$

$$C = \frac{1}{\sum_{i=1}^N \frac{1}{u_i^2}} \quad (13)$$

The uncertainty of the KCRV, pH_R , is usually calculated under the assumption of a Gaussian error distribution and completely given by the individual uncertainties according to equation (14)

$$u(pH_R)^2 = C \quad (14)$$

In order to take the spread of the results into account, the uncertainty for the KCRV of CCQM-K17 is determined by the external consistency method [15, p.6-6], [13, p.46] according to equation (15). The Birge ratio R_{Birge} [15], [16] is given by equation (16).

$$u_R^2 = \frac{\sum_{i=1}^N (w_i (pH_i - pH_R)^2)}{(N-1) \cdot \sum_{i=1}^N w_i} \quad (15)$$

$$R_{\text{Birge}}^2 = \frac{\sum_{i=1}^N \frac{(\text{pH}_i - \text{pH}_R)^2}{u_i^2}}{(N-1)} \quad (16)$$

In Tables A8 the Birge ratios R_{Birge} calculated according to equation (16) are listed together with the KCRV and its uncertainty for the sample. Additionally the uncertainty, $u(\text{pH}_R)$, ($k = 1$) calculated by the internal consistency method [13], [15] according to equation (14) is given.

Temperature °C	KCRV (pH_R) (equ. 12)	$u(\text{pH}_R)$ ($k = 1$) (equ. 14)	u_R ($k = 1$) (equ. 15)	Birge ratio R_{Birge} (equ. 16)
15	4.0093	0.00031	0.00089	2.85
25	4.0156	0.00035	0.00109	3.08
37	4.0343	0.00041	0.00125	3.02

Table A8. KCRV and its uncertainty for the sample $0.05 \text{ mol} \cdot \text{kg}^{-1}$ potassium hydrogen phthalate

7 Evaluation of equivalence (according to Appendix B of the MRA)

The degree of equivalence, D_i , of each laboratory with respect to the key comparison reference value is given by a pair of terms,

$$D_i = (\text{pH}_i - \text{pH}_R). \quad (17)$$

The value of U_i the expanded uncertainty in D_i , ($k = 2$) is calculated according to equation (18):

$$U_i = 2\sqrt{u_i^2 + u(\text{pH}_R)^2}. \quad (18)$$

The degree of equivalence between two laboratories is given by a pair of terms,

$$D_{ij} = D_i - D_j = \text{pH}_i - \text{pH}_j. \quad (19)$$

The value U_{ij} the expanded uncertainty in D_{ij} , ($k = 2$) is calculated according to equation (20)

$$U_{ij} = 2\sqrt{u_i^2 + u_j^2}. \quad (20)$$

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