

Final report for CCQM-K9

pH determination on two phosphate buffers by Harned cell measurements

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Abstract

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.

The CCQM-K9 comparison allows estimations of the capability of ten national metrology institutes (NMIs) to determine the pH of two phosphate buffers 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 Slovak Institute of Metrology (SMU) and the National Institute of Standards and Technology (NIST)

A high degree of agreement of the measurement results of the NMIs is evident. The majority of the results obtained agree within the uncertainty stated by the participants.

1 Introduction

The primary measurement procedure for pH at the top of the traceability chain 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 February 1999 the CCQM Working Group on pH measurement, since April 2000 the CCQM WG on Electrochemical Analysis, initiated the first key comparison on pH, CCQM-K9, on two phosphate buffers in order to evaluate the degree of equivalence of the national primary measurement procedures for pH.

Ten national metrology institutes participated. The comparison started in October 1999 and the results were reported until February 2000. The comparison was restricted to the use of Harned cells. Since pH measurement is a well developed field of metrology, a fact which was confirmed by the results of three EUROMET projects [3-5], including NIST participation, it was not regarded as necessary to carry out a pilot study before the key comparison.

2 Participation in CCQM-K9

In table 1 the names of all National Metrology Institutes (NMIs) are listed that participated in CCQM-K9.

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 Materials and Chemical Research	NIMC/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
National Institute of Standards and Technology	NIST	US

Table1. CCQM-K9 key comparison participants

3 Description of the samples

Two phosphate buffers, both containing potassium dihydrogen phosphate (KH_2PO_4) and disodium hydrogen phosphate (Na_2HPO_4) at different molalities were chosen as transfer standards. The molality ($\text{mol}\cdot\text{kg}^{-1}$) was known to the participants only for sample (1).

Sample (1): $0.025 \text{ mol}\cdot\text{kg}^{-1} \text{ KH}_2\text{PO}_4 + 0.025 \text{ mol}\cdot\text{kg}^{-1} \text{ Na}_2\text{HPO}_4$

Sample (2): $0.02 \text{ mol}\cdot\text{kg}^{-1} \text{ KH}_2\text{PO}_4 + 0.02 \text{ mol}\cdot\text{kg}^{-1} \text{ Na}_2\text{HPO}_4$

The samples were prepared from NIST Standard Reference Materials. Sample (1) was distributed in solid form as NIST SRM 186If and NIST SRM186IIf together with the description how to prepare the buffer solution to obtain the stated molality. The pH of the SRM's used for sample preparation was not known within the level of uncertainty desirable in this key comparison.

Sample (2) was prepared by the pilot laboratory with the assistance of the Zentrum für Messen und Kalibrieren GmbH Sachsen-Anhalt (Germany). A single batch of 40 l from NIST SRM 186 If and NIST SRM 186IIf at the molality of $0.02 \text{ mol}\cdot\text{kg}^{-1}$ each was prepared and distributed in 1 litre bottles. The homogeneity of the batch was tested by the pilot laboratory in determining the pH of three randomly-selected bottles. The electrolytic conductivity of the deionized water used for preparation was $0.5 \mu\text{S cm}^{-1}$. The participants were given the total mass of the sample and the amount of water in the sample.

Each participant received three bottles together with a description how to store the sample. The amount of materials (1) and (2) 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 pa so that there are only measurable quantities on the right hand side of equation (3) pa is measured as a function of m_{Cl} .

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

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

The acidity function

$$pa_0 = -\lg(a_{\text{H}^+} \gamma_{\text{Cl}^-} / m^0)_{m_{\text{Cl}} \rightarrow 0} \quad (4)$$

corresponding to zero chloride molality is determined by linear extrapolation according to equation (5) of pa as a function of the chloride molality, using measurements at at least three values of m_{Cl} in the range from 0.005 to 0.02 mol·kg⁻¹. It has been shown [8] that a linear extrapolation is appropriate if the change in ionic strength produced by the addition of chloride is restricted to less than 20%.

$$pa = pa_0 + bm_{\text{Cl}} \quad (5)$$

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).

$$\text{pH} = pa_0 + \lg \gamma_{\text{Cl}} \quad (7)$$

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

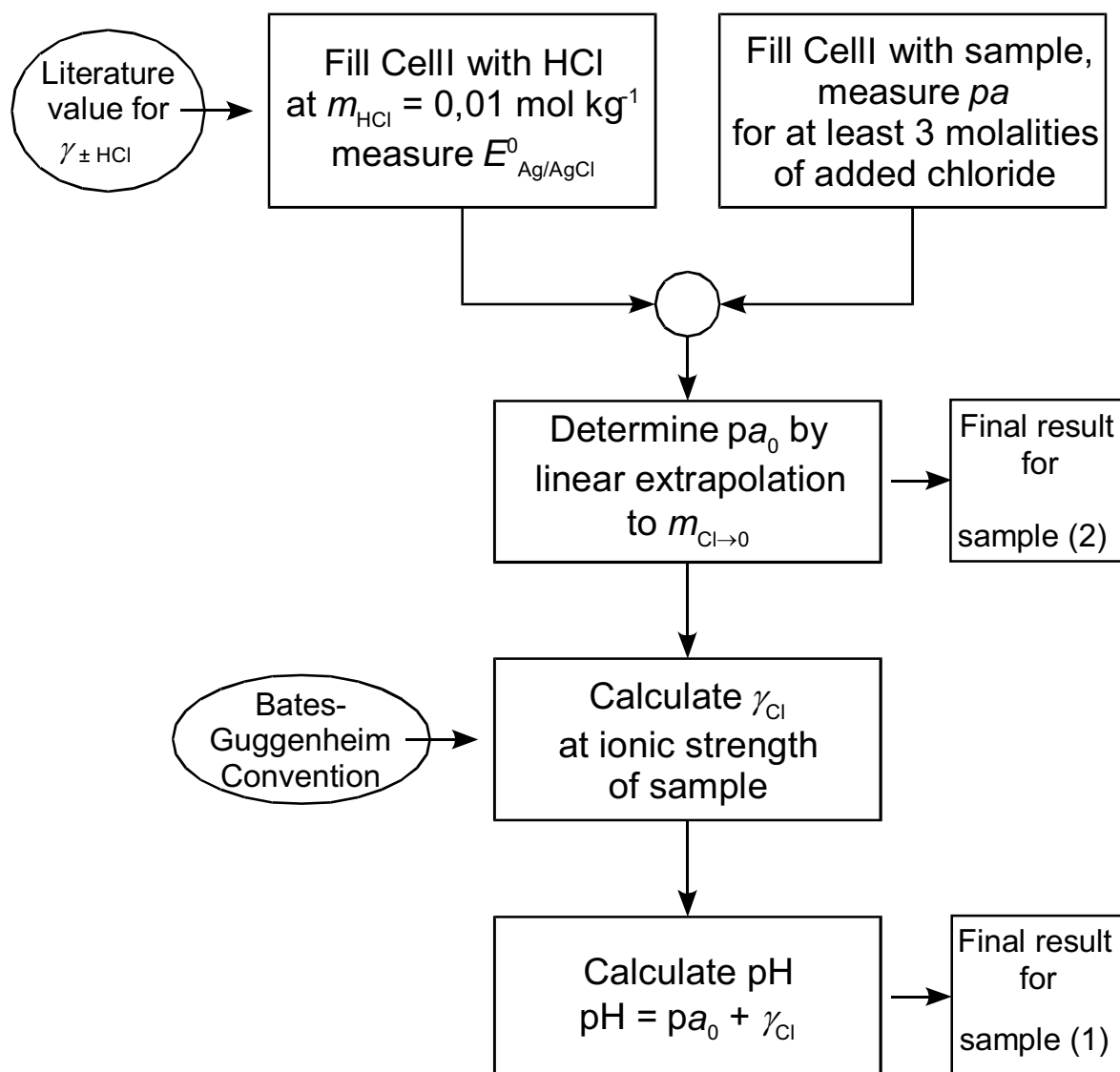


Figure 1. Primary measurement procedure of pH

5 Brief description of the measurement protocol

The samples for CCQM-K9 were sent to the participants together with an instruction package including a result reporting form and an uncertainty budget form for each of the two samples. A working paper on pH measurement was agreed upon by the WG members before the comparison, 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-K9 to carry out the measurements between 5 °C and 50 °C in steps of 5 °C, but at least at 15 °C, 25 °C and 37 °C, because not all were able to measure in the whole temperature range.

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. 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 sample (1) and the acidity function at zero chloride molality at the measurement temperatures for sample (2). The pH for sample (2) was calculated by the pilot laboratory, using the value for the ionic strength which was only known to the pilot laboratory.

An instruction how to calculate the uncertainties according to GUM [10] is given in the above mentioned CCQM working paper on pH [6]. Participants were asked to evaluate the uncertainty according to the example given in [6].

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

6 Deviation from the protocol

Because of technical problems, NIMC reported results for buffer (2) only. CENAM erroneously chose 35 °C instead of 37 °C as measurement temperature for buffer (1). SMU used a modified procedure for determination of E^0 .

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

The measurement equation to determine the pH of sample (1) and (2) is equation (1).

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

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 :

$$u(pH) = u(pa_0)$$

$$\text{and } u(pa_0) = \sqrt{u^2(pa_{m=0.005}) + u^2(\text{intercept})} \quad (9)$$

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

$$u(\text{intercept}) = s \sqrt{\frac{1}{N} + \frac{\bar{m}_{\text{Cl}}^2}{\sum_{i=1}^N (m_{\text{Cl}} - \bar{m}_{\text{Cl}})^2}}, \quad s^2 = \frac{\sum_{i=1}^N [pa_{m_{\text{Cl}}} - (pa_0 + b \cdot m_{\text{Cl}})]^2}{N - 2} \quad (10)$$

s is the residual standard deviation, N the number of measurements used to get p_a at different molalities of chloride, b is the slope of the regression line.

DPL used an approach slightly different from (10), by replacing the residual standard deviation s by $u(p_{a_{m=0.005}})$. As far as the scatter around the regression line is small, both approaches give very similar results.

It was known from the evaluation of previous EUROMET comparisons [3-5] that the uncertainty of the acidity function at the smallest amount of added chloride, $m_{Cl} = 0.005 \text{ mol kg}^{-1}$, $u(p_{a_{m=0.005}})$, 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 the main component 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 1 of Annex A for one typical example, namely sample (2) at a measurement temperature of 25 °C. The standard uncertainties $u(m_{HCl})$, $u(E^0)$, $u(p_a)$, $u(\text{intercept})$ and $u(p_{a_0})$ are also summarized in the Annex for this example.

8 Results and uncertainties of the measurements of the individual laboratories

The results obtained by the laboratories for samples (1) and (2) at different temperatures together with the associated uncertainties ($k = 2$), as reported to the pilot laboratory, are given in Tables 2 to 11 for sample (1), $0.025 \text{ mol kg}^{-1} \text{ KH}_2\text{PO}_4 + 0.025 \text{ mol kg}^{-1} \text{ Na}_2\text{HPO}_4$; and in Table 12 to 21 for sample (2), $0.02 \text{ mol kg}^{-1} \text{ KH}_2\text{PO}_4 + 0.02 \text{ mol kg}^{-1} \text{ Na}_2\text{HPO}_4$. The graphs showing the results are numbered correspondingly.

9 Changing of results and follow-up bilateral comparisons

One participant (SMU) discovered a calculation error which influenced the result, but not to an extent which was immediately obvious. This observation was stated after the results of the K9 had been disclosed. After discussion in the CCQM Plenary Meeting it was decided to use the uncorrected result for Appendix B of the MRA and the correct result for evaluating the KCRV.

A follow-up bilateral comparison was agreed by the pilot laboratory (PTB) and the SMU.

The sample was a phosphate buffer containing KH_2PO_4 and Na_2HPO_4 .

The comparison took place in January 2000. The buffer was prepared by the pilot laboratory.

The measurement protocol was similar to the K9 key comparison. The value obtained for the acidity function of the sample as reported by SMU and PTB is taken as the final result of the bilateral comparison.

10 Discussion of the results

CCQM-K9 was very successful in terms of the degree of equivalence of the results obtained by the measurement procedures used by the participants to determine the pH of primary buffer solutions. All participants supplied full uncertainty budgets.

The evaluation of K9 confirms the results obtained in the comparisons which performed under EUROMET co-operation, which have demonstrated the comparability of measurements within $\Delta\text{pH} = 0.005$ in different laboratories using samples from a single batch [3], [4], [5]. The uniformity of the results obtained with sample (1) with known molality is negligibly better than the uniformity of sample (2) with unknown composition. This confirmed the competence of the participants.

All participants carried out the measurements at 15 °C, 25 °C and 37 °C. For sample (1) six of nine participants also reported results for 5 °C, 10 °C, 20 °C, 30 °C, 40 °C, 45 °C and 50 °C, DPL only for 40 °C and 45 °C. For sample (2) four of ten participants measured at 5 °C, 10 °C, 20 °C, 30 °C, 40 °C, 45 °C and 50 °C, too. DPL reported a result for 40 °C. The degree of equivalence is not significantly influenced by the measurement temperature. Most of the participants determined the amount content of HCl by coulometric titration. A high-precision gravimetric method was used by KRISS, CENAM and 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

According to the high degree of overlap of the uncertainties stated by the participants, the individual laboratory uncertainties play a major role in determining the uncertainty of the KCRV. Assuming that all participants of CCQM-K9 are equally competent, there is no reason to doubt their uncertainty statements, so these can be regarded as credible.

Two different approaches to assign the KCRV and the uncertainty associated with it are taken into consideration.

1. In the first approach [11], the value provided by each laboratory is considered as an unbiased estimate of the quantity of concern. 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.

The uncertainty of the KCRV, $u(\text{pH}_R)$, is completely given by the individual uncertainties according to equation (14)

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

A problem with this classical method 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].

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) 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-K9 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.

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

A more 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).

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

2. As a more robust estimator of a reference value, the median has been proposed. This estimator is less influenced by the presence of extreme values. The median absolute deviation (MAD) permits the corresponding standard uncertainty to be estimated [14]. As an alternative for the assignment of a KCRV to CCQM-K9 a maximum weight method developed at SMU has been tested as a robust method:

The reference value x_w is calculated according to equation (11) but using in this case an iterative procedure. The weights are calculated according to equation (18) and (19); the adjustable parameter k is set to be 1. The s^2 is the variance.

$$w_i = \frac{1}{u_i} \cdot e^{-k \left(\frac{(\text{pH}_i - \text{pH}_w)^2}{s} \right)} \quad (17)$$

$$s^2 = \frac{\sum_{i=1}^N (\text{pH}_i - \text{pH}_{\text{mean}})^2}{N} \quad (18)$$

The uncertainty of the reference value is calculated according to equation (16) also for this method.

The results obtained by both methods are compared in the Annex. Because no practically significant difference in the KCRV could be observed between the two methods, the variance-based weighted mean is stated as the KCRV. The uncertainty of the KCRV is calculated according the external consistency concept.

It is proposed to continue the work on robust approaches and other statistical estimators for the assignment of key comparisons reference values in order to treat more consistently certain problems e.g, those related to extreme values or associated with comparisons involving small numbers of laboratories.

In order to investigate the reasons leading to increased interlaboratory spread even though the experimental designs used are very similar, it is proposed to perform a study. This study on fundamental investigations of the primary measurement procedure for pH will be 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.

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 sample (2).

13 References

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Annex A

1 Schedule

Key comparison agreed	February 99 (5 th CCQM)
Starting date:	October 1999
Deadline for the receipt of the individual reports	December 1999
Draft A report	April 00 (6 th CCQM)
Draft B report	November 00 (WG meeting)
KCRV agreed/ Final report	April 01 (7 th CCQM)

2 Date of Measurement

Participant	Date of Measurement	Report received
NRCCRM	Oct 99 –Dec 99	29/12/99
PTB (pilot)	9-13 Nov 99 (1); 12-22 Oct 99 (2)	
DPL for pH	25-30 Nov 99 (1); 13-18 Oct 99(2)	22/12/99
NIMC	Dec 99	31/12/99
KRISS	11 Dec 99 (1); 29. Oct 99 (2)	01/01/00
CENAM	27 Dec 99 (1); 17 Nov 99 (2)	29/02/00
GUM	29 Nov 99-14 Dec 99 (1); 12-26 Nov 99 (2)	31/12/99
VNIIFTRI	25 Oct-04-Nov 99 (1) and(2)	21/12/99
SMU	01-08 Feb 00	08/02/00
NIST	12-13, 20-21, 24-27 Jan 00 (1) 17-19 Nov 99 (2)	18/02/00

3 Uncertainty budget

Neglecting the uncertainties associated with the Bates-Guggenheim convention and regarding the small uncertainty of the ionic strength I as insignificant, the uncertainty of the pH value is stated as:

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

$$\text{and } u(\text{p}a_0) = \sqrt{u^2(\text{p}a_{m=0,005}) + u^2(\text{intercept})} \quad (9)$$

The complete uncertainty budget taking into account all known components which affect the measurement result is given in Tables 1 to 3 for a representative example, namely sample (2) at a measurement temperature of 25 °C.

Table 1. 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(\text{pa}) $	Uncertainty contribution $u_i(\text{pa})$ in %
E / V	0.772	$2 \cdot 10^{-5}$	16.9 V^{-1}	$3 \cdot 10^{-4}$	17.14
E^0 / V (see table)	0.222	$5.5 \cdot 10^{-5}$	16.9 V^{-1}	$1 \cdot 10^{-3}$	57.14
T / K	298.15	$8 \cdot 10^{-3}$	0.033 K^{-1}	$2.5 \cdot 10^{-4}$	14.29
$m_{\text{Cl}} / \text{mol kg}^{-1}$	0.005	$2.2 \cdot 10^{-6}$	86.9 kg mol^{-1}	$1.9 \cdot 10^{-4}$	10.86
$P_{\text{H}_2} / \text{Pa}$	$1.01 \cdot 10^5$	3	$2.2 \cdot 10^{-6} \text{ Pa}^{-1}$	$1 \cdot 10^{-5}$	0.57

$$u(\text{pa}) = 0.001$$

Table 2. Standard uncertainty of the standard potential of the silver-silver chloride electrode (E^0) from measurements in $m_{\text{HCl}} = 0.01 \text{ mol kg}^{-1}$.

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 / V	0.464	$2 \cdot 10^{-5}$	1	$2 \cdot 10^{-5}$	26.03
T / K	298.15	$8 \cdot 10^{-3}$	$8 \cdot 10^{-4} \text{ V K}^{-1}$	$6.4 \cdot 10^{-6}$	8.33
$m_{\text{HCl}} / \text{mol kg}^{-1}$	0.01	$1 \cdot 10^{-5}$	$5.1 \text{ V kg}^{-1} \text{ mol}^{-1}$	$5.1 \cdot 10^{-5}$	65.09
$P_{\text{H}_2} / \text{Pa}$	$1.01 \cdot 10^5$	3	$1.3 \cdot 10^{-7} \text{ V Pa}^{-1}$	$4.2 \cdot 10^{-7}$	0.55

$$u(E^0) = 5.5 \cdot 10^{-5} \text{ V}$$

Table 3. Standard uncertainty of the acidity function at zero chloride molality pa_0

$u(\text{pa}_0) = \sqrt{u^2(\text{pa}_{m_{\text{Cl}}=0.005}) + u^2(\text{intercept})}^*$ <p>(*) variance of the ordinate intercept as obtained by the linear regression of the $\text{p} a$ values at (mol kg^{-1}): 0,005; 0,010; 0,015)</p> $u(\text{intercept}) = s \sqrt{\left[\frac{1}{N} + \frac{\bar{m}_{\text{Cl}}^2}{\sum_{i=1}^N (m_{\text{Cl}} - \bar{m}_{\text{Cl}})^2} \right]}$ <p>N (number of measurements) = 9</p> $s = \sqrt{\left[\frac{\sum_{i=1}^N (\text{pa}_i - (b + \text{pa}_0 m_{\text{Cl}}))^2}{(N - 2)} \right]}$; $b = \text{slope of the regression line}$ $u(\text{intercept}) = 3.6 \cdot 10^{-4}$ $u(\text{pa}_0) = \sqrt{0.0011^2 + 0.00036^2} = 0.0012$	(9)	(10)
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The figures 1 and 2 show the relative contributions to the total uncertainty of E^0 and pa .

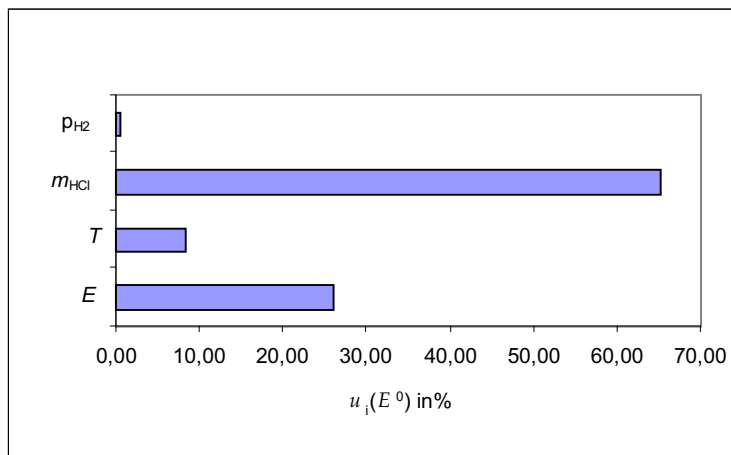


Figure 1. Relative contributions to the uncertainty of the standard potential E^0

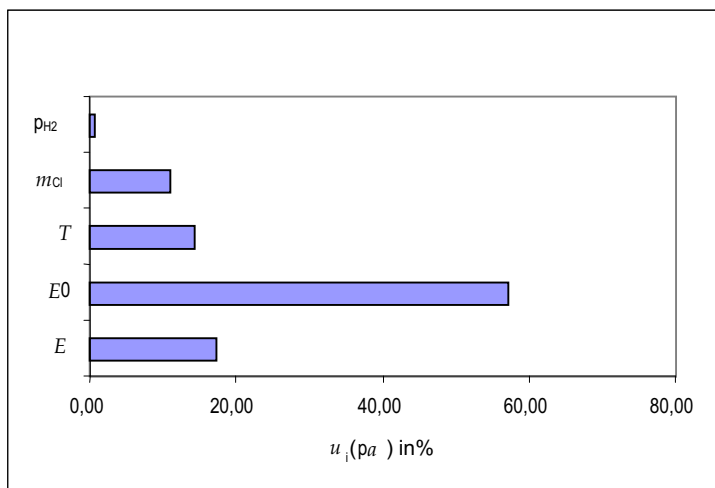


Figure 2. Relative contributions to the uncertainty of the acidity function pa

4 Individual uncertainties

The standard uncertainties reported by the participants for the acidity function at the smallest amount of added chloride, $u(pa_0)$ for the standard potential difference, $u(E^0)$, the standard uncertainties $u(m_{HCl})$ and for the acidity function at zero molality of chloride, $u(pa_0)$ are summarized in table 4. The values at 25°C for sample (2) are selected as typical examples. The uncertainties reported for sample (2) are not significantly different from the values stated for sample(1).

The uncertainty of the intercept has also been calculated by the pilot laboratory according to equation (9).

Table 4. Uncertainties reported by the participants at 25°C for sample (2)

Participant	$u(m_{\text{HCl}})$ mol kg ⁻¹	$u(E^0)$ in V	$u(\text{pa})$ at $m_{\text{Cl}^-}=0.005$ mol kg ⁻¹)	u (intercept) calculated by pilot lab	u (pa_0) reported by participant
NRCCRM	$1.0 \cdot 10^{-5}$	$5.6 \cdot 10^{-5}$	0.0014	0.0010	0.0020
PTB	$1.0 \cdot 10^{-5}$	$5.2 \cdot 10^{-5}$	0.0010	0.00036	0.0011
DPL for pH	$4.5 \cdot 10^{-6}$	$2.7 \cdot 10^{-5}$	0.00064	0.00037	0.0008
NIMC	$3.7 \cdot 10^{-5}$	$2.2 \cdot 10^{-4}$	0.0041	0.0023	0.0042
KRISS	$6.8 \cdot 10^{-6}$	$4.1 \cdot 10^{-5}$	0.00079	0.00021	0.0008
CENAM	$2.3 \cdot 10^{-6}$	$1.2 \cdot 10^{-5}$	0.00023	0.0067	0.0067
GUM	$4.8 \cdot 10^{-6}$	$3.5 \cdot 10^{-5}$	0.00067	0.00038	0.0008
VNIIFTRI	$2.0 \cdot 10^{-5}$	$1 \cdot 10^{-4}$	0.0018	0.00077	0.0018
SMU	$3.0 \cdot 10^{-6}$	$3.1 \cdot 10^{-5}$	0.0009	0.00012	0.0009
NIST	$1.7 \cdot 10^{-7}$	$4.8 \cdot 10^{-5}$	0.00032	0.0018	0.0018

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 5 .

Table 5. Experimental details

Participant	HCl			Alkali Chloride	
	Source Preparation	Amount of content determination	Molality reported mol kg ⁻¹	Source Drying conditions	Addition to the buffer mol kg ⁻¹
NRCCRM		Coulometry	0.00982	KCl 100±0.01% 500°C /2h	0.005, 0.01 0.02
PTB	analytical grade product	Coulometry	0.01002	NaCl Merck Suprapur 110°C/2h	0.005, 0.01 0.015
DPL for pH	stock solution 0.10017 mol kg ⁻¹	Coulometry	0.010	NaCl Merck Urtiter 500°C/4h	0.005, 0.01 0.015
NIMC	Cica-Merck Ultrapur grade product	Coulometry	0.00927	KCl Merck Supur 110°C/2h	0.01, 0.014 0.017
KRISS	stock solution 0.10008 mol kg ⁻¹	AgCl gravimetry	0.010	KCl Aldrich 99.999 % 110°C/2h	0.005, 0.01 0.015
CENAM	0.01004 mol kg ⁻¹	Gravimetric preparation	0.01004	NaCl Baker ULTREX; Ultrapure reagent	0.005, 0.01 0.015
GUM	analytical grade twice distilled	AgCl precipitation titration	0.009782	KCl analytical grade; add. purification 500°C/4h	0.005, 0.01 0.015
VNIIFTRI	HCl 34% Impurities: 10 ⁻⁴ %	Coulometry	0.00999	NaCl, 99.999% inorg impu. 10 ⁻⁴ % 110°C/2h	0.005, 0.01 0.015
SMU	analytical grade purified by isothermal distillation	Coulometry	0.0061 to 0.02379	NaCl Merck Suprapur 450°C/4h	0.005,0.0075 0.01, 0.013 0.016, 0.019
NIST	analytical grade Baker 19 L batch	Coulometry	0.01002	NaCl Merck Suprapur 110°C/2h	0.005, 0.01 0.015

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),

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

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, $u(\text{pH}_R)$, is in this case completely given by the individual uncertainties according to equation (14)

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

In order to take the spread of the results into account, the uncertainty for the KCRV of CCQM-K9 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).

$$u'(\text{pH}_R)^2 = \frac{\sum_{i=1}^N (w_i (\text{pH}_i - \text{pH}_R)^2)}{(N-1) \cdot \sum_{i=1}^N w_i} \quad (15)$$

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

In Tables 6 and 7 the Birge ratios R_{Birge} calculated according to equation (16) are listed together with the KCRV and its uncertainty for sample (1) and sample (2), respectively. Additionally the uncertainty calculated by the internal consistency method [13], [15] is given.

Table 6. Sample (1) $0.025 \text{ mol}\cdot\text{kg}^{-1} \text{ KH}_2\text{PO}_4 + 0.025 \text{ mol}\cdot\text{kg}^{-1} \text{ Na}_2\text{HPO}_4$

Temperature °C	Number of laboratories <i>i</i>	pH _R	$u(\text{pH}_R)$ ($k = 1$)	$u'(\text{pH}_R)$ ($k = 1$)	Birge ratio R_{Birge}
5	6	6.9497	0.00042	0.00093	2.214
10	6	6.9213	0.00044	0.00082	1.882
15	9	6.8975	0.00032	0.00049	1.548
20	6	6.8781	0.00040	0.00070	1.760
25	9	6.8633	0.00034	0.00056	1.642
30	6	6.8512	0.00040	0.00069	1.708
37	8	6.8394	0.00034	0.00064	1.588
40	7	6.8360	0.00046	0.00094	2.023
45	7	6.8325	0.00045	0.00110	2.473
50	6	6.8290	0.00058	0.00150	2.541

Table 7. Sample (2) $0.02 \text{ mol}\cdot\text{kg}^{-1} \text{ KH}_2\text{PO}_4 + 0.02 \text{ mol}\cdot\text{kg}^{-1} \text{ Na}_2\text{HPO}_4$

Temperature °C	Number of laboratories <i>i</i>	pH _R	$u(\text{pH}_R)$ ($k = 1$)	$u'(\text{pH}_R)$ ($k = 1$)	Birge ratio R_{Birge}
5	4	6.9756	0.00055	0.00130	2.295
10	4	6.9471	0.00051	0.00110	2.142
15	10	6.9248	0.00037	0.00086	2.336
20	4	6.9046	0.00053	0.00100	1.957
25	10	6.8905	0.00036	0.00070	1.903
30	4	6.8771	0.00048	0.00080	1.646
37	10	6.8667	0.00038	0.00078	2.046
40	4	6.8614	0.00055	0.00090	0.809
45	5	6.8592	0.00044	0.00130	3.011
50	4	6.8563	0.00056	0.00130	2.559

Reference values obtained as the variance-weighted mean (equation 12) and according to the maximum-weight method (robust mean, equations 17, 18) are compared in Table 8 for the data set of sample (1) at 15°C, 25°C and 37°C. In addition, the uncertainties of the reference values (equation 15) are given.

The corresponding data for sample (2) are presented in Table 9.

$$x_w = \frac{\sum_{i=1}^N w_i \text{pH}_i}{\sum_{i=1}^N w_i} \quad (17)$$

$$w_i = \frac{1}{u_i} \cdot e^{-k \left(\frac{(\text{pH}_i - \text{pH}_w)}{s} \right)^2} \quad (18)$$

Table 8. Sample (1) $0.025 \text{ mol}\cdot\text{kg}^{-1} \text{ KH}_2\text{PO}_4 + 0.025 \text{ mol}\cdot\text{kg}^{-1} \text{ Na}_2\text{HPO}_4$

Temperature °C	variance weighted mean	$u(\text{pH}_R)$ ($k=1$)	robust mean	$u'(\text{pH}_R)$ ($k=1$)
15	6.8975	0.00049	6.8981	0.00029
25	6.8633	0.00056	6.8638	0.00028
37	6.8394	0.00062	6.8398	0.00042

Table 9. Sample (2) $0.02 \text{ mol}\cdot\text{kg}^{-1} \text{ KH}_2\text{PO}_4 + 0.02 \text{ mol}\cdot\text{kg}^{-1} \text{ Na}_2\text{HPO}_4$

Temperature °C	variance weighted mean	$u(\text{pH}_R)$ ($k=1$)	robust mean	$u'(\text{pH}_R)$ ($k=1$)
15	6.9248	0.00086	6.9244	0.00069
25	6.8905	0.00070	6.8905	0.00063
37	6.8667	0.00078	6.8654	0.00055

There is no apparent difference between the two estimates either for sample (1) or sample (2).

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 numbers,

$$D_i = (\text{pH}_i - \text{pH}_R) \quad (19)$$

and U_i , the expanded uncertainty of D_i , ($k=2$), which is calculated according to equation (20):

$$U_i = 2\sqrt{u_i^2 + u(\text{pH}_R)^2}. \quad (20)$$

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

$$D_{ij} = D_i - D_j \quad (21)$$

and U_{ij} , the expanded uncertainty of D_{ij} , ($k=2$), which is calculated according to equation (22)

$$U_{ij} = 2\sqrt{u_i^2 + u_j^2}. \quad (22)$$

Tables and Figures

Sample (1): $0.025 \text{ mol}\cdot\text{kg}^{-1} \text{ KH}_2\text{PO}_4 + 0.025 \text{ mol}\cdot\text{kg}^{-1} \text{ Na}_2\text{HPO}_4$

Table 1. pH values for sample (1) at 15 °C

	Temperature	
	15 °C	
Participant	pH	$U (k = 2)$
KRISS	6,8941	0,0020
NRCCRM	6,8950	0,0060
SMUcor	6,8970	0,0018
NIST	6,8973	0,0010
VNIIFTRI	6,8980	0,0038
DPL	6,8983	0,0016
CENAM	6,8990	0,0060
GUM	6,8990	0,0020
PTB	6,8992	0,0020
SMU	6,8930	0,0020

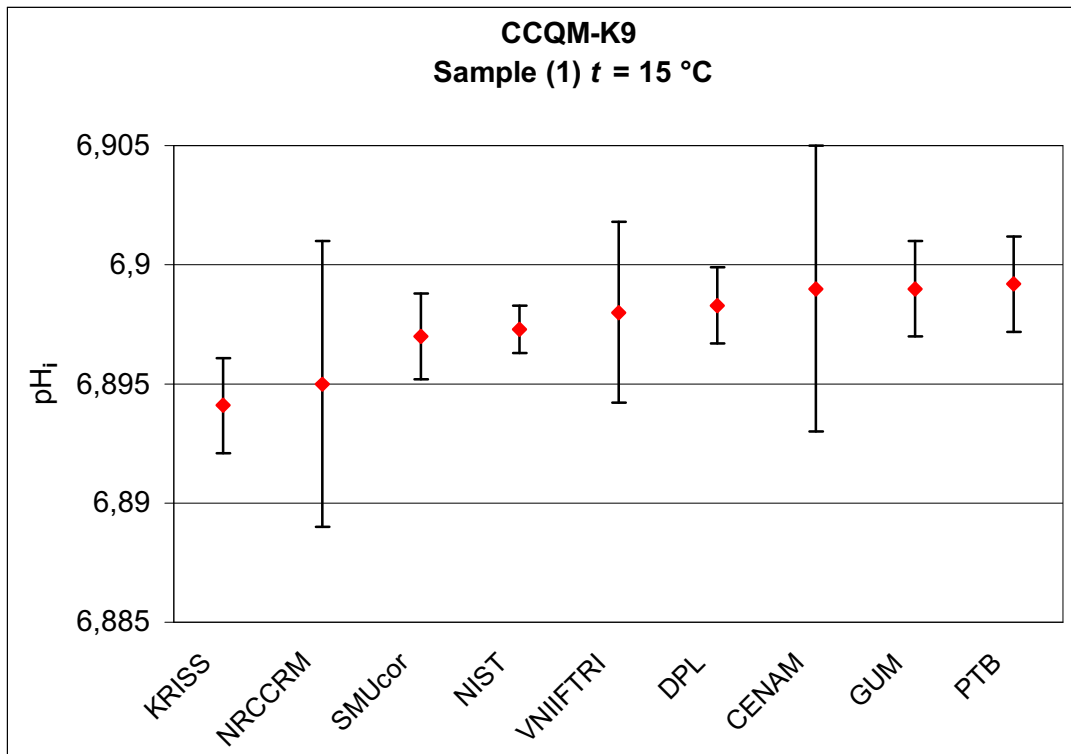


Table 2. pH values for sample (1) at 25 °C

	Temperature	
	25 °C	
Participant	pH	$U(k=2)$
CENAM	6,8580	0,0120
KRISS	6,8597	0,0020
NRCCRM	6,8600	0,0040
NIST	6,8630	0,0014
VNIIFTRI	6,8640	0,0036
SMUcor	6,8640	0,0018
PTB	6,8643	0,0022
DPL	6,8643	0,0016
GUM	6,8645	0,0018
SMU	6,8590	0,0020

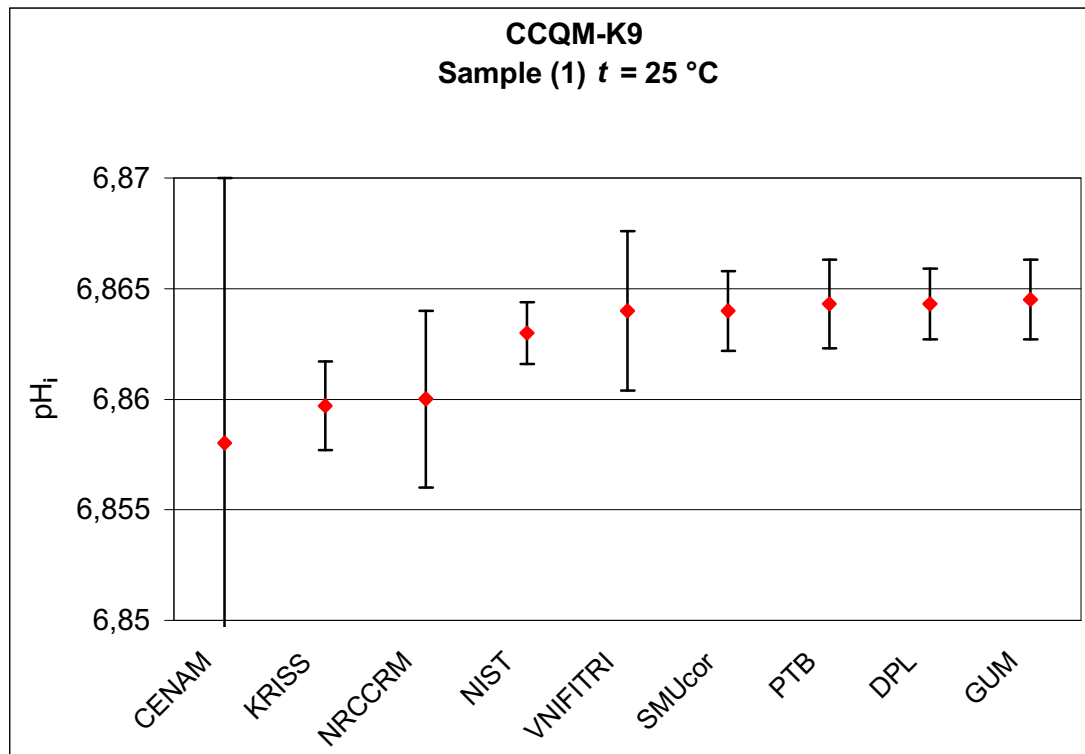


Table 3. pH values for sample (1) at 37 °C

	Temperature	
	37 °C	
Participant	pH	$U(k=2)$
KRISS	6,8360	0,0020
NRCCRM	6,8370	0,0040
GUM	6,8382	0,0018
VNIIFTRI	6,8390	0,0038
SMUcor	6,8397	0,0018
PTB	6,8406	0,0022
DPL	6,8407	0,0016
NIST	6,8406	0,0044
SMU	6,8350	0,0020

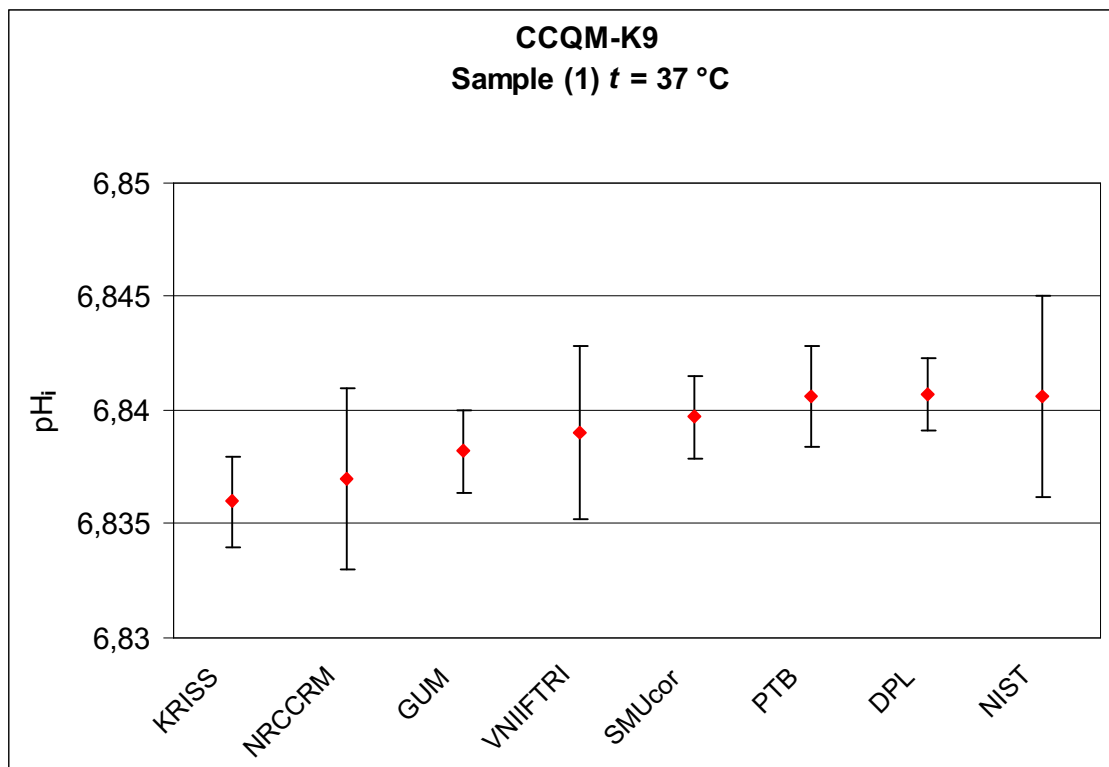


Table 4. pH values for sample (1) at 5 °C

Participant	Temperature	
	5°C	
Participant	pH	$U(k = 2)$
CENAM	6,9420	0,0160
KRISS	6,9466	0,0022
NIST	6,9490	0,0013
VNIIFTRI	6,9500	0,0036
PTB	6,9514	0,0024
GUM	6,9532	0,0020

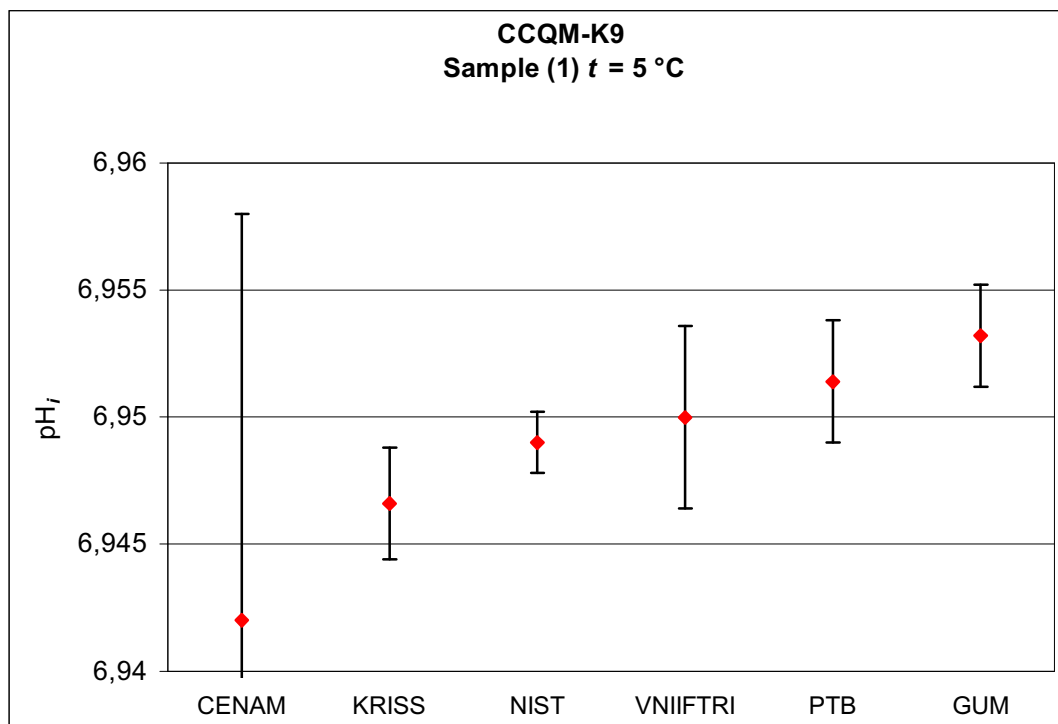


Table 5. pH values for sample (1) at 10 °C

	Temperature 10 °C	
Participant	pH	$U(k=2)$
CENAM	6,9130	0,0180
KRISS	6,9183	0,0020
NIST	6,9208	0,0014
VNIIFTRI	6,9220	0,0038
PTB	6,9229	0,0024
GUM	6,9234	0,0018

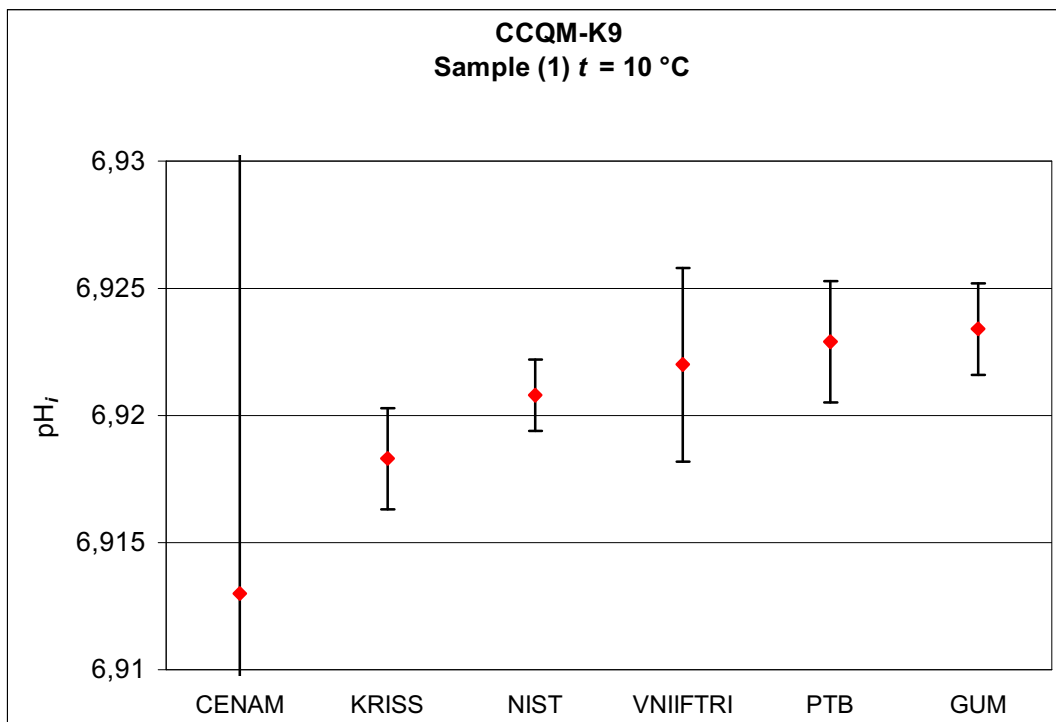


Table 6. pH values for sample (1) at 20 °C

	Temperature	
	20 °C	
Participant	pH	$U(k=2)$
KRISS	6,8751	0,0020
NIST	6,8779	0,0012
VNIIFTRI	6,8790	0,0036
GUM	6,8792	0,0018
PTB	6,8799	0,0022
CENAM	6,8840	0,0100

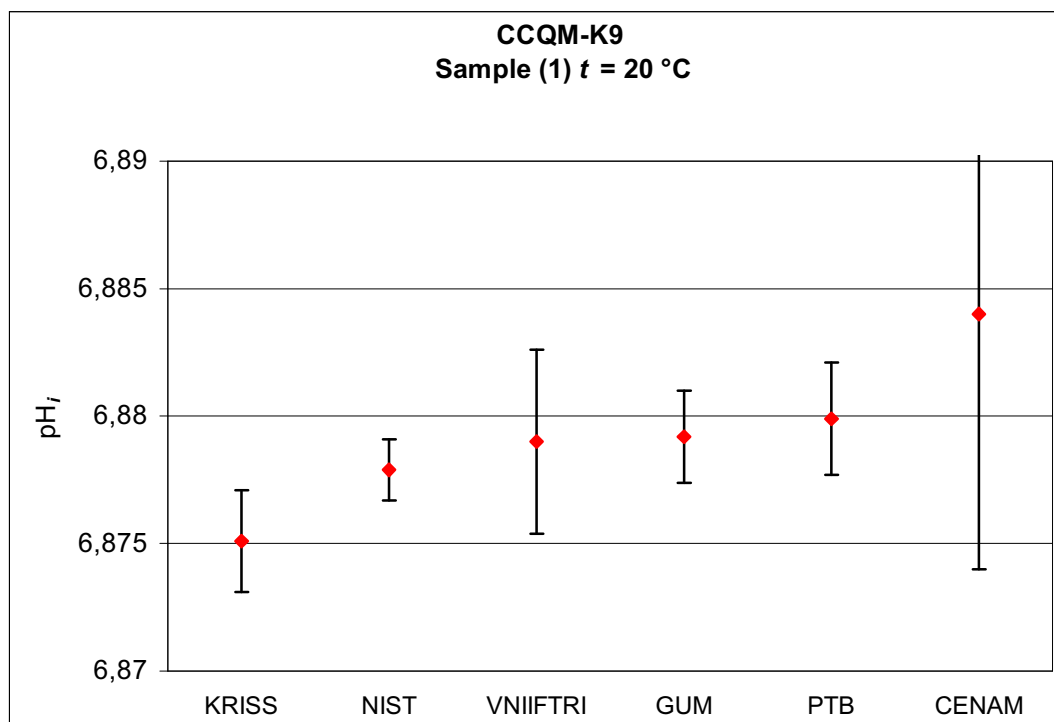


Table 7. pH values for sample (1) at 30 °C

	Temperature	
	30 °C	
Participant	pH	$U(k=2)$
KRISS	6,8478	0,0020
GUM	6,8511	0,0018
NIST	6,8520	0,0043
VNIIFTRI	6,8520	0,0036
PTB	6,8522	0,0022
CENAM	6,8540	0,0120

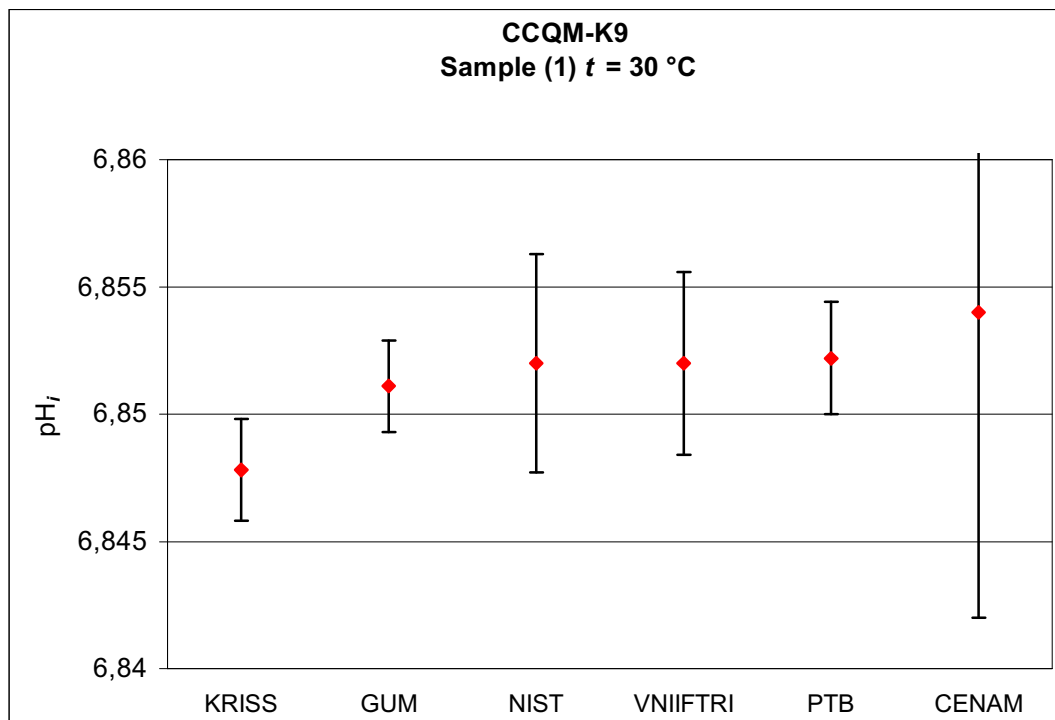


Table 8. pH values for sample (1) at 40 °C

	Temperature	
	40 °C	
Participant	pH	$U (k = 2)$
KRISS	6,8326	0,0020
VNIIFTRI	6,8340	0,0038
GUM	6,8344	0,0024
CENAM	6,8370	0,0080
PTB	6,8373	0,0022
DPL	6,8382	0,0016
NIST	6,8382	0,0042

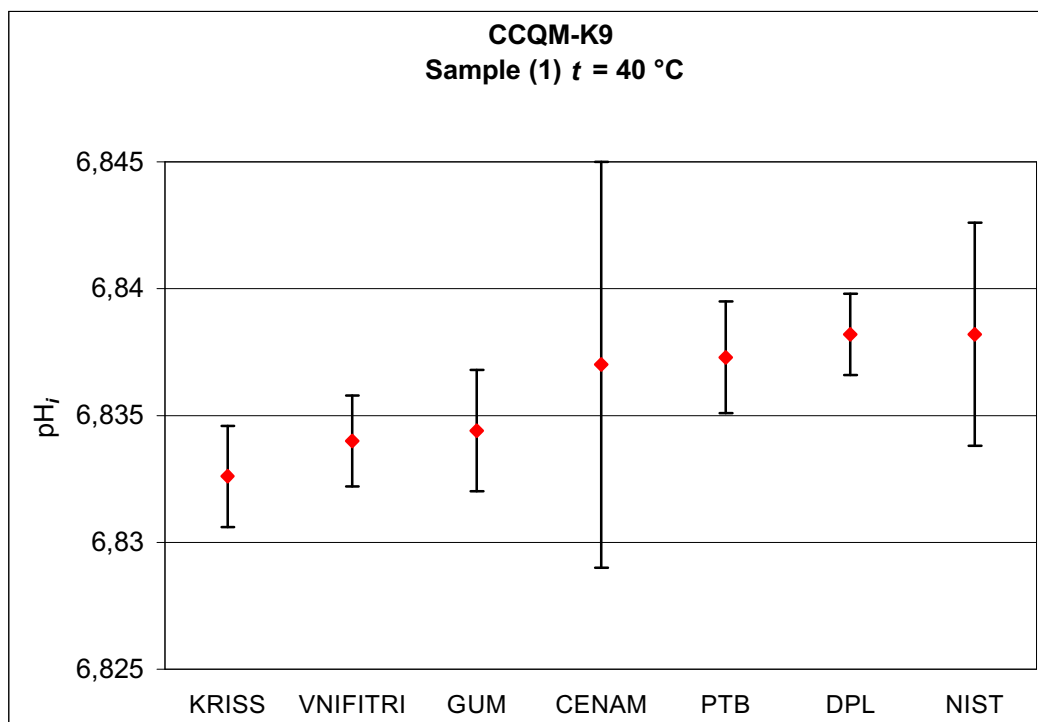


Table 9. pH values for sample (1) at 45 °C

	Temperature	
	45 °C	
Participant	pH	$U (k = 2)$
KRISS	6,8294	0,0018
GUM	6,8297	0,0024
VNIIFTRI	6,8310	0,0038
PTB	6,8336	0,0022
DPL	6,8346	0,0016
NIST	6,8347	0,0045
CENAM	6,8400	0,0080

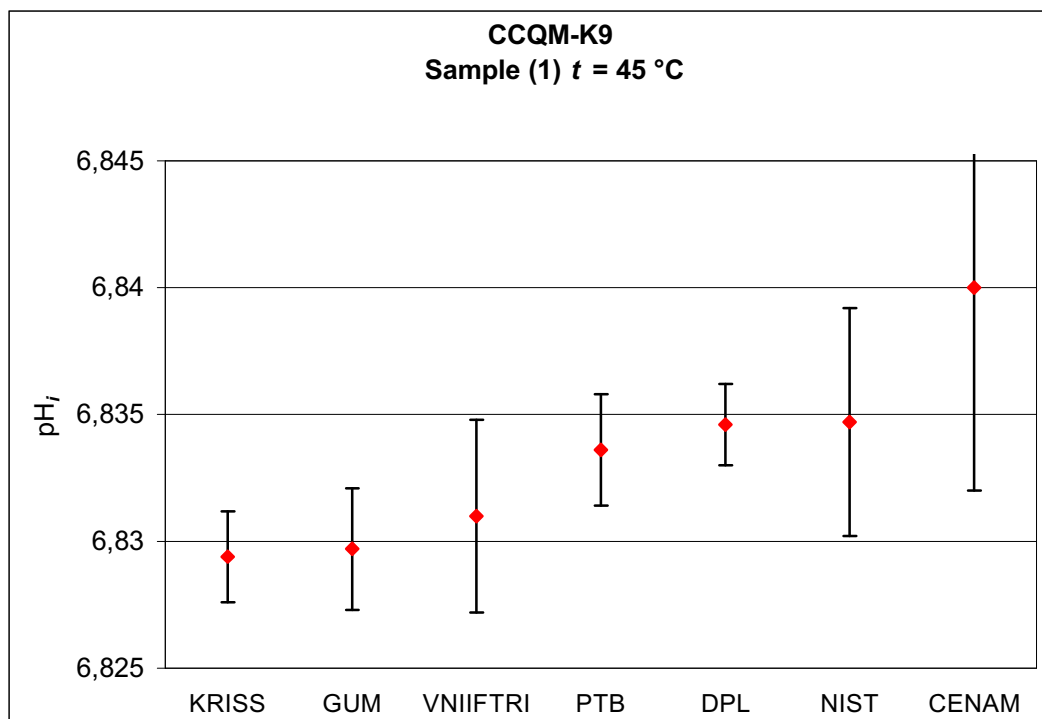
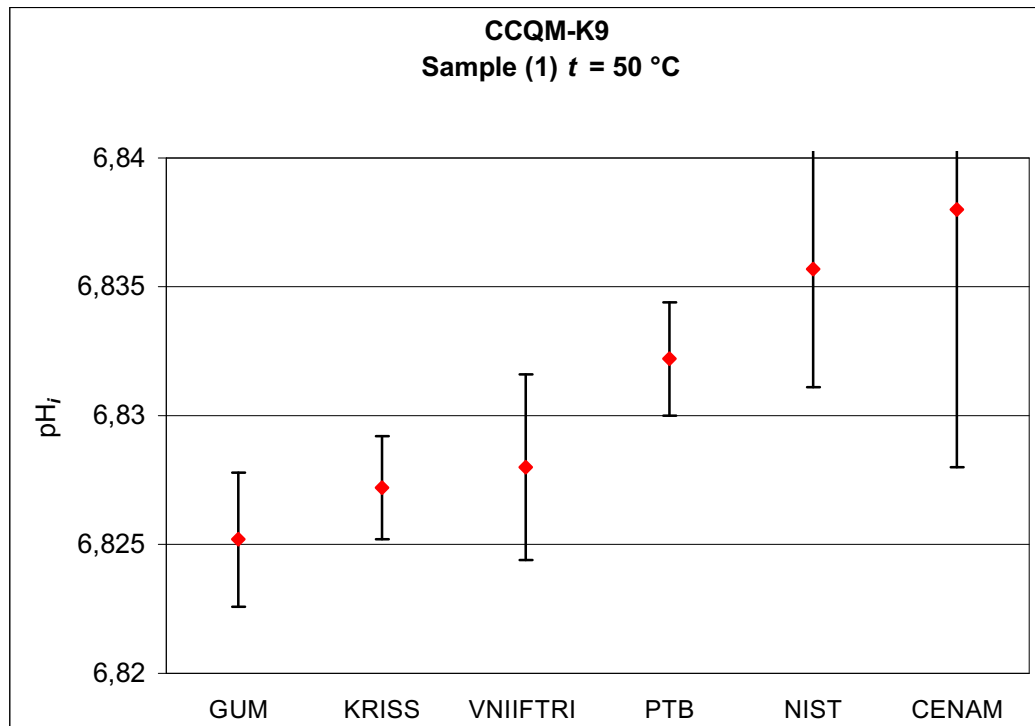


Table 10. pH values for sample (1) at 50 °C

	Temperature	
	50 °C	
Participant	pH	$U (k = 2)$
GUM	6,8252	0,0026
KRISS	6,8272	0,0020
VNIIFTRI	6,8280	0,0036
PTB	6,8322	0,0022
NIST	6,8357	0,0046
CENAM	6,8380	0,0100



Sample (2): $0.02 \text{ mol}\cdot\text{kg}^{-1} \text{ KH}_2\text{PO}_4 + 0.02 \text{ mol}\cdot\text{kg}^{-1} \text{ Na}_2\text{HPO}_4$

Table 11. pH values for sample (2) at 15 °C

	Temperature	
	15 °C	
Participant	pH	$U (k = 2)$
KRISS	6,9217	0,0016
NRCCRM	6,9232	0,0040
GUM	6,9233	0,0018
SMUcor	6,9242	0,0018
PTB	6,9259	0,0022
DPL	6,9265	0,0016
VNIIFTRI	6,9272	0,0038
NIST	6,9295	0,0026
NIMC	6,9352	0,0086
CENAM	6,9362	0,0110
SMU	6,9192	0,0020

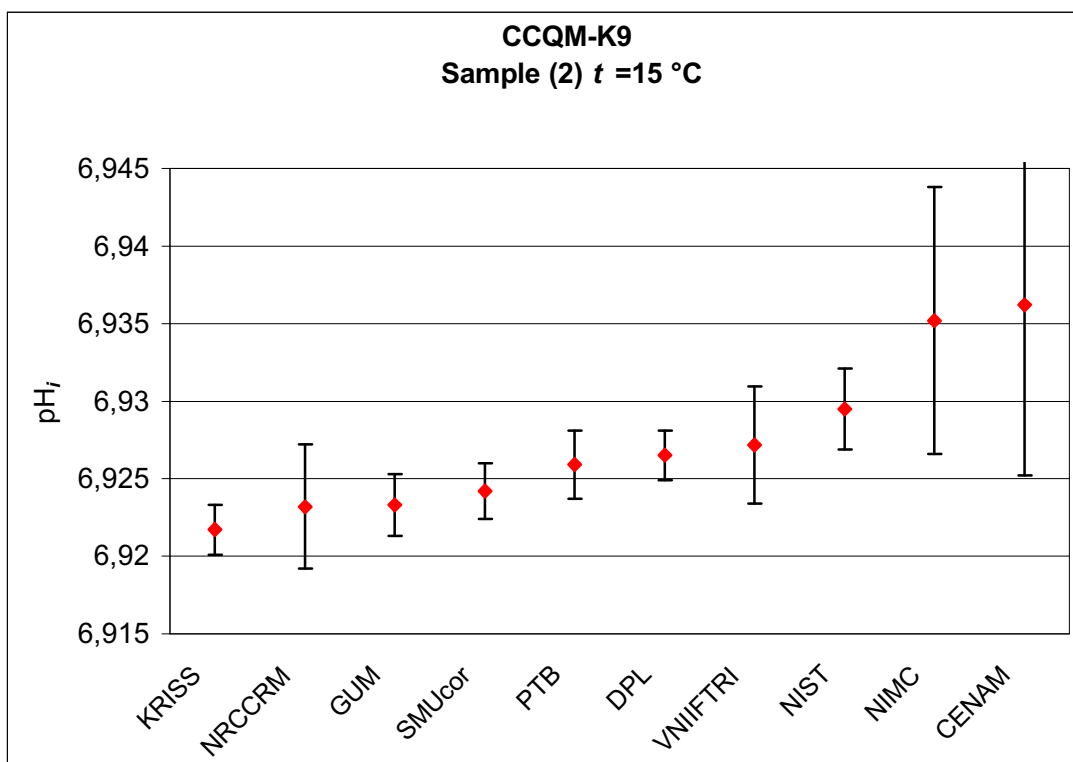


Table 12. pH values for sample (2) at 25 °C

	Temperature	
	25 °C	
Participant	pH	$U(k=2)$
KRISS	6,8877	0,0016
NRCCRM	6,8886	0,0040
SMUcor	6,8896	0,0018
GUM	6,8903	0,0016
PTB	6,8914	0,0022
DPL	6,8923	0,0016
NIMC	6,8933	0,0084
VNIIFTRI	6,8936	0,0036
NIST	6,8941	0,0042
CENAM	6,9066	0,0130
SMU	6,8846	0,0020

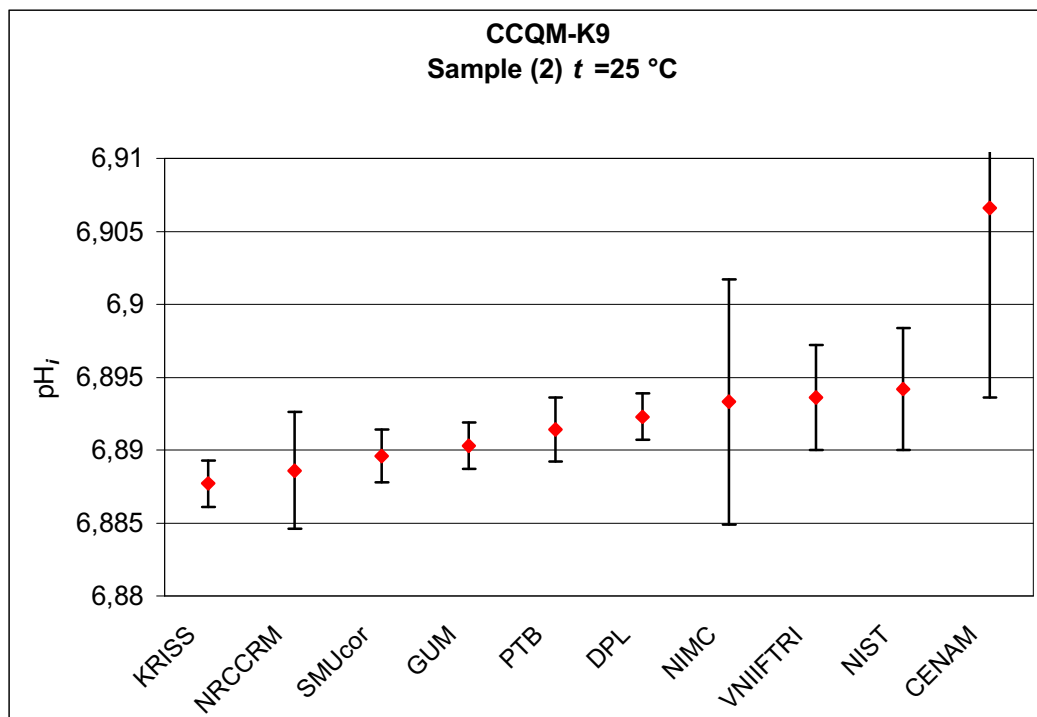


Table 13. pH values for sample (2) at 37 °C

	Temperature	
	37 °C	
Participant	pH	$U(k=2)$
NRCCRM	6,8635	0,0040
KRISS	6,8643	0,0016
GUM	6,8648	0,0022
NIMC	6,8655	0,0074
SMUcor	6,8657	0,0018
VNIIFTRI	6,8665	0,0038
PTB	6,8673	0,0022
DPL	6,8695	0,0016
NIST	6,8707	0,0030
CENAM	6,8745	0,0110
SMU	6,8605	0,0020

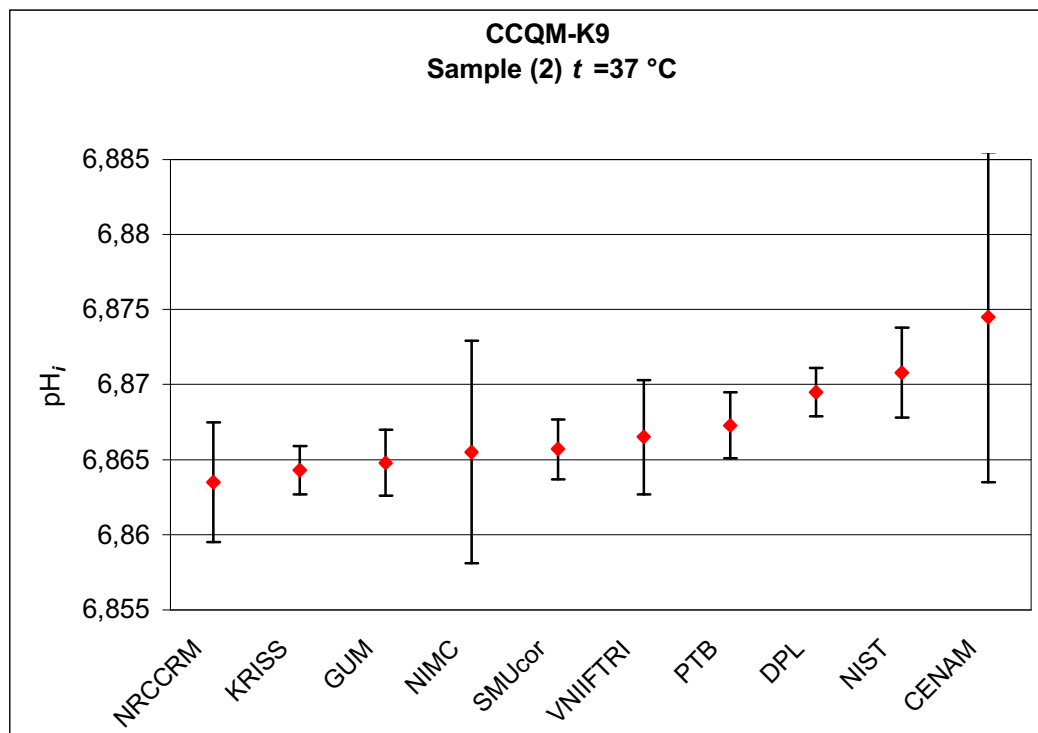


Table 14. pH values for sample (2) at 5 °C

	Temperature	
	5 °C	
Participant	pH	$U(k=2)$
KRISS	6,9733	0,0016
PTB	6,9770	0,0030
GUM	6,9776	0,0020
VNIIFTRI	6,9787	0,0038

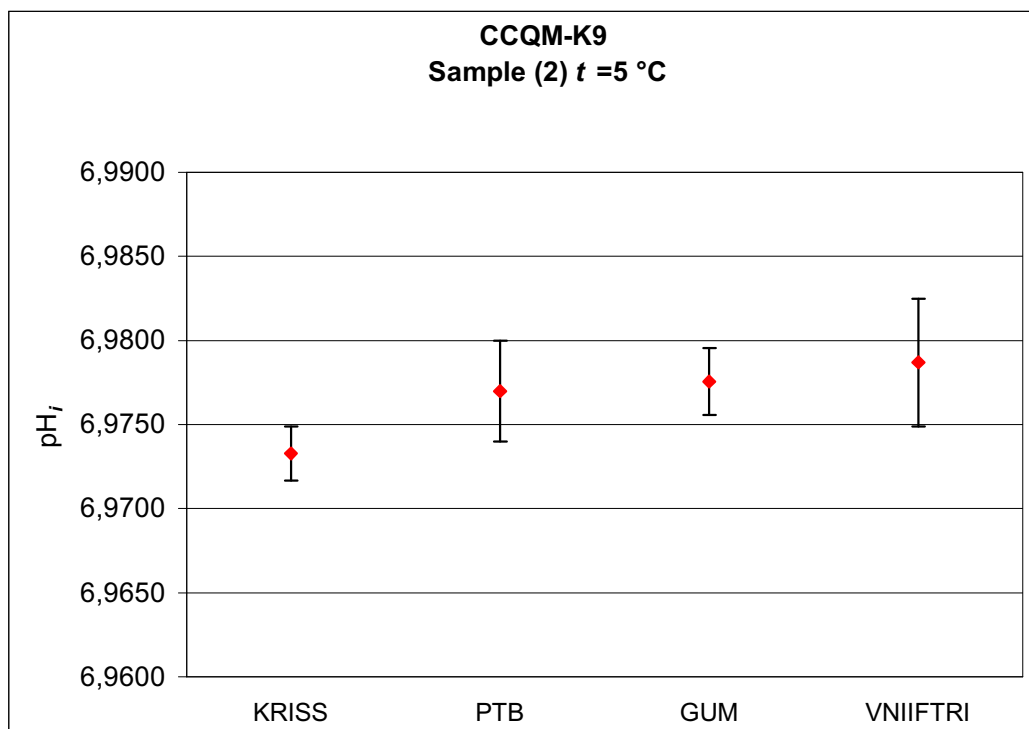


Table 15. pH values for sample (2) at 10 °C

	Temperature	
	10 °C	
Participant	pH	$U(k=2)$
KRISS	6,9450	0,0016
GUM	6,9480	0,0016
PTB	6,9490	0,0030
VNIIFTRI	6,9509	0,0038

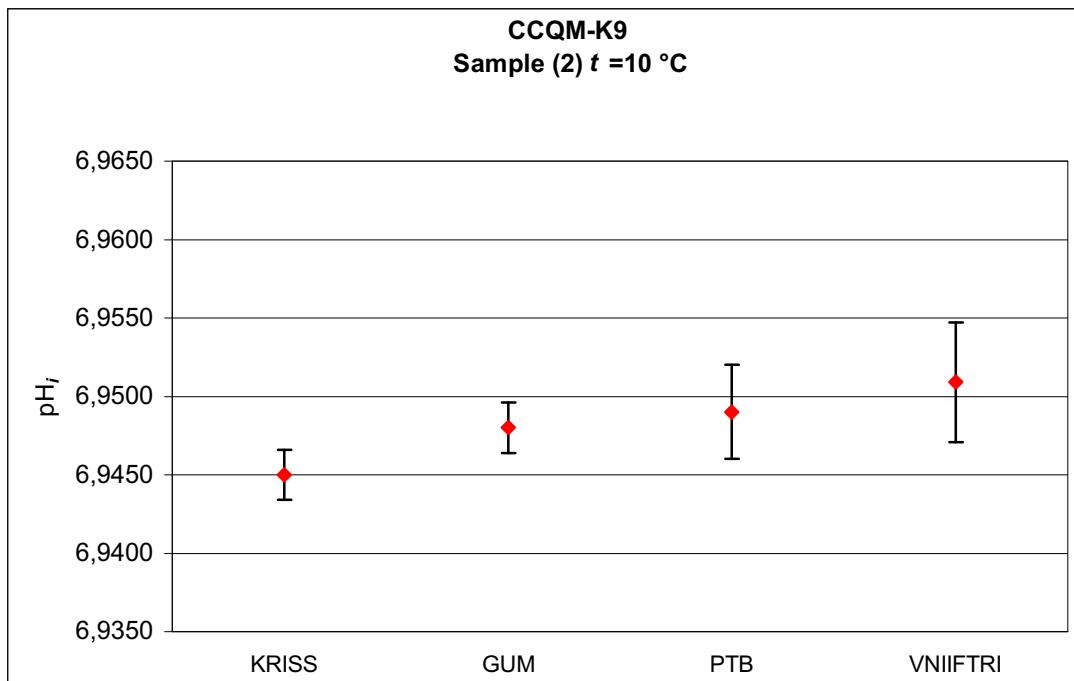


Table 16. pH values for sample (2) at 20 °C

	Temperature	
	20 °C	
Participant	pH	$U(k=2)$
KRISS	6,9028	0,0016
GUM	6,9047	0,0022
PTB	6,9068	0,0022
VNIIFTRI	6,9074	0,0036

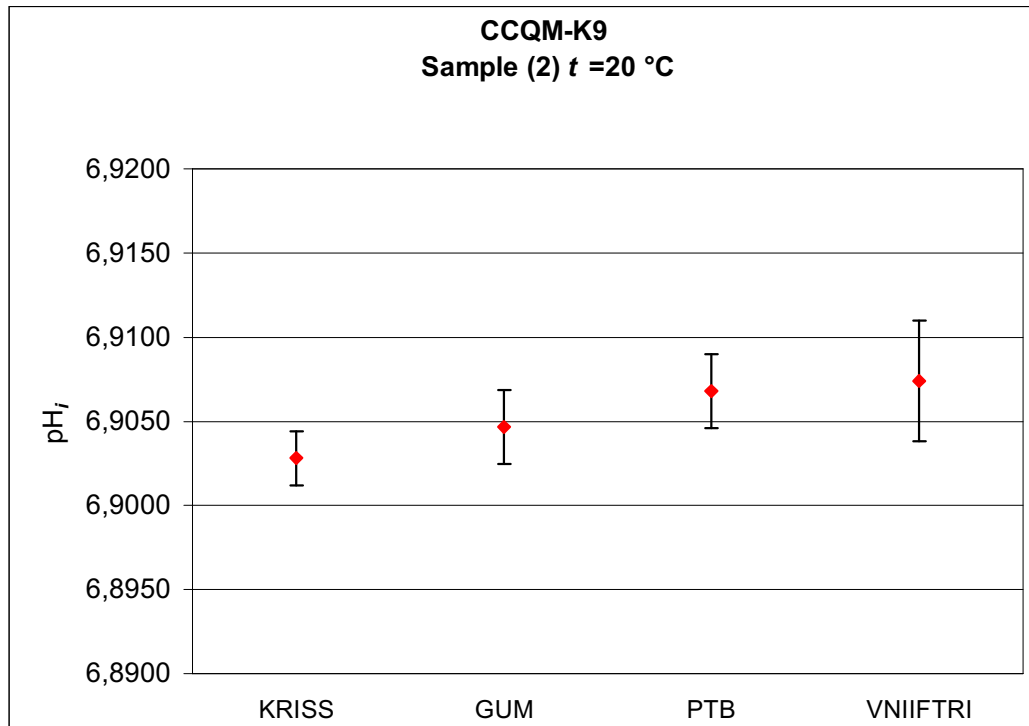


Table 17. pH values for sample (2) at 30 °C

	Temperature	
	30 °C	
Participant	pH	$U(k=2)$
KRISS	6,8757	0,0016
GUM	6,8771	0,0016
PTB	6,8790	0,0022
VNIFFTRI	6,8797	0,0036

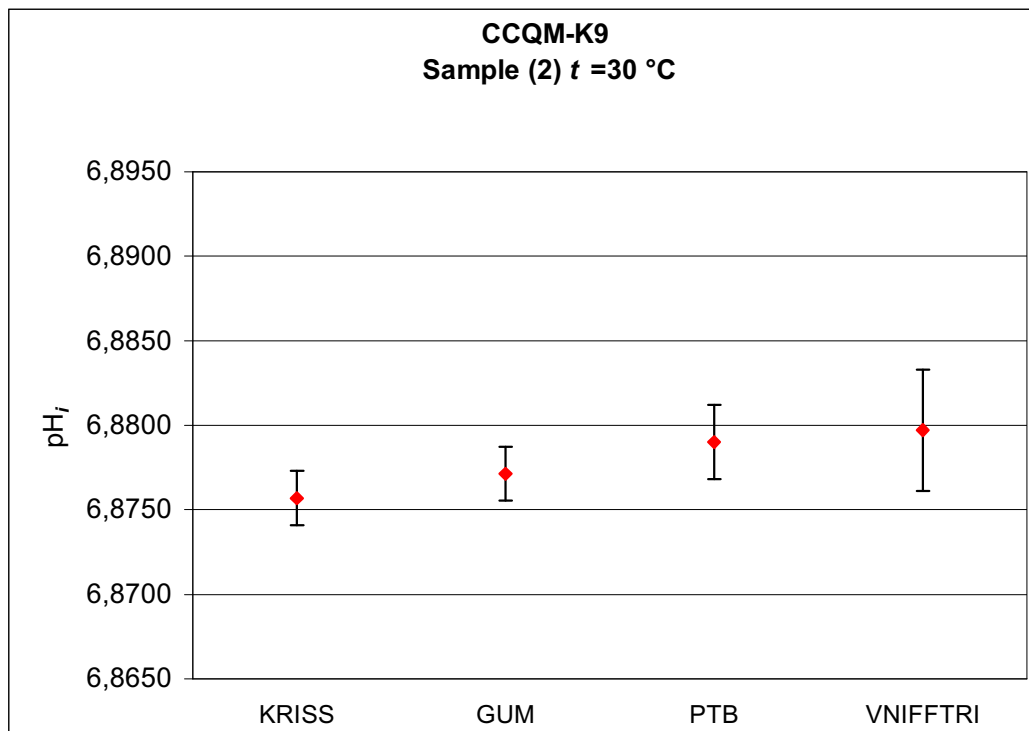


Table 18 pH values for sample (2) at 40 °C

		Temperature
		40 °C
Participant	pH	$U(k=2)$
GUM	6,8607	0,0022
KRISS	6,8611	0,0016
VNIIFTRI	6,8619	0,0038
PTB	6,8631	0,0030

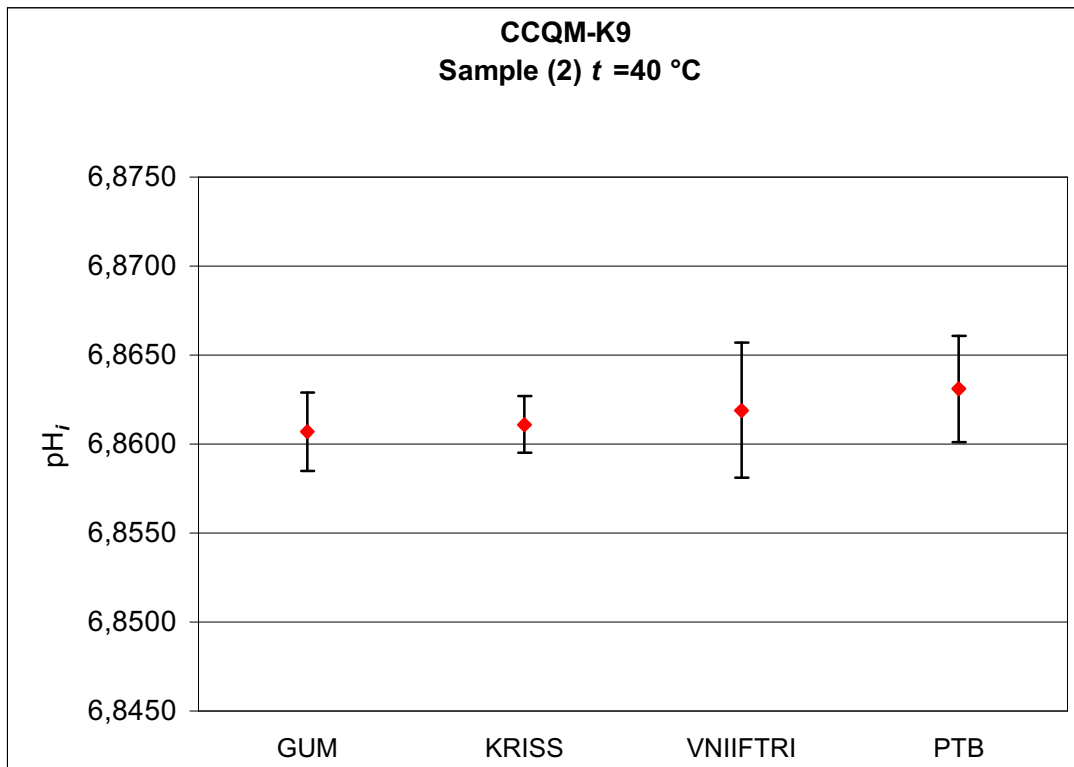


Table 19. pH values for sample (2) at 45 °C

		Temperature
		45 °C
Participant	pH	$U(k=2)$
VNIIFTRI	6,8559	0,0040
GUM	6,8566	0,0018
KRISS	6,8578	0,0016
PTB	6,8605	0,0030
DPL	6,8629	0,0016

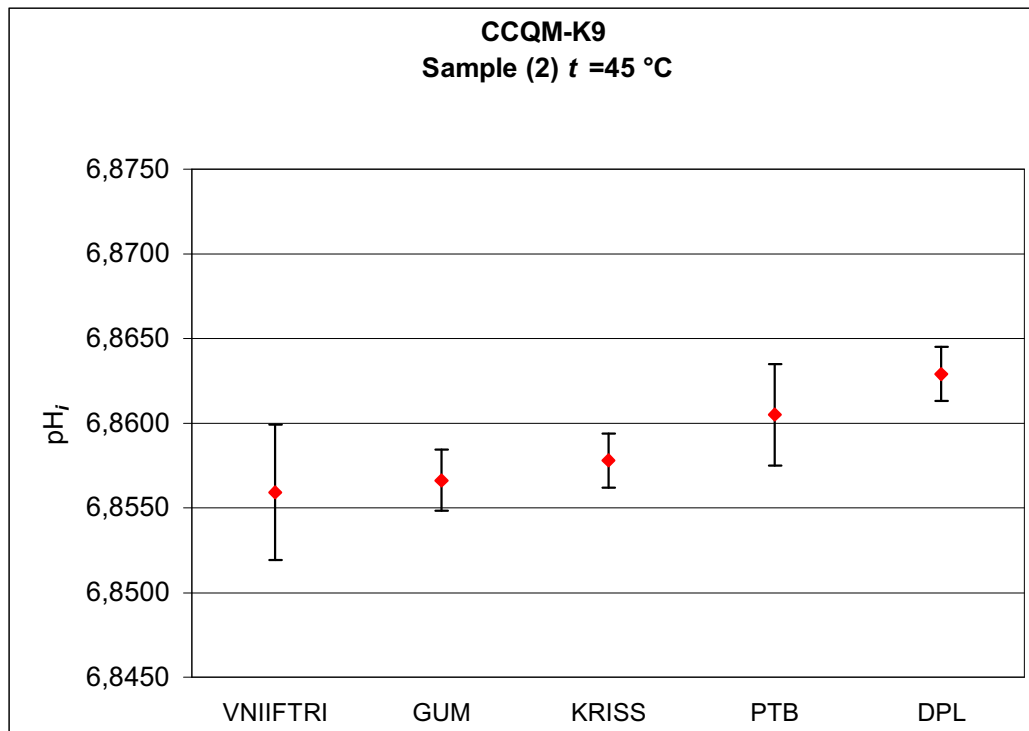


Table 20. pH values for sample (2) at 50 °C

	Temperature	
	50 °C	
Participant	pH	$U(k=2)$
GUM	6,853	0,0022
VNIIFTRI	6,8569	0,0036
KRISS	6,857	0,0016
PTB	6,8596	0,0030

