# Report on IPQ-DFM bilateral comparison on phosphate buffer 2008

30 April 2009
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## Summary

In 2008 IPQ asked DFM to participate in a bilateral comparison on pH following the transfer of the Portuguese set-up for primary pH measurements from the University of Lisbon to IPQ. IPQ wanted to test their capability in primary pH measurements through the bilateral comparison. The bilateral comparison is registered as EURAMET project 1051.

DFM acted as coordinating laboratory for the bilateral comparison. Due to limitations of DFM's production capacity and ability to do stability and homogeneity testing the comparison did not fulfil the rules of a supplementary key comparison and cannot formally link to a CCQM key comparison.

This report contains the details of the comparison including the results of the two institutes and an evaluation of the equivalence of these.

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# Contents

# 1 Background, participants and time schedule

## 1.1 Background

The Portuguese primary pH set-up was transferred from the University of Lisbon Faculty of sciences to Instituto Português da Qualidade (IPQ) in 2008. After the transfer of the set-up IPQ wanted to test their capability in primary pH measurements.

Danish Fundamental Metrology (DFM) and IPQ agreed on a bilateral comparison coordinated by DFM. The comparison was carried out as EURAMET project 1051.

Due to limitations of DFM's production capacity and ability to do stability and homogeneity testing the comparison was bilateral. The comparison did not fulfil the rules of a supplementary key comparison and cannot be formally linked to a CCQM key comparison.

## 1.2 Participants

The participants were:

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## 1.3 Time schedule

The originally agreed time schedule was:

Dispatch of samples: 2008-07-16
Measurement period: 2008-07-16 to 2008-08-15
Deadline for receipt of report: 2008-09-30
Draft report: 2008-11-15
Deadline for receipt of comments to draft report: 2008-12-31
Final report sent to EURAMET: 2009-02-28

However, the writing of the draft report was delayed. The draft report was sent from DFM to IPQ on 2009-02-27. IPQ and DFM agreed on 2009-04-01 as deadline for comments to the draft report. And the final report will be sent to EURAMET by 2009-05-30.

# 2 Measurement sample and conditions

## 2.1 Sample

The comparison was carried out on a physiological phosphate buffer, that is an aqueous solution containing 0.03043 mol $kg^{-1}$ $Na_2HPO_4$ (disodium hydrogen phosphate) and 0.008695 mol $kg^{-1}$ $KH_2PO_4$ (potassium dihydrogen phosphate).

The buffer was prepared by dissolving weighed quantities of NIST SRM 186g I and II in a weighed quantity of argonbubbled, deionised water with conductivity lower than 200 µS/m. The salts are weighed and transferred to a glass bottle to which the water is added. The bottle is shaken until the salts are dissolved and left to stand for an hour. After renewed shaking the samples for measurement are taken from this solution. The production method used at DFM differs somewhat from the method recommended by NIST and thus the pH of the produced buffer does not necessarily match that stated in the certificate from NIST for SRM 186g.

DFM took the aliquots used for the measurements directly from the large bottle in which the buffer was produced.

For the buffer to be sent to IPQ was prepared three 1 L glass bottles with plastic screw caps (so-called bluecap bottles). The bottles and their caps were soaked over night in 2% solution of Extran® MA01. Extran® MA01 is an alkaline detergent solution from Merck. The bottles and caps were then rinsed thoroughly in high purity water and dried at 120 °C for 6 hours.

After cooling the bottles, the buffer was filled into the bottles and the screw caps screwed on. The bottles were labelled, the screw cap re-tightened a couple of times and then the bottles were sealed using Parafilm®. After weighing the bottles, they were cooled in a refrigerator over night, packed in a large box containing styrofoam insulation material and shipped to Portugal by courier service. IPQ had been instructed to refrigerate the buffer immediately after receipt and keep it refrigerated for at least two days. IPQ was further instructed to store the bottles with buffer at room temperature not exceeding 30 °C from the day before the start of the measurements.

The DFM did not provide IPQ with the hydrochloric acid and the chloride salt (sodium or potassium chloride) that must be used for the measurements.

## 2.2 Measurement conditions

The measurement conditions stated in the protocol were:

> It is recommended to use HCl with SI traceable known molality close to a molality of 0.01 mol/kg to measure the standard potential of the Ag/AgCl electrodes.

Alkali chloride of certified high quality should be added at at least three different molalities in the range of 0.005 mol/kg to 0.02 mol/kg.

The pH measurements are to be carried out at 15 °C, 25 °C, and 37 °C using the primary measurement for pH (Harned cell). Use the standard protocol of your laboratory for this measurement.

For the Faraday constant and for the gas constant the 2006 CODATA[a] values are to be used. These are F = 96 485.3399(24) C·mol$^{-1}$ and R = 8.314 472(15) J mol$^{-1}$ K$^{-1}$. The standard pressure to be used in the evaluation is 101 325 Pa.

The protocol of the comparison is appendix 1 of this report.

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[a] Values available at http://physics.nist.gov/cuu/Constants/index.html.

# 3 Participants results

## 3.1 Results of DFM

The measurement report of DFM is appendix 2 of this report. The results of DFM are summarised in the table below.

In the table $E°_{Ag/AgCl}$ is the standard potential of the silver/silver chloride electrodes, $U(E°_{Ag/AgCl})$ is the expanded uncertainty of this at the 95 % confidence level, $p°(a_H\gamma_{Cl})$ is the acidity function at zero chloride molality, $U(p°(a_H\gamma_{Cl}))$ is the expanded uncertainty of this, pH is the pH value and U(pH) is the expanded uncertainty of this.

| *Tempe-rature* | $E°_{Ag/AgCl}$ | $U(E°_{Ag/AgCl})$ | $p°(a_H\gamma_{Cl})$ | $U(p°(a_H\gamma_{Cl}))$ | *pH* | *U(pH)* |
|---|---|---|---|---|---|---|
| (°C) | (V) | (V) | (1) | (1) | (1) | (1) |
| 15 | 0.228569 | 0.000053 | 7.5596 | 0.0012 | 7.4520 | 0.0012 |
| 25 | 0.222405 | 0.000061 | 7.5254 | 0.0011 | 7.4160 | 0.0011 |
| 37 | 0.214227 | 0.000094 | 7.5044 | 0.0011 | 7.3926 | 0.0011 |

## 3.2 Results of IPQ

The report from IPQ was received on 2008-09-30. The report submitted by IPQ is appendix 3 of this report. The results of IPQ are summarised in the table below.

| *Tempe-rature* | $E°_{Ag/AgCl}$ | $U(E°_{Ag/AgCl})$ | $p(a_H\gamma_{Cl})$ | $U(p(a_H\gamma_{Cl}))$ | *pH* | *U(pH)* |
|---|---|---|---|---|---|---|
| (°C) | (V) | (V) | (1) | (1) | (1) | (1) |
| 15 | 0.22839 | 0.00010 | 7.5607 | 0.0065 | 7.4529 | 0.0068 |
| 25 | 0.22227 | 0.00015 | 7.5241 | 0.0042 | 7.4146 | 0.0049 |
| 37 | 0.21375 | 0.00018 | 7.5013 | 0.0044 | 7.3895 | 0.0053 |

### 3.2.1 Communication with IPQ

IPQ was asked to expand on a number of details in the submitted report. Further IPQ was asked to recheck the calculation at 25 °C.

# 4 Evaluation of results

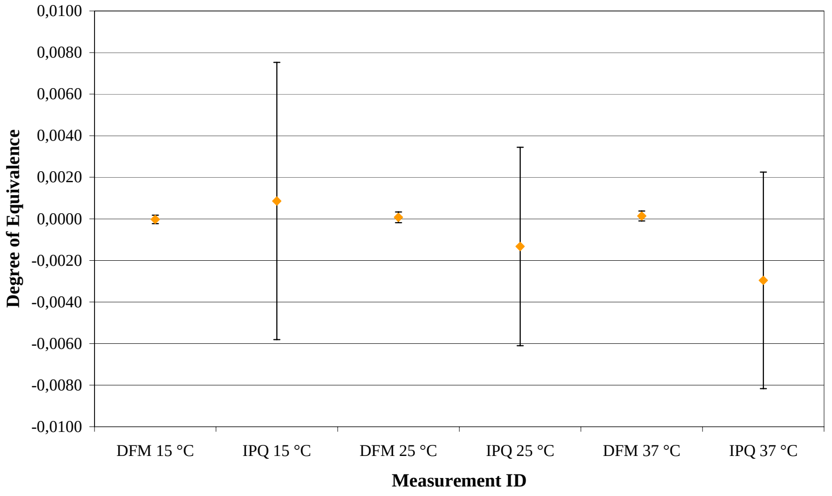
The standard potentials of the silver/silver chloride electrodes are not directly comparable, as the exact standard potential of a silver/silver chloride electrode will depend on the manufacturing of the electrode. However, large discrepancies from the tabulated, theoretical value of the standard potential indicate problems. However, in this case both participants report satisfactory standard potentials of the silver/silver chloride electrodes.

Both the acidity functions at zero chloride molality and the pH can be compared, but the only difference between these values is the correction for the chloride activity coefficient at zero molality based on the Bates-Guggenheim convention. The reported results show that both participants are able to apply the Bates-Guggenheim convention correctly at all three temperatures. Thus only the pH values were compared.

The equivalence of the reported pH values were evaluated based on a weighted mean of DFM's and IPQ's results. The calculated degrees of equivalence are:

| | **DFM** | | **IPQ** | |
|---|---|---|---|---|
| *Temperature* | *D* | *U(D)* | *D* | *U(D)* |
| 15 °C | 0.0000 | 0.0002 | 0.0009 | 0.0067 |
| 25 °C | 0.0001 | 0.0003 | -0.0013 | 0.0048 |
| 37 °C | 0.0001 | 0.0002 | -0.0030 | 0.0052 |

The degrees of equivalence are shown in the graph below. The error bars in the graph are 95% confidence level error bars.



# 5 Conclusion

The result of this bilateral comparison is that IPQ has demonstrated equivalence with DFM for measurement of pH of phosphate buffer.

# 6 Appendix 1

The protocol of the comparison is given on the following 4 pages.

# IPQ-DFM bilateral comparison on phosphate buffer 2008

# Measurement protocol

## Introduction

The Portuguese primary pH set-up was transferred from the University of Lisbon Faculty of sciences to Instituto Português da Qualidade (IPQ). After the transfer of the set-up IPQ wants to test their capability in primary pH measurements and that is the purpose of this bilateral comparison coordinated by DFM. The comparison is registered as EURAMET project 1051.

The buffer to be measured in this comparison will be a physiological phosphate buffer (0.03043 mol kg$^{-1}$ $Na_2HPO_4$ and 0.008695 mol kg$^{-1}$ $KH_2PO_4$).

Due to limitations of DFM's production capacity and ability to do stability and homogeneity testing the comparison is bilateral. The comparison does not fulfil the rules of a supplementary key comparison and cannot formally link to a CCQM key comparison.

## Participating laboratories and contact persons

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## Time schedule

Dispatch of samples: 2008-07-16
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Deadline for receipt of report: 2008-09-30
Draft report: 2008-11-15
Deadline for receipt of comments to draft report: 2008-12-31
Final report sent to EURAMET: 2009-02-28

## Sample

The sample will be prepared at DFM from high purity water and NIST SRM 186g I and II ($Na_2HPO_4$ and $KH_2PO_4$). However, the method of preparation at DFM differs slightly from that recommended by NIST, and thus the pH of the produced buffer does not necessarily match that stated in the certificate of NIST for SRM 186g. The water mass fraction will be given on each bottle. The ionic strength of the buffer is 0.1 mol $kg^{-1}$.

IPQ will receive three 1 L glass bottles with plastic screw caps ("Blue cap" bottles) with buffer from DFM. The screw caps will be sealed by plastic film (Parafilm®). The bottles will be shipped in a cardboard box by courier.

Hydrochloric acid and sodium or potassium chloride will not be provided. It is recommended to dry the alkali chloride at least at 400 °C for at least two hours.

## Actions at receipt

1. Do not remove the Parafilm® seal or uncap the bottles. Immediately after receipt inspect the received bottles for damage, leakage or visible contaminants in the solution. Confirm the receipt of the samples by e-mail to the coordinating laboratory. In the e-mail report the condition of the bottles.
2. Place the bottles in a refrigerator for at least two days. Do not remove the Parafilm® seal or uncap the bottles.
3. On the day before the use of the solution the bottle(s) should be taken out of the refrigerator and stored at room temperature (not exceeding 30 °C). Do not remove the Parafilm® seal or uncap the bottles.
4. Before uncapping the bottles or removing the Parafilm® seal weigh each bottle to a resolution of at least 0.01 g. The bottle mass in air (apparent mass)[1] should be reported together with the pressure, humidity and temperature of the weighing laboratory at the time of the weighing. Report the results of the weighing of the bottles by e-mail to the coordinating laboratory.
5. Check that the apparent mass of each bottle does not deviate by more than 0.2 gram from that stated by the coordinating laboratory. If the apparent mass deviates more, please contact the coordinating laboratory before uncapping the bottle.
6. Shake the bottle well for about 30 seconds before opening it in order to assure homogeneity of the solution.

## Measurement conditions

It is recommended to use HCl with SI traceable known molality close to a molality of 0.01 mol/kg to measure the standard potential of the Ag/AgCl electrodes.

Alkali chloride of certified high quality should be added at at least three different molalities in the range of 0.005 mol/kg to 0.02 mol/kg.

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[1] This means that the balance indication should be corrected according to the balance calibration but no correction for air buoyancy should be performed.

The pH measurements are to be carried out at 15 °C, 25 °C, and 37 °C using the primary measurement for pH (Harned cell). Use the standard protocol of your laboratory for this measurement.

For the Faraday constant and for the gas constant the 2006 CODATA[2] values are to be used. These are F = 96 485.3399(24) C mol$^{-1}$ and R = 8.314 472(15) J mol$^{-1}$ K$^{-1}$. The standard pressure to be used in the evaluation is 101 325 Pa.

## Instructions for reporting

The participants must submit an Excel report form prepared by the coordinating laboratory and e-mailed to the participants together with this protocol. The measurement report form has seven worksheets: *Summary, Results at 15 ºC, Results at 25 ºC, Results at 37 ºC, Graphs at 15 ºC, Graphs at 25 ºC* and *Graphs at 37 ºC*.

The *Summary* sheet contains information about the participant, the samples including weighing to check the integrity of the bottles and a summary of the results, namely the standard potentials, the acidity functions at zero chloride molality and the pH. Further there is the possiblity to make comments. The cells with green colour must be filled in, however the comments are optional.

The *Results at 15 ºC, Results at 25 ºC* and *Results at 37 ºC* sheets contain more detailed information about the results. Again the green cells must be filled in (except for comments which are optional), but also the tables for cell voltage and acidity functions must be filled in. In the cell voltage table information regarding the acid cells must be given for as many cells as the participant use. In both tables information must be given for at least three different chloride concentrations and again for as many cells as the participant use. The result of any cell that is not included in the calculation should be given, but please mark it as disregarded by changing the font colour to red. Do so in both tables, if it is a buffer cell that is not included in the calculation. If a cell is disregarded please state the reason for disregarding it in the comments field.

Further to the numerical data in the *Results at 15 ºC, Results at 25 ºC* and *Results at 37 ºC* sheets, data must also be given graphically in the *Graphs at 15 ºC, Graphs at 25 ºC* and *Graphs at 37 ºC* sheets. Also here the greens cells must be filled in, but comments are optional. Graphs must be pasted in over the yellow squares. The text in the yellow squares can be covered by the graph. Preferably the raw data from which the graphs are plotted should be inserted elsewhere in the sheets.

The uncertainty must be evaluated in accordance with GUM.[3] All significant sources of uncertainty must be taken into account. Remember to include an uncertainty from the extrapolation of the acidity function to zero chloride molality. Include at least uncertainty budgets for the acid concentration, the molality of chloride at one level, the standard potential of the Ag|AgCl electrodes at each temperature and the acidity function at zero chloride molality at each temperature. The uncertainty budgets must be given in Excel sheets.

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[2] Values available at http://physics.nist.gov/cuu/Constants/index.html. These values are those recently approved as the 2006 CODATA values (see http://physics.nist.gov/cuu/Reference/versioncon.shtml and “background information” in that link). The difference in *F* from the 2002 CODATA value [Mohr PJ and Taylor BN 2005 *Rev. Modern Phys.* **77**(1) 1-107] is insignificant for this Key Comparison. *R* remains unchanged.

[3] ISO 1003 *Guide to the Expression of Uncertainty in Measurement*, ISBN 92-67-10188-9, 1st Ed., International Organization for Standardization, Geneva, Switzerland, 1993.

Further to this the participants must submit at written description of their measurement procedure. This must contain information on:

- Source and quality of the hydrochloric acid and sodium or potassium chloride used for the measurements. State also whether sodium or potassium chloride was used and drying conditions for the salt.
- Description of the method of determination of the concentration of the hydrochloric acid.
- Description of preparation of Ag|AgCl electrodes including age of the used electrodes.
- Description of preparation of the Pt|$H_2$ electrodes including age of the used electrodes.
- Description of how each set of electrodes are stored.
- Description of any preconditioning and/or comparison procedures used for either set of electrodes.
- Description of method of preparation of hydrochloric acid used in the cells.
- Description of method of preparation of chloride containing buffer.
- Description of the measurement procedure including details such as number of cells used, which solutions are measured at the same time, interval between potential measurements, stabilisation time, criteria for signal stability, criteria for temperature stability, are different temperatures measured independently, etc.
- Description of calculation procedure to evaluate the pH including equations used. Please detail how the voltages used in the calculation are extracted from the measured data. Include also an example of calculation of the chloride molality in buffer solution.
- Volume of the electrochemical cell (portion of the Harned cell in which the Pt|$H_2$ and Ag|AgCl electrodes are immersed).
- Volume of humidifier portion of the Harned cell.
- Flow rate of $H_2$ in the Harned cells (at least approximate flow rate).
- A picture of the measurement cell.

# 7 Appendix 2

DFM's measurement report for this comparison is given on the following 16 pages.

# DFM report for IPQ-DFM bilateral comparison on pH 2008

27 February 2009
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## Summary

This document gives details of the measurement procedure and uncertainty calculation used at DFM for the IPQ-DFM bilateral comparison on pH carried out in 2008. The comparison is registered as EURAMET project 1051.

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# 1 Measurement procedure and details

## 1.1 Acid and chloride salt

DFM produces the acid for the Harned cell measurements by a two-step procedure. In the first step, an approximate 0.1 mol/kg HCl(aq) solution is prepared from Merck suprapur 30% HCl. The ~0.1 mol/kg HCl(aq) solution is called the stock acid. One batch of stock acid weighs around 10 kg and last for about 5 years.

The exact molality of the stock acid is determined by coulometric titration. This is done immediately after the production of the stock acid and at intervals as long as there remains stock acid. One round of coulometric titration consists in ten repeat measurements. Immediately after production a round of coulometry is done. This results in a molality with uncertainty. The stock acid molality is assigned this molality until the next round of coulometry is done. A new round of coulometric titration is performed at a time where the molality of the stock acid is still assumed to be within the 95% confidence level of the uncertainty determined at the first round of coulometry. If this is confirmed by the new round, the stock acid is assigned this molality until the next round of coulometry. New rounds of coulometry are done until no more stock acid remains. If any round of coulometry does not confirm the previous value, corrective actions have to be taken.

The second step of the production of acid for Harned cell measurements is gravimetric dilution of the stock acid. The amounts of water and stock acid to be weighed to produce the desired quantity of HCl(aq) with molality 0.01 mol/kg are calculated from the molality of the stock acid, $b_{stock}$, the target molality of the acid (that is 0.01 mol/kg), $b_{acid}$, the desired quantity, $m_{acid}$, and the molar mass of HCl, $M_{HCl}$. To perform the calculation one needs the mass fraction of HCl in both the stock acid and the 0.01 mol/kg HCl(aq). To calculate these mass fractions one assumes to have a quantity of solution containing 1000 g of water. This applies to both the stock acid and the 0.01 mol/kg HCl(aq). With $b_{stock}$ and $b_{acid}$ in mol/kg, $M_{HCl}$ in g/mol and $m_{acid}$ in g, the mass of stock solution to be weighed, $m_{stock}$ in g, is given by:

$$m_{stock} = \frac{\dfrac{m_{acid} \frac{1000\,g}{1000\,g/kg} b_{acid} M_{HCl}}{1000\,g + \frac{1000\,g}{1000\,g/kg} b_{acid} M_{HCl}}}{\dfrac{\frac{1000\,g}{1000\,g/kg} b_{stock} M_{HCl}}{1000\,g + \frac{1000\,g}{1000\,g/kg} b_{stock} M_{HCl}}}$$

The mass of water to be weighed, $m_{water}$, is given in g by:

$$m_{water} = m_{acid} - m_{stock}$$

In the above equations the masses $m_{acid}$, $m_{stock}$ and $m_{water}$ are true masses (i. e. masses in vacuum). Buoyancy correction has to be applied to get the apparent masses that must be used for performing the actual weighing.

Chloride is added to the buffer as sodium chloride. The sodium chloride used is a Merck Urtitersubstanz. Merck has found the following analysis results for the batch of Urtitersubstanz used:

> The amount after drying at 110°C determined by argentometry is found to be within the range 99.95% - 100.05%

| | |
|---|---|
| Bromide | max. 0.005% |
| Hexacyanoferrate | max. 0.000 1% |
| Iodide | max. 0.001% |
| Phosphate | max. 0.000 5% |
| Sulphate | max. 0.001% |
| Total nitrogen | max. 0.001% |
| Heavy metals (as Pb) | max. 0.000 5% |
| Ba (barium) | max. 0.001% |
| Ca (calcium) | max. 0.002% |
| Fe (iron) | max. 0.000 1% |
| K (potassium) | max. 0.01% |
| Mg (magnesium) | max. 0.001% |

The sodium chloride is dried at 500 °C for at least 4 hours, allowed to cool to between 100 °C and 200 °C in the oven, then transferred to a desiccator and left in this over night before being weighed.

The chloride containing buffer is prepared by weighing the sodium chloride, adding this to a flask and then adding buffer to the flask. The buffer is added first by pouring, but as the target mass of buffer is approached the buffer is added using a single use syringe without needle. A little of the buffer is poured into a single use beaker, then drawn into the syringe and added to the flask.

Before producing the chloride containing buffer it is decided what mass of buffer should be used for each molality. This is denoted $m_{buffer}$. The mass of sodium chloride, $m_{NaCl}$, to be added to this mass of buffer is calculated from the molar mass of sodium chloride, $M_{NaCl}$, the water fraction of the buffer, $f_{buffer}$, and the target molality of (sodium) chloride, $b_{Cl}$. With $m_{buffer}$ in g, $M_{NaCl}$ in g/mol and $b_{Cl}$ in mol/kg the mass of sodium chloride to be added, $m_{NaCl}$ in g, is given by:

$$m_{NaCl} = \frac{M_{NaCl} b_{Cl} m_{buffer} f_{buffer}}{1000 g / kg}$$

In the above equation the masses $m_{NaCl}$ and $m_{buffer}$ are true masses (i. e. masses in vacuum). Buoyancy correction has to be applied to get the apparent masses that must be used for performing the actual weighing.

### 1.1.1 Calculation examples

Example of calculation of target for acid production and realised molality:

$b_{stock}$ = 0.100 062 mol/kg with u =0.000 012 mol/kg

$M_{HCl}$ = 36.460 94 g/mol with u = 0.002 0 g/mol

$m_{acid}$ = 1000 g (Specified value, thus no uncertainty)

$b_{acid,\ target}$ = 0.01 mol/kg (Specified value, thus no uncertainty)

$$m_{stock,target} = \frac{\dfrac{1000\ g \cdot \frac{1000\ g}{1000\ g/kg} \cdot 0.01 mol/kg \cdot 36.46094 g/mol}{1000\ g + \frac{1000\ g}{1000\ g/kg} \cdot 0.01 mol/kg \cdot 36.46094 g/mol}}{\dfrac{\frac{1000\ g}{1000\ g/kg} \cdot 0.100062 mol/kg \cdot 36.46094 g/mol}{1000\ g + \frac{1000\ g}{1000\ g/kg} \cdot 0.100062 mol/kg \cdot 36.46094 g/mol}} \Leftrightarrow$$

$$m_{stock,target} = 100.27 g$$

$$m_{water,target} = 1000\ g - 100.27\ g = 899.73\ g$$

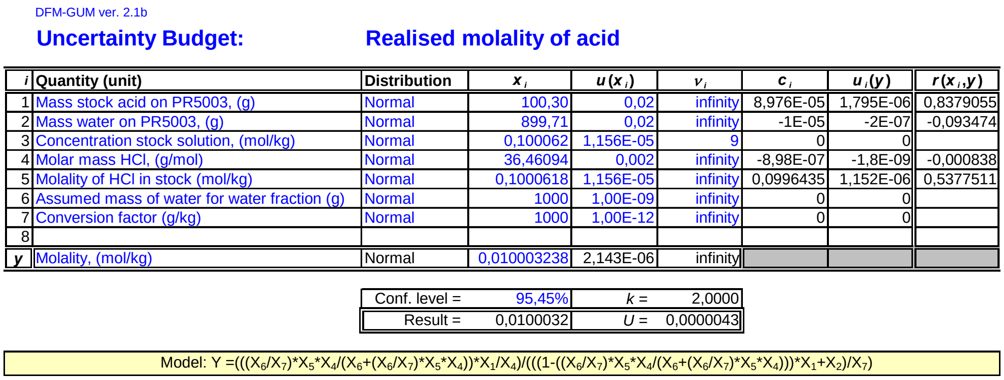
DFM actually uses no correction for buoyancy for the production of the hydrochloric acid. Thus these masses are also the target masses in air.

The realised weighing results for the IPQ-DFM bilateral comparison run were (both as masses in air):

$m_{stock,\ target}$ = 100.30 g

$m_{water,\ target}$ = 899.71 g

These are inserted into an uncertainty spreadsheet. The calculation and result is seen from the picture below. Both the assumed mass of water for calculating the water fraction and the conversion factor between g and kg must be given an uncertainty for the calculation to work. Very small uncertainties are assigned to these quantities, to make the contribution to the uncertainty of the molality insignificant.



DFM-GUM ver. 2.1b

**Uncertainty Budget:** **Realised molality of acid**

| $i$ | Quantity (unit) | Distribution | $x_i$ | $u(x_i)$ | $\nu_i$ | $c_i$ | $u_i(y)$ | $r(x_i,y)$ |
|---|---|---|---|---|---|---|---|---|
| 1 | Mass stock acid on PR5003, (g) | Normal | 100,30 | 0,02 | infinity | 8,976E-05 | 1,795E-06 | 0,8379055 |
| 2 | Mass water on PR5003, (g) | Normal | 899,71 | 0,02 | infinity | -1E-05 | -2E-07 | -0,093474 |
| 3 | Concentration stock solution, (mol/kg) | Normal | 0,100062 | 1,156E-05 | 9 | 0 | 0 | |
| 4 | Molar mass HCl, (g/mol) | Normal | 36,46094 | 0,002 | infinity | -8,98E-07 | -1,8E-09 | -0,000838 |
| 5 | Molality of HCl in stock (mol/kg) | Normal | 0,1000618 | 1,156E-05 | infinity | 0,0996435 | 1,152E-06 | 0,5377511 |
| 6 | Assumed mass of water for water fraction (g) | Normal | 1000 | 1,00E-09 | infinity | 0 | 0 | |
| 7 | Conversion factor (g/kg) | Normal | 1000 | 1,00E-12 | infinity | 0 | 0 | |
| 8 | | | | | | | | |
| $y$ | Molality, (mol/kg) | Normal | 0,010003238 | 2,143E-06 | infinity | | | |

| | | | |
|---|---|---|---|
| Conf. level = | 95,45% | $k$ = | 2,0000 |
| Result = | 0,0100032 | $U$ = | 0,0000043 |

Model: $Y =(((X_6/X_7)*X_5*X_4/(X_6+(X_6/X_7)*X_5*X_4))*X_1/X_4)/(((1-((X_6/X_7)*X_5*X_4/(X_6+(X_6/X_7)*X_5*X_4)))*X_1+X_2)/X_7)$

Example of calculation of target for addition of chloride to buffer and realised molality:

$b_{Cl,\ target}$ = 0.01 mol/kg (Specified value, thus no uncertainty)

$m'_{buffer}$ = 800 g in air (Specified value, thus no uncertainty)

$f_{buffer}$ = 0.994 526 98 g/g with u = 0.000 000 14 g/g

$M_{NaCl}$ = 58.442 769 28 g/mol with u = 0.002 0 g/mol

In the target calculation is used a buoyancy correction factor $\alpha_{buffer}$ = 1.001 053 g in vacuum/g in air for correction of the buffer mass in air to true mass. This buoyancy correction factor is chosen to reflect typical climate conditions during weighing at DFM. Using this buoyancy correction factor it is found that:

$m_{buffer} = m'_{buffer}\alpha_{buffer}$ = 800.842 4 g in vacuum.

This is inserted in the equation for calculating the target mass of NaCl in vacuum, i. e.

$$m_{NaCl,\,target} = \frac{58.44276928\ g/mol \cdot 0.01\ mol/kg \cdot 800.8424\ g \cdot 0.99452698\ mol/kg}{1000\ g/kg} \Leftrightarrow$$

$$m_{NaC,\,target} = 0.46547\ g$$

The buoyancy correction factor used in the target calculation for NaCl is $\alpha_{NaCl}$ = 1.000 406 g in vacuum/g in air. This buoyancy correction factor too is chosen to reflect typical climate conditions during weighing at DFM. Thus the target mass of NaCl in air is found as:

$m'_{NaCl,\ target} = m_{NaCl,\ target}/\alpha_{NaCl}$ = 0.465 28 g in air.

The realised weighing results for the IPQ-DFM bilateral comparison run were:

$m'_{buffer}$ = 799.98 g in air

$m'_{NaCl}$ = 0.465 29 g in air

For the conversion of realised masses in air to true masses are used buoyancy correction factors based on the climate conditions at the time of the weighing. For the IPQ-DFM bilateral comparison the buoyancy correction factors are:

$\alpha_{buffer}$ = 1.001 031 g in vacuum/g in air

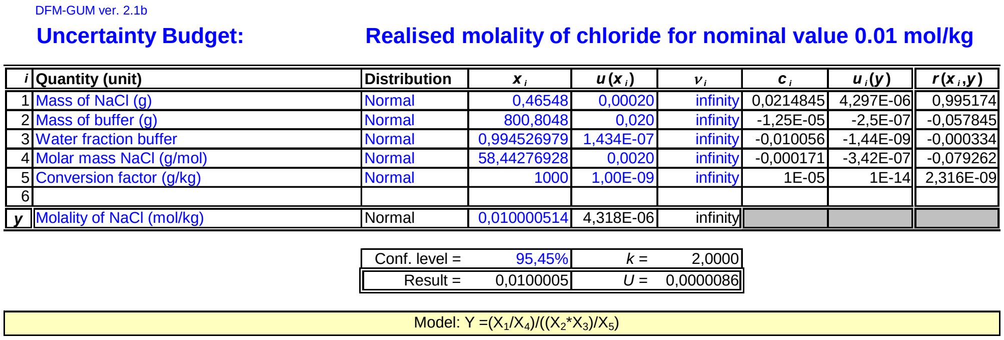
$\alpha_{NaCl}$ = 1.000 397 g in vacuum/g in air

The corresponding masses in vacuum are then found to be:

$m_{buffer}$ = 800.804 8 g in vacuum

$m_{NaCl}$ = 0.465 48 g in vacuum

These values are inserted into an uncertainty spreadsheet. The calculation and result is seen from the picture below. The conversion factor between g and kg must be given an uncertainty for the calculation to work. A very small uncertainty is assigned to this quantity, to make the contribution to the uncertainty of the molality insignificant.



DFM-GUM ver. 2.1b

**Uncertainty Budget:** **Realised molality of chloride for nominal value 0.01 mol/kg**

| *i* | **Quantity (unit)** | **Distribution** | $x_i$ | $u(x_i)$ | $\nu_i$ | $c_i$ | $u_i(y)$ | $r(x_i,y)$ |
|---|---|---|---|---|---|---|---|---|
| 1 | Mass of NaCl (g) | Normal | 0,46548 | 0,00020 | infinity | 0,0214845 | 4,297E-06 | 0,995174 |
| 2 | Mass of buffer (g) | Normal | 800,8048 | 0,020 | infinity | -1,25E-05 | -2,5E-07 | -0,057845 |
| 3 | Water fraction buffer | Normal | 0,994526979 | 1,434E-07 | infinity | -0,010056 | -1,44E-09 | -0,000334 |
| 4 | Molar mass NaCl (g/mol) | Normal | 58,44276928 | 0,0020 | infinity | -0,000171 | -3,42E-07 | -0,079262 |
| 5 | Conversion factor (g/kg) | Normal | 1000 | 1,00E-09 | infinity | 1E-05 | 1E-14 | 2,316E-09 |
| 6 |  |  |  |  |  |  |  |  |
| *y* | Molality of NaCl (mol/kg) | Normal | 0,010000514 | 4,318E-06 | infinity |  |  |  |

| | | | |
|---|---|---|---|
| Conf. level = | 95,45% | *k* = | 2,0000 |
| Result = | 0,0100005 | *U* = | 0,0000086 |

Model: $Y = (X_1/X_4)/((X_2 * X_3)/X_5)$

## 1.2 Electrodes

Silver oxide is prepared by mixing a solution of analytical grade silver nitrate with a solution of analytical grade sodium hydroxide. The molarity of the silver nitrate solution is ~0.98 mol/L and the sodium hydroxide solution has molarity ~1 mol/L. The resulting precipitate is washed repeatedly in deionised water until the conductivity of the water after washing is constant and below 30 μS/cm. The precipitate is then filtered using vacuum, and the silver oxide stored for minimum one month prior to use. The silver oxide is stored humid and in darkness.

The silver/silver chloride electrodes are prepared by a paste of the silver oxide prepared above and deionised water being deposited onto a platinum helix. The silver oxide is thermally decomposed to silver. When a sufficient amount of silver (100 mg - 250 mg) has been deposited, about 20% of the silver is converted to silver chloride by electrolytic oxidation in 0.1 mol/L hydrochloric acid. The silver/silver chloride electrodes are then stored in hydrochloric acid with molality 0.005 mol/kg for at least one month before use. The silver/silver chloride electrodes used by DFM for the IPQ-DFM bilateral comparison were prepared between 2008-01-02 and 2008-01-10 both dates included. The electrodes were first used for measurements in March 2008.

Prior to every experiment the electrodes are checked for consistency of the set. Starting two days before the measurements are started the electrodes are placed in deionised water for between 1 hour and 3 hours, then in argon bubbled sodium chloride with molality 0.01 mol/kg for at least 24 hours. The potential of each electrode against a silver/silver chloride electrode of a different batch is then measured in this solution. The electrodes are only used if the difference between highest and lowest potential does not exceed 40 μV. The electrodes are left in the sodium chloride solution over night. Before mounting in the cells, the electrodes again are placed in deionised water for between 1 hour and 3 hours. Just before mounting, they are dabbed gently with filter paper to remove adhering water.

DFM regenerates the platinum hydrogen electrodes prior to every primary pH experiment. Two days before starting the measurements the platinum hydrogen electrodes are cleaned by boiling in 6 mol/L nitric acid, rinsed three times in deionised water and boiled in deionised water. Then the electrodes are annealed until redglowing by heating in a pure methanol flame. The electrodes are then electrolytically cleaned in 0.1 mol/L nitric acid, first as anode for 1 minute, then as cathode for 4 minutes. After this a fresh layer of platinum black is electrodeposited onto the electrodes. The electrodes are left in deionised water over night. The next day the electrodes are placed in a hydrogen bubbled hydrochloric acid with molality 0.01 mol/kg for at least 3 hours. One electrode is chosen as reference and the potentials of the others measured against this. If the difference between highest and lowest potential exceeds 40 μV, the electrodes are not used. After measuring the potentials the electrodes are left in deionised water over night. Before inserting the electrodes in the Harned cells, they are dabbed gently with filter paper to remove adhering water.

## 1.3 Cells and hydrogen flow

The cell is shown in the picture below. The total volume of the cell is ~100 mL of which the humidifier part is ~60 mL. The flowrate of hydrogen in each cell is not really known, but is 4 mL/min to 8 mL/min.

## 1.4 Experimental procedure

Twelve cells are used for the experiment. They are placed in a 150 L water bath used for temperature control of the cells. The cells are divided into four groups of three cells each. The groups are hydrochloric acid with molality 0.01 mol/kg, buffer with sodium chloride molality ~0.005 mol/kg, buffer with sodium chloride molality ~0.010 mol/kg and buffer with sodium chloride molality ~0.015 mol/kg.

The twelve cells are connected to a vacuum pump and an argon source. The cells are evacuated to a pressure low than 10 mbar. Then argon is applied to get atmospheric pressure in the cells. This is repeated three times totally. Then the cells are opened towards the atmosphere and argon is flushed through the cells at about 5 mbar overpressure for 10 minutes. Then the cells are closed, and each cell filled with the appropriate measurement solution which is forced into the cell by an overpressure of argon. The hydrogen flow in each cell is started as soon as the cell is filled. Filling all the cells takes between 90 minutes and 120 minutes.

During filling, the temperature control is not applied. The set-up is placed in a room with the room temperature controlled to be 23 °C ± 0.5 °C. The experiment is started at 25 °C and it takes typically around 2 hours to achieve a temperature close to 25 °C in the water bath and thus in the cells. Then the temperature setpoint often has to be adjusted to achieve an operating temperature that is 25 °C ± 0.005 °C. This may take up to 2 hours more. Between completion of the filling and achieving the correct operating temperature the hydrogen flow in each cell is adjusted to an appropriate flow.

Measurements start automatically when the temperature is within 0.2 °C of the nominal temperature. A round of measurements consists in measuring the temperature three times, then the twelve potentials, then the atmospheric pressure and finally temperature another three times. The six temperature measurements are averaged, and the potentials and pressure are assigned to have been measured at the average temperature. One round of measurements is done every 30 minutes.

The stability criteria are described below, but typically it takes 5 hours - 6 hours from completion of the filling before stability is achieved. When changing the temperature during the experiment, there is a time lapse of 2 hours to 4 hours during which no measurements are done. This is the time it takes to heat or cool to the new temperature. Measurements start automatically when the temperature is within 0.2 °C of the nominal temperature. From the time where measurements start, it usually takes between 30 minutes and 2 hours to achieve stability at the new temperature including adjustment of the temperature setpoint to achieve an operating temperature that is within ± 5 mK of the nominal temperature.

Once sufficient data has been collected at 25 °C, the nominal temperature is changed to 37 °C and data are collected at this temperature. When sufficient data are acquired at 37 °, the temperature is changed to 15 °C and measurements done at this temperature. Finally, the temperature is changed back to 25 °C to check that no changes in buffer properties have occurred during the experiment.

## 1.5 Potential selection and stability criteria

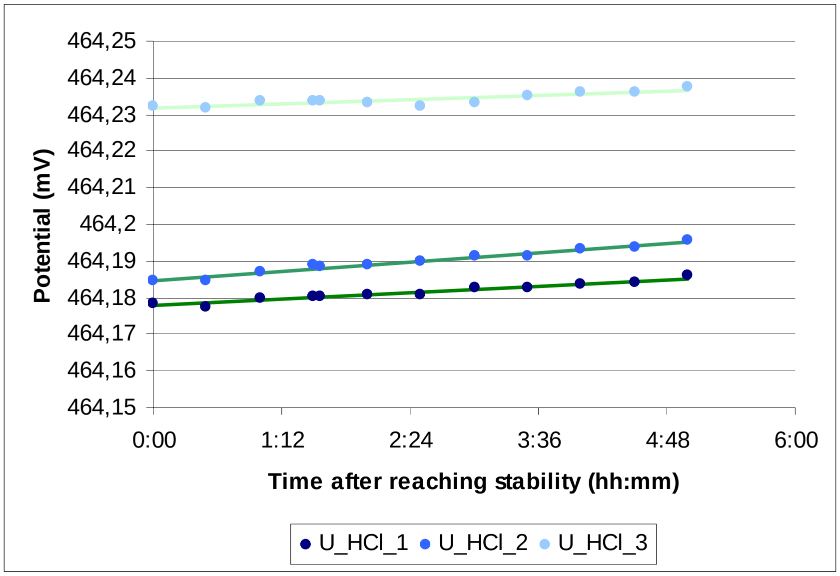
A time interval of minimum 4 hours is used for the calculation of the acidity function at zero chloride molality. This time interval is chosen to be the same for each of the four groups of cells. This time interval is chosen so, that each group of cells fulfil the criteria given below and the measured temperature is stable within ±2 mK in the time interval. The time interval is chosen to be as long as possible. The time interval may start at any time after the start of the experiment, where the stability criteria are met, and will end if the stability criteria are no longer met. In practice, less than twelve cells might be used, as some cells might not fulfil the criteria and are thus left out of the calculation.

The measured potentials are considered stable if the potential changes by no more than ±10 μV/h for each cell. Single points may deviate more than this, but this is an exception. During the time interval used the potentials in the three cells with hydrochloric acid measured at nominally the same time are not allowed to differ more from each other than 60 μV. For cells containing buffer with the same molality of sodium chloride the potentials measured at nominally the same time are not allowed to differ more from each other than 100 μV.

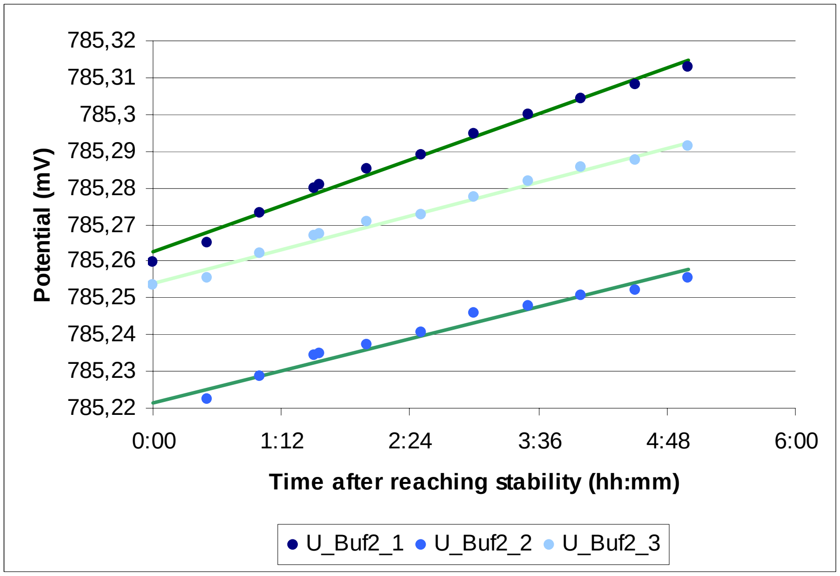
The measurement software automatically corrects the measured voltage for calibration error of the digital voltmeter used for the measurements and for the hydrogen pressure. The partial pressure of hydrogen is calculated from the measured atmospheric pressure and the measured average temperature using an equation for the vapour pressure of water as a function of temperature. The vapour pressure of water is subtracted from the atmospheric pressure and the result of this is taken as the partial pressure of hydrogen.

Examples of curves of potential as a function of time during the time when the potentials are considered stable are shown below. The temperature in both cases is 25ºC. The first curve is the hydrochloric acid cells and the second is buffer with ~0,010 m chloride. The potentials used in the calculation of the pH value are the intercept of linear regressions of the potential of a cell as a function of time. The potentials are referred to the time when stability is achieved. The linear fits are also shown on the figures below.

The uncertainty of each potential is found by combining two contributions. The first contribution, which is by far the smallest, is the uncertainty of the intercept of the regressions. The second contribution is the uncertainty associated with the allowed scatter between the cells within a group. For the hydrochloric acid cells the standard uncertainty of this second contribution is equal to 60 μV divided by two times the squareroot of 3, that is $u_{scatter} = 60\mu V/(2\sqrt{3}) = 17\mu V$ . For the buffer cells one finds analogously $u_{scatter} = 100\mu V/(2\sqrt{3}) = 29\mu V$ .



Potential (mV)
464,25
464,24
464,23
464,22
464,21
464,2
464,19
464,18
464,17
464,16
464,15
0:00
1:12
2:24
3:36
4:48
6:00
Time after reaching stability (hh:mm)
● U_HCl_1 ● U_HCl_2 ● U_HCl_3



Potential (mV)
785,32
785,31
785,3
785,29
785,28
785,27
785,26
785,25
785,24
785,23
785,22
0:00
1:12
2:24
3:36
4:48
6:00
Time after reaching stability (hh:mm)
● U_Buf2_1 ● U_Buf2_2 ● U_Buf2_3

# 2 Calculation of result and uncertainty

DFM has employed a new scheme of calculating uncertainty based on a method and software developed by Lars Nielsen, DFM[a].

The scheme takes as its input the vector of the directly observed (that is measured or otherwise estimated) quantities $\{z\}$ with the covariance matrix $\{\{\Sigma\}\}$. A model is set up based on:

1) the 'true value' of the directly observed quantities $\{\zeta\}$, which have been estimated by $\{z\}$
2) parameters with no prior information $\{\beta\}$
3) physical or mathematical constraints between the parameters $\{f(\zeta, \beta)=0\}$.

The direct observables $\{\zeta\}$ and the parameters $\{\beta\}$ are then found using Lagrange multipliers $\{\lambda\}$ by minimising the quantity $\Theta$, given by

$$\Theta(\beta,\zeta,\lambda;z)=(z-\zeta)^T\,\Sigma^{-1}(z-\zeta)+2\lambda^T\ f(\beta,\zeta)$$

The uncertainties of the directly observed quantities $\{z\}$ are propagated via the minimised quantity $\Theta$, thus the uncertainties and correlation coefficients of $\zeta$ and $\beta$ are found directly from the calculation.

The example values given below are for carbonate buffer and have nothing to do with the measurements done for the bilateral comparison between DFM and IPQ.

For calculating uncertainty of a complete primary pH experiment, we have the following 49 directly observed quantities, the $z$-vector, which are estimates of the corresponding 'true values' in the $\zeta$-vector. The standard uncertainties of the $z$-quantities are shown (the correlations among the balance parameters are used, but not shown).

---

[a] L. Nielsen, "Least-squares estimation using Lagrange multipliers", Metrologia 35 (1998), 115–118. Erratum, Metrologia 37 (2000), 183. Implemented in the software package DFM-GUM Analyzer©.

| **Quantity group** | **Quantity name** | $z_i$ | $x$ | $u(x)$ | **Unit** |
|---|---|---|---|---|---|
| Buoyancy corrections | WeighingLabTemperature | $z_1$ | 26 | 0,5 | $^{o}$C |
| | WeighingLabRH | $z_2$ | 0,36 | 0,05 | 1 |
| | WeighingLabPressure | $z_3$ | 101750 | 100 | Pa |
| | CO2MolefractionLab | $z_4$ | 0,0004 | 0,0001 | 1 |
| | AirDensCorrection | $z_5$ | 1 | 0,000065 | 1 |
| | HClDensity | $z_6$ | 998 | 1 | kg/m$^3$ |
| | NaClDensity | $z_7$ | 2160 | 1 | kg/m$^3$ |
| | WaterDensity | $z_8$ | 998 | 1 | kg/m$^3$ |
| | SolutionDensity | $z_9$ | 998 | 1 | kg/m$^3$ |
| Buffer production | Water fraction in buffer | $z_{10}$ | 0,995221 | 0,000001 | |
| Buffer with chloride | MassIndicationBufferLC | $z_{11}$ | 800,42 | 0,02 | g |
| | MassIndicationNaClLow-Chloride | $z_{12}$ | 0,23281 | 0,00005 | g |
| | MassIndicationBufferMC | $z_{13}$ | 800,03 | 0,02 | g |
| | MassIndicationNaClMed-Chloride | $z_{14}$ | 0,46557 | 0,00005 | g |
| | MassIndicationBufferHC | $z_{15}$ | 800,04 | 0,02 | g |
| | MassIndicationNaClHigh-Chloride | $z_{16}$ | 0,69845 | 0,00005 | g |
| | MolarMassNaCl | $z_{17}$ | 58,4428 | 0,002 | kg/mol |
| Acid | MassIndicationStockAcid | $z_{18}$ | 100,19 | 0,01 | div |
| | MassIndicationWaterAcid | $z_{19}$ | 899,8 | 0,02 | div |
| | MolarMassHCl | $z_{20}$ | 36,46094 | 0,002 | kg/mol |
| | ConcentrationStockAcid | $z_{21}$ | 0,10013 | 1,41E-05 | 1 |
| | MassFractionHClInStock | $z_{22}$ | 0,0036376 | 0,0000001 | 1 |
| Balance parameters | f_AT201 | $z_{23}$ | 1,0000013 | 0,0000007 | g/div |
| | A_AT201 | $z_{24}$ | -1,37E-08 | 1,017E-08 | 1/div |
| | B_AT201 | $z_{25}$ | 5,425E-11 | 3,462E-11 | 1/div$^2$ |
| | f_PR5003 | $z_{26}$ | 1,0000023 | 1,49E-06 | g/div |
| | A_PR5004 | $z_{27}$ | 2,004E-09 | 1,417E-09 | 1/div |
| | B_PR5005 | $z_{28}$ | -2,93E-13 | 2,498E-13 | 1/div$^2$ |
| | LongtermStabilityAT201 | $z_{29}$ | 1 | 7,5E-07 | 1 |
| | LongtermStabilityPR5003 | $z_{30}$ | 1 | 4,0E-06 | 1 |
| Constants | GasConstant | $z_{31}$ | 8,314472 | 0,000015 | J/(mol K) |
| | StandardPressure | $z_{32}$ | 101325 | 0,1 | Pa |
| | FaradayConstant | $z_{33}$ | 96485,3383 | 0,0083 | C/mol |
| Potentials referred to start | PotentialHCl1 | $z_{34}$ | 0,4643078 | 1,70E-05 | V |
| | PotentialHCl2 | $z_{35}$ | 0,4643084 | 1,70E-05 | V |
| | PotentialHCl3 | $z_{36}$ | 0,4642843 | 1,70E-05 | V |
| | PotentialLowCl1 | $z_{37}$ | 0,9562611 | 2,90E-05 | V |
| | PotentialLowCl2 | $z_{38}$ | 0,9562573 | 2,90E-05 | V |
| | PotentialLowCl3 | $z_{39}$ | 0,9561499 | 1,00E+02 | V |
| | PotentialMedCl1 | $z_{40}$ | 0,9379536 | 1,00E+02 | V |
| | PotentialMedCl2 | $z_{41}$ | 0,9379927 | 1,00E+02 | V |
| | PotentialMedCl3 | $z_{42}$ | 0,9380784 | 2,90E-05 | V |
| | PotentialHighCl1 | $z_{43}$ | 0,9273226 | 2,90E-05 | V |
| | PotentialHighCl2 | $z_{44}$ | 0,9273425 | 2,90E-05 | V |
| | PotentialHighCl3 | $z_{45}$ | 0,9273234 | 2,90E-05 | V |
| DVM | DVMError | $z_{46}$ | 0 | 8,00E-06 | 1 |
| Environment | AveragePressure | $z_{47}$ | 101325 | 10 | Pa |
| | AverageTemperature | $z_{48}$ | 25,0048 | 0,005 | $^{o}$C |
| Activity | ActivityCoefficientHCl | $z_{49}$ | 0,90426 | 0,0001 | 1 |

Cells that are excluded, have uncertainty $u$ = 100 V. This will cause them to have negligible weight in the adjustment of $\zeta$ and $\beta$.

We identify 21 quantities with no prior information (i. e. which we want to determine), the $\beta$-vector, here shown with the result from the mathematical solution:

| Quantity group | Quantity name | $\beta_i$ | $x$ | $u(x)$ | Unit |
|---|---|---|---|---|---|
| Buoyancy corrections | AirDensity | $\beta_1$ | 1,1798764 | 0,0025432 | kg/m$^3$ |
| | HClBuoyancyCorrection | $\beta_2$ | 1,001036 | 2,531E-06 | |
| | NaClBuoyancyCorrection | $\beta_3$ | 1,000399 | 8,969E-07 | |
| | WaterBuoyancyCorrection | $\beta_4$ | 1,001036 | 2,531E-06 | |
| | SolutionBuoyancyCorrection | $\beta_5$ | 1,001036 | 2,531E-06 | |
| Buffer with chloride | MolalityLowChloride | $\beta_6$ | 0,0049975 | 1,09E-06 | mol/kg |
| | MolalityMedChloride | $\beta_7$ | 0,0099989 | 1,151E-06 | mol/kg |
| | MolalityHighChloride | $\beta_8$ | 0,0150001 | 1,249E-06 | mol/kg |
| Acid | MolalityAcid | $\beta_9$ | 0,0099992 | 1,678E-06 | mol/kg |
| HCl potential | AveragePotentialHCl | $\beta_{10}$ | 0,4643001 | 9,823E-06 | V |
| Acidity function | AcidityFunctionLowCl1 | $\beta_{11}$ | 10,101822 | 0,0004446 | |
| | AcidityFunctionLowCl2 | $\beta_{12}$ | 10,101822 | 0,0004446 | |
| | AcidityFunctionLowCl3 | $\beta_{13}$ | 10,101822 | 0,0004446 | |
| | AcidityFunctionMedCl1 | $\beta_{14}$ | 10,096002 | 0,000353 | |
| | AcidityFunctionMedCl2 | $\beta_{15}$ | 10,096002 | 0,000353 | |
| | AcidityFunctionMedCl3 | $\beta_{16}$ | 10,096002 | 0,000353 | |
| | AcidityFunctionHighCl1 | $\beta_{17}$ | 10,090183 | 0,0003946 | |
| | AcidityFunctionHighCl2 | $\beta_{18}$ | 10,090183 | 0,0003946 | |
| | AcidityFunctionHighCl3 | $\beta_{19}$ | 10,090183 | 0,0003946 | |
| Linear regression | AcidityFunctionSlope | $\beta_{20}$ | -1,163672 | 0,045676 | |
| | AcidityFunctionIntercept | $\beta_{21}$ | 10,107638 | 0,0006126 | |

The quantities are constrained by a set of 30 functional constraints describing the relations among the parameters, put in a form of $f(\zeta, \beta)=0$. The purpose of the functions is to ensure the propagation of uncertainties from the measured quantities. One advantage of this form is the possibility to use multivariate and implicit expressions. The following illustrates how the constraints are set up.

Air density: The 'unknown quantity' $\beta_1$ is the air density, which is 'constrained' by the BIPM standard formula with the laboratory environmental parameters temperature, humidity, etc., $\zeta_1$ through $\zeta_5$ by

$$f_1 : \rho_{air}(\zeta_1, \zeta_2, \zeta_3, \zeta_4, \zeta_5) - \beta_1 = 0$$

Buoyancy correction: There are four buoyancy correction factors, $\beta_2$ through $\beta_5$, for HCl, NaCl, water and solution, again handled as 'unknown quantities'. Each is constrained to substance density and air density by a relation, e.g. here given for HCl:

$$f_2 : \left(1 - \frac{\beta_1}{8000}\right) / \left(1 - \frac{\beta_1}{\zeta_6}\right) - \beta_2 = 0$$

Molalities: Four molalities are used, given by the parameters $\beta_6$ through $\beta_9$. The starting point for the constraint function is the indication on the balance of the aliquot of buffer solution and NaCl, e.g. for the buffer with low chloride addition, $\zeta_{11}$ and $\zeta_{12}$. The measurement capability of the balance is taken into account by using a scale factor and a second order correction of the indication, determined from calibration, a long term stability factor and the buoyancy correction factor, hence a relation similar to

$$m_{true} = f_{stability}\ f_{scale}\ m_I \left(1 + A m_I + B m_I^2\right) f_{buoyancy}$$

E.g. the true mass of the weighed low chloride expanded becomes

$$m_{true} = \zeta_{29}\ \zeta_{23}\ \zeta_{11}\left(1 + \zeta_{24}\,\zeta_{11} + \zeta_{25}\,\zeta_{11}^2\right)\beta_3$$

This expression is incorporated into the molality constraint that, again for low chloride addition, using the molar mass for NaCl and the water fraction of the buffer becomes:

$$f_6 : \frac{m_{true,\,NaCl}}{\zeta_{17}\ m_{true,\,buffer}\ \zeta_{10}} - \beta_6 = 0$$

Similar equations apply for the other chloride molalities and for the acid molality.

The measured potentials in the HCl cells are used to determine an average potential[a], which is introduced as parameter $\beta_{10}$. The constraint functions are:

$$f_{10\ldots12} : \zeta_{34\ldots36} - \beta_{10} = 0$$

The nine acidity function values are $\beta_{11}$ through $\beta_{19}$. The cell potentials ($\zeta_{37}$ through $\zeta_{45}$) are quantities estimated from the measurement, while natural constants (e.g. the Faraday constant, $\zeta_{33}$) are taken from tables and literature. The constraint functions have the form (here for low chloride, cell 1)

$$f_{13} : \frac{(\zeta_{37} - \beta_{10})(1 + \zeta_{46})\zeta_{33}}{\zeta_{31}(\zeta_{48} + 273.15)\ln 10} - 2\log\beta_9\zeta_{49} + \log\beta_6 + \tfrac{1}{2}\log\frac{\zeta_{32}}{\zeta_{47}} - \beta_{11} = 0$$

The linear regression is parameterised through slope and intercept as parameters $\beta_{20}$ and $\beta_{21}$. Constraint functions then relate the acidity function values $\beta_{11}$ through $\beta_{19}$ to the linear fit using the relevant chloride molality ($\beta_6$ through $\beta_8$):

$$f_{22\ldots30} : \beta_{20}\ \beta_{6/7/8} + \beta_{21} - \beta_{11\ldots19} = 0$$

The example given here has the acidity function intercept at zero chloride molality, $\beta_{21}$, as the final result of calculation.

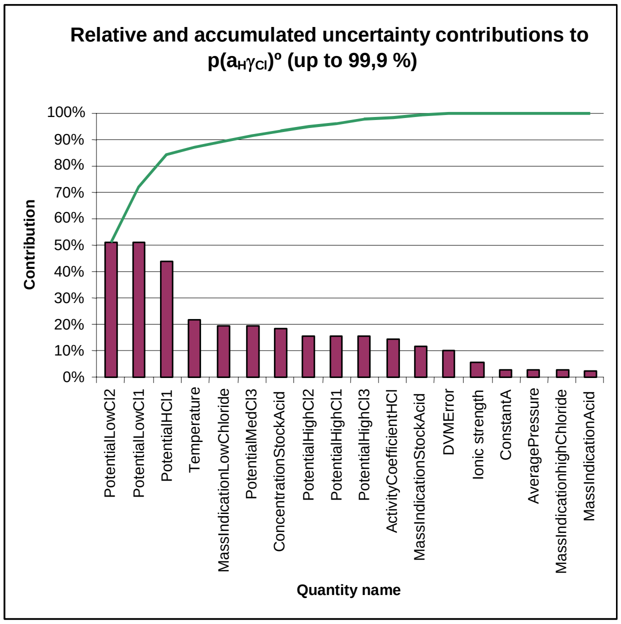
---

[a] The standard potential of the silver/silver chloride electrode is not calculated as part of the calculation of the pH value. Instead the term involving the mean activity of HCl is included in the equation for the acidity function.

Usually the pH value is the final result of the calculation. In that case the scheme is expanded with the ionic strength of the buffer and the two ‘constants’ of the Bates-Guggenheim convention as directly observed quantities, with the logarithm of the chloride ion activity coefficient at zero chloride molality and the pH as quantities with no prior information and finally with two constraint functions tied to the logarithm of the chloride ion activity coefficient at zero chloride molality and the pH.

The minimisation of the quantity $\Theta$ is (usually) done iteratively and a solution yields not only adjusted values (solutions) to $\zeta$ and $\beta$, but also uncertainties and the complete covariance or correlation matrix, and allows for a chi-square test of the overall consistency of the model. Consistency is rejected, if the chi-square probability is less than 5 %. If a solution requires that, say $\zeta_{37}$ must be adjusted more than twice the uncertainty of the measured value $z_{37}$, then one should look closer at the uncertainty estimate of this quantity. A plot of the normalized deviations $(\zeta - z)/u(\zeta - z)$ give an overview of possible problematic quantities.

From the resulting covariance matrix it is possible to calculate the contribution of the measured quantities to the final parameter, the acidity function intercept at zero chloride molality, $\beta_{21}$. In case the calculation has the pH value as the final result, this type of calculation is done for the pH value instead of the acidity function intercept at zero chloride molality.



Relative uncertainty contribution $u(x_i)/u(y)$
Acidity function intercept

# 8 Appendix 3

The report of IPQ is given on the following 12 pages.

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# EURAMET Project 1051

# IPQ Report for

# IPQ-DFM Bilateral Comparison on Phosphate Buffer- 2008

Instituto Português da Qualidade
Ministério da Economia e Inovação

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**This work was conducted in cooperation between the Portuguese Institute for Quality (IPQ) and Danish Fundamental Metrology Ltd. (DFM) by**

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## Contents

## 1. Introduction

The aim of this study was a bilateral comparison on phosphate buffer.

The buffer measured was a physiological phosphate buffer 0,03043 mol kg$^{-1}$ $Na_2HPO_4$ and 0,008695 mol kg$^{-1}$ $KH_2PO_4$. This buffer was prepared by DFM.

Measurements were performed from 2008-07-20 to 2008-08-05.

## 2. Solution preparation

### 2.1. Hydrochloric acid solution

Hydrochloric acid solution (molality 0,01 mol kg$^{-1}$) was prepared by measuring the appropriate volume of a stock solution of HCl / 30% (Merck Suprapur®; lot no ZC812418735, Ref. 1.00318.0250), and adding the corresponding weight of ultra pure water (Millipore® Milli-Q Advantage system).

The molality (± expanded uncertainty, $k$ = 2) of the hydrochloric acid used for measurement of standard potential, mol kg$^{-1}$, was:

$$m_{\mathrm{HCl}} = 0{,}009687 \pm 0{,}000005$$

### 2.2. Buffer with Chloride ion solution

NaCl (Merck Suprapur®; 99,99; lot no BO144006734, Ref. 1.06406.0050) was added to aliquots of the phosphate buffer to yield solutions with added molalities of NaCl, $m_{\mathrm{NaCl}}$, equal to 0,005 mol kg$^{-1}$, 0,010 mol kg$^{-1}$, and 0,015 mol kg$^{-1}$. NaCl was dried at 110 °C before use until constant weight.

## 3. Electrodes

The electrodes used on this bilateral comparison have been prepared in November 2007. The electrodes consist of a glass body with sealed-in platinum wire.

### 3.1. Ag│AgCl Electrodes

The base for the each silver-silver chloride electrode is a helix of platinum wire sealed into the end of a glass tube.

Before preparation is started, the electrodes are chemically cleaned.

Silver chloride electrodes were prepared by means of the thermal-electrolytic method. For each silver-silver chloride electrode a thick paste of well-washed silver oxide and water is applied to each helix. The electrodes are suspended in a furnace heated to about 450 ºC until they are completely white. Successive layers of silver oxide are applied until a smooth surface is obtained. A part of the silver formed in this way is then converted to silver chloride by electrolysis in a 0,1 M solution of hydrochloric acid from Merck Suprapur®, HCl / 30%. The completed electrodes are stored in a 0,005 mol kg$^{-1}$ HCl for 2 weeks prior to their first use in Harned cells. Their potentials are then compared and individual electrodes that differ from the average of the group by more than 0,1 mV are rejected.

Between measurements, the electrodes were stored in 0,005 mol kg$^{-1}$ HCl.

### 3.2. Pt│$H_2$ Electrodes

For the hydrogen electrodes the platinum wire is spot-welded to the edge of the platinum foil.

The platinization of each hydrogen electrode is made with the platinum black. Each electrode is electrolyticaly platinized under a current of 200 mA to 400 mA for 1 to 3 minutes.

Following platinization, the Pt electrodes were rinsed in a stream of water and stored in deionized water between uses.

Electrodes are highly stable and reproducible.

## 4. Measurement cell

The picture of the measurement cell is in Figure 1.

The material of the hydrogen inlet tubing is PVC.

Volume of solution for filling one measurement cell ca. 50 mL.

Volume of buffer solution in $H_2$ gas bubbler is ca. 2 mL.

Flow rate of hydrogen is about 1-2 bubbles/s

Hydrogen bubbles diameter in measurement space is about 1-2 mm.

The criterion for voltage stability is below 30 µV and average voltage stabilisation time is about 1 hour.

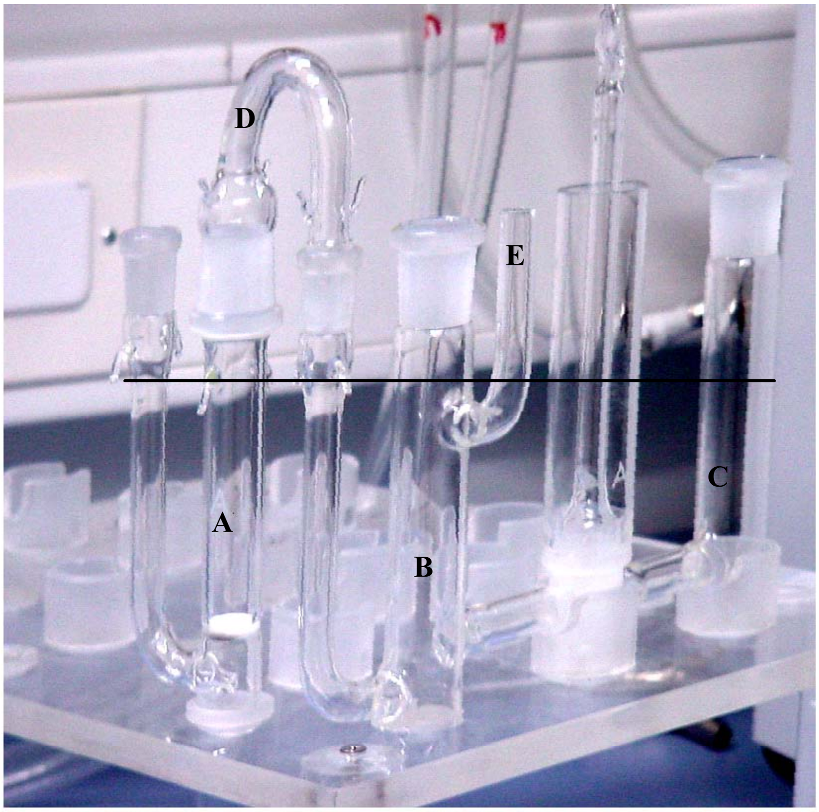

Fig. 1. Harned cell vessel. The horizontal line indicates the cell vessel immersion level.

A - $H_2$ gas bubbler

B - Pt, $H_2$ (g) electrode compartment

C - Ag, AgCl electrode compartment

D - Head space

E - $H_2$ (g) outlet

## 5. Measurement Procedure

The primary procedure for pH assessment is our standard protocol laboratory 43000.08506-01. This is based on measurement of the potential difference between a platinum-hydrogen electrode and a silver-silver chloride reference electrode of an electrochemical cell without liquid junction, known as the Harned cell:

$$\mathrm{Pt} \mid \mathrm{H_2}\ (\mathrm{g},\ 101325\ \mathrm{Pa}) \mid \mathrm{Buffer} + \mathrm{Cl^-} \mid \mathrm{AgCl, Ag} \qquad (1)$$

This electrochemical cell is filled with a selected buffer solution, to which chloride ions are added at chloride molalities of 0,005 mol $kg^{-1}$, 0,010 mol $kg^{-1}$ and 0,015 mol $kg^{-1}$, enabling use of the silver-silver chloride electrode.

The experiment is performed in a ‘‘WALKIN’’ climatic chamber with temperature control of ± 0,01 ºC. The primary measurement device is shown in figure 2.

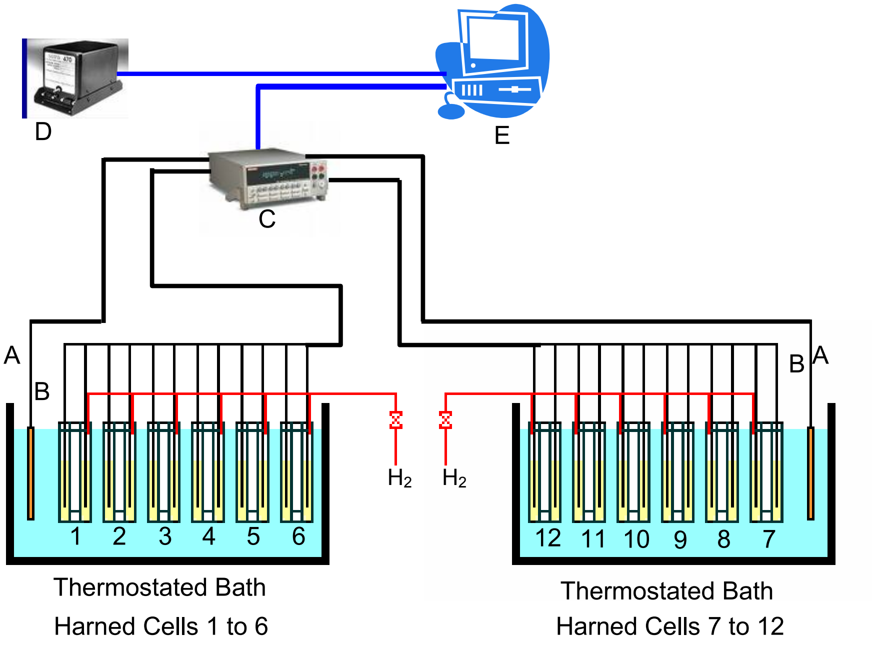

Figure 2. Experimental device for primary measurement of pH.

A – Thermometer.

B – Harned Cells.

C – Digital Multimeter, Keithley 2700.

D – Pressure meter, SETRA 470.

E – Computer equiped with XLINX software for data acquisition .

Operation of the primary system for the pH measurement involves two series of measurements with 6 cells each one. In the first series, measurements of $E^{o}$ are performed with the cells 1 to 3 filled with solution of HCl at 0,01 mol $kg^{-1}$ molality. Measurements of $E$ are performed with the cells 4 to 6 filled with buffer solution with chloride ion at 0,005 mol $kg^{-1}$, 0,010 mol $kg^{-1}$ and 0,015 mol $kg^{-1}$ molalities, respectively.

In the second series, measurements of $E$ are performed with the cells 1 to 3 and 4 to 6 filled with buffer solution with chloride ion at 0,005 mol $kg^{-1}$, 0,010 mol $kg^{-1}$ and 0,015 mol $kg^{-1}$ molalities, respectively.

During data acquisition, which was continued for a few hours, searching for stability (approximately 30 min potential variation less than 30 μV), the electrolytic cells were kept in a Clear View Lauda® model LSC 1067 precision thermostatic bath (± 0.005 ºC) connected to a refrigeration unit Lauda® model WK 500; temperature was measured with a Pt 100 resistance thermometer Type MPM1 1041/300, 1/10DIN. Cell potentials were acquired with a Keithley 7001-DVM system connected to a Keithley 2010 digital multimeter. The DVM is controlled by an IEEE interface.

## 6. Determination of pH Value

In the operation of the primary system for pH measurement fundamental steps, recommended by IUPAC, are required:

1. The potential, $E$, of Cell (1) defined by the Nernst equation (2) is the quantity to be measured:

$$E = E^{0}_{\mathrm{Ag,AgCl}} - \left[ \left( \frac{RT}{F} \right) \ln \left( \frac{m_H \gamma_H}{m_0} \right) \left( \frac{m_{Cl} \gamma_{Cl}}{m_0} \right) \right] \qquad (2)$$

where:

- $E$ is the potential of Cell (1) (corrected to 101325 Pa partial pressure of hydrogen gas);
- $E^{0}_{\mathrm{Ag,ACl}}$ is the standard potential of the cell, which conventionally coincides with that of the silver-silver chloride electrode, in V;
- $R$ = 8,314472(15) J $mol^{-1}K^{-1}$, is the molar gas constant;

- $T$ is temperature in K;
- $F = 96485{,}3399(24)$ C mol$^{-1}$, is the Faraday constant;
- $m_\mathrm{H}$ and $m_\mathrm{Cl}$ are the molalities of hydrogen ion and chloride ion, respectively, in mol kg$^{-1}$;
- $m^0$ is the standard molality (1 mol kg$^{-1}$);
- $\gamma_\mathrm{H}$ e $\gamma_\mathrm{Cl}$ are the activity coefficients of the hydrogen ion and chloride ion, respectively.

Considering $a_\mathrm{H} = m_\mathrm{H}\gamma_\mathrm{H,}$ equation (2) stay:

$$E = E^0_{\mathrm{Ag,AgC}l} - \left[\left(\frac{RT}{F}\right)\ln\left(a_\mathrm{H} m_\mathrm{Cl}\gamma_\mathrm{Cl}\right)\right] \qquad (3)$$

or

$$-\lg\left(\frac{a_\mathrm{H}\gamma_\mathrm{Cl}}{m_0}\right) = \frac{E - E^0_{\mathrm{Ag,AgC}l}}{(RT/F)} + \lg\left(\frac{m_\mathrm{Cl}}{m_0}\right) \qquad (4)$$

where $-\lg\left(\frac{a_\mathrm{H}\gamma_\mathrm{Cl}}{m_0}\right)$ is the acidity function, p($a_\mathrm{H}\gamma_\mathrm{Cl}$).

2. Extrapolation to zero chloride concentration by linear regression of the acidity function, that conduct to p$(a_\mathrm{H}\gamma_\mathrm{Cl})^0$;
3. Calculation of the chloride ion activity coefficient, $\gamma_\mathrm{Cl}$, using the Bates-Guggenheim convention:

$$\lg \gamma_{Cl} = -\frac{A\,I^{1/2}}{1 + 1{,}5\,I^{1/2}} \qquad (5)$$

and finally,

4. Calculation of hydrogen ion activity $a_\mathrm{H}$ and primary standard pH values:

$$\mathrm{pH} = \mathrm{p}a_H = \mathrm{p}(a_H\gamma_{Cl})^0 + \lg\gamma_{Cl} \qquad (6)$$

## 7. Results and Uncertainties

Results and uncertainties are presented on tables. Additional data, namely graphs are given in the Excel Report form.

Table 1. Standard uncertainty of the standard potential of the Ag|AgCl electrodes ($E^{o}$) from measurements in hydrochloric acid ($m_{HCl} = 0{,}01$ mol kg$^{-1}$) at 15 ºC.

| Quantity | Estimate $x_i$ | Standard uncertainty $u(x_i)$ | Sensitivity coefficient $\lvert c_i \rvert$ | Uncertainty contribution $u_i(E^{o})$ | Uncertainty contribution $u_i(E^{o})$ / % |
|---|---|---|---|---|---|
| $E$ / V | 0,463444 | $4{,}1\times10^{-5}$ | 1 | $4{,}1\times10^{-5}$ | 50,8 |
| $T$ / K | 288,18 | $5\times10^{-3}$ | $8{,}2\times10^{-4}$ | $4{,}3\times10^{-6}$ | 5,3 |
| $m_{HCl}$ / mol kg$^{-1}$ | 0,01 | $4{,}7\times10^{-6}$ | 5,10 | $2{,}4\times10^{-5}$ | 29,7 |
| $P_{H_2}$ / Pa | $1{,}018\times10^{5}$ | 3 | $7{,}5\times10^{-8}$ | $2{,}3\times10^{-7}$ | 0,3 |
| $\Delta E$ BIAS / V | $2{,}4\times10^{-5}$ | $1{,}1\times10^{-5}$ | 1 | $1{,}1\times10^{-5}$ | 14,0 |

$u_c(E^{o}) = 4{,}9\times10^{-5}$ V

$$E^{o} = (0{,}22839 \pm 0{,}00010)\ \mathrm{V}$$

Table 2. Standard uncertainty of the acidity function (p($a_H\gamma_{Cl}$)) at 15 ºC.

| Quantity | Estimate $x_i$ | Standard uncertainty $u(x_i)$ | Sensitivity coefficient $\lvert c_i \rvert$ | Uncertainty contribution $u_i(E^{o})$ | Uncertainty contribution $u_i(E^{o})$ / % |
|---|---|---|---|---|---|
| $E$ / V | 0,791681 | $6{,}9\times10^{-6}$ | 17,5 | $1{,}2\times10^{-4}$ | 8,1 |
| $E^{o}$ /V | 0,228389 | $4{,}9\times10^{-5}$ | 17,5 | $8{,}6\times10^{-4}$ | 57,9 |
| $T$ / K | 288,18 | $5\times10^{-3}$ | $3{,}4\times10^{-2}$ | $1{,}8\times10^{-4}$ | 12,0 |
| $m_{Cl}$ / mol kg$^{-1}$ | 0,005 | $1{,}1\times10^{-6}$ | 85,35 | $9{,}5\times10^{-5}$ | 6,4 |
| $P_{H_2}$ / Pa | $1{,}017\times10^{5}$ | 3 | $1{,}3\times10^{-6}$ | $3{,}9\times10^{-6}$ | 0,3 |
| $\Delta E$ BIAS / V | $1{,}9\times10^{-5}$ | $1{,}3\times10^{-5}$ | 17,5 | $2{,}3\times10^{-4}$ | 15,4 |

$u_c(\mathrm{p}(a_H\gamma_{Cl})) = 9\times10^{-4}$

$u(\mathrm{intercept}) = 3{,}3\times10^{-3}$

$$\mathrm{p}(a_H\gamma_{Cl})^{o} = 7{,}5607 \pm 0{,}0065$$

$u_c(\mathrm{pH}) = 0{,}0034$

$U(\mathrm{pH}) = 0{,}0068$

$$\mathrm{pH} = 7{,}4529 \pm 0{,}0068 \text{ at 15 ºC}$$

Table 3. Standard uncertainty in the standard potential of the Ag|AgCl electrodes ($E^{o}$) from measurements in hydrochloric acid ($m_{\mathrm{HCl}}$ = 0,01 mol kg$^{-1}$) at 25 ºC.

| Quantity | Estimate $x_i$ | Standard uncertainty $u(x_i)$ | Sensitivity coefficient $\lvert c_i \rvert$ | Uncertainty contribution $u_i(E^{o})$ | Uncertainty contribution $u_i(E^{o})$ / % |
|---|---|---|---|---|---|
| $E$ / V | 0,465343 | $6,8\times10^{-5}$ | 1 | $6,8\times10^{-5}$ | 60,8 |
| $T$ / K | 298,14 | $5\times10^{-3}$ | $8,2\times10^{-4}$ | $3,9\times10^{-6}$ | 3,5 |
| $m_{\mathrm{HCl}}$ / mol kg$^{-1}$ | 0,01 | $4,7\times10^{-6}$ | 5,28 | $2,5\times10^{-5}$ | 22,4 |
| $P_{H_2}$ / Pa | $1,019\times10^{5}$ | 3 | $7,5\times10^{-8}$ | $2,3\times10^{-7}$ | 0,2 |
| $\Delta E$ BIAS / V | $1,7\times10^{-5}$ | $1,5\times10^{-5}$ | 1 | $1,5\times10^{-5}$ | 13,1 |

$u_c(E^{o}) = 7,4\times10^{-5}$ V

$$E^{o} = (0,22227 \pm 0,00015)\ \mathrm{V}$$

Table 4. Standard uncertainty of the acidity function ($\mathrm{p}(a_{\mathrm{H}}\gamma_{\mathrm{Cl}})$) at 25 ºC.

| Quantity | Estimate $x_i$ | Standard uncertainty $u(x_i)$ | Sensitivity coefficient $\lvert c_i \rvert$ | Uncertainty contribution $u_i(E^{o})$ | Uncertainty contribution $u_i(E^{o})$ / % |
|---|---|---|---|---|---|
| $E$ / V | 0,802843 | $5,8\times10^{-6}$ | 16,9 | $9,8\times10^{-5}$ | 5,4 |
| $E^{o}$ /V | 0,222270 | $7,4\times10^{-5}$ | 16,9 | $1,2\times10^{-3}$ | 67,9 |
| $T$ / K | 298,14 | $5\times10^{-3}$ | $3,3\times10^{-2}$ | $1,6\times10^{-4}$ | 8,5 |
| $m_{\mathrm{Cl}}$ / mol kg$^{-1}$ | 0,005 | $1,1\times10^{-6}$ | 86,39 | $9,6\times10^{-5}$ | 5,2 |
| $P_{H_2}$ / Pa | $1,019\times10^{5}$ | 3 | $2,5\times10^{-6}$ | $7,6\times10^{-6}$ | 0,4 |
| $\Delta E$ BIAS / V | $1,6\times10^{-5}$ | $1,4\times10^{-5}$ | 16,9 | $2,3\times10^{-4}$ | 12,6 |

$u_c(\mathrm{p}(a_{\mathrm{H}}\gamma_{\mathrm{Cl}})) = 1,3\times10^{-3}$

$u(\mathrm{intercept}) = 2,1\times10^{-3}$

$$\mathrm{p}(a_{\mathrm{H}}\gamma_{\mathrm{Cl}})^{o} = 7,5241 \pm 0,0042$$

$u_c(\mathrm{pH}) = 0,0024$

$U(\mathrm{pH}) = 0,0049$

$$\mathrm{pH} = 7,4146 \pm 0,0049 \text{ at } 25\ ºC$$

Table 5. Standard uncertainty in the standard potential of the Ag|AgCl electrodes ($E^{\mathrm{o}}$) from measurements in hydrochloric acid ($m_{\mathrm{HCl}}$ = 0,01 mol kg$^{-1}$) at 37 ºC.

| Quantity | Estimate $x_i$ | Standard uncertainty $u(x_i)$ | Sensitivity coefficient $\lvert c_i \rvert$ | Uncertainty contribution $u_i(E^{\mathrm{o}})$ | Uncertainty contribution $u_i(E^{\mathrm{o}})$ / % |
|---|---|---|---|---|---|
| $E$ / V | 0,466366 | $8{,}4\times10^{-5}$ | 1 | $8{,}4\times10^{-5}$ | 64,4 |
| $T$ / K | 310,15 | $7\times10^{-3}$ | $8{,}2\times10^{-4}$ | $5{,}5\times10^{-6}$ | 4,2 |
| $m_{\mathrm{HCl}}$ / mol kg$^{-1}$ | 0,01 | $4{,}7\times10^{-6}$ | 5,5 | $2{,}6\times10^{-5}$ | 19,9 |
| $P_{H_2}$ / Pa | $1{,}019\times10^{5}$ | 3 | $1{,}2\times10^{-7}$ | $3{,}6\times10^{-7}$ | 0,3 |
| $\Delta E$ BIAS / V | $1{,}7\times10^{-5}$ | $1{,}5\times10^{-5}$ | 1 | $1{,}5\times10^{-5}$ | 11,2 |

$u_c(E^{\mathrm{o}}) = 8{,}9\times10^{-5}$ V

$$E^{\mathrm{o}} = (0{,}21375 \pm 0{,}00018)\ \mathrm{V}$$

Table 6. Standard uncertainty of the acidity function ($\mathrm{p}(a_{\mathrm{H}}\gamma_{\mathrm{Cl}})$) at 37 ºC.

| Quantity | Estimate $x_i$ | Standard uncertainty $u(x_i)$ | Sensitivity coefficient $\lvert c_i \rvert$ | Uncertainty contribution $u_i(E^{\mathrm{o}})$ | Uncertainty contribution $u_i(E^{\mathrm{o}})$ / % |
|---|---|---|---|---|---|
| $E$ / V | 0,815890 | $5{,}1\times10^{-6}$ | 16,2 | $8{,}3\times10^{-5}$ | 4,0 |
| $E^{\mathrm{o}}$ /V | 0,213750 | $8{,}9\times10^{-5}$ | 16,2 | $1{,}5\times10^{-3}$ | 70,0 |
| $T$ / K | 310,15 | $7\times10^{-3}$ | $3{,}2\times10^{-2}$ | $2{,}1\times10^{-4}$ | 10,3 |
| $m_{\mathrm{Cl}}$ / mol kg$^{-1}$ | 0,005 | $1{,}1\times10^{-6}$ | 85,25 | $9{,}5\times10^{-4}$ | 4,6 |
| $P_{H_2}$ / Pa | $1{,}019\times10^{5}$ | 3 | $2{,}4\times10^{-6}$ | $7{,}3\times10^{-6}$ | 0,4 |
| $\Delta E$ BIAS / V | $1{,}6\times10^{-5}$ | $1{,}4\times10^{-5}$ | 16,2 | $2{,}2\times10^{-4}$ | 10,8 |

$u_c(\mathrm{p}(a_{\mathrm{H}}\gamma_{\mathrm{Cl}})) = 1{,}5\times10^{-3}$

$u(\mathrm{intercept}) = 2{,}2\times10^{-3}$

$$\mathrm{p}(a_{\mathrm{H}}\gamma_{\mathrm{Cl}})^{\mathrm{o}} = 7{,}5013 \pm 0{,}0044$$

$u_c(\mathrm{pH}) = 0{,}0027$

$U(\mathrm{pH}) = 0{,}0053$

$$\mathrm{pH} = 7{,}3895 \pm 0{,}0053 \text{ at } 37\ ºC$$