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ABSTRACT

A pilot study organised by the Consultative Committee for Amount of Substance (CCQM) was carried out to assess the capabilities of twelve NMIs for preparing Ag|AgCl electrodes. Each participant prepared at least three Ag|AgCl electrodes representative of those employed in their primary pH calibration facilities. The electrodes were sent to a coordinating laboratory where comparative measurements of their potential difference to a *de-facto* reference, slope as a function of chloride ion concentration and electrochemical impedance were made. Electrodes from most institutes were highly repeatable and consistent within the typical rejection criteria applied during production. An analysis of the electrode slopes in a phosphate buffer containing different concentrations of NaCl revealed the influence of variances in the Ag|AgCl electrodes between institutes on the certified pH value of a buffer solution. The difference between National Metrology Institutes (NMIs) is consistent with submitted values in CCQM-K9 although biases were smaller in the analysis here, suggesting the presence of other unknown contributions to the uncertainty such as cell design. The smaller biases observed in this work may also reflect improvements in the Ag|AgCl electrodes since CCQM-K9 was performed. Electrochemical impedance spectroscopy suggests a similar microstructure for electrodes prepared by most institutes.

This is the first time a practical comparison of the characteristics of Ag|AgCl electrodes at different NMIs has been carried out. As the reference potential of Ag|AgCl electrodes is the second largest contribution to the measurement uncertainty of pH, this work is essential to improving future repeatability and stability of Ag|AgCl electrodes and comparability between institutes in pH measurement.

CONTENTS

1 INTRODUCTION

The accuracy of primary pH measurement depends on the performance of Ag|AgCl electrodes. These electrodes are used in the Harned cell (an electrochemical cell arrangement which does not contain a liquid junction) for assigning primary pH values to buffer solutions. A small change in the potential of a Ag|AgCl reference electrode makes a significant contribution to the measurement uncertainty. In metrological applications, excluding the determination of the molality of HCl used in the Harned cell, the reference potential of Ag|AgCl electrodes employed is the largest contribution to the measurement uncertainty of pH (figure 1). NMIs usually follow procedures developed in house for preparing Ag|AgCl electrodes. These often involve a number of subtle changes made to published methods following many years of experimental work and refinement. The difference in fabrication methods employed at each NMI may lead to significant changes in their performance which may compromise international comparability of pH measurement. A recent paper-based study of fourteen NMIs [1] focussed on understanding the influence of several variables in the preparation of Ag|AgCl electrodes on the accuracy of Harned cell measurements of pH. The performance of each NMI in the last decade was assessed on their results in eight key comparisons involving the measurement of pH of phosphate, phthalate, carbonate, borate and tetroxalate buffer materials (in CCQM - K9 and K9.2, K17, K18 and K18.1, K19 and K19.1 and K20 respectively). [2] The performance of each laboratory was correlated to the results of a questionnaire to determine the critical parameters in the preparation of Ag|AgCl electrodes and their sensitivities with respect to the accuracy of pH measurement. This study revealed that the parameters most closely correlated to performance in comparisons were area of electrode wire exposed to the electrolyte, diameter and porosity of the Ag sphere prior to anodisation, amount of Ag converted to AgCl during anodisation, stability times employed for electrodes to reach equilibrium in solution prior to measurement, electrode rejection criteria employed and purity of reagents.

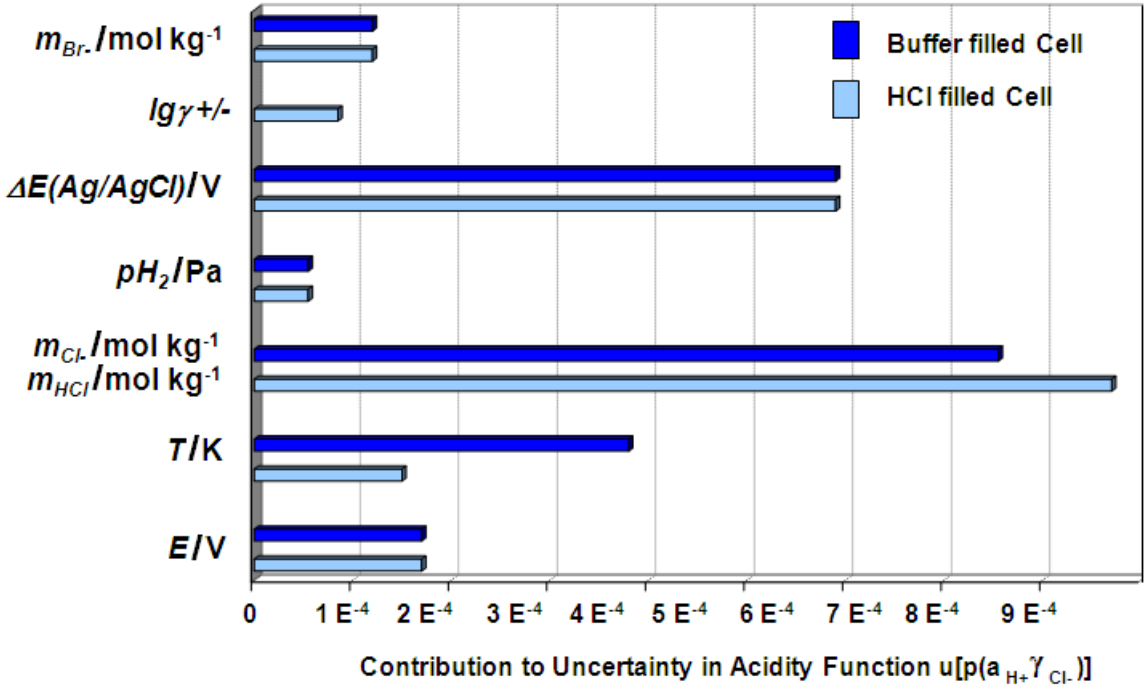

Figure 1 Uncertainty budget for the determination of the acidity function.

Although this study provided some useful observations, these were semi-quantitative and made some assumptions. In order to determine quantitative differences in the performance of Ag|AgCl prepared at NMIs providing traceability for pH measurement, a preparative comparison was proposed. This study is the successor to CCQM-P37.1 and focusses on comparing the potential against a *de-facto* reference, repeatability, stability, electrical impedance spectroscopy and acidity function of Ag|AgCl electrodes

prepared at NMIs maintaining calibration facilities for pH measurement. This is the first time that such a preparative comparison has been undertaken and it is an important step towards understanding the sensitivities in the preparation method on repeatability of the electrode potential and performance. The results of this study will be used to work towards better international comparability in pH measurement.

The time schedule was as follows:

Comparison proposed	February 2012
Electrodes sent to NPL for analysis	June 2012
Electrodes returned to participants	September 2012
Preliminary results presented	April 2013
Draft report circulated	March 2014
Report approved	April 2014

2 PARTICIPANTS

Table 1 CCQM-P37.2 participants

Acronym	Participant	Country
NPL	National Physical Laboratory	UK
MSL	Measurement Standards Laboratory	NZ
PTB	Physikalisch-Technische Bundesanstalt	DE
DFM	Danish Fundamental Metrology	DK
LNE	Laboratoire national de métrologie et d'essais	FR
NMIJ	National Metrology Institute of Japan	JP
SMÚ	Slovenský metrologický ústav	SK
NIST	National Institute of Standards and Technology	US
CENAM	Centro Nacional de Metrología	MX
ČMI	Český metrologický institut	CZ
TÜBİTAK	Türkiye Bilimsel ve Teknolojik Araştırma Kurumu	TR
IPQ	Laboratório Nacional de Metrologia	PT

3 RESULTS AND DISCUSSION

Electrodes were sent from twelve institutes (MSL, TÜBİTAK, LNE, NMIJ, SMÚ, PTB, DFM, NIST, ČMI, CENAM, NPL and IPQ). Electrodes from IPQ were received after the start date of the comparison so were not included in some of the measurements. All electrodes were stored in an aqueous solution of 0.01 mol dm^{-3} HCl on receipt and when not in use. The sections which follow describe the measurements carried out to compare the electrodes.

3.1 POTENTIAL DIFFERENCE MEASUREMENTS

Figure 2 shows the two different methods employed for comparing the potential of the Ag|AgCl electrodes received from the participants against a *de-facto* reference (a thermal electrolytic Ag|AgCl electrode prepared at NPL). The potential of the *de-facto* reference against a standard hydrogen electrode was (0.464167 ± 0.000010) V [E^0= (0.2219 ± 0.0002) V]. The set-up for experiment 1 is shown in figure 2 (a). The electrodes were placed in an aqueous solution of 0.01 mol dm^{-3} HCl in a large vessel to allow for all electrodes to be measured simultaneously. The benefit of this approach is that all electrodes experience the same experimental conditions (i.e. temperature and concentration of the electrolyte) and the drift in the *de-facto* reference is the same for the measurement of each electrode. The drawback of this approach however is that the homogeneity of the electrolyte could be compromised due to the large volume used. Figure 2 (b) shows the set-up for experiment 2, where measurements were carried out in a smaller vessel (approximately 250 ml electrochemical cell) containing an aqueous solution of 0.01 mol dm^{-3} HCl. In this approach it is easier to control the homogeneity of the solution with stirring. Measurements were performed in series with a batch of six Ag|AgCl electrodes being measured at a time. In order to ensure similar conditions, the electrolyte was filled from the same batch and replaced before each experiment. Temperature was maintained at 20 °C and the electrodes (including the reference) were allowed at least twelve hours to stabilise. In experiments 1 and 2, the distance of all electrodes to the reference was kept approximately constant as the reference was placed in the middle of the electrolyte and the measured electrodes were attached to the walls of the container. The electrolyte was bubbled with argon before each measurement and an over pressure was maintained during the experiment. The potential difference between the electrodes and the reference (ΔE) was measured as a function of time using a high accuracy Keithley 2001 multimeter which was calibrated to national standards. Measurements were taken every 30 s and were acquired using in house software written in LabVIEW 8.6. All measurements were shielded from RF radiation.

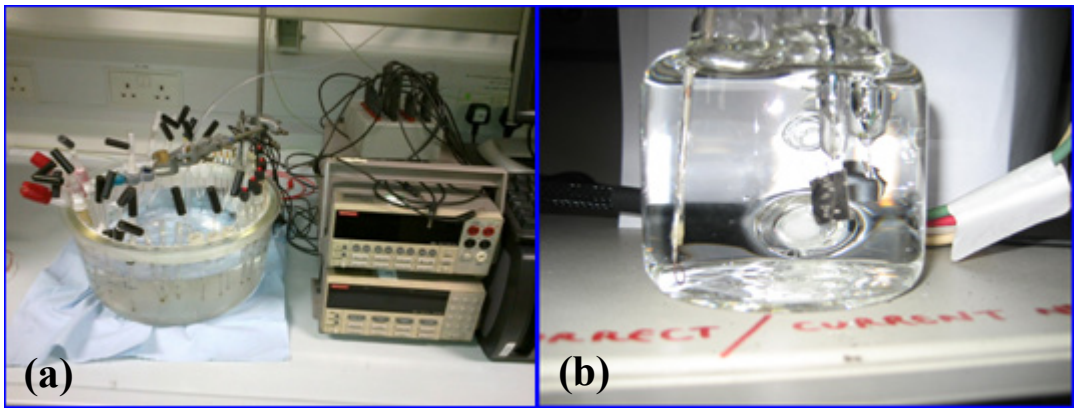

Figure 2 Methods used to compare electrode potential against a *de-facto* reference. (a) shows the large vessel approach (experiment 1), (b) shows the smaller electrochemical cell (experiment 2).

In experiment 1, three sets of measurements were made in series after one day, two days and five days of the electrodes being inserted into the electrolyte. The mean of the transient measurements for all three sets of data (after equilibrium had been achieved) are presented in figure 3. The standard deviation of the transient potential measurements (after equilibrium had been achieved) is presented in figure 4. The figures show that the repeatability of the electrode ensemble and stability of the individual electrodes improves as the electrodes are given a longer period to stabilise in the solution.

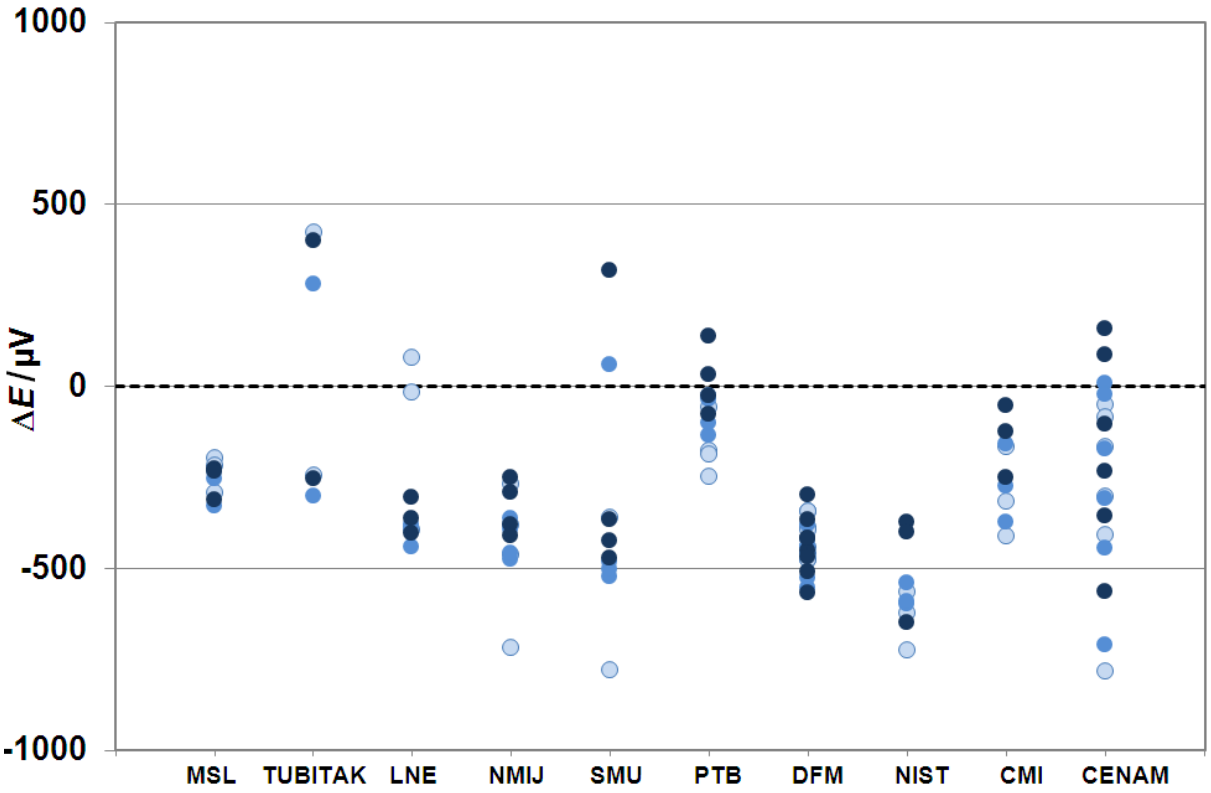

Figure 3 Mean of the potential difference (Δ*E*) of the Ag|AgCl electrodes vs a *de-facto* reference. The shade of the data points indicates the sequence of the measurements with light blue representing measurements from the first run and dark blue from the last run.

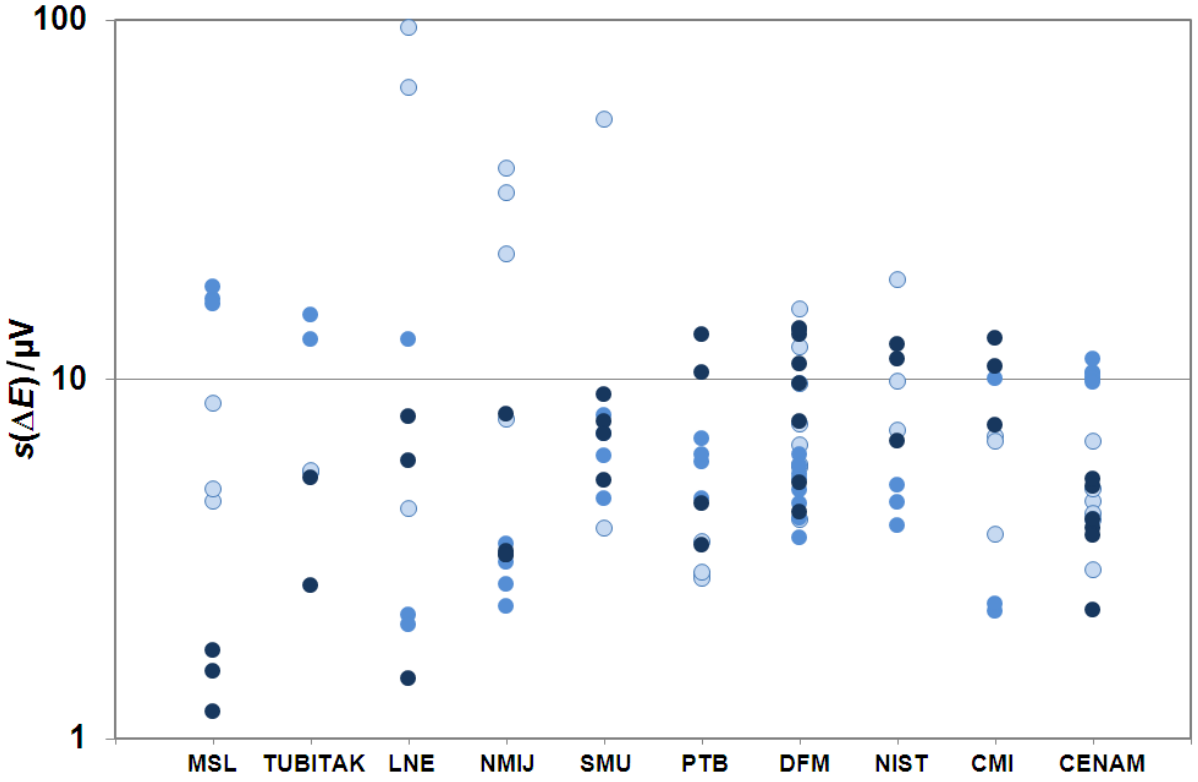

Figure 4 Standard deviation of the potential difference *s*(ΔE) of the Ag|AgCl electrodes vs a *de-facto* reference. The *y*-axis is plotted on a logarithmic scale. The shade of the data points indicates the sequence of the measurements with light blue representing measurements from the first run and dark blue representing the last run.

The results from the measurements made after a five day stabilisation period display the best repeatability and stability. This confirms the conclusion in CCQM-P37.1 where the smallest E^0 deviation of the Ag|AgCl electrodes used in pH measurement from the median occurred for NMIs that employ longer equilibrium times. For these data, the mean potential difference of the electrode ensemble from each institute has been calculated and a median was determined from the eleven mean values. The difference from the mean value for each participant's ensemble and the median is shown in figure 5, where the bars indicate 1 standard deviation of each electrode ensemble. When primary pH measurements are made, in an attempt to select a set of similar reference electrodes and reduce the risk of changes in potential between electrodes, it is common practice to reject individual reference electrodes which differ from the average of the group by more than 100 μV [3]. Although figure 5 shows larger deviations than this between institutes, only the repeatability of electrodes from each institute should be considered. This is because simultaneous measurements of the standard potential of the Ag|AgCl electrode in 0.01 mol dm^{-3} HCl solution are made during buffer certifications, which will correct for differences in absolute potential between institutes.

Electrodes from three of the participants (CENAM, SMÚ and TÜBİTAK) display a repeatability that does not meet the rejection criterion of 100 μV. However, due to the large volume of solution used in this experiment and the issues surrounding homogeneity, these differences are most likely to be attributed to the changes in solution environment as opposed to the performance of the electrodes themselves.

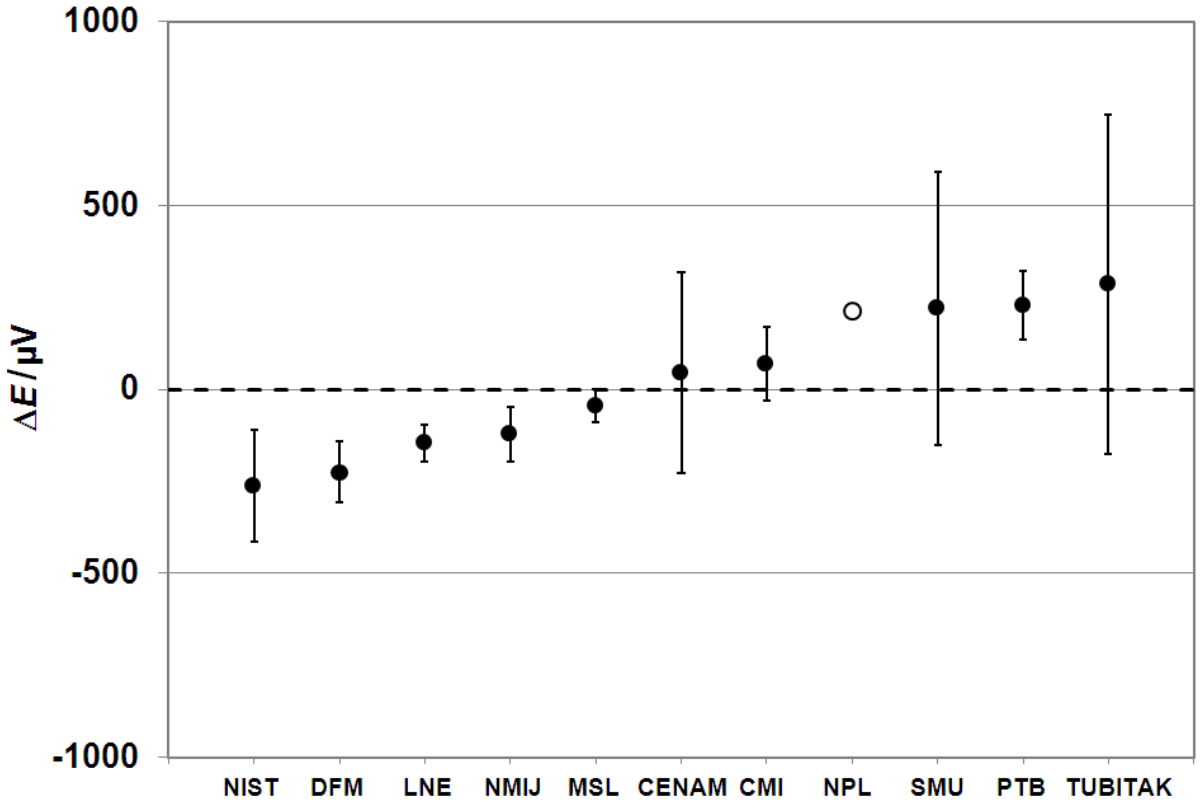

Figure 5 Difference of the mean potential difference (Δ*E*) of each electrode ensemble vs a *de-facto* reference from the median of the eleven participants.

Experiment 2 provides conditions much closer to the Harned cell as similar volumes of electrolyte were used and the solution was stirred adequately to ensure that it was homogenous. In the same format as experiment 1, data of the mean transient response of the electrode potential and the standard deviation after equilibrium had been achieved are shown in figures 6 and 7 respectively.

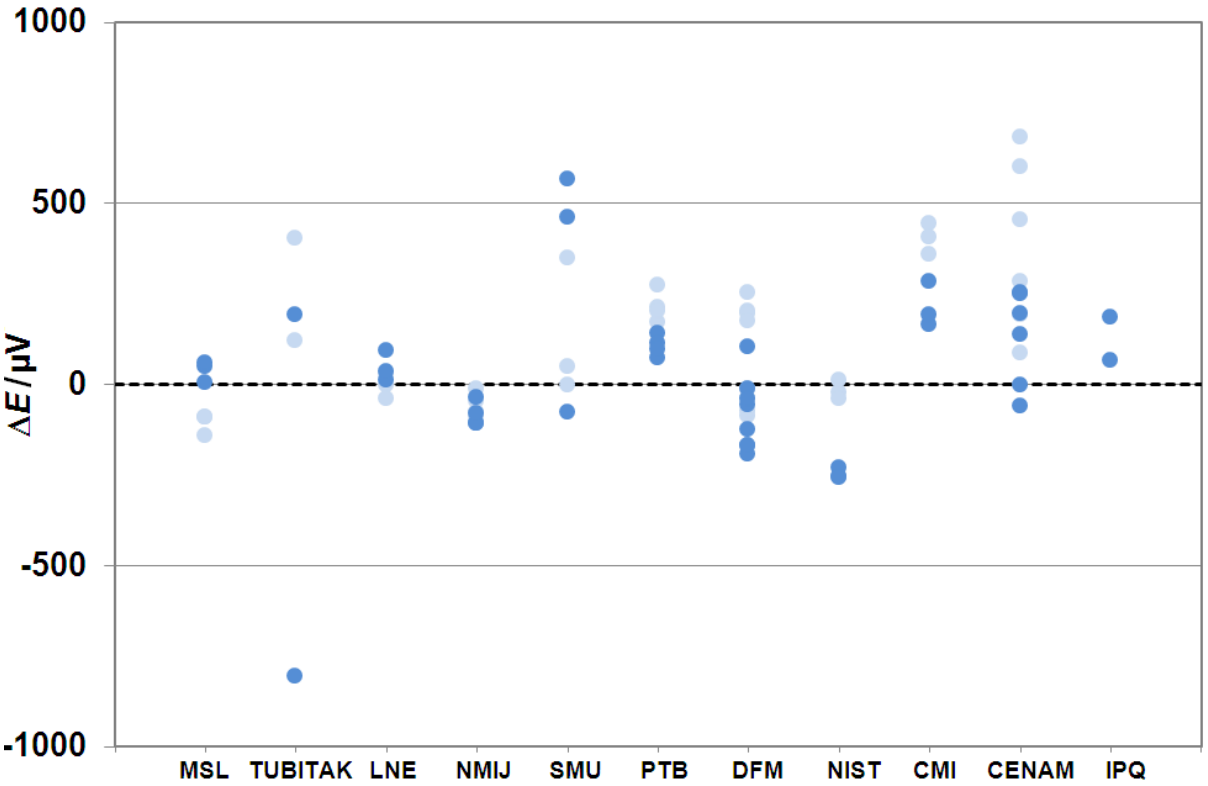

Figure 6 Mean of the potential difference (Δ*E*) of the Ag|AgCl electrodes vs a *de-facto* reference. The shade of the data points indicates the sequence of the measurements with light blue representing measurements from the first run and dark blue from the last run.

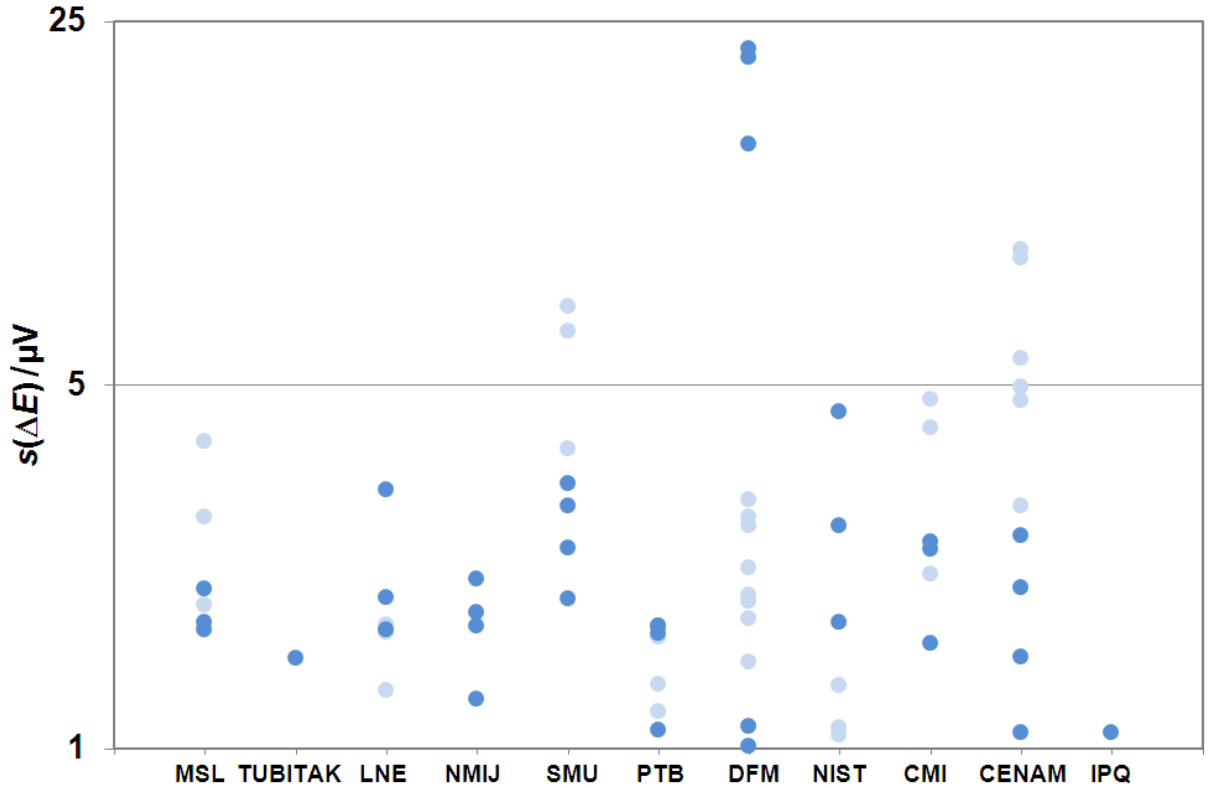

Figure 7 Standard deviation of the potential difference *s*(Δ*E*) of the Ag|AgCl electrodes vs a *de-facto* reference. The *y*-axis is plotted on a logarithmic scale. The shade of the data points indicates the sequence of the measurements with light blue representing measurements from the first run and dark blue the last run.

The figures show better repeatability and stability compared to the measurements conducted in the larger vessel. This is as anticipated and confirms the hypotheses previously articulated that the experiment involved a more homogenous and stable solution. As with the data in experiment 1, the longer conditioning time results in improved repeatability across the ensemble of electrodes from each participant and improved stability for each electrode. Four electrodes from DFM display significantly larger standard deviations in the second run. This is likely to be attributed to connection and shielding issues.

The data from the second set of measurements in experiment 2 are plotted in figure 8. As before, the mean potential difference of the electrode ensemble from each institute has been calculated and a median was determined from the eleven mean values. The difference of the mean value for each participant's ensemble from the median is shown, where the bars indicate 1 standard deviation of the measurements for each electrode ensemble. The results are a considerable improvement to those from the large vessel with the mean from most participants lying within 100 μV of the median. The repeatability of the electrodes from each participant now easily meets the rejection criterion (with the exception of SMÚ and TÜBİTAK). The NPL *de-facto* reference (open circle) is now very close to the median.

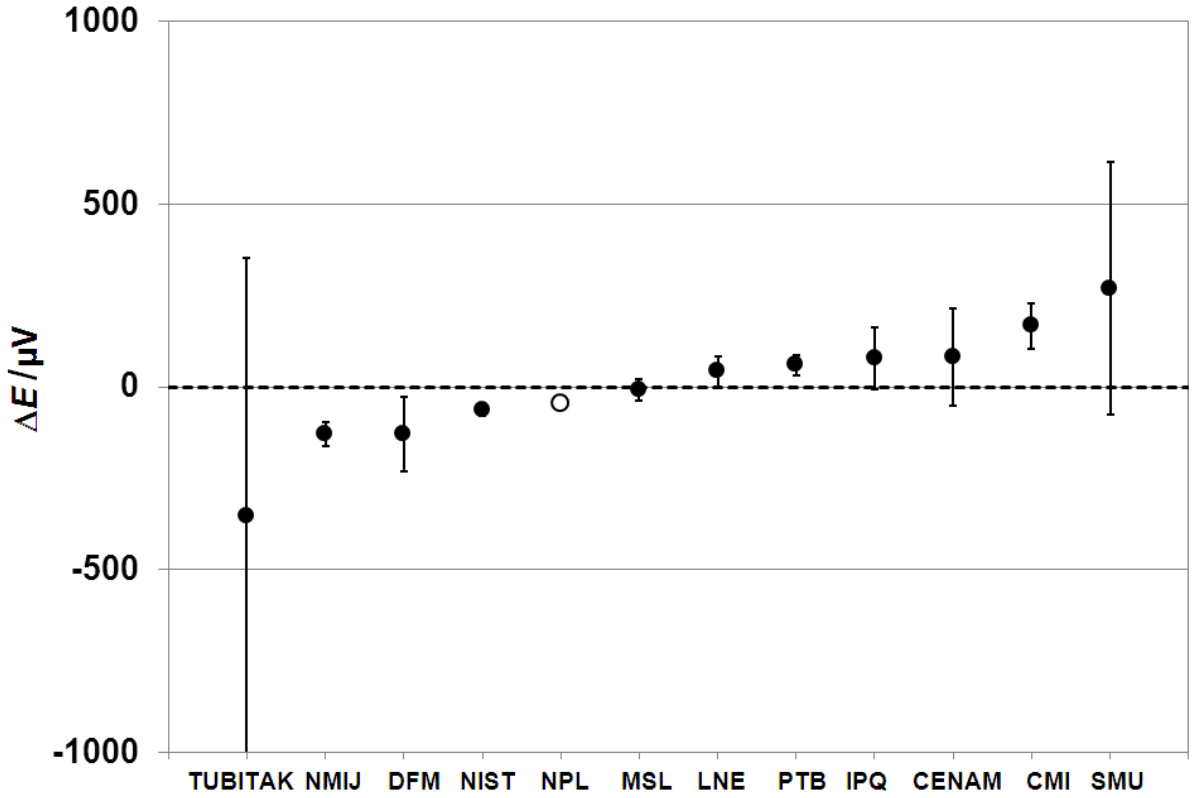

Figure 8 Difference of the mean potential difference (Δ*E*) of each electrode ensemble vs a *de-facto* reference from the median of the eleven participants.

Measurements of the three electrodes from NIST display excellent repeatability with a range of only 4 μV across the ensemble. CCQM-P37.1 identified that Ag|AgCl electrodes prepared at NIST are unique in that Ag wire is used in place of Pt. When Pt is exposed to the electrolyte, one would expect a mixed potential to be set up, hence causing a deviation in the value of E^0. Electrodes made from Ag wire would not suffer from this effect as Ag makes up the majority of the coated sphere. Hence the superior repeatability for the NIST electrodes may be attributable to the use of Ag wire.

The larger variance in the potential difference of electrodes from TÜBİTAK and SMÚ may be due to issues in sealing the electrodes. SMÚ reported cracking of the glass at the Pt-glass seal for several electrodes as a result of modifying their preparation procedure. This may account for the poorer

repeatability observed. Similarly, cracking at the seal in the electrodes from TÜBİTAK was observed during the measurements. Given the delicate nature of these electrodes it is also likely that defects may have been introduced from transportation.

Figure 9 shows the last set of data reproduced from figure 6 for measurements of DFM and CENAM Ag|AgCl electrodes. DFM provided three recently prepared electrodes, one used in the current pH calibration facility (the single open circle between data points for the new and old batch) and four from an older batch (used to the point where it no longer fulfilled DFM's acceptance criterion for potential difference within the ensemble). CENAM provided three recently prepared electrodes and three from an older batch. The data shows a shift in potential difference of the aged batch of DFM electrodes vs the *de-facto* reference electrode compared to the new batch. The potential of the older batch vs the *de-facto* reference is much closer to the median in figure 8. The electrode currently employed in the pH facility compares closely to the potential from the new batch. The newer batch shows better repeatability of the ensemble. The reference potential and repeatability of the CENAM electrodes vs the *de-facto* reference is shown to be independent of the age of the electrode. This observation is consistent with the analysis in CCQM-P37.1 which found no correlation between an NMI's performance in a key comparison and the age of the Ag|AgCl electrodes used. Although the DFM electrodes show some small dependency, measurements conducted at DFM (not shown here) suggest the change in potential is attributed to differences between batches (such as purity of the silver oxide used) rather than the age of the electrodes. Measurements at DFM also show that the potential difference between electrodes from the same batch increases with number of uses which is consistent with the data presented here.

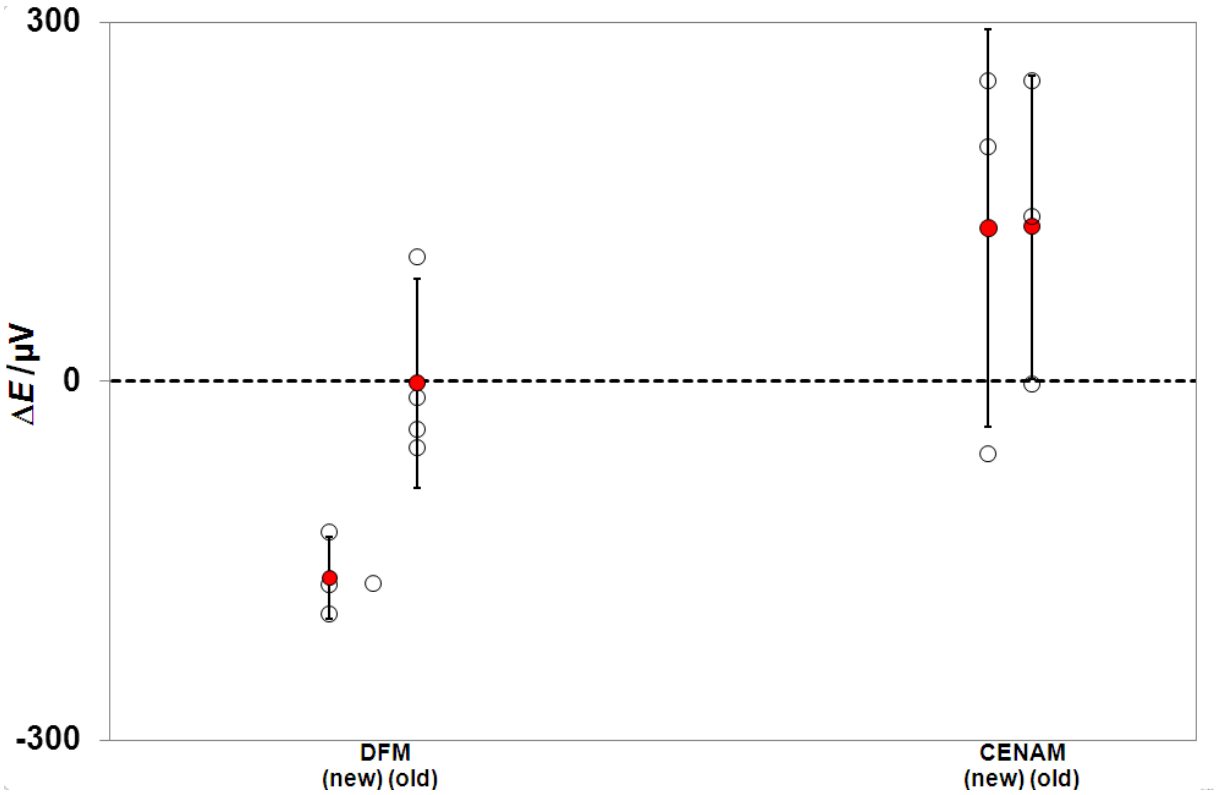

Figure 9 Influence of electrode age on measured potential difference (Δ*E*) against the *de-facto* reference for DFM and CENAM electrodes. The red data points show the mean of the measurements for each electrode ensemble. The bars indicate one standard deviation of the measurements.

3.2 DETERMINING THE SLOPE OF THE ACIDITY FUNCTION

The potentials of all Ag|AgCl electrodes in the study were compared to a standard hydrogen electrode in three buffer solutions of 0.0125 mol kg^{-1} Na_2HPO_4, 0.0125 mol kg^{-1} KH_2PO_4, containing nominal molalities of 0.001, 0.01 and 0.1 mol kg^{-1} of NaCl at 25 °C. A mean of the slopes of the electrodes for each participant was taken. Figure 10 shows the difference between the mean slope for each participant and the median (60.3 mV per molality decade) of the mean slope for all twelve participants. Of the twelve participants, ten agree within 200 μV per molality decade from the median. Reference electrodes from TÜBİTAK (5.1 mV per molality decade from the median) and SMÚ (1.5 mV per molality decade from the median) are clear outliers. This is likely to be due to the leakage at the Pt/glass seal, as described earlier, due to the potential of the Ag|AgCl electrode becoming more negative when Pt is exposed to a H_2-saturated solution. The negative deviation is likely to be greater in the solution containing 0.001 mol kg^{-1} of NaCl (largest cell potential) and lowest in the solution containing 0.1 mol kg^{-1} of NaCl (smallest cell potential). Hence the slope would be lower, as is shown in figure 10. Also, if there is any effect from the Pt substrate in the other NMIs' electrodes, the NIST electrodes would have a higher slope, as they are made from Ag wire. This is observed in Figure 10 with the exception of the electrodes from ČMI.

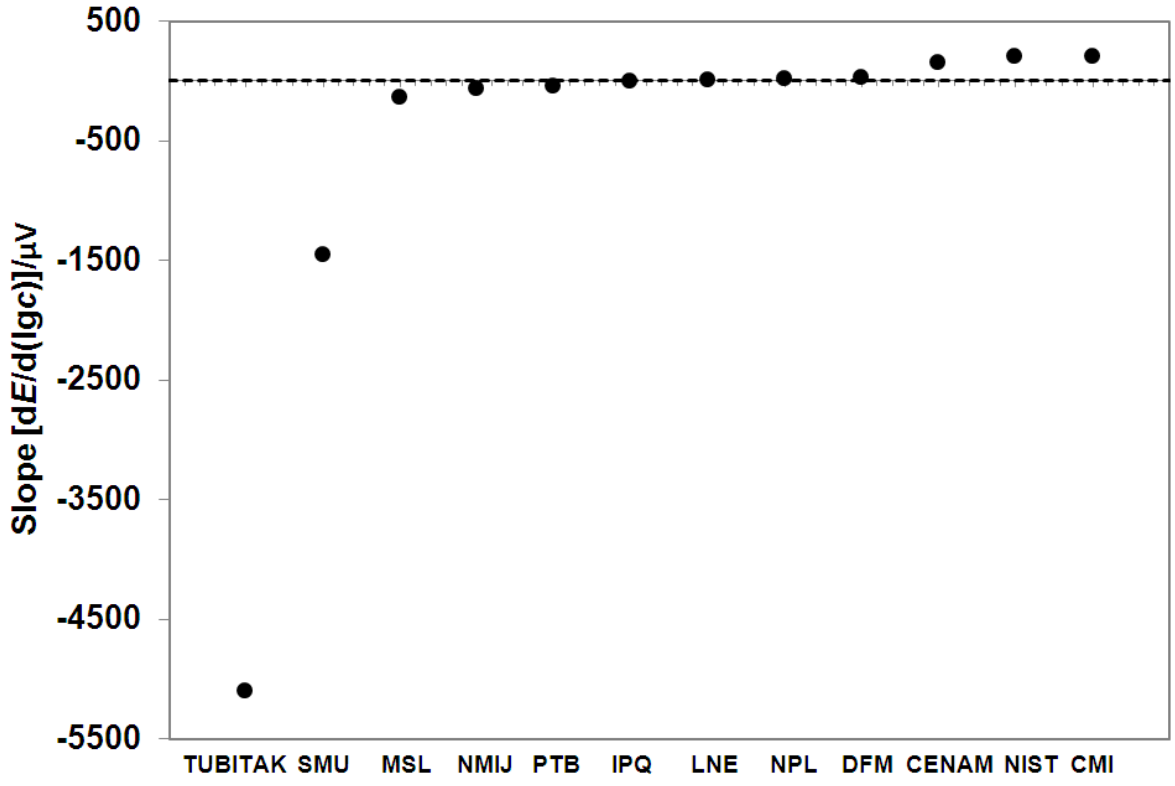

Figure 10 Difference between the mean slope of each participant's electrode ensemble and the median. The slope of each electrode was determined from the potential difference from a standard hydrogen electrode vs Cl^- molality.

Figure 11 presents the same data with the 2 outliers removed.

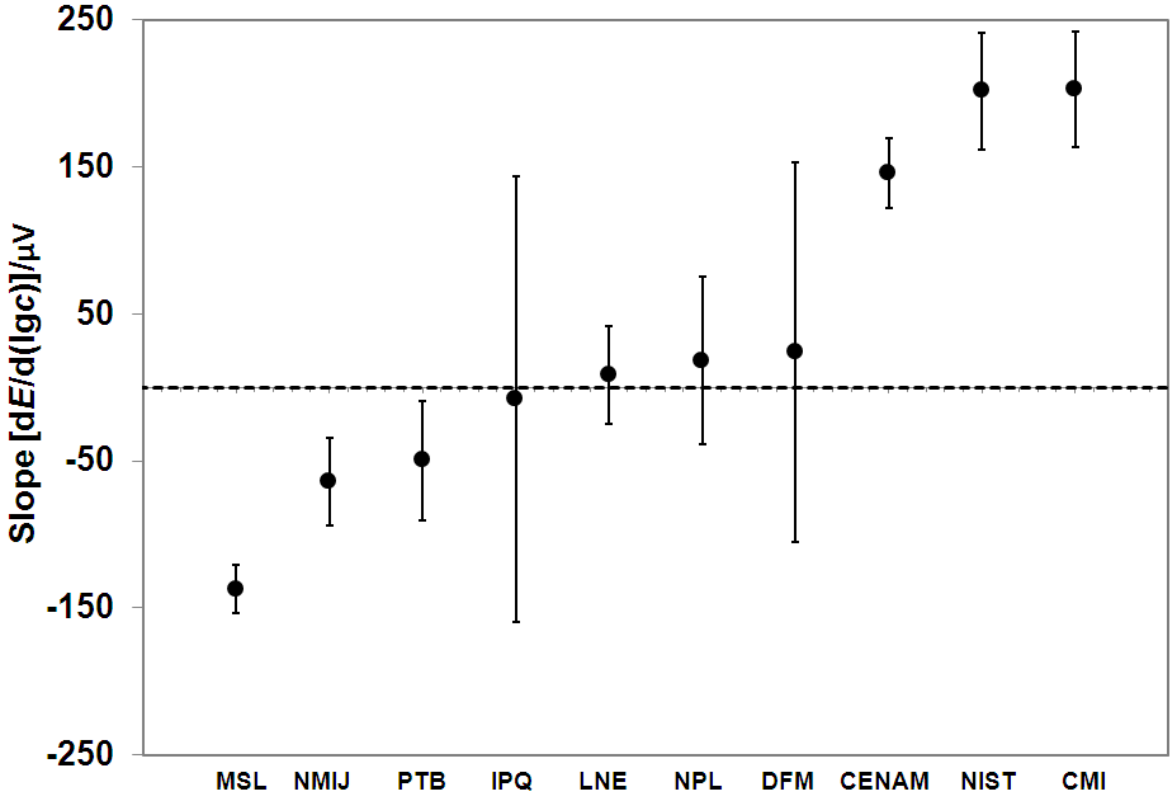

Figure 11 Data from figure 10 with outliers removed. The median is calculated from the full data set in figure 10. Bars indicate one standard deviation of the slope data for all electrodes from each institute.

In order to assess the influence of these differences in slopes (and hence Ag|AgCl electrode performance) on the results in key comparisons, the slopes were normalised to Harned cell measurements performed at NPL. These measurements were carried out using NPL Ag|AgCl electrodes and three different buffer solutions of 0.0125 mol kg^{-1} Na_2HPO_4 and 0.0125 mol kg^{-1} KH_2PO_4, each containing three nominal molalities of NaCl (0.005, 0.01 and 0.015 mol kg^{-1}) at 25 °C. Measurements of two of the NPL Ag|AgCl reference electrodes against a standard hydrogen electrode were made in a nominal 0.01 mol kg^{-1} HCl solution. The molality of the HCl solution was determined by gravimetric titration. The acidity function at each point was determined from:

$$\mathrm{p}(\mathrm{a}_{\mathrm{H}}\gamma_{Cl})_m = \frac{F(E_2 - E_1)}{RT\ln(10)} - 2\lg(m_{HCl}) - 2\lg(\gamma_{\pm HCl}) + \lg(m_{Cl^-})$$

Where $\mathrm{p}(a_{\mathrm{H}}\gamma_{\mathrm{Cl}})_m$ is the acidity function, F is the Faraday constant, R is the ideal gas constant, T is the temperature of the cells, E_1 is the potential of the cell containing the buffer, E_2 is the potential of the cell containing 0.01 mol kg^{-1} HCl, m_{HCl} is the molality of the HCl solution, $\gamma_{\pm\mathrm{HCl}}$ is the mean activity coefficient and m_{Cl}- is the molality of Cl^- in the buffer solution.

Data from the participants' Ag|AgCl electrodes normalised to the NPL electrodes measured in the three buffers are presented in figure 12. The potential of the participants' Ag|AgCl electrodes (hence $\mathrm{p}(a_{\mathrm{H}}\gamma_{\mathrm{Cl}})$ was fixed to the measurement of the NPL electrodes in the 0.0125 mol kg^{-1} Na_2HPO_4 and 0.0125 mol kg^{-1} KH_2PO_4 buffer containing a nominal molality of 0.01 mol kg^{-1} NaCl (filled circles in figure 12). The participants' electrodes were not measured in the 0.0125 mol kg^{-1} Na_2HPO_4 and 0.0125 mol kg^{-1} KH_2PO_4 buffer containing 0.005 and 0.015 mol kg^{-1} NaCl. The acidity function for the participants' Ag|AgCl electrodes at these molalities of NaCl was then determined by using the normalised slopes used in figure 10 (extrapolated points are shown with open circles in figure 12). The

difference in the slopes is very small as all the fitted lines are superimposed with the exception of TÜBİTAK (dotted red line) and SMÚ (dotted yellow line).

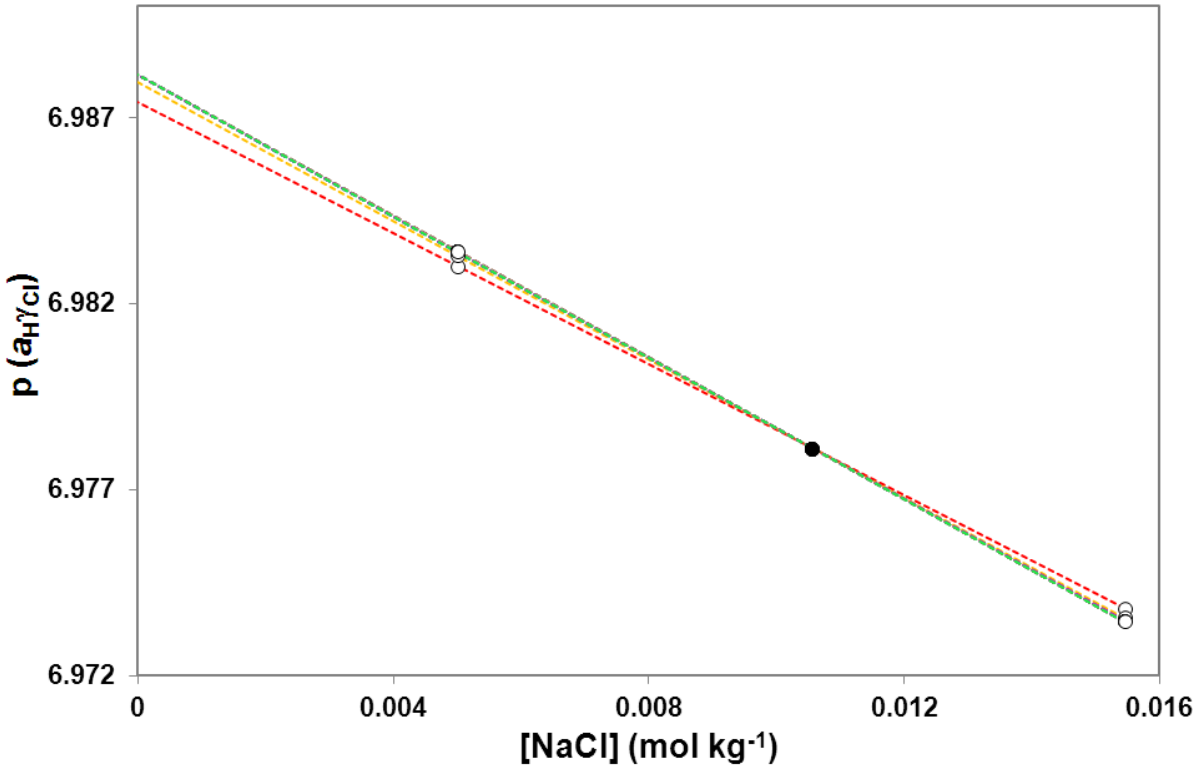

Figure 12 Acidity function ($p(a_H\gamma_{Cl})$) vs Cl^- molality. Slope measurements of the Ag|AgCl electrodes from each participant have been normalised to Harned cell measurements of NPL Ag|AgCl electrodes in three buffer solutions containing different chloride molalities.

From this analysis, a value of pH was determined for each NMI by extrapolating to zero chloride molality and using $-\lg\gamma_{Cl^-} = 0.0854$ (based on the 0125 mol kg^{-1} Na_2HPO_4 and 0.0125 mol kg^{-1} KH_2PO_4 at 25 °C). The data is plotted in figure 13 for each participant. The results from the analysis are plotted in increasing order of pH from left to right. Data from CCQM-K9 (sample 2 at 25 °C) has been overlaid as it involves the same buffer to which these measurements in 0.01 mol kg^{-1} are normalised to and at almost the same molalities. They show a similar trend to the values submitted in the key comparison with the smallest value being obtained by SMÚ and with CENAM being amongst the largest. This demonstrates the systematic influence of Ag|AgCl electrode performance can have on international comparability. However, the differences in pH values between institutes, calculated from the slope of the Ag|AgCl electrodes, are much smaller than the differences in the submitted results in the key comparison. This suggests for the first time that differences in Ag|AgCl electrodes are not the main cause of biases between institutes in key comparisons. It is also important to note that SMÚ used different methods for fabricating Ag|AgCl electrodes in CCQM-K9 and this study.

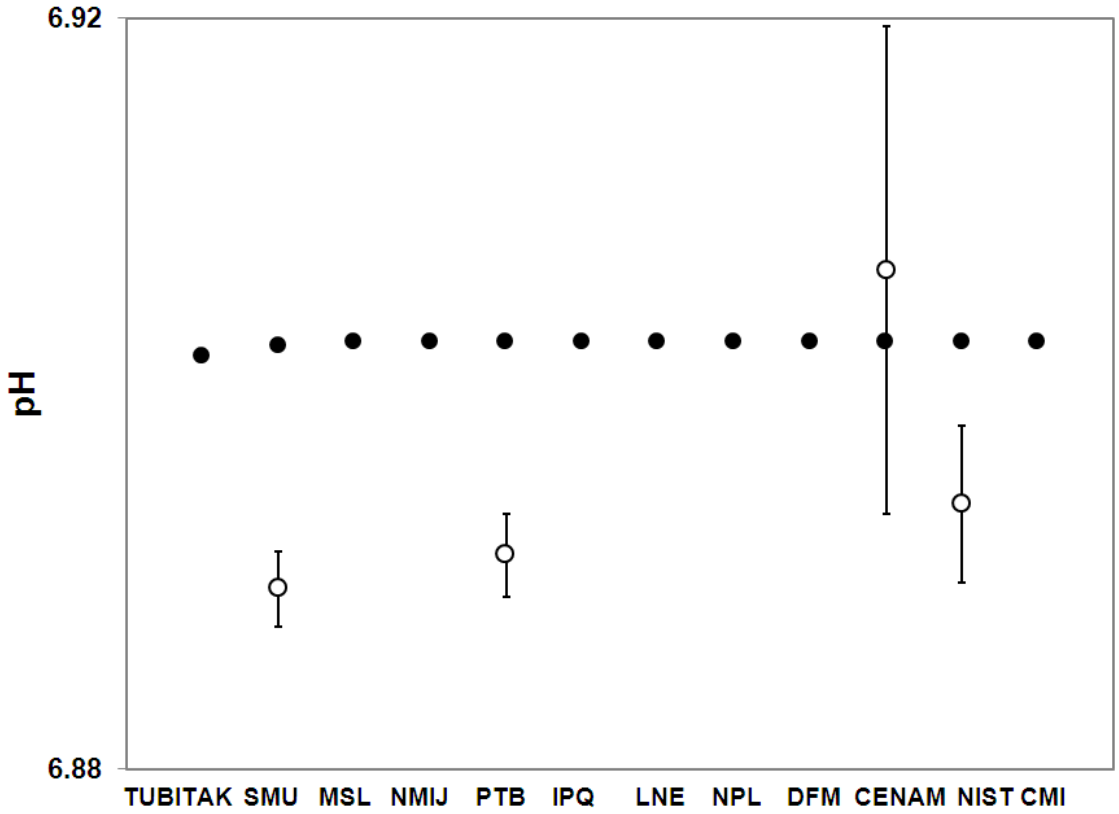

Figure 13 Calculated pH from the acidity function in figure 12 (filled circles) against institute. The results from sample 2 (0.02 mol kg^{-1} KH_2PO_4, 0.02 mol kg^{-1} Na_2HPO_4) in CCQM-K9 (25 °C) have been overlaid (open circles). Expanded uncertainties are shown with bars.

Figure 14 shows an alternative analysis of the data in figure 12 using a different normalisation procedure to fixing the potential of the participants' Ag|AgCl electrodes to the measurement of the NPL electrodes in the 0.0125 mol kg^{-1} Na_2HPO_4 and 0.0125 mol kg^{-1} KH_2PO_4 buffer containing a nominal molality of 0.01 mol kg^{-1} NaCl (filled circles in figure 12). In this instance values from the participants' Ag|AgCl electrodes from the measurements against the standard hydrogen electrode in 0.0125 mol kg^{-1} Na_2HPO_4, 0.0125 mol kg^{-1} KH_2PO_4, 0.01 mol kg^{-1} of NaCl were normalised to the Harned cell measurement at the same NaCl molality using the measurements of the NPL electrodes in both experiments (filled circles). The acidity function for the participants' Ag|AgCl electrodes at 0.005 and 0.015 mol kg^{-1} of NaCl was then determined by using the normalised slopes used in figure 10 (extrapolated points are shown with open circles).

Unlike before, where the plots were mostly superimposed (with the exception of TÜBİTAK and SMÚ), plots from all institutes can now be clearly identified. This approach does not account for the possible cancelling of potential differences between measurements in acid and in buffer. Hence this highlights the impact of simultaneously measuring the standard potential of the Ag|AgCl electrode in 0.01 mol kg^{-1} HCl solution during buffer certifications in order to account for the absolute difference in potential of the Ag|AgCl electrodes between institutes.

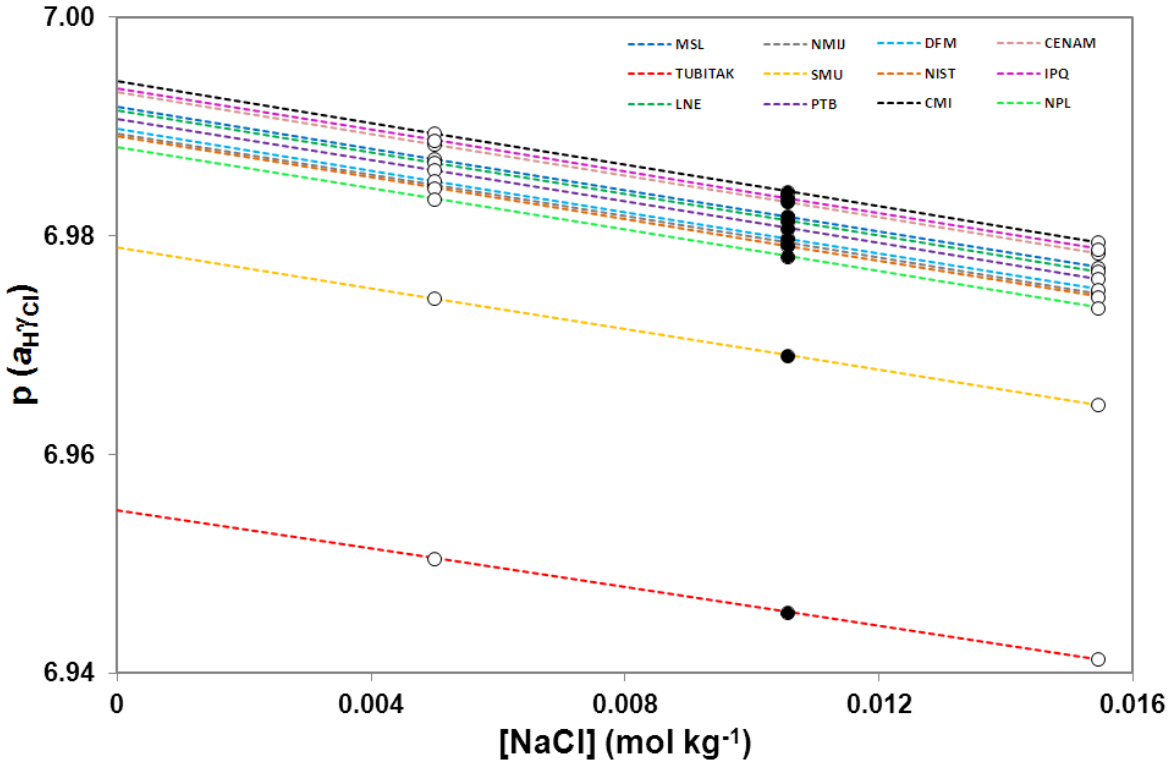

Figure 14 Acidity function ($p(a_H\gamma_{Cl})$) vs Cl^- molality. Slope measurements for each participant have been normalised to Harned cell measurements of NPL Ag|AgCl electrodes in three buffer solutions containing different chloride molalities.

Figure 15 shows the calculated values of pH when the slopes in figure 14 are used. It shows much larger differences in the projected pH values between institutes as absolute potential differences are used as well as slopes. The observation from figure 13 is thereby exaggerated, showing that the pH values determined from the measurements from the Ag|AgCl electrodes track the trend in submitted values in CCQM-K9.

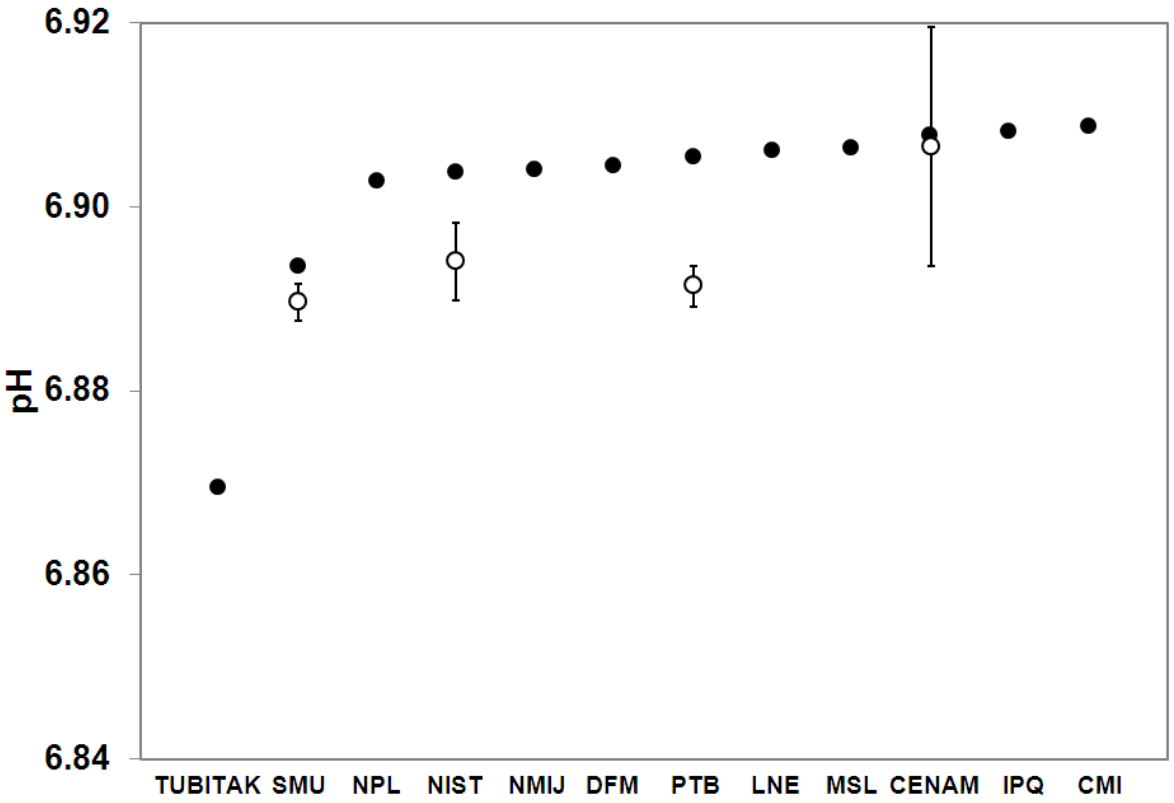

Figure 15 Calculated pH from the acidity function in figure 14 (filled circles) against institute. The results from sample 2 (0.02 mol kg^{-1} KH_2PO_4, 0.02mol kg^{-1} Na_2HPO_4) in CCQM-K9 (25 °C) have been overlaid (open circles). Expanded uncertainties are shown with bars.

Whilst any differences in potential of Ag|AgCl electrodes between institutes should cancel out when the HCl cell and buffer cell measurements are made, electrodes which show some deviation from ideal behaviour in HCl solution (ie. larger differences in potential) may have a greater chance of causing a bias or non-ideal behaviour when used for measurements of a buffer solution. Ag|AgCl electrodes are rarely checked for their potential in the buffer alone and the differences between this and the performance in acid. In fact measurements to test repeatability to meet acceptance criteria are usually performed only in 0.01 mol dm^{-3} HCl solution. Therefore it is possible that deviations from ideal behaviour may be exaggerated or change in buffer solution resulting in biased extrapolations. For example, the absolute voltage may still be more important than is currently believed to be the case. To investigate this, absolute deviations in the potential of electrodes from each institute (figure 8) were plotted against the pH determined from slope measurements in the phosphate buffer (figure 13). The analysis showed no obvious correlation, indicating that deviations in the potential of an electrode does not influence its behaviour in buffer solutions of varied chloride molality in a linear fashion. Figure 16 shows one standard deviation of the potential measurements of each ensemble from each institute (data from figure 8) plotted against the calculated pH value from the slope data. A correlation is shown here when the electrodes from TÜBİTAK and SMÚ are included in the analysis. This indicates that when electrodes are prepared that produce a batch with poor repeatability, their behaviour in buffer solutions is affected. Given that the deviation in these electrodes is due to issues with the sealing at the glass/Pt interface, this result is to be expected. Analysis of the data from the other ten institutes does not reveal a linear correlation. This suggests that the differences observed in electrode behaviour are not linked to their performance in buffer solutions and are not likely to make a significant contribution towards the differences observed in submitted values in key comparisons. Other factors such as long term electrode drift (its significance is shown in figure 3 and 6) are more likely to influence measurements. Drift may also be a function of the ideality of the Ag|AgCl electrode and therefore linked to absolute voltage difference.

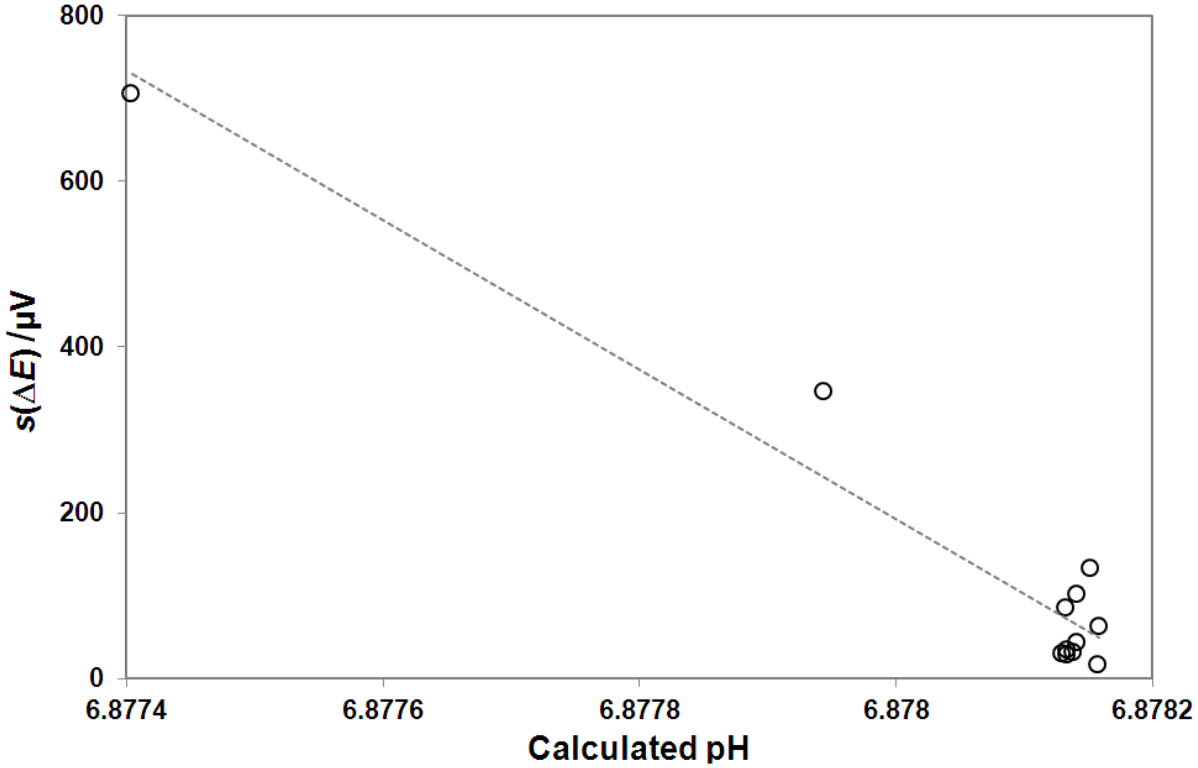

Figure 16 Standard deviation of the potential data *s*(Δ*E*) shown in figure 8 for each institute as a function of calculated pH from the analysis in figure 13. The grey line shows a linear least squares fit to the data.

3.3 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY ANALYSIS

Electrochemical Impedance Spectroscopy (EIS) measurements were carried out for all electrodes from each NMI and a characteristic Nyquist plot from each NMI is presented in figure 17 (Z_{Im} is the imaginary component and Z_{Re} is the real component of the complex impedance). A representative measurement from the electrode ensemble from each participant is shown.

The spectra have been multiplied by the geometric area of the electrode. Three distinct regions are usually identified from this analysis. Firstly the partial contribution of electrolyte and cell configuration at high frequencies (the frequency range is too limited to reveal the entire arc). Secondly, a semicircle at intermediate frequencies when the system is under kinetic control, as a result of an electrochemical charge transfer step at the electrode–electrolyte interface. Lastly a straight, or slightly curved, line at low frequencies which is characteristic of diffusion processes. Since all the electrodes have been analysed in the same 0.01 mol dm^{-3} HCl solution, the shift of their respective ohmic resistance is due to the difference in the active surface (real area), and thus is related to the porosity.

The signatures for TÜBİTAK, SMÚ and NMIJ showed larger impedance values compared to the electrodes from the other participants. These indicate less porous structures. The absence of a significant diffusion process (lack of curved or straight line at low frequencies for the SMÚ and NMIJ electrodes) is consistent with their denser structure. The different method used at SMÚ for electrode fabrication, as outlined in CCQM-P37.1 [1], may account for the change in electrode microstructure. Alternatively, leaks at the Pt/glass interface as suggested previously for the SMÚ and TÜBİTAK electrodes, may account for the different EIS profiles.

Given the similarity in the EIS data of the electrodes from the other nine participants, it is likely that the differences previously observed in slope and potential difference are not attributable to significant differences in the microstructures of the electrodes.

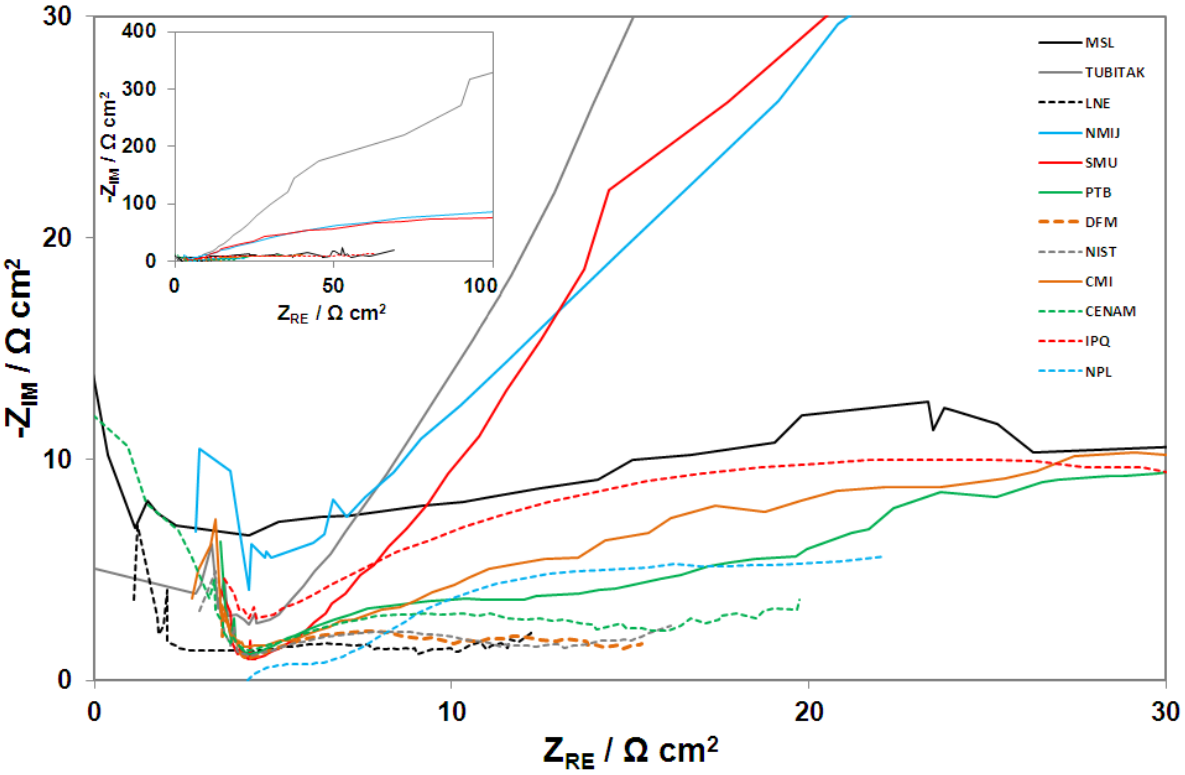

Figure 17 Complex plane impedance between 100 kHz and 0.1 Hz for an electrode from each participant selected to represent the ensemble. Measurements were carried out in a 0.01 mol.dm^{-3} HCl solution against a Pt flag counter electrode. The minimum point for each plot has been normalised to 4.3 Ω cm^2 to account for differences in the resistance of the solution. The inset shows the same data on a larger scale.

3.4 SCANNING ELECTRON MICROSCOPY

DFM provided a Ag|AgCl electrode for Scanning Electron Microscopy (SEM) measurements. An image from the analysis is shown in figure 18. The microstructure is very similar to previous analyses on NPL electrodes [4]. The elemental analysis for Ag and Cl on the surface of the electrode yielded 76 % Ag and 24 % Cl. This is also in close agreement to data collected from NPL electrodes where a surface composition of 67 % Ag and 33 % Cl was observed. The difference in composition between electrodes from the two institutes may result from a change in concentration of the electrolyte used in the anodisation process (1 mol dm^{-3} HCl used at DFM compared to 0.1 mol dm^{-3} HCl used at NPL). The microstructure may also account for the difference, with a more porous electrode allowing deeper penetration of the electrolyte. These results confirm previous work [4] where an EDX image with elemental analysis of the cross section of a Ag|AgCl electrode showed the formation of AgCl on the outer layers of the Ag sphere penetrating no further than about a quarter of the distance from the surface to the Pt wire. It is likely that a similar distribution of AgCl will be present in electrodes from all institutes that use an anodisation process to convert the Ag to AgCl due to the reduced penetration of the electrolyte as a resistive AgCl layer builds up on the surface.

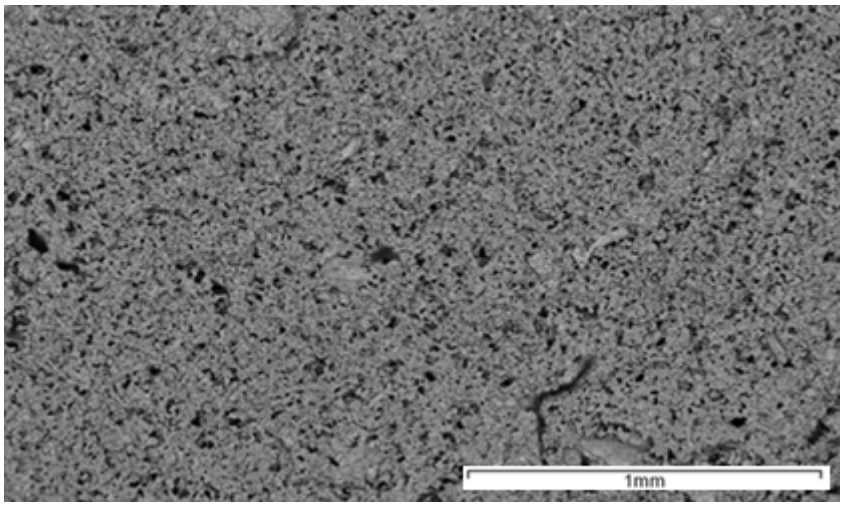

Figure 18 SEM image of a Ag|AgCl **electrode from DFM.**

It is known that 10-25 % of the Ag should be converted to AgCl to produce electrodes with good repeatability and stability [5]. However the implications of an uneven distribution of AgCl within the sphere of material are not known. The performance of this distribution compared to an homogenous arrangement of Ag and AgCl would be an interesting future study. We can hypothesise that this electrode may be less stable than one where the Ag|AgCl is evenly distributed, since it may be more difficult for an electrochemical couple with high exchange current density to be established.

4 CONCLUSIONS

The first international comparison has been carried out to assess the preparative capabilities of twelve laboratories fabricating Ag|AgCl electrodes for pH measurement. Measurements of the potential difference of the electrodes to a *de-facto* reference revealed important information about their repeatability and stability. The standard deviation of the electrode ensemble from most institutes was less than 100 μV, which is consistent with the typical rejection criteria applied. Further measurements suggested that for a particular fabrication process at one institute, newer electrodes are more repeatable. EIS analysis for a representative electrode from each institute showed a similar microstructure for each. An analysis of the electrode slopes in a phosphate buffer containing different concentrations of NaCl has revealed, for the first time, the influence of variances in the Ag|AgCl electrodes between institutes on the certified pH value of a buffer solution. The analysis displayed a similar trend to the values from key comparison CCQM-K9. The differences in pH values between institutes obtained using the analysis of Ag|AgCl electrode slopes were much smaller than those observed in the key comparison, suggesting that variances in the Ag|AgCl electrodes are probably not the main cause of the bias between institutes. The smaller biases observed in this work may also reflect improvements in the Ag|AgCl electrodes since CCQM-K9 was performed (1999). The difference in concentration between the buffers used in this study and in CCQM-K9 may also account for the change in differences amongst institutes and may affect the conclusions drawn.

This is the first comparison to provide quantitative information on the differences in the performance of Ag|AgCl electrodes prepared at NMIs providing traceability for pH measurement. It is an important step towards understanding the sensitivities in the preparation method on repeatability of the electrode potential and performance and will be used to improve future international comparability in pH measurement.

5 REFERENCES

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