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CCQM P37.1:
Preparation of Ag/AgCl Electrodes for Harned cell Measurements

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Approved on behalf of NPLML by Alan Brewin, Division Head.

ABSTRACT

A questionnaire was completed by 14 participants (INMETRO, NIM, PTB, DFM, LNE, NMIJ, SMU, NIST, CENAM, GUM, NPLI, IPQ, BIM and KRISS) to study 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 national metrology institute in the last decade has been assessed based on their results in 8 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). The performance of each laboratory has been correlated to the results of the 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 reveals that the parameters most closely correlated to performance in comparisons are 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.

CONTENTS

1 INTRODUCTION

The performance of Ag/AgCl reference electrodes is of paramount importance for accurate pH measurement. A small change in the potential of a Ag/AgCl reference electrode makes a significant contribution to the measurement uncertainty. Usually, 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 (as shown in figure 1). Ag/AgCl electrodes are usually prepared at National Metrology Institutes (NMIs) by following procedures developed by standardisation bodies or bespoke methods developed in house. A large number of NMIs have gained a wealth of experience in electrode preparation from investing a significant effort into refining methods to improve performance. However the sensitivities of various processes in the procedures and their impact on electrode performance are still poorly understood. To date, a detailed investigation has not been carried out.

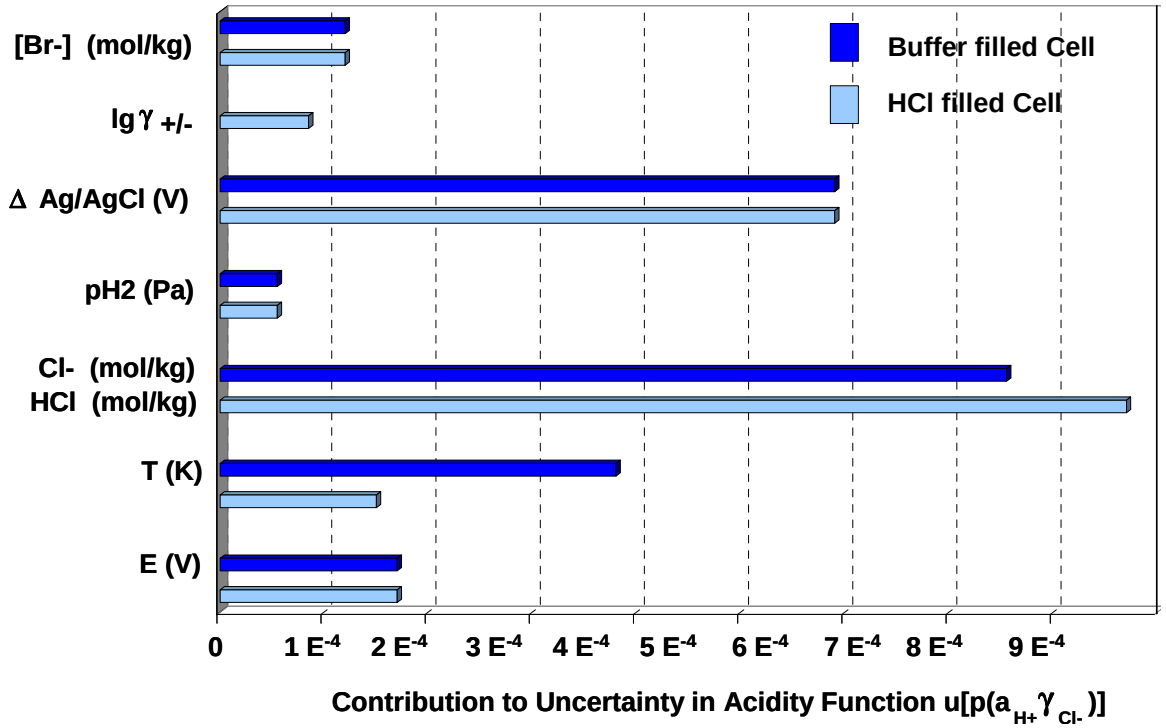

Figure 1 Uncertainty budget for the determination of acidity function.

The aim of this study is to meet this requirement and improve performance of Ag/AgCl electrodes by understanding the sensitivities of various parameters involved in the manufacturing process. This study identifies differences in preparation techniques between NMIs in order to understand the causes of any discrepancies in the potential of electrodes produced. It is an important step towards understanding the sensitivities in the preparation method on repeatability of the electrode potential and performance. This intention of this study is to improve future international comparability in pH measurement.

The time schedule was as follows:

Questionnaire 1 sent to participants	03 August 2009
Deadline for responses	01 March 2010
Review of data	13 April 2010
Questionnaire sent to participants	23 July 2010
Deadline for responses	31 August 2010

P37.1 was discussed at the meeting of the CCQM-EAWG on 20 April 2009 at BIPM, Paris. NPL was appointed to coordinate the study.

2 PARTICIPANTS

Table 1 CCQM P37.1 participants

Acronym	Participant	Country	Analyst
INMETRO	Instituto Nacional de Metrologia, Normalização e Qualidade Industrial	BR	Fabiano Barbieri Gonzaga
NIM	National Institute of Metrology, China	CN	Xiu Hongyu; Wu Bing
PTB	Physikalisch-Technische Bundesanstalt	DE	Petra Spitzer
DFM	Danish Fundamental Metrology	DK	Pia Tønnes Jakobsen
LNE	Laboratoire National de métrologie et d'Essais	FR	Rachel Champion, Paola Fisicaro
NMIJ	National Metrology Institute of Japan	JP	Masaki Ohata,
SMU	Slovensky Metrologicky Ustav	SK	Leos Vyskocil
NIST	National Institute of Standards and Technology	US	Kenneth Pratt
CENAM	Centro Nacional de Metrologia	MX	Marcela Monroy, Adrian Reyes
GUM	Central Office of Measures	PL	Wladyslaw Kozlowski
NPLI	National Physical Laboratory of Israel	IL	Elena Kardash
IPQ	Laboratorio Central de Metrologia	PT	Maria Filomena Camoes
BIM	National Centre of Metrology	BG	Dimka Ivanova
KRISS	Korea Research Institute of Standards and Science	KR	Hwashim Lee, Euijin Hwang

3 RESULTS AND DISCUSSION

Figure 2 shows the number of CCQM-EAWG key comparisons involving pH measurement that each NMI has participated in over the last decade. The results of the key comparisons listed here have been used as an indicator of NMI performance.

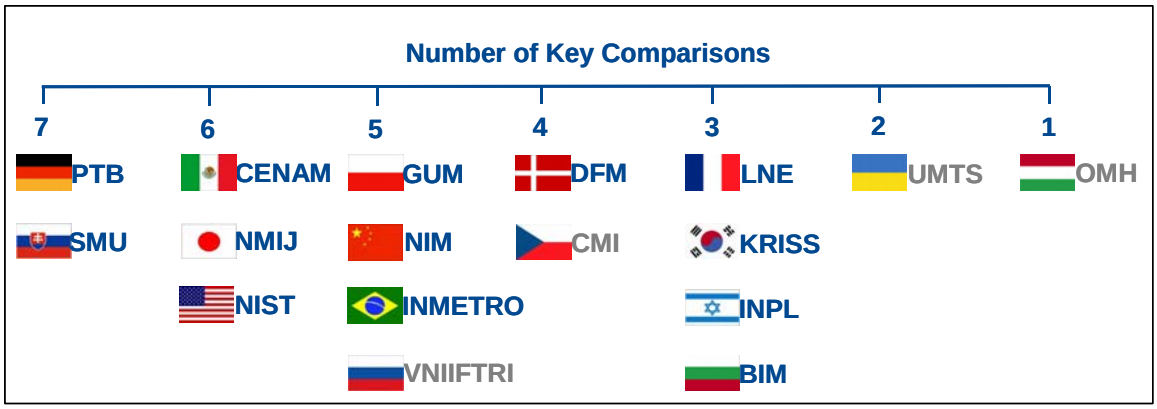

Figure 2 The number of CCQM-EAWG key comparisons of pH that each NMI has participated in the last decade. Institutes in grey are those which did not participate in P37.1.

Figure 3 shows the results of plotting the mean absolute degree of equivalence (DOE) against the mean absolute difference of E^0 from the median (used as an indicator of electrode performance) for all key comparisons of pH.1. Each sphere represents a different NMI with size being proportional to participation in key comparisons (the larger the sphere, the more key comparisons an NMI has participated in). A large mean absolute DOE of pH was observed for one NMI and was deemed as an outlier. Data from this institute has not been included in the analysis.

The data shows a positive correlation between these two variables and suggests that institutes with the capability to produce high accuracy Ag/AgCl electrodes (small deviation of E^0 from the median) demonstrate good performance in key comparisons of pH (demonstrated by small mean DOE). There are some outliers to the line of best fit (weighted by participation). However with the exception of one, these NMIs have participated in 3 or fewer key comparisons. Hence one could argue that there is insufficient data to observe a correlation for these institutes. One of the outliers has participated in 5 key comparisons and demonstrates a capability to produce high performing Ag/AgCl electrodes with a poor mean performance in key comparisons. In this case there is likely to be other factors influencing their pH measurement capability. This analysis demonstrates the impact of Ag/AgCl electrode performance on comparability in pH measurement.

1 Although the slope of the acidity function might be a better indicator of electrode performance, E^0 has been used in this study due to more data being available. Should data for the slope be obtained for the comparisons studied here, this might represent useful future work. However we make the assumption that electrodes exhibiting non ideal E^0 (due to impurities etc.) are likely to exhibit similarly non-ideal slopes.

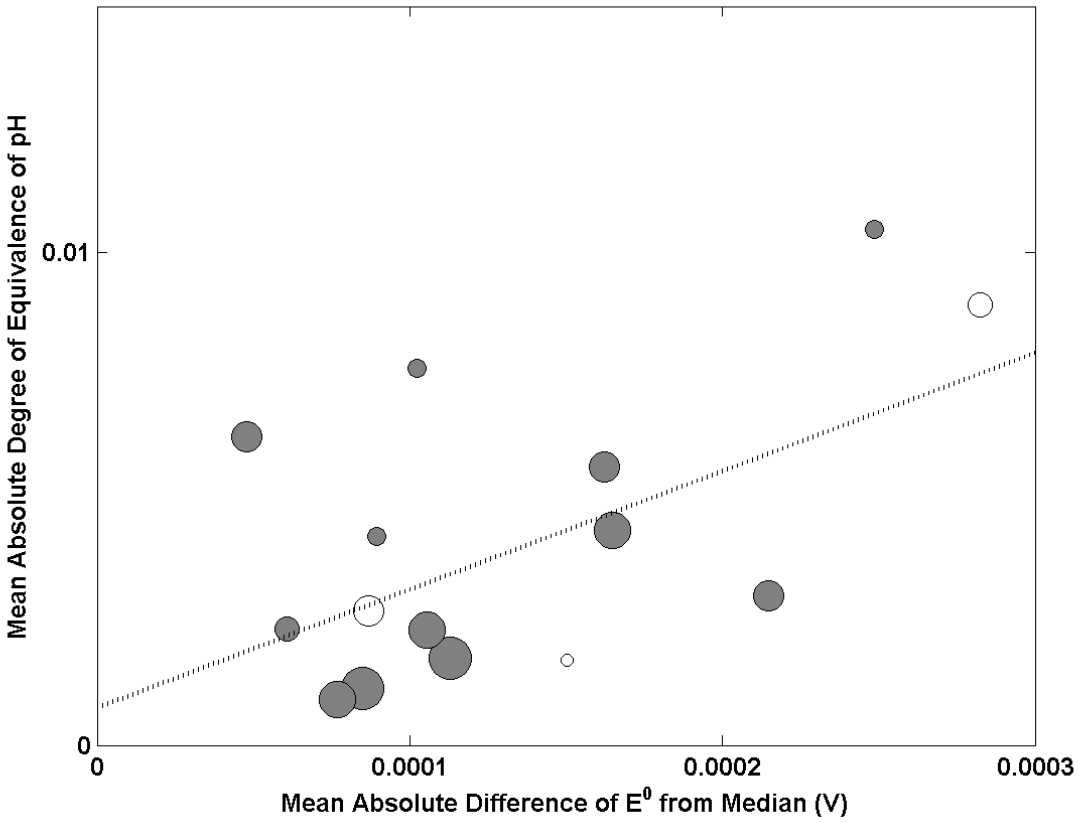

Figure 3 Correlating degree of equivalence in key comparisons of pH to Ag/AgCl electrode performance. A line of best fit has been added to the graph which has been weighted by an NMI's participation. The white circles indicate the NMI's which have not participated in P37.1.

The questionnaire was divided into two phases. The first addressed a broad range of variables in the preparation of Ag/AgCl electrodes. The second phase involved supplementary questions which were formulated from a discussion of the results from phase one.

3.1 QUESTIONNAIRE 1 RESULTS

The questionnaire was divided into 6 sections relating to different stages of the fabrication method. Table 2 provides a summary of the results. Answers were divided into 3 different categories. Answers were classified as similar for 10 or more identical responses, intermediate for 5 – 9 identical responses and different for fewer than 5 identical responses. A full table of the results is provided in table 4 of the appendix.

Table 2 Results from phase 1 of the study.

Section 1: General	Similar	Intermediate	Different
(a) Do you follow a specific standard or published method?		X	
(b) if yes to (a) which standard method is employed?		X	
(c) What material is used to seal the electrodes?	X		
(d) Is the sealant in contact with the electrolyte?	X		
(e) Is any wire on the electrode exposed to the electrolyte?	X		
(f) if yes to (e) what is the surface area of exposed wire?			X

Section 2: Preparation of Ag_2O Paste	Similar	Intermediate	Different
(a) Quality of the water used for washing and solution preparation?	X		
(b) What is the resistivity of water used (if known)?	X		
(c) Is Ag_2O prepared from a reaction of $AgNO_3$ and NaOH?	X		
(i) What is the purity of $AgNO_3$?			X
(ii) What are the main impurities in the $AgNO_3$?	Data set is too small		
(iii) What is the concentration of the $AgNO_3$ solution?		X	
(iv) Approximate mass of $AgNO_3$ solution used in reaction with NaOH?			X
(v) How is the NaOH solution prepared?	X		
(vi) What is the purity of the NaOH used to prepare the solution?			X
(vii) What are the main impurities in the NaOH solution?	Data set is too small		
(viii) What is the concentration of the NaOH solution?		X	
(ix) Mass of NaOH solution used in the reaction with $AgNO_3$?			X
(x) Temperature of $AgNO_3$ solution when the NaOH solution is added?	X		
(xi) Is the solution stirred?	X		
(xii) How is the NaOH solution added to the $AgNO_3$ solution?	X		
(xiii) Time Ag_2O is left to stand before it is decanted and washed?			X
(xiv) How many times is the precipitate washed?			X
(xv) What criterion is applied to determine the number of washings?	X		
(xvi) Is precipitate filtered after each washing (is all the water removed)?		X	
(xvii) How is the Ag_2O stored?	X		

Section 3: Preparation of Electrode Wire (for coating with Ag_2O)	Similar	Intermediate	Different
(a) What material is used for the wire?	X		
(b) What is the shape of the wire before addition of Ag_2O?	X		
(c) What is the diameter of the wire?		X	
(d) How is the wire cleaned before applying the Ag_2O paste?	X		
(e) Is the wire washed in distilled water after the cleaning procedure?	X		
(f) What is the purity of the wire?			X
(g) What are the main impurities in the wire?	Data set is too small		

Section 4: Application of Ag_2O Paste and Reduction to Ag	Similar	Intermediate	Different
(a) What device is used to transfer the Ag_2O paste to the wire?		X	
(b) How many coats are added to the wire?	X		
(c) What furnace temperature is used for reducing the Ag_2O paste?	X		
(d) What is the approximate mass of the Ag after reduction of all coats?			X
(e) What is the diameter of the Ag after reduction of all coats?			X
(f) what is the shape of the Ag/AgCl material?		X	

Section 5: Anodisation	Similar	Intermediate	Different
(a) Is the anodisation carried out between coats or in 1 stage?	X		
(b) What is the electrolyte used?	X		
(c) What are the main impurities of the electrolyte?	Data set is too small		
(d) What is the concentration of the electrolyte?	X		
(e) Is anodisation carried out at constant voltage or constant current?	X		
(f) What current is passed?	X		
(g) What voltage is applied?	Data set is too small		
(h) What is the current density?	Data set is too small		
(i) What counter electrode is used in the cell?	X		
(j) What percentage of Ag is converted to AgCl?		X	

Section 6: Comparative Electrode Measurements and Storage	Similar	Intermediate	Different
(a) What are the electrodes stored in when not in use?		X	
(b) After manufacture when are comparative measurements made?		X	
(c) Is an electrode aging process employed?		X	
(d) What electrolyte is used for the comparative measurements?		X	
(e) Electrodes equilibration time prior to comparative measurements?		X	
(f) What reference is used for the electrode potential measurements?	X		
(g) Time period for which the potential of the electrode is measured?			X
(h) Is solution deoxygenated during comparative measurements?		X	

The graphs which follow feature responses to questions that received fewer than 5 identical responses and show a good correlation to the mean absolute difference of E^0 from the median of the 8 key comparisons listed above. It is clear from the outliers in figure 3, that there are some parameters other than the performance of Ag/AgCl electrodes that affect the DOE in the key comparisons. By comparing parameters in the preparation of Ag/AgCl electrodes to E^0, we are able to de-convolute all other factors contributing uncertainty to the measurement of pH. Also, given that a good correlation exists between E^0 and DOE in most cases, E^0 can be taken to act as a surrogate for an NMI's performance in pH comparisons. Due to the often randomly scattered nature of the data reported in comparisons, absolute values of DOE and E^0 were used so that the calculated mean of all comparisons represented the average deviation of an NMI from the reference value and the median of E^0. The advantage of this is that random variations are captured, rather than summing to zero. A drawback to this approach is that any systematic information will be lost. In order to investigate the cause of systematic effects in electrode preparation, parameters from the questionnaire would need to be benchmarked against the respective DOEs and E^0 for each comparison. This would involve a substantial amount of work and would probably not provide any further information on the sensitivities of the parameters investigated.

Figure 4 shows a positive correlation between the surface area of electrode wire that is exposed to the electrolyte with the electrode performance (mean deviation of E^0 from the median). The graph suggests that as the surface area of exposed wire is reduced, the electrode performance improves. One NMI is anomalous to this observation with a large surface area of wire exposed (50 – 70 mm^2) and good performance (mean absolute difference of E^0 from median < 0.0001 V). This NMI produces electrodes from Ag wire where all other institutes use Pt. Hence with Pt exposed to the electrolyte, one

would expect a mixed potential to be set up, hence causing a deviation in the value of E^0 (the correlation observed supports this). Electrodes made from Ag wire would not suffer from this effect as Ag makes up the majority of the coated sphere. Hence this accounts for why good electrode performance was achieved with a large amount of wire exposed to the electrolyte. When using Pt wire it is important to keep the exposed area of wire to a minimum.

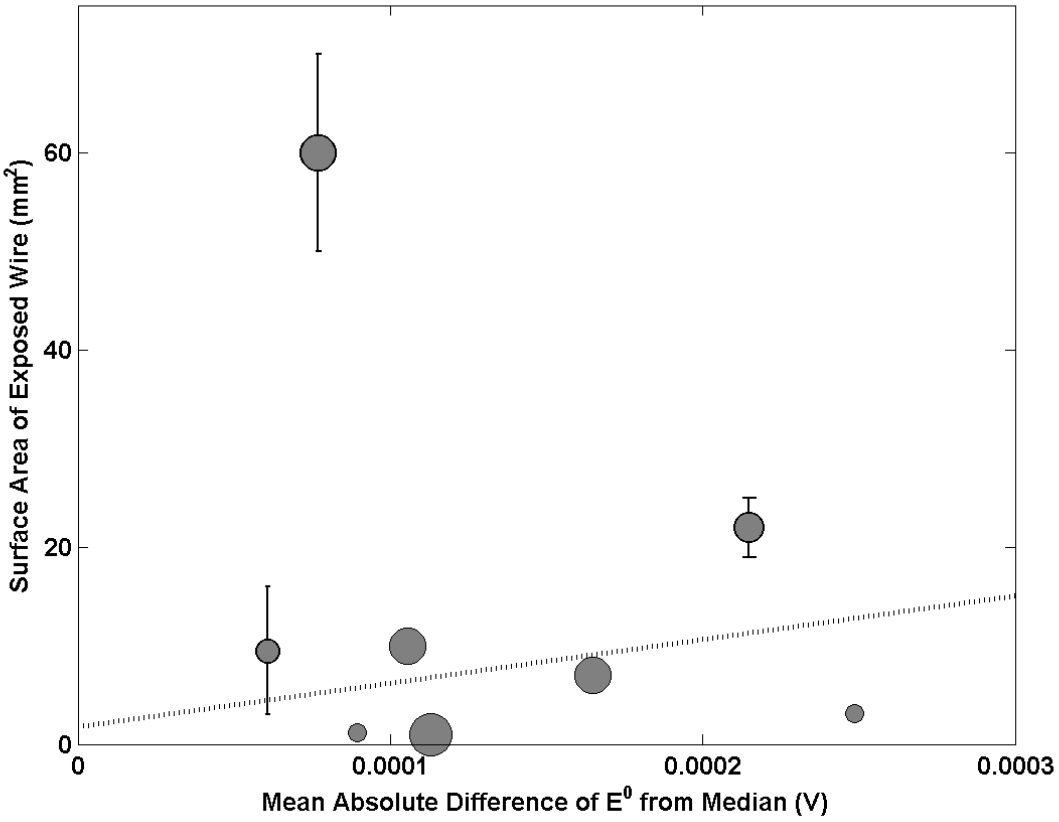

Figure 4 Surface area of the electrode wire that is exposed to the electrolyte as a function of the mean absolute difference E^0 from the median. The data is taken from responses to question 1(f) in table 4. Each sphere represents a different NMI with size being proportional to amount participation in key comparisons. Bars on the data points indicate that a range of values were submitted. A line of best fit has been added and is weighted by an NMI's participation. The anomalous data point at 60 mm^2 has been removed from the fit.

Figure 5 presents data on the time for which Ag_2O paste is left to stand before it is used in electrode fabrication. Results from 9 NMI's were received and the open circles indicate greater than values. The graph suggests that longer wait times after production of the Ag_2O paste result in better electrode performance. However the difference in the time intervals shown between NMIs is small (~0.2 hours) and there is no obvious explanation for the observed trend.

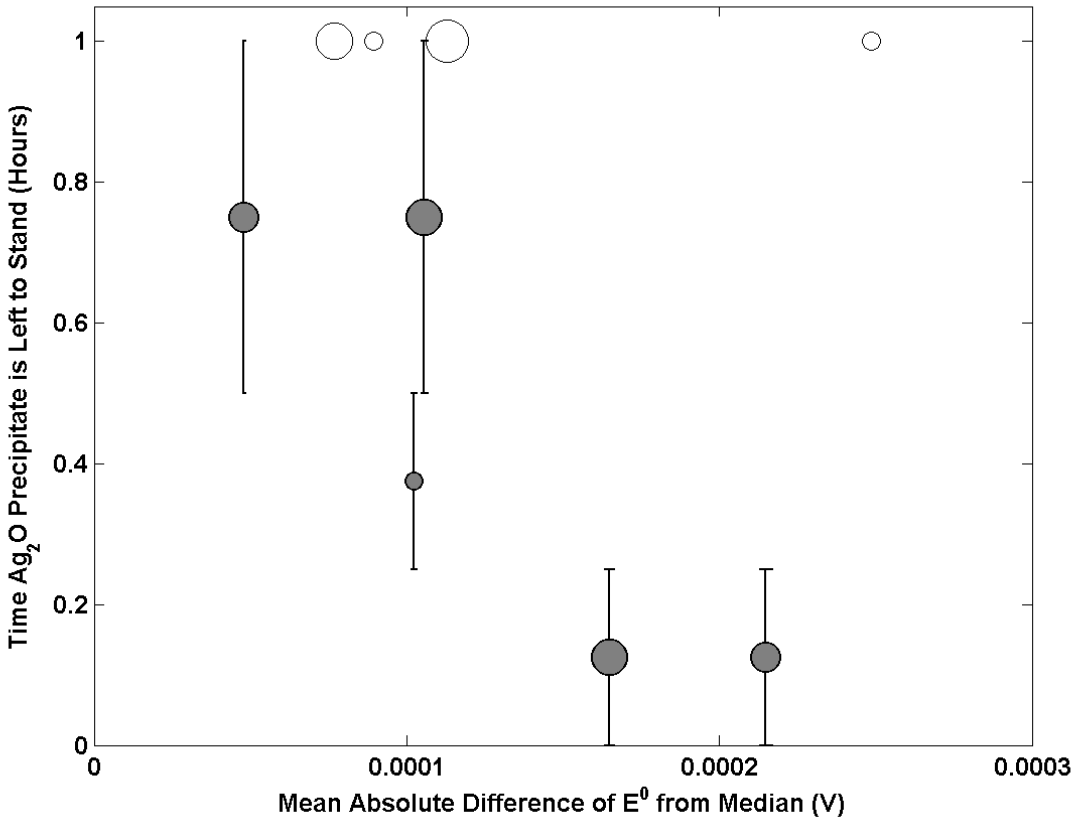

Figure 5 Time Ag_2O precipitate is left to stand before use as a function of the mean absolute difference of E^0 from the median. The data is taken from responses to question 2(cxiii) in table 4. Each sphere represents a different NMI with size being proportional to amount of participation in key comparisons. Bars on the data points indicate that a range of values were submitted. White circles indicate laboratories that have submitted greater than values.

Figure 6(a) shows the relationship between the mass of Ag added to produce an electrode and the mean absolute difference of E^0 from the median. The data shows no obvious correlation. The weighted line of best fit tentatively suggests a tendency for smaller Ag spheres to result in poorer electrodes. However, the slope is very small showing no obvious relationship between electrode performance and mass of Ag. Interestingly, when mass is substituted for diameter of the Ag sphere deposited (figure 6(b)), a positive correlation is exhibited with larger spheres resulting in poorer electrode performance. This effect has been described in recent work [1-2] and is due to the presence of a microporous structure that limits the rate at which traces of any previous solutions are diluted by any new environment. Larger diameter spheres of Ag/AgCl were shown to require longer times to reach equilibrium which is consistent with the process being described by diffusion whereby traces of the previous solution diffuses out of the pore structure while the new solution diffuses in. This increases the probability of contaminating the solution with a previous storage/measurement solution. The observed correlation in figure 6(b) supports this theory and highlights the requirement to produce electrodes with spheres of smaller diameter. A correlation between mass and diameter of the Ag sphere would be expected. However the fact that figure 6(a) does not show the same trend as figure 6(b) suggest that the porosity of the material may be the cause. Data from the 2 NMIs with the poorest electrodes produce Ag spheres with large diameters compared to the others but with a similar mass of material. This would suggest the Ag/AgCl material contains a larger degree of porosity. The performance would then be compromised due to increased equilibrium times and solution contamination.

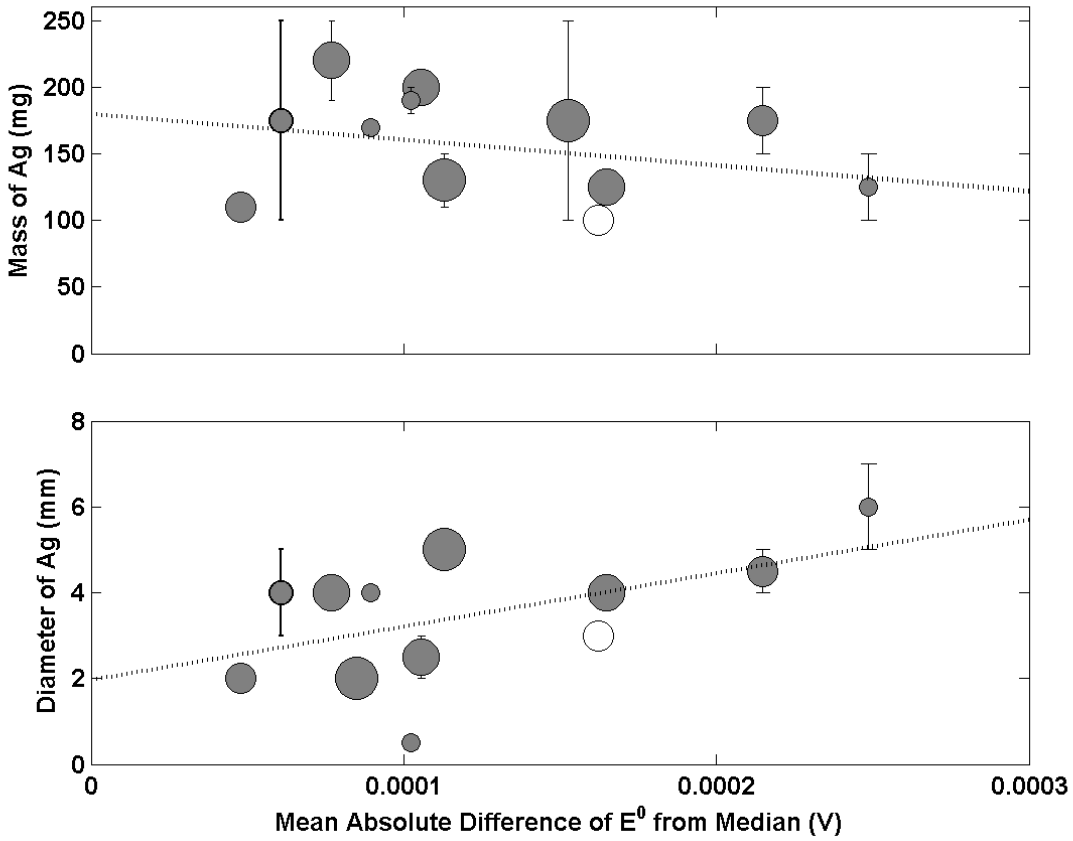

Figure 6 (a) Mass of Ag sphere before anodisation and (b) diameter of Ag sphere before anodisation, each as a function of the mean absolute difference E^0 from the median. The data is taken from responses to question 4(d) and 4(e) respectively in table 4. Each sphere represents a different NMI with size being proportional to amount of participation in key comparisons. Bars on the data points indicate that a range of values were submitted. A line of best fit has been added to the data (weighted by participation). White circles indicate laboratories that have submitted less than values (and have not been included in the line of best fit).

3.2 QUESTIONNAIRE 2 RESULTS

The second phase of the study focused on refining a sub-set of the questions from the first phase following a discussion of the results. Further questions omitted from questionnaire 1 were also added. A selection of the data with a clear correlation between parameters in the method and performance in key comparisons is presented here. A full table of the results with the questionnaire is provided in tables 6 and 7 of the appendix.

Figure 7 reports the influence of altering the content of Ag converted to AgCl during anodisation, on electrode performance. The data suggests an optimum at around 15-20% AgCl exists with laboratories converting higher and lower amounts of Ag to AgCl than this range producing poorer electrodes. The best performing lab uses 17%, a cluster at 20% and 15% show intermediate performance and the poorest performance electrodes contain 5% AgCl in one case, 20-25 % in another and one at 15%. However the data provided is not enough to strongly support this statement as the uncertainty in the AgCl content reported is expected to be large. Further research is required to understand the relationship between composition and electrode performance.

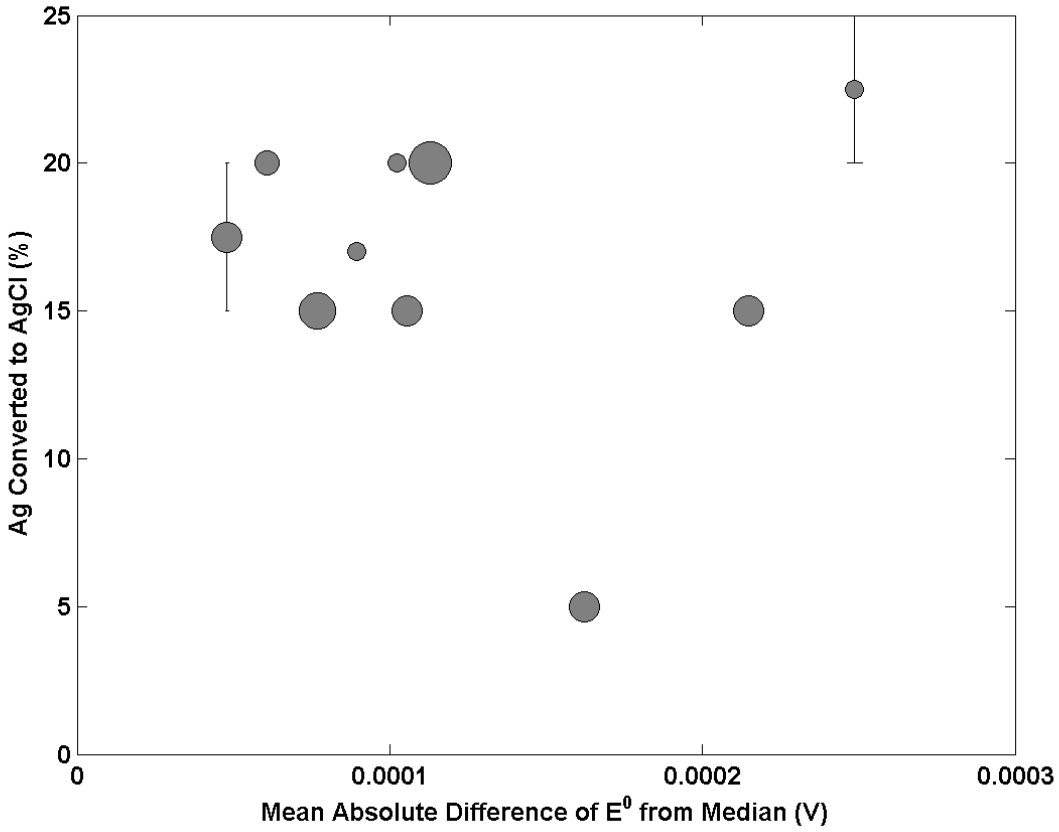

Figure 7 Amount of Ag converted to AgCl as a function of the mean absolute difference E^0 from the median. The data is taken from responses to question 1(a) in table 6. Each sphere represents a different NMI with size being proportional to amount of participation in key comparisons. Bars on the data points indicate that a range of values were submitted.

Figure 8 presents the results of the time in which an electrode is allowed to reach equilibrium in solution prior to measurement. The data exhibits an interesting trend with the smallest E^0 deviation from the median occurring for NMIs that employ longer equilibrium times. This relationship sharply plateaus for wait times below 3 hours (which the majority of institutes use). The data suggests a requirement to adopt longer equilibration times prior to measurement. This will be dependent on the porosity of the Ag/AgCl material with longer times being required for higher degrees of porosity. The solution the electrode was stored in prior to transfer to the Harned cell will also have an effect. This was addressed in question 2(d) of questionnaire 2 (see table 6 of the appendix). The majority of NMI's use a low concentration of HCl solution (ie. 0.01 $mol.Kg^{-1}$). However some use saturated AgCl solution. This may require longer times for the previous solution to diffuse out and new in and may contaminate the HCl solution depending on the porosity of the Ag/AgCl sphere.

Question 6(h) provides information on whether solutions are deoxygenated when making comparative Ag/AgCl electrode measurements (see table 4 of the appendix). It is surprising that 6 out of the 14 institutes do not deoxygenate the solution. Although the data suggests no correlation between this parameter and electrode performance (graph not shown).

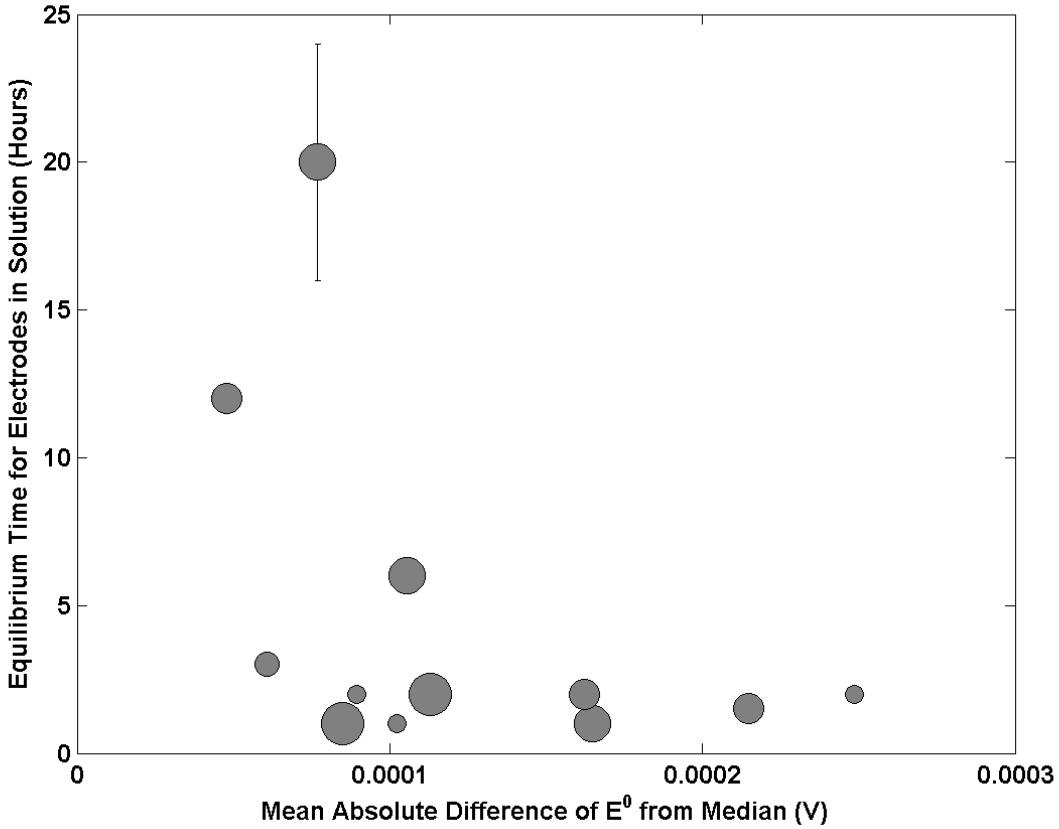

Figure 8 Time electrodes are in solution prior to measurement as a function of the mean absolute difference of E^0 from the median. The data is taken from responses to question 3(c) in table 6. Each sphere represents a different NMI with size being proportional to amount of participation in key comparisons. Bars indicate a range of times were employed.

An investigation into the impact of electrode history on electrode performance is presented in figure 9. The age of a batch of Ag/AgCl electrode used in each key comparison is plotted as a function of the mean absolute difference E^0 from the median. Generally the data suggests no correlation between electrode age and performance. However if we consider the data for each NMI there appears to be some tendency for older electrodes to display E^0 values with a larger deviation from the median.

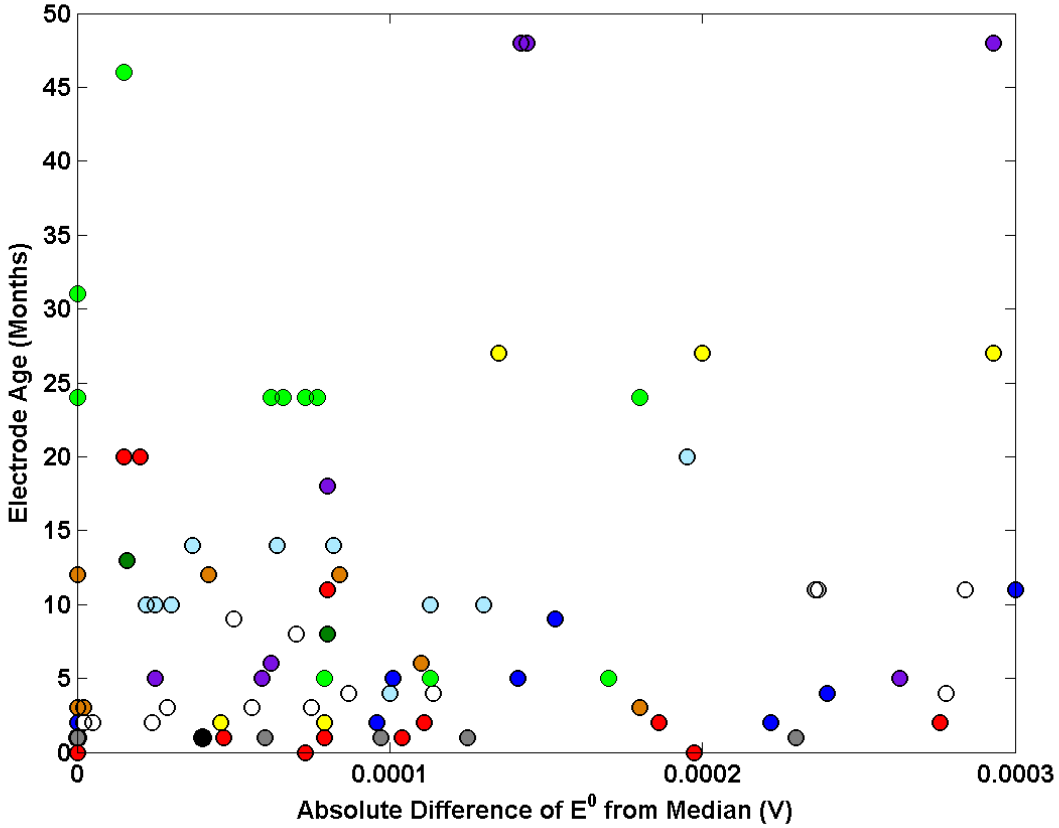

Figure 9 Electrode age as a function of the mean absolute difference of E^0 from the median. The data is taken from responses to question 2(a) in table 6.The results from each comparison are plotted and each NMI is represented with a different colour.

Another important parameter in the history of an electrode is the solutions and temperatures it has been subjected to prior to measurement. Details for each institute are provided in question 2(b) of questionnaire 2 in table 7 of the appendix.

The long and short term stability of Ag/AgCl reference electrodes is of paramount importance for accurate pH measurement as a small change in the potential of a Ag/AgCl reference electrode makes a significant contribution to the measurement uncertainty. Therefore 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 micro volts. Figure 10 shows the relationship between this rejection criterion employed at each NMI and electrode performance. An excellent linear relationship is observed with electrode performance improving when the criterion is more stringent. This outlines the importance of reducing potential differences between electrodes when making a selection.

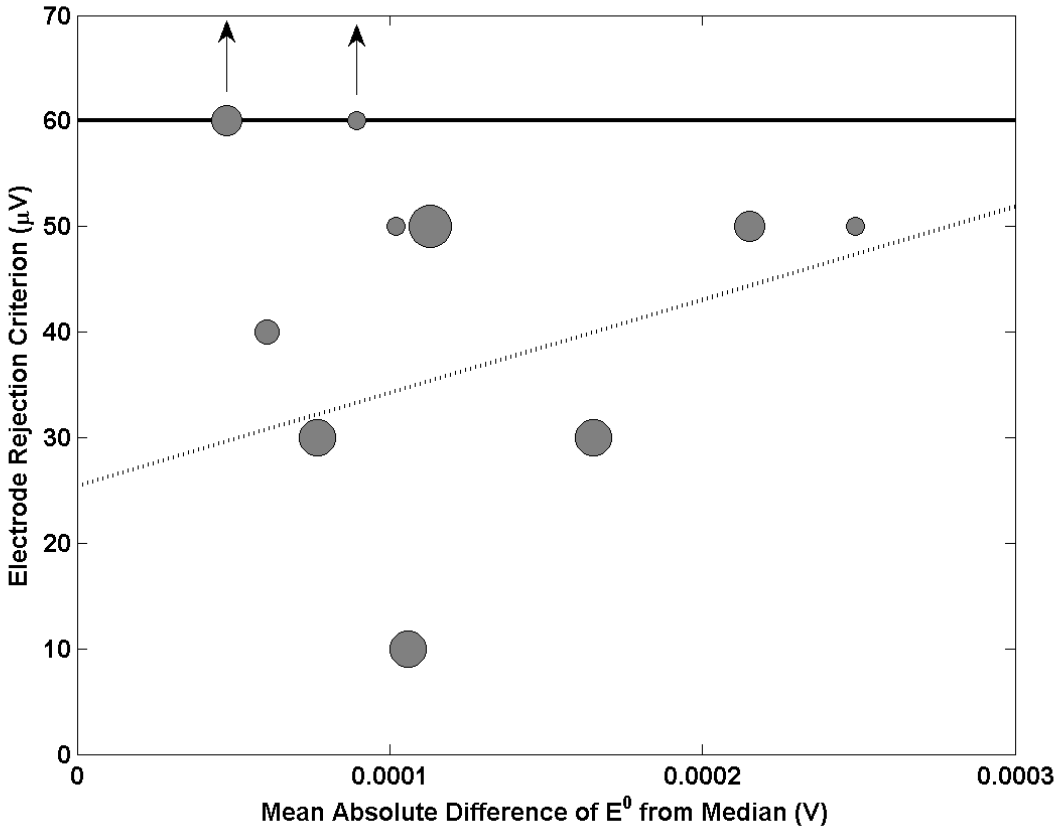

Figure 10 Electrode rejection criterion as a function of the mean absolute difference of E^0 from the median. The data is taken from responses to question 2(c) in table 6. Each sphere represents a different NMI with size being proportional to amount of participation in key comparisons. The graph has been scaled to exclude the results of 2 NMI's that were substantially larger than the others (these are indicated on the solid line with arrows and represent rejection criteria of 250 and 5000 μV). A line of best fit has been added to the graph which has been weighted by an NMI's participation.

The first half of section 3 on the Harned cell and section 4 on HCl molality in questionnaire 2 (see table 5 in the appendix) investigate parameters which may affect pH comparability which are independent of electrode performance. For this reason Figures 11 and 12 are plotted against the mean absolute DOE of pH from the 8 key comparisons. Figure 11 shows the correlation between the uncertainty in the molality of the HCl solution with performance of NMIs in key comparisons. The data reveals a positive correlation which is expected as the uncertainty in the molality of HCl is the largest contributor to pH measurement.

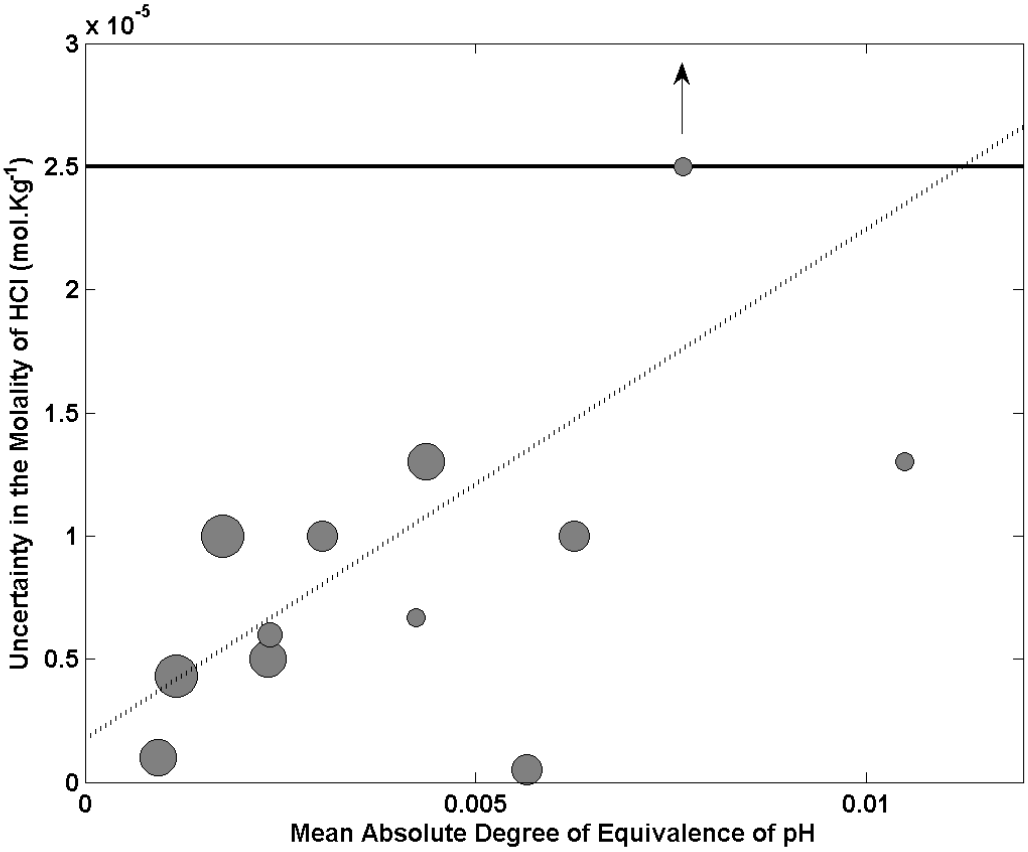

Figure 11 Uncertainty in the molality of HCl as a function of the mean absolute degree of equivalence of pH. The data is taken from responses to question 4(c) in table 6. Each sphere represents a different NMI with size being proportional to amount of participation in key comparisons. The uncertainty quoted is at the 95% confidence interval (*k*=2). The graph has been scaled to exclude the results from 1 NMI that was substantially larger than the others (this is indicated on the solid line with an arrow and represents an uncertainty of 5 x 10^{-5} mol/Kg). A line of best fit has been added to the graph which has been weighted by an NMI's participation.

Figure 12 shows the relationship between the dimensions of Harned cells used at different NMIs and their performance in key comparisons. Circles in dark blue, red, yellow, orange, green, purple and light blue represent dimensions *t*, *u*, *v*, *w*, *x*, *y* and *z* on diagram in questionnaire 2 in table 5 in the appendix respectively. The y-axis is plotted on a log scale. No correlation is observed for each of the Harned cell dimensions.

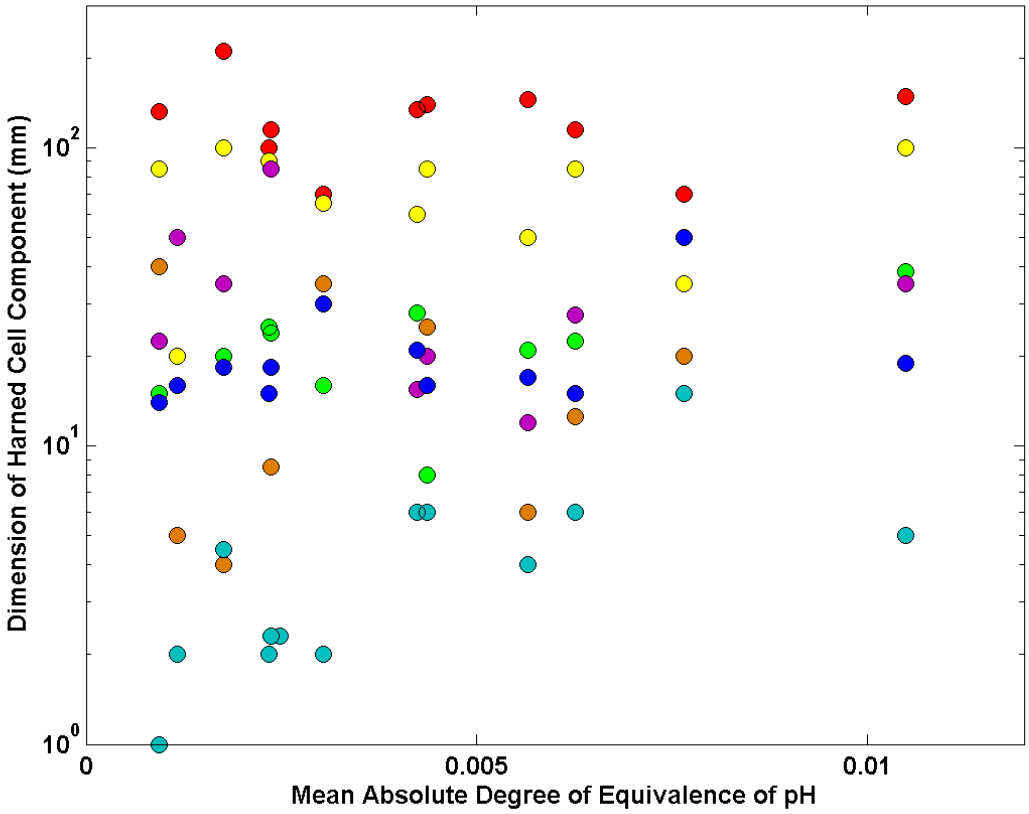

Figure 12 Dimension of Harned cell components as a function of the mean absolute degree of equivalence of pH for each NMI. The data is taken from responses to question 4(c) in table 6. Circles in dark blue, red, yellow, orange, green, purple and light blue represent dimensions *t, u, v, w, x, y* and *z* on the diagram in questionnaire 2 in table 5 of the appendix respectively. A mean was taken for institutes that responded with a range of dimensions.

3.3 FURTHER OBSERVATIONS

This study revealed some further information which is informative to understand the sensitivities of the various stages in the preparation protocol on electrode performance. From the data provided there is some evidence that the purity of reagents used in the preparation of Ag_2O (such as $AgNO_3$ and NaOH) and the purity of the electrode wire influenced electrode performance (data not plotted- see purity data in tables 4 and 6 of the appendix). However, most data provided was taken from assays quoted on purchased reagents (often indicated with greater than values). Therefore for a thorough analysis to be performed laboratories would be required to measure the impurities in materials which is outside the scope of this study.

One laboratory claimed to purchase Ag_2O from third party instead of producing it in house. It is likely that the material has not be produced with the same rigour that would be exercised following a standard preparation procedure. For example, the number of times the material is washed after formation is likely to be reduced. Hence the purchase material would be expected to contain more impurities and result in poorer electrodes.

Two laboratories have reported a different procedure to the conventional anodisation, for converting some of the Ag to AgCl. The convertion is achieved by reacting Ag with Cl_2 using a 0.01M HCl solution saturated with Cl_2. The reason provided by the laboratory for adopting this alternative method is that it produces a more homogenous layer. However, there is not enough data to determine its effect

on electrode performance. Similarly, one institute reports a different route to preparing Ag (Ag_2CO_3 paste is prepared from $AgNO_3$ and $NaHCO_3$ instead of Ag_2O from $AgNO_3$ and NaOH). The reason for this is that it is believed that HCO_3^- does not adhere to the precipitate as much as OH^-. A further alteration to the conventional method for producing Ag_2O is that one institute uses KOH instead of NaOH.

Three institutes state that they apply thinner final Ag_2O layers when coating the electrode. This is believed to result in a more uniform morphology of the final Ag/AgCl sphere. However, once again further work is required to established its influence on electrode performance.

4 CONCLUSIONS

A questionnaire was completed by 14 participants 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 reveals that the parameters most closely correlated to performance in comparisons are 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, equilibrium time for electrodes in solution prior to measurement and electrode rejection criteria employed. From the data provided there is some evidence that the purity of reagents used in the preparation of Ag_2O (such as $AgNO_3$ and NaOH) and the purity of the electrode wire influenced electrode performance. Although the influence of several of these parameters on Ag/AgCl electrode performance might be expected [1-6], this study provides for the first time, information on the sensitivities of these parameters on repeatability of the electrode potential and performance at the international level, and how variations between institutes may affect the accuracy of primary pH measurement. Although this study is qualitative, it highlights a clear correlation for a number of parameters to performance in key comparisons. This allows for a unified strategy within the CCQM-EAWG for electrode design and may lead to improved future international comparability in pH measurement.

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6 APPENDIX

Table 3 Questionnaire 1.

Section 1: General

(a) Do you follow a specific standard or published method?
(b) If yes to (a) which standard method is employed?
(c) What material is used to seal the electrodes? (*if possible include an electrode diagram in section 7*)
(d) Is the sealant in contact with the electrolyte?
(e) Is any wire on the electrode exposed to the electrolyte?
(f) If yes to (e) approximately what is the surface area of exposed wire?

Section 2: Preparation of Ag_2O Paste

(a) What is the quality of water used for washing and solution preparation?
(b) What is the resistivity of water used (if known)?
(c) Is Ag_2O prepared from a reaction of $AgNO_3$ and NaOH?
(d) If answer to (c) is yes:
(i) What is the purity of $AgNO_3$?
(ii) What are the main impurities in the $AgNO_3$?
(iii) What is the concentration of the $AgNO_3$ solution?
(iv) What approximate mass of the $AgNO_3$ solution is used in the reaction with NaOH?
(v) How is the NaOH solution prepared?
(vi) What is the purity of the NaOH used to prepare the solution?
(vii) What are the main impurities in the NaOH solution?
(viii) What is the concentration of the NaOH solution?
(ix) What approximate mass of the NaOH solution is used in the reaction with $AgNO_3$?
(x) What is the temperature of the $AgNO_3$ solution when the NaOH solution is added?
(xi) Is the solution stirred?
(xii) How is the NaOH solution added to the $AgNO_3$ solution?
(xiii) How long after the reaction of $AgNO_3$ and NaOH is the Ag_2O precipitate left to stand before it is decanted and washed?
(xiv) How many times is the precipitate washed?
(xv) what criterion is applied to determine the number of washings?
(xvi) Is the precipitate filtered after each washing (ie is all the water removed)?
(xvii) How is the Ag_2O stored?

Section 3: Preparation of Electrode Wire (for Coating with Ag_2O)

(a) What material is used for the wire?
(b) What is the shape of the wire before addition of Ag_2O?
(c) What is the diameter of the wire?
(d) How is the wire cleaned before applying the Ag_2O paste?
(e) Is the wire washed in distilled water following the cleaning procedure?
(f) What is the purity of the wire?
(g) What are the main impurities in the wire?

Section 4: Application of Ag_2O Paste and Reduction to Ag

(a) What device is used to transfer the Ag_2O paste to the wire?
(b) How many coats are added to the wire?
(c) What furnace temperature is used for reducing the Ag_2O paste?
(d) What is the approximate mass of the Ag after reduction of all coats?
(e) What is the approximate diameter of the Ag after reduction of all coats?
(f) What is the shape of the Ag/AgCl material?

Section 5: Anodisation

(a) Is the anodisation carried out in between coats or in 1 stage after adding all coats?
(b) What is the electrolyte used?
(c) What are the main impurities of the electrolyte?
(d) What is the concentration of the electrolyte?
(e) Is the anodisation carried out at constant voltage or constant current?
(f) What current is passed?
(g) What voltage is applied?
(h) What is the current density?
(i) What counter electrode is used in the cell?
(j) What percentage of Ag is converted to AgCl?

Section 6: Comparative Electrode Measurements (not Harned Cell measurements) and Storage

(a) What are the electrodes stored in when not in use?
(b) How soon after manufacture are comparative electrode measurements made?
(c) Is an elecrtrode aging process employed?
(d) What electrolyte is used for the comparative electrode measurements?
(e) How much time is allowed for electrodes to equilibriate in solution prior to comparative measurements?
(f) What reference is used for the electrode potential measurements?
(g) What is the time period for which the potential of the electrode is measured?
(h) Is the solution deoxygenated when comparative electrode measurements are carried out?

Section 7: Further Details of Preparation Procedure

Please provide a description of your preparation procedure to include any processes / techniques not covered by the questionnaire.

Table 4 Full results from questionnaire 1.

Question	PTB	DFM	KRISS	NMIJ	CENAM	GUM	SMU	NIST	LNE	BIM	INMETRO	NPLI	IPQ	NIM
1(a)	Y (mods)	N	Y	Y (mods)	Y	Y (mods)	N	Y (mods)	N	Y	Y	Y	Y (mods)	Y
1(b)	-	-	**	***	**	-	-	**	-	-	*	****	-	-
1(c)	glass	glass	glass	glass	glass	glass	glass	other	glass	other	glass	glass	glass	glass
1(d)	Y	Y	N	Y	Y	Y	Y	Y	Y	N	Y	Y	Y	Y
1(e)	Y	Y	Y	Y	Y	Y	N	Y	Y	N	N	Y	Y	N
1(f)	1	3-16	1.15	10	7	19-25	-	50-70	3.14	-	-	1.3	1.75	-
2(a)	ultra pure	-	-	ultra pure	deionised	ultra pure	ultra pure	deionised	ultra pure	laboratory	deionised	deionised	ultra pure	ultra pure
2(b)	18.2 MΩcm	0.67-3.3 MΩcm	-	18.2 MΩcm	18.2 MΩcm	18.2 MΩcm	18.2 MΩcm	18.2 MΩcm	18.2 MΩcm	<2 µS/cm	18.2 MΩcm	1 MΩcm	18.2 MΩcm	17 MΩcm
2(c)	Y	Y	Y	Y	Y	Y	N	Y	Y	N	N	purchased	Y	Y
2(di)	>99%	>99%	>99%	99.8%	>99.999%	>99.9%	>99.9%	>99.999%	>99.99%	>99.9%	-	-	>99.9%	>99.99%
2(dii)	-	Pb,Tl <0.001% Ni,Mn,Cl<0.000 5%,Zn,Cd,0.0 001%,Fe,Cu< 0.0002%, SO4 < 0.002 %	-	SO_4 < 0.01 %, Cl 0.001 %	-	Pb<0.001%, Tl<0.001%, Ni<0.0005%, Mn<0.0005%, SO_4 0.002%	Fe, Cu, Bi, Pb	HNO_3 PO_4<30, SO_4<200, As<2, Cr 9, Pb<10, Sn<10, h metals<50	-	SO_4 0.0024%	-	-	-	SO_4 0.002(%)
2(diii)	0.7 M	0.7 M	0.67 M	0.03 M	0.714 M	0.66 M	0.3 M	~2 M	0.714 M	0.67 M	-	-	0.67 M	0.1 M
2(div)	700 g	800 g	3300 g	5 g	84.9 g	133.5 g		(275±25) ml	5.86 g	6.79 g	-	-	338 g	200 g
2(dv)	gravimetry	gravimetry	gravimetry	gravimetry	gravimetry	gravimetry	-	gravimetry	gravimetry	gravimetry	-	-	gravimetry	gravimetry
2(dvi)	>99%	>99%	>99.99%	>97.0%	>99.99%	>99%	-	>99%	>99.99%	>95%	-	-	>99.9%	>99.9%
2(dvii)	<(0.0005%Pb 0.0005%Fe 0.001%Al 0.0005%Cl 0.0005%SO_4 0.0005%PO_4 0.005%SiO_2 1%Na_2CO_3	Na_2CO_3<1% SiO_2<0.005% SO_4<0.0005% Ca<0.0005%, Fe<0.0005% K<0.05% Al<0.0005%	-	Na_2CO_3 <1 %, K 0.05 %, Cl 0.005 %	-	Na_2CO_3<1% SiO_2<0.0005% SO_4<0.0005% Ca<0.0005%, Fe<0.0005% K<0.0002% Al<0.0002%	-	Cu <10. H metals as Ag < 5, Fe < 0.8, Hg < 0.1, PO_4 < 2	-	K_2CO_3 1%	-	-	-	K 0.01 Al 0.01 Ca 0.01 (%)
2(dviii)	5 M	5 M	5 M	0.03 M	4.98 M	3.9 M	-	2 M	3.944 M	0.2 M	-	-	5 M	0.1 M
2(dix)	100 g	140 g	480 g	1.2 g	-	18.5 g	-	240 g	1.3753 g	-	-	-	80 g	200 g
2(dx)	20-30 °C	20-30 °C	20-30 °C	20-30 °C	20-30 °C	20-30 °C	-	20-30 °C	20-30 °C	20-30 °C	-	-	20-30 °C	20-30 °C
2(dxi)	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	-	-	Y	Y
2(dxii)	dropwise	intermed	dropwise	dropwise	dropwise	dropwise	-	dropwise	dropwise	dropwise	-	-	dropwise	dropwise
2(dxiii)	>60 mins	-	2 days	30-60 mins	0-15 mins	0-15 mins	-	>60 mins	>60 mins	15-30 mins	-	-	-	30-60 mins
2(dxiv)	-	-	30-40	50-60	10-15	40	5-10	10-15	-	15-20	-	-	-	15-20
2(dxv)	-	conductivity remains constant	-	conductivity remains constant	conductivity < 35 µs/cm	conductivity remains constant	conductivity remains constant	conductivity < 8 µS·cm-1	-	conductivity ≤ $5x10^{-6}$ S/m	-	-	Bates and experience	conductivity remains constant
2(dxvi)	-	-	N	N	Y	N	-	N	Y	N	-	-	Y	Y
2(dxvii)	kept hydrated	kept hydrated	-	kept hydrated	kept hydrated	kept hydrated	kept hydrated	allowed to dry	kept hydrated	kept hydrated	-	-	kept hydrated	kept hydrated

Question	PTB	DFM	KRISS	NMIJ	CENAM	GUM	SMU	NIST	LNE	BIM	INMETRO	NPLI	IPQ	NIM
3(a)	Pt	Pt	Pt	Pt	Pt	Pt	Pt	Ag	Pt	Pt	Pt	Pt	Pt	Pt
3(b)	helix	helix	helix	helix	helix	fish hook	helix	fish hook	fish hook	helix	helix	helix	helix	helix
3(c)	0.5-1.0 mm	0.5-1.0 mm	0.7 mm	<0.5 mm	<0.5 mm	0.5-1.0 mm	<0.5 mm	0.5-1.0 mm	0.5-1.0 mm	0.5-1.0 mm	0.05 mm	0.5 mm	<0.5 mm	0.5-1.0 mm
3(d)	nitric acid	nitric acid	nitric acid	nitric acid	nitric acid	other	annealing	nitric acid	nitric acid	nitric acid	nitric acid	water	nitric acid	piranha
3(e)	Y	Y	Y	Y	Y	Y	N	Y	Y	Y	Y	Y	Y	Y
3(f)	<99.99%	>99.99%	99%	> 99.95%	<99.999%	<99.9%	<99.9%	<99.999%		<99.999%	99.99%	<99.9%	<99.999%	<99.99%
3(g)	-	Cu 6ppm Al 1ppm Sn 1ppm Ge 1ppm	-	-	-	Pd 0.012% Rh 0.0029% Fe 0.0011% As 0.001% Ir <0.001% Ru<0.001% Sb<0.001%	-	Si 3.5 no others detected (high DL for Hg<100,As<30,W<100)	-	-	-	Al 96, B 380, Co 5.3, Cu 1.9, Fe 38, Mg 12, Mn 0.7, Ni 0.6, Ti 0.9, Zn 7.4 ppm	-	Rh 0.002% Ir 0.002%
4(a)	plastic	glass	metallic	immersed	glass	glass	plastic	plastic	no device	glass	other	wooden	metallic	glass
4(b)	>4	>4	2-3	>4	>4	>4	3	>4	>4	>4	>4	1	>4	>4
4(c)		400-500 °C	400-500 °C	400-500 °C	400-500 °C	400-500 °C	300-400 °C	400-500 °C	400-500 °C	400-500 °C	400-500 °C	400-500 °C	400-500 °C	400-500 °C
4(d)	110-150 mg	100-250 mg	~ 170 mg	200 mg	125 mg	150-200 mg	-	190-250 mg	100-150 mg	180-200 mg	<100 mg	-	110 mg	110 mg
4(e)	5 mm	3-5 mm	4 mm	2-3 mm	4 mm	4-5 mm	2 mm	4 mm	5-7 mm	0.5 mm	<3 mm	4 mm	3 mm	2 mm
4(f)	spherical	spherical	helix	spherical	spherical	spherical	cylindrical	spherical	other	spherical	cylindrical	cylindrical	spherical	cylindrical
5(a)	1 stage	1 stage	1 stage	1 stage	1 stage	1 stage	-	1 stage	1 stage	1 stage	-	1 stage	1 stage	1 stage
5(b)	HCl	HCl	1M HCl	HCl	HCl	HCl	-	HCl	HCl	HCl	-	HCl	HCl	HCl
5(c)	-	Br<5ppm, Cl<100ppb, PO_4<10ppm, SO_4<300ppm, SO_3<500ppm, GE<10ppm, NH_4<500ppm	-	<10 ppt for Cu, Al, Ge, Sn, W, Se, Fe, Ni and Pt	-	Br ~0.0004%, SO_4- ~0.000008 %, SO_3 ~ 0.000008 %	-	Br<5, As>0.005	-	br <50 ppm	-	-	-	SO_4 0.0002(%) SO_3 0.0002(%) Sn 0.0002(%)
5(d)	1 M	1 M	1 M	1 M	1 M	1 M	-	1 M	1 M	1 M	-	1 M	1 M	1 M
5(e)	constant current	constant current	constant current	constant current	constant current	constant current	-	constant current	constant current	constant current	-	constant current	constant current	constant current
5(f)	10 mA	10 mA	10 mA	10 mA	10 mA	10 mA	-	10 mA	10 mA	10 mA	-	20 mA	10 mA	10 mA
5(g)	-	-	-	<1V	-	-	-	-	-	10 V	-	-	-	0.3~0.4 (V)
5(h)	13 mA/cm^2	-	-	5 mA/cm^2	-	3.2-5 mA/cm^2	-	-	-	-	-	4 mA/cm^2	-	10 mA/cm^2
5(i)	Pt	Pt	Pt	Pt	Pt	Pt	-	Pt	Pt	Pt	-	Pt	Pt	Pt
5(j)	-	20%	17%	15%	-	>15%	-	15%	>15%	>15%	~5%	-	>15%	15%
6(a)	0.005M HCl	0.005M HCl	0.05M HCl	0.005M HCl	0.01M HCl	sat AgCl	sat AgCl	0.01M HCl	0.005M HCl	water	0.01M HCl	0.01M HCl	0.005M HCl	0.01M HCl
6(b)	1 week	-	1 day	1 months	4-7 days	1 week	3-4 days	1 week	1 week	1 week	-	1 week	3-4 days	1 week
6(c)	Y	N	Y	Y	N	Y	N	Y	N	Y	-	Y	N	Y
6(d)	other	other	0.05M HCl	0.01M NaCl	other	0.01M KCl	0.01M HCl	0.01M HCl	other	0.01M HCl	-	0.01M HCl	0.01M HCl	0.01M HCl
6(e)	24 hours	24 hours	2 hours	2-6 hours	-	24 hours	0-2 hours	0-2 hours	2-6 hours	>24 hours	-	40 mins	0-2 hours	>24 hours
6(f)	from batch	other	from batch	from batch	from batch	other	from batch	from batch	from batch	from batch	-	H_2electrode	from batch	from batch
6(g)	30-60 mins	<30 mins	~2 months	30-60 mins	>60 mins	<30 mins	30-60 mins	<30 mins	>60 mins	30-60 mins	-	3 months	<30 mins	>60 mins
6(h)	Y	Y	Y	Y	Y	N	Y	N	Y	N	-	N	N	N

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Table 5 Questionnaire 2.

Section 1 - Follow-up Questions

			Unc
(a) What percentage of Ag is converted to AgCl during the anodisation process?		%	
(b) State the quality grade of $AgNO_3$ used to prepare the Ag_2O paste?			
(c) State the quality grade of NaOH used to prepare the Ag_2O paste?			
(d) What is the metallic purity of the Pt/Ag support wire? (*quote uncertainty*)*		%	
(e) How long is the Ag_2O paste heated (during the reduction process to Ag)?		minutes	

**Based on metallic impurities*

Section 2 Electrode History

(a) Enter the approximate age (in months) of the Ag/AgCl electrodes used in each comparison in the table below (shaded boxes indicate that an NMI did not paricipate in a comparison).

	PTB	DFM	KRISS	NMIJ	CENAM	GUM	SMU	NIST	LNE	BIM	INMETRO	INPL	IPQ	NIM
K9														
P37														
K9.2														
K17														
K18														
K19														
K18.1														
K20														

(b) For each comparison participated in, list the types of solutions and temperatures the Ag/AgCl electrodes were subjected to in the month leading up to the comparison.

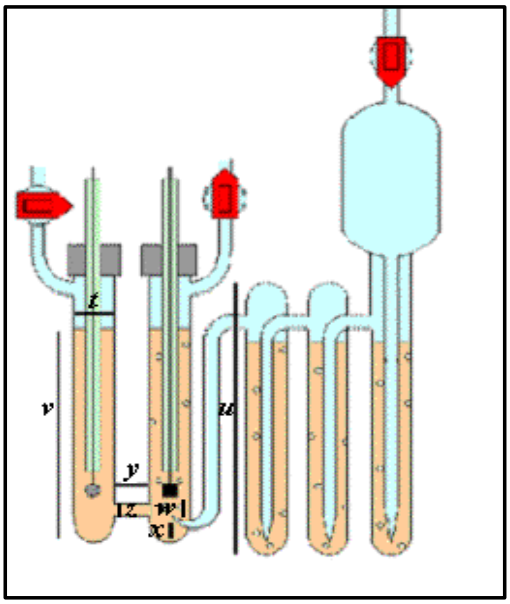
	1	T(°C)	2	T(°C)	3	T(°C)	4	T(°C)	5	T(°C)	6	T(°C)	7	T(°C)
K9														
P37														
K9.2														
K17														
K18														
K19														
K18.1														
K20														

(c) What criteria is used for Ag/AgCl electrode rejection?

(d) What solution are Ag/AgCl electrodes stored in before transfer to the Harned cell?

Section 3 The Harned Cell

(a) Provide a schematic of your Harned cell with dimensions. If different cells have been used, please draw each different type and state which key comparison each cell has been used in.



The dimensions we are paricularly interested in are shown on the diagram and are:

(i) Inner diameter of the working compartment (t)
(ii) The compartment length (u)
(iii) Height of the column of solution (v)
(iv) Distance between H_2 inlet and electrode (w)
(v) Distance between H_2 inlet and bottom of cell (x)
(vi) Distance between H_2 electrode and Ag/AgCl electrode compartments (y)
(vii) The inner diameter of the connecting tube between the compartments (z)

(b) Is there a difference when measuring Ag/AgCl electrodes vs the hydrogen electrode in a Harned cell compared to vs each other? If so give details of the E^0 difference.

(c) What is the time period from inserting the Ag/AgCl electrodes in the Harned cell to taking readings?

Section 4 HCl Molality

(a) What method is used to determine HCl molality?
(b) What is the concentration of bromide impurities in the solution?
(c) What is the uncertainty in the HCl molality?

If procedures have been changed since K9, please state for each answer the nature and date(s) when the change(s) was (were) made

Table 6 Results from questionnaire 2.

Question	PTB	DFM	KRISS	NMIJ	CENAM	GUM	SMU	NIST	LNE	BIM	INMETRO	NPLI	IPQ	NIM
1(a)	20%	20%	17%	15%	-	>15%	-	15%	20-25%	20%	5%	-	-	15-20%
1(b)	> 99%	99.9%	99%	> 99.8%	99.9999%	> 99.9%	-	99.999%	99.995%	-	> 99.8%	-	-	> 99.9%
1(c)	> 99%	99%	99.99%	> 97%	99.99%	> 99%	-	98.6%	99.998%	-	> 99.0%	-	-	> 99.5%
1(d)	> 99.99%	99.998%	99%	99.95%	99.997%	> 99.9%	99%	99.999%	> 99%	≥99.99%	99.99%	99.90%	-	99.99%
1(e)	15 mins	16 mins	120 mins	15 mins	15 mins	10 mins	-	10 mins	15 mins	75 mins	3 mins	250 mins	-	30-40 mins
K9	3	-	2	-	24	5	0	5	-	-	-	-	-	3
P37	1	-	15	-	6	6	10	1	-	1		1	-	-
K9.2	2	-	-	10	-	-	-	-	-	-	-	-	-	-
K17	4	-	27	10	48	2	1	24	-	-	-	-	-	12
K18	9	-	-	4	18	11	11	31	1	1	-	1.5	-	6
K19	11	-	-	14	5	9	2	24	-	1	-	-	-	-
K18.1	8	8	-	-	2	-	20	-	1	-	-	0.5	-	3
K20	-	13	-	20	6	4	20	46	-	1	-	1	-	-
2(c)	deviation <50 µV	deviation <40 µV	deviation < 5000 µV	deviation <10 µV	deviation <30 µV	deviation <50 µV	-	deviation <30 µV	deviation <50 µV	deviation <50 µV	-	deviation <100 µV	-	deviation <250 µV
2(d)	0.005M HCl	0.005M HCl	0.005M HCl	0.005M HCl	0.01M HCl	sat. AgCl	sat. AgCl	soln to be measured	0.005M HCl	sat. AgCl	0.01M HCl + sat. AgCl	-	-	0.01M HCl
3(ai)	18.4 mm	18.4 mm	21 mm	15 mm	16 mm	30 mm	16 mm	14 mm	19 mm	50 mm	17 mm	14 mm	-	15 mm
3(aii)	210 mm	115 mm	134 mm	100 mm	140 mm	70 mm	-	130-135 mm	149 mm	70 mm	145 mm	120 mm	-	115 mm
3(aiii)	100 mm	80-90 mm	60 mm	90 mm	85 mm	65 mm	20 mm	80-90 mm	100 mm	35 mm	50 mm	80 mm	-	80-90 mm
3(aiv)	4 mm	2-15 mm	6 mm	15 mm	25 mm	35 mm	5 mm	40 mm	5 mm	20 mm	6 mm	1 mm	-	10-15 mm
3(av)	20 mm	20-28 mm	28 mm	25 mm	8 mm	16 mm	-	15 mm	38.5 mm	0.5 mm	21 mm	20 mm	-	20-25 mm
3(avi)	35 mm	80-90 mm	15.5 mm	15 mm	20 mm	35 mm	50 mm	20-25 mm	35 mm	15 mm	12 mm	40 mm	-	25-30 mm
3(avii)	4.5 mm	2.3 mm	6 mm	2 mm	6 mm	2 mm	2 mm	1 mm	5 mm	15 mm	4 mm	18 mm	-	5-7 mm
3(b)	Y*	Y	N	< 10 µV	< 200 µV	Y	~ 100 µV	2 x larger in Harned cell	Y**	-	~ 300 µV	N	-	< 100 µV
3(c)	2 hrs	3 hrs	2 hrs	6 hrs	1 hr	1.5 hrs	1 hr	16-24 hrs	2 hrs	1 hr	2 hrs	0.66 hrs	-	12 hrs
4(a)	coulometry	coulometry	coulometry	coulometry	potent. titration	potent. titration	coulometry	coulometry	potent. titration	potent. titration	coulometry	potent. titration	-	coulometry
4(b)	below detection limit : 20µg/kg	less than 5 ppm	-	-	-	max. = ca. 0,05 mg/1000g	less than 10 ppm	stated as < 0.005 % (50 ppm)	less than 5 ppm	-	< 13 µg/kg	-	-	1×10^{-7} mol/kg
4(c)	0.00001 mol/Kg	0.000006 mol/kg	0.0000067 mol/kg	0.000005 mol/kg	0.000013 mol/kg	0.00001 mol/kg	0.0000043 mol/kg	0.000001 mol/Kg	0.000013 mol/kg	0.000052 mol/kg	0.0000005 mol/kg	0.0000377 mol/kg	-	$1\times10-5$ mol/kg

* E^0 in the pH set-up is determined as the mean using three cells. The standard deviation in general is below 30µV. E^0 measured at 3 HCl molalities after aging and before used in pH measurements: E^0 calculated with fixed gamma+/- deviate at maximum 40 µV from E^0 (taken from extrapolation).
** K18 : the range is 40µV when comparing the electrodes to each other, and the range is 150 µV when measuring E°. K18.1 the range is 20µV when comparing the electrodes to each other, and the range is 50 µV when measuring E°.

Table 7 Results from questionnaire 2, question 2(b).

PTB	Solution 1	Temp (°C)	Solution 2	Temp (°C)	Solution 3	Temp (°C)	Solution 4	Temp (°C)	Solution 5	Temp (°C)	Solution 6	Temp (°C)	Solution 7	Temp (°C)
K9	phthalate	5-50	phthalate	5-50	phthalate	5-50	oxalate	5-50	phosphate	5-50	oxalate	5-50	oxalate	5-50
K9.2	carbonate	15-25	carbonate	37	carbonate	37	carbonate	37	phosphate	5-50	phosphate	5-50	phosphate	5-50
K17	phthalate	5-50	phthalate	5-37	phthalate	5-37	phthalate	5-37	phthalate	5-37	HCl	15-25	phthalate	5-37
K18	carbonate	25	carbonate	25	carbonate	37	borate	15-37	carbonate	15-37	carbonate	15-37	carbonate	15-37
K19	borate	15-37	borate	15-37	borate	15-37	borate	15-37	borate	15-37	borate	15-37	borate	15-37
K18.1	HCl	25	HCl	10-50	oxalate	10-50	oxalate	10-50	oxalate	10-50	HCl	5-50	HCl	5-50
K20	oxalate	10-50	oxalate	10-50	-	-	-	-	-	-	-	-	-	-
DFM	**Solution 1**	**Temp (°C)**	**Solution 2**	**Temp (°C)**	**Solution 3**	**Temp (°C)**	**Solution 4**	**Temp (°C)**	**Solution 5**	**Temp (°C)**	**Solution 6**	**Temp (°C)**	**Solution 7**	**Temp (°C)**
K20	carbonate	25,37,15,25	carbonate	25,37,15,25	phosphate	25,37,15,25	phthalate	25,37,15,25	-	-	-	-	-	-
KRISS	**Solution 1**	**Temp (°C)**	**Solution 2**	**Temp (°C)**	**Solution 3**	**Temp (°C)**	**Solution 4**	**Temp (°C)**	**Solution 5**	**Temp (°C)**	**Solution 6**	**Temp (°C)**	**Solution 7**	**Temp (°C)**
K9	sat AgCl	room temp.	-	-	-	-	-	-	-	-	-	-	-	-
P37	sat AgCl	room temp.	0.005M HCl	room temp	-	-	-	-	-	-	-	-	-	-
K17	0.005M HCl	room temp.	-	-	-	-	-	-	-	-	-	-	-	-
NMIJ	**Solution 1**	**Temp (°C)**	**Solution 2**	**Temp (°C)**	**Solution 3**	**Temp (°C)**	**Solution 4**	**Temp (°C)**	**Solution 5**	**Temp (°C)**	**Solution 6**	**Temp (°C)**	**Solution 7**	**Temp (°C)**
K9.2	HCl	15,25,37	phthalate	15,25,37	borate	15,25,37	carbonate	15,25,37	-	-	-	-	-	-
K17	HCl	15,25,37	phthalate	15,25,37	-	-	-	-	-	-	-	-	-	-
K18	HCl	15,25,37	phthalate	15,25,37	phosphate	15,25,37	carbonate	15,25,37	-	-	-	-	-	-
K19	HCl	15,25,37	borate	15,25,37	-	-	-	-	-	-	-	-	-	-
K20	HCl	15,25,37	tetraoxalate	15,25,37	borate	15,25,37	carbonate	25	-	-	-	-	-	-
NIST	**Solution 1**	**Temp (°C)**	**Solution 2**	**Temp (°C)**	**Solution 3**	**Temp (°C)**	**Solution 4**	**Temp (°C)**	**Solution 5**	**Temp (°C)**	**Solution 6**	**Temp (°C)**	**Solution 7**	**Temp (°C)**
K9	HCl	22	tetroxalate	5-50	-	-	-	-	-	-	-	-	-	-
P37	HCl	22	HCl 1M	22	-	-	-	-	-	-	-	-	-	-
K17	HCl	-	-	-	-	-	-	-	-	-	-	-	-	-
K19	HCl	22	phthalate	15-37	-	-	-	-	-	-	-	-	-	-
K20	HCl	22	tetroxalate	25	-	-	-	-	-	-	-	-	-	-
CENAM	**Solution 1**	**Temp (°C)**	**Solution 2**	**Temp (°C)**	**Solution 3**	**Temp (°C)**	**Solution 4**	**Temp (°C)**	**Solution 5**	**Temp (°C)**	**Solution 6**	**Temp (°C)**	**Solution 7**	**Temp (°C)**
K9	0.01M HCl	21	-	-	-	-	-	-	-	-	-	-	-	-
P37	0.01M HCl	21	-	-	-	-	-	-	-	-	-	-	-	-
K17	0.01M HCl	21	-	-	-	-	-	-	-	-	-	-	-	-
K18	0.01M HCl	21	-	-	-	-	-	-	-	-	-	-	-	-
K19	0.01M HCl	21	-	-	-	-	-	-	-	-	-	-	-	-
K18.1	0.01M HCl	21	-	-	-	-	-	-	-	-	-	-	-	-
K20	0.01M HCl	21	-	-	-	-	-	-	-	-	-	-	-	-
LNE	**Solution 1**	**Temp (°C)**	**Solution 2**	**Temp (°C)**	**Solution 3**	**Temp (°C)**	**Solution 4**	**Temp (°C)**	**Solution 5**	**Temp (°C)**	**Solution 6**	**Temp (°C)**	**Solution 7**	**Temp (°C)**
K18	0.005M HCl	room temp	-	-	-	-	-	-	-	-	-	-	-	-
K19	0.01M NaCl	room temp	-	-	-	-	-	-	-	-	-	-	-	-
K18.1	0.005M HCl	room temp	-	-	-	-	-	-	-	-	-	-	-	-
K20	0.01M NaCl	room temp	-	-	-	-	-	-	-	-	-	-	-	-
BIM	**Solution 1**	**Temp (°C)**	**Solution 2**	**Temp (°C)**	**Solution 3**	**Temp (°C)**	**Solution 4**	**Temp (°C)**	**Solution 5**	**Temp (°C)**	**Solution 6**	**Temp (°C)**	**Solution 7**	**Temp (°C)**
P37	phosphate	25	-	-	-	-	-	-	-	-	-	-	-	-
K18	carbonate	25	-	-	-	-	-	-	-	-	-	-	-	-
K19	borate	15,25,37	-	-	-	-	-	-	-	-	-	-	-	-
K20	tetroxalate	25,37	-	-	-	-	-	-	-	-	-	-	-	-
INMETRO	**Solution 1**	**Temp (°C)**	**Solution 2**	**Temp (°C)**	**Solution 3**	**Temp (°C)**	**Solution 4**	**Temp (°C)**	**Solution 5**	**Temp (°C)**	**Solution 6**	**Temp (°C)**	**Solution 7**	**Temp (°C)**
K9.2	0.01M HCl	21	Sat AgCl	21	-	-	-	-	-	-	-	-	-	-
K18	0.01M HCl	21	Sat AgCl	21	-	-	-	-	-	-	-	-	-	-
K18.1	0.01M HCl	21	Sat AgCl	21	-	-	-	-	-	-	-	-	-	-
K20	0.01M HCl	21	Sat AgCl	21	-	-	-	-	-	-	-	-	-	-
NPLI	**Solution 1**	**Temp (°C)**	**Solution 2**	**Temp (°C)**	**Solution 3**	**Temp (°C)**	**Solution 4**	**Temp (°C)**	**Solution 5**	**Temp (°C)**	**Solution 6**	**Temp (°C)**	**Solution 7**	**Temp (°C)**
P37	0.01M HCl	25	-	-	-	-	-	-	-	-	-	-	-	-
K18	0.01M HCl	25	-	-	-	-	-	-	-	-	-	-	-	-
K18.1	0.01M HCl	25	-	-	-	-	-	-	-	-	-	-	-	-
K20	0.01M HCl	25	-	-	-	-	-	-	-	-	-	-	-	-
NIM	**Solution 1**	**Temp (°C)**	**Solution 2**	**Temp (°C)**	**Solution 3**	**Temp (°C)**	**Solution 4**	**Temp (°C)**	**Solution 5**	**Temp (°C)**	**Solution 6**	**Temp (°C)**	**Solution 7**	**Temp (°C)**
K9	phosphate	15	phosphate	25	phosphate	37	-	-	-	-	-	-	-	-
K17	phthalate	15	phthalate	25	phthalate	37	-	-	-	-	-	-	-	-
K18	carbonate	15	carbonate	25	carbonate	37	-	-	-	-	-	-	-	-
K18.1	carbonate	15	carbonate	25	carbonate	37	-	-	-	-	-	-	-	-