REVIEW OF NMIJ STUDIES USING THE PRIMARY pH METHOD

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Abstract. In the field of pH measurements, the NMIJ, as designated metrology body, provides the traceability to international pH standards for a country, disseminate the certified buffer solutions for JCSS [1] and develops new measurements technologies. In this review we would like to present the last topic with the short description of some recent studies involving the Harned cell

1. Silver-silver chloride reference electrodes
Ag/AgCl electrode is used in wide range of pH measurements spreading from the primary pH method to everyday routine acidity determination. Its standard potential, $E^0_{Ag/AgCl}$, is estimated to make up between 30 % to 80 % of contribution to the final pH uncertainty; i.e. the accuracy of pH is substantially predetermined at this stage of measurement. Surprisingly, there are almost no publication about such important characteristic of standard potential as its temporal stability. Subsequently, in 2012 we published the results of several-years-long monitoring of standard potentials of a set of reference electrodes [2], with the conclusion: “The maximal observed change of $E^0_{Ag/AgCl}$ in the studied temperature range from 15 °C to 37 °C is about 200 µV for overall period of four years”.

Since the publication [2], we have continued to observe the temporal evolution of a selected set of Ag/AgCl electrodes presented at the Figure 1 as set A in the form of moving average (arithmetic mean of $E^0_{Ag/AgCl}$ covering the period of monitoring) with its expanded uncertainty, $k = 2$.

![Figure 1. Evolution of moving average $E^0$, set A, 25 °C](image)

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The uncertainty of moving average $E^o$ increases expectedly with time, but its final value after ten-years-exploitation was equal to 50 µV, i.e. less 0.001 in terms of pH. We could continue to use further the set $A$ for our routine measurements, but due to mechanical breakdowns, the metal fatigue for the wire with a silver bulb, the number of electrodes fell below the required quantity of six pieces for our primary pH measurement set-up.

The Figure 2 illustrates the possibility to use the Ag/AgCl electrodes several years with good $E^o_{\text{Ag/AgCl}}$ temporal stability for the other set of reference electrodes $B$.

![Figure 2. Evolution of moving average $E^o$, set $B$, 25 °C](image)

In such way, we demonstrated that temporal stability of standard potential of ca. 30-50 µV can be guaranteed at conditions of good maintenance of electrodes (regular change of storage solution, storage in the dark place between measurements etc.) and their using only in the dilute aqueous solutions with low halides content, typically for the ionic strength of studied solutions $I \leq 0.1$ mol/kg

2. pH of bioethanol
At present time, there is no reliable instrument to precisely measure pH values in pure ethanol. The commercial glass electrode does not work properly for ethanol content more than 70 % and the observed pH depends on the type of used electrode, time of measurement, intensity of stirring, depth of electrode immersion etc.

Consequently, CCQM- P152 pilot comparison was started at 2014 to determine the pH of an 0.05 m phthalate buffer in water-ethanol mixture (mass fraction 50 %) with the purpose to assign the pH standard for this field of measurements.

The measurand of this study was the acidity function of the above-mentioned solution at the temperature 25 °C and almost all participants (seven metrology institutes) demonstrated a quite good
agreement of results within the range ±0.005. However, the stability study of the samples performed by the pilot laboratory, Physikalisch-Technische Bundesanstalt (PTB), Germany, discovered a linear increase of the measurand, ca. 0.005 per month, due to supposed slow esterification reaction between phthalic acid and ethanol [3].

As a result of CCQM-P152 pilot comparison, the metrological society is now faced with the task of finding other pH reference buffer solutions for ethanol, a rather difficult task due to the low solubility of common buffer inorganic solutes in alcohol. Another possible alternative to deal with this task is to use a unified pH scale, investigated in the recent EMPIR project “Uniphied” [4].

3. pH of seawater
The SCOR, Scientific Committee on Oceanic Research, had created in 2015 the Working Group WG145 with the aim “to document the current status, and basis in laboratory measurements, of Pitzer models of seawater and estuarine water focusing on the chemistry of ocean acidification and micronutrient trace metals” and “…to implement the web-based tool for (such) chemical speciation calculation”.

In 2017 four National Metrology Institutes (Laboratoire National de Métrologie et d’Essai, France; National Institute of Standards and Technology, USA; NMIJ and PTB) had joined this project with the purpose to prepare buffer solutions of a mixture of Tris and electrolytes relevant for seawater and to conduct metrologically sound primary Harned cell measurements.

The developed Pitzer ionic interaction model is based on the publication [5], which provided the principles of the program to calculate the speciation of full seawater at a fixed pH. The ion-interaction Pitzer model extends the ionic strength range of the Bates–Guggenheim convention by incorporating both long and short-range interactions of ions in solution. The long-range interactions are given by a Debye–Hückel term and the short-range interactions can be divided into interactions between dissimilar ions of same and opposite charges. The activity coefficient of a single ions in solution is expected be both long and short range interactions of ions in solution. The long-range interactions are given by a Debye–Hückel term and the short-range interactions can be divided into interactions between dissimilar ions of same and opposite charges. The activity coefficient of a single ions in solution is expected be found from the experimentally determined parameters describing pairwise and triplet interactions, which are also functions of temperature and pressure.

In the case of seawater pH, the 0.04 m Tris buffer in artificial seawater was designated as a candidate standard buffer. The artificial seawater with the salinity $S=35$ and the ionic strength $I = 0.72285$ mol·kg$^{-1}$ contains the following components: H*, Na*, Mg$^{2+}$, Ca$^{2+}$, K*, Sr$^{2+}$ and SO$_{4}^{2-}$ ions.

In the framework of this study NMIJ has finished Harned cell measurements of potentials for fifteen H*/TrisH*/Cl$^{-}$ solutions, $m_{Cl^{-}}$, from 1.0 to 5.0 mol/kg, with ratio $y_{H^{+}} = m_{H^{+}}/(m_{H^{+}} + m_{TrisH^{+}})$ equal to 0.1, 0.3 and 0.5, and other fifteen H*/TrisH*/Na*/Cl$^{-}$ solutions, $m_{Cl^{-}}$ from 1.0 to 5.0 mol/kg, with ratio $y_{Na^{+}} = m_{Na^{+}}/(m_{Na^{+}} + m_{TrisH^{+}})$ to 0.3, 0.5 and 0.7. Both sets of solutions were measured at the temperatures 5, 10, 15, 20, 25, 30 and 40 °C.

It is difficult yet to estimate the quality of our experimental results in terms of Pitzer modelling, but we can make a comparison of calculated mean activity coefficient of hydrochloric acid in Tris solution with the available literature data [6]. As shown at Figures 3 and 4, the good agreement of above-mentioned values was observed at different ionic strengths of solutions.

The NMIJ contribution to the SCOR project "Chemical Specification of Natural Waters and Determination of pH" is made in hope to obtain eventually a Tris buffer solution with a thermodynamic pH value for measuring the acidity of seawater.
Figure 3. Comparison of experimental results with the literature data of activity coefficients at the ionic strength $I = 1 \text{ mol/kg}, 25 ^\circ \text{C}$ (open circles – NMIJ values, closed circles – data from [6])

Figure 4. Comparison of experimental results with the literature data of activity coefficients at the ionic strength $I = 3 \text{ mol/kg}, 25 ^\circ \text{C}$ (open triangles – NMIJ values, closed circles – data from [6])
4. Conclusion

The review of some NMIJ recent studies show the different applications of electrochemical cell without liquid junction in the field of precise potentiometric measurements. In particular, the temporal stability of standard potential of reference silver-silver chloride electrodes was re-estimated from few years to the period of one decade. In other studies, the Harned cell method was used to assign the pH values for seawater buffers or mixed water-organic solvent solutions.

References

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