

Enhancing the Metrological Quality of Buffer Solutions CRMs for more Accurate Water pH Measurements

Rashed A. Aldosari, AbdulRahman R. Alaskar, Fahad, R. AlMutairi and Adel B. Shehata
SASO / NMCC, KSA

Introduction

It has been reported that, the production of primary pH CRMs is carried out using complex equipment and takes long time with high cost. Therefore, the calibration of glass electrodes by secondary buffer certified reference materials (CRMs) is more convenient. The secondary buffer solutions can be certified for their pH values with regard to primary buffer solutions of the same nominal composition using Baucke cell. The well-known Nernst equation (1) is the mathematical model for this pH certification [1].

$$pH_x = pH_p + \frac{\Delta E \times F}{RT \ln 10} \quad (1)$$

Based on this model, three sources of uncertainty, used to be reported by the National Metrology Institutes producing such buffers CRMs. In this work we introduce three additional sources of uncertainty which were not dealt with in any previous published work on the secondary buffer certification.

Experimental

The Baucke cell allows the standardization of a secondary buffer with respect to a primary buffer provided their pH values are between 3 and 11 and differ by not more than +0.02 pH. The water bath was set at 25 °C and the Baucke cell was placed in it, then the primary and the secondary buffers were added into the half-cell. The two Pt/H₂ electrodes were immersed in the half-cell and connected to a multimeter, which was switched-on and left for one hour to stabilize. The flow rate of the pure hydrogen gas into the cell was adjusted at 8.5 mL/min and the potential, ΔE was measured at 25°C (See Figure 1).

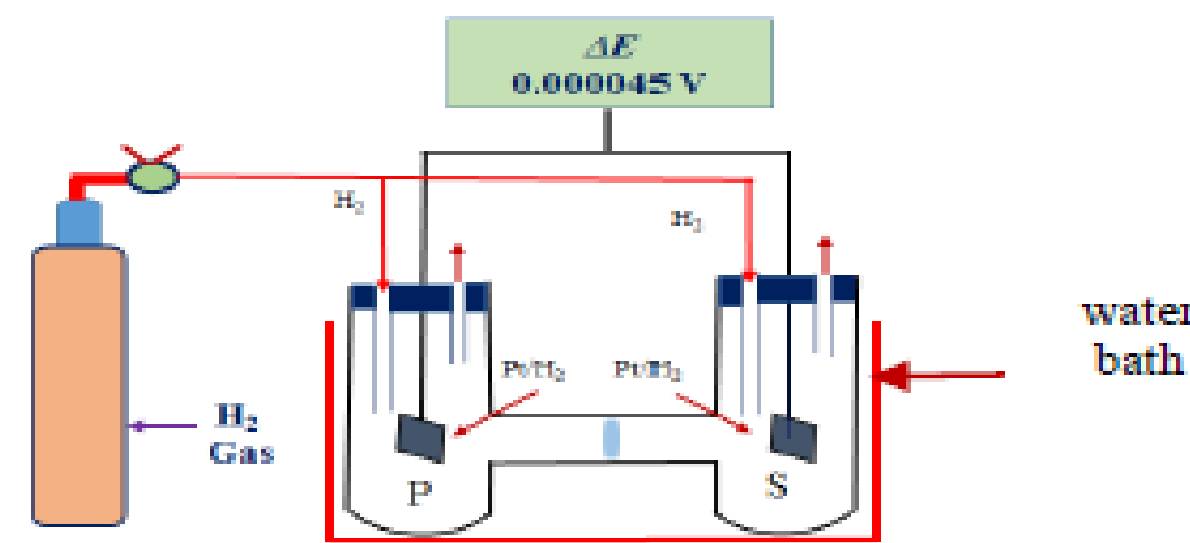


Figure 1. Schematic for the Baucke cell

Sources of Uncertainty

The uncertainty of measurements was calculated according to the Eurachem/CITAC Guide for quantifying uncertainty [2].

- The Explicit sources of uncertainty used to be reported by NMIs
 - CRM primary buffer
 - Cell potential
 - Effect of temperature

- Implicit sources of uncertainty
 - Electrode stability
 - Signal stability
 - Effect of temperature

The three implicit sources of uncertainty have been incorporated into Nernst equation as f_1 , f_2 and f_3 (eq 2) in condition that the pH value of each of them equals one in order not to influence the measured pH value. [3].

$$pH_x = pH_p + \frac{\Delta E \times F}{RT \ln 10} \cdot f_1 \cdot f_2 \cdot f_3 \quad (2)$$

All the uncertainty sources were shown as a fishbone structure given in Figure 2 and the estimation of them was made as described below.

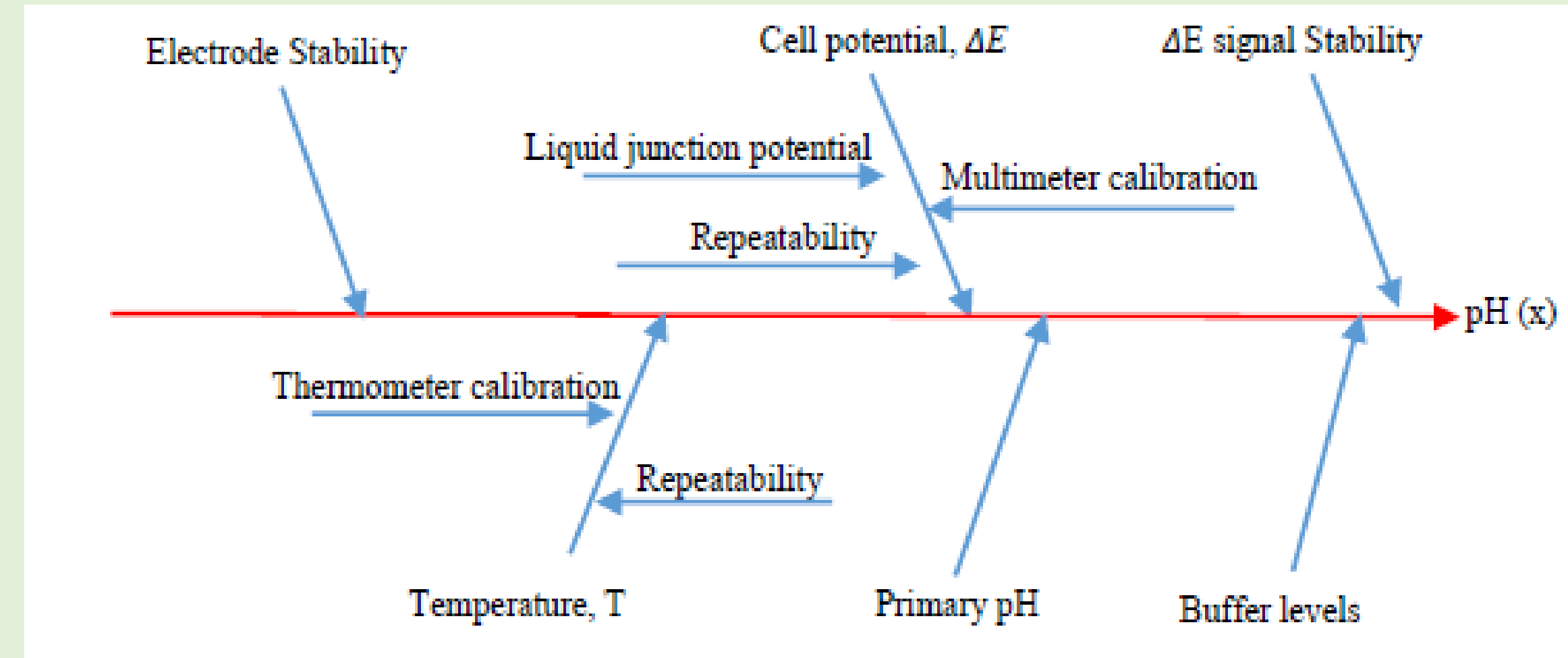


Figure 2: Fish bone structure showing the characterization uncertainty sources

Estimation of the explicit uncertainty sources

Calibration of the voltammeter, u_{cal}	Liquid junction potential, u_{LJP}	Repeatability, u_{rept}
The maximum error is a technical specification of the voltammeter taken from its manual. The U_{cert} is taken from the calibration certificate. Eq 3	According to IUPAC Recommendation 2002, the liquid junction potential is estimated as 10% of the measured potential, E. Eq 4.	The uncertainty of the repeatability was obtained as SD divided by $\sqrt{n}$. Eq 5.

$$u_{cal} = \sqrt{\left(\frac{\max \text{ error}}{\sqrt{3}}\right)^2 + \left(\frac{U_{Cert}}{2}\right)^2} \quad u_{LJP} = \frac{10\% E}{\sqrt{3}} \quad u_{rept} = \frac{SD}{\sqrt{n}}$$

The three uncertainty contributions were combine by eq 6 to give the uncertainty due to cell potential, u_c , ΔE .

$$u_{c \Delta E} = \sqrt{(c_1 \cdot u_{cal})^2 + (c_2 \cdot u_{LJP})^2 + (c_3 \cdot u_{rept})^2}$$

Effect of temperature, u_T	The CRM, u_{CRM}
This uncertainty is composed from the SD of 5 measurements, the range which is the difference between the highest and lowest measured temperatures and the contribution from the thermometer calibration certificate.	The uncertainty contribution from the certificate of the CRM divided by 2.
$u_T = \sqrt{\left(\frac{U_{Cert}}{2}\right)^2 + (SD)^2 + \left(\frac{Range}{2}\right)^2} \quad (7)$	$u_{CRM} = \frac{U_{exp}}{2} \quad (8)$

Estimation of the implicit uncertainty sources

The electrode stability (f1):

Estimation is done by measuring E between the same buffer solution in both half-cell (Z) then measuring E between different buffer solutions (S) in both half-cell according to the sequence: $Z_1 - S - S - Z_2 - S - S - Z_3 - S - S - Z_4$. The number of Z samples is plotted against the corresponding E values and the slope of the line is calculated. The uncertainty is calculated using equation 9, where E_{x1} is the potential of Z_1 and E_{x2} is the potential of Z_2 .

$$u = Slope \times \frac{E_{x1} - E_{x2}}{2} \quad (9)$$

Signal stability (f2):

Baucke proposed the stability condition as: $t \geq 5\text{min}$, $dV/dt \leq 6 \mu V$ and the uncertainty of this contribution is considered as $6 \mu V$.

Solution level difference (f3)

A difference in levels of the buffer solutions in the two half-cells (l_1-l_2) is created as a result of the difference in atmospheric pressure on the surface of buffer solutions. This level difference is taken as 1 mm and the uncertainty in the measured potential arising from this source is calculated according to equation 10.

$$\Delta E = \frac{RT}{nF} \times \log \left(1 + \frac{(l_1 - l_2) \cdot \rho \cdot g}{p_0} \right) / \sqrt{3} \quad (10)$$

R - universal gas constant
 T - temperature in K (273.15 + t)
 n - umber of charges
 F - Faraday constant
 l_1-l_2 - difference in solution levels
 ρ - density of solution
 g - gravity (980 cm/s²)
 P_0 - atmospheric pressure (Pa)

The combined standard uncertainty

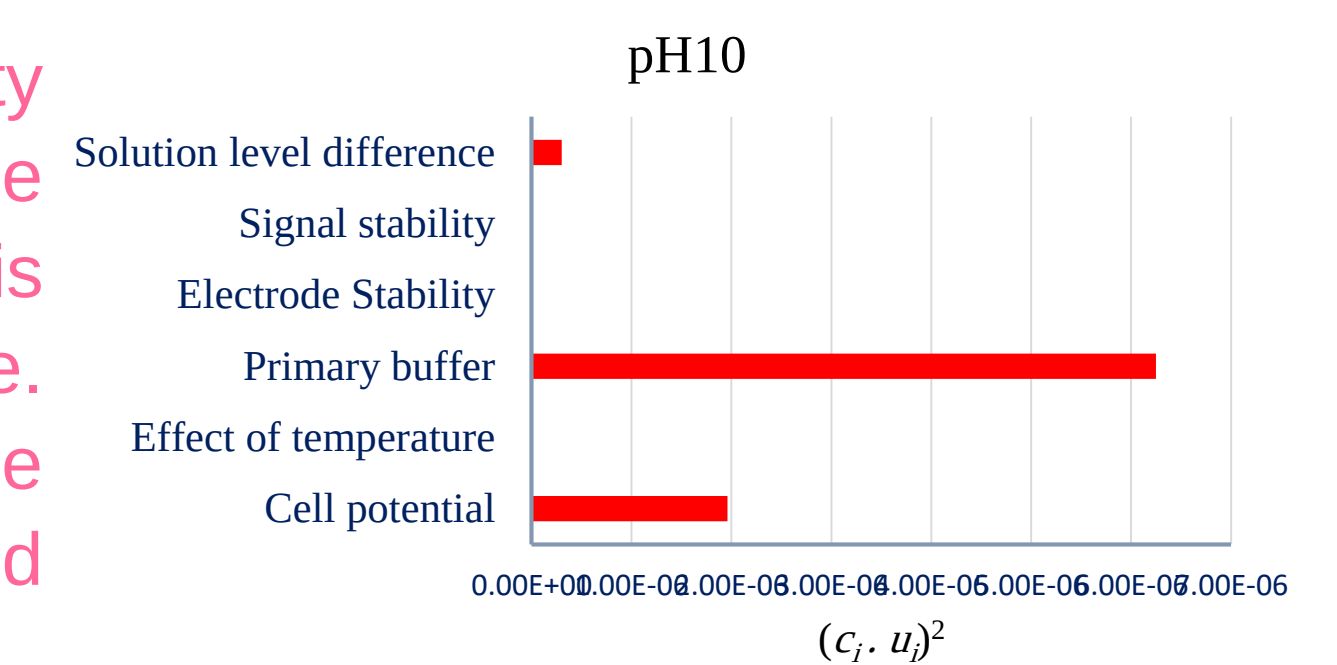
The combined standard uncertainty of characterization, u_{char} is calculated using equation 11.

$$u_{char} = \sqrt{\left(\frac{\partial pH(x)}{\partial pH(s)} \cdot u_{CRM}\right)^2 + \left(\frac{\partial pH(x)}{\partial \Delta E} \cdot u_E\right)^2 + \left(\frac{\partial pH(x)}{\partial T} \cdot u_T\right)^2 + \left(\frac{\partial pH(x)}{\partial f_1} \cdot u_{f1}\right)^2 + \left(\frac{\partial pH(x)}{\partial f_2} \cdot u_{f2}\right)^2 + \left(\frac{\partial pH(x)}{\partial f_3} \cdot u_{f3}\right)^2}$$

Uncertainty source	pH4	pH7	pH10
Cell potential	1.00E-06	2.21E-05	1.96E-06
Effect of temperature	7.11E-17	7.10649E-17	7.10649E-17
Primary buffer	6.25E-06	6.25E-06	6.25E-06
Electrode Stability	2.86E-18	2.8561E-18	2.8561E-18
Signal stability	1.00E-08	1.00E-08	1.00E-08
Solution level difference	3.03E-07	3.025E-07	3.025E-07
Combined standard uncertainty, u_c	0.0028	0.0054	0.0029

Conclusion

The study found that the largest uncertainty comes from the buffer CRM, followed by the cell potential. The third largest uncertainty is from the implicit solution level difference. Uncertainty from temperature, electrode stability, and signal stability is very small and can be neglected.



References

- [1] B. Koleva, L. Dimitrova, D. Stoica and P. Fisicaro (2021). Application of secondary pH measurement method for homogeneity and stability assessment of reference materials, *Accred. Qual. Assur.* 26, 113-120.
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- [3] A. B. Shehata, A. R. Alaskar, R. A. Aldosari and F. R. Almutari (2023). Certification of buffer solutions reference materials using Baucke cell for supporting the quality of pH measurements, *J. Chem. Metrol.* 17:1, 100-113.