CRM REPORT

ACG publications

J. Chem. Metrol. X:X (202X) X-X

journal of chemical metrology

Certification of buffer solutions reference materials using Baucke cell for supporting the quality of pH measurements[§]

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(Received, March 30, 2023; Revised May 04, 2023; Accepted May 08, 2023)

Abstract: The need for certified pH reference materials to support the traceability claims and quality of the daily large volume of pH measurements is very strong. In this work, three batches of buffer solutions were prepared, and their pH values were certified in accordance with the IUPAC Recommendation 2002. The first batch was prepared from potassium tetraoxalate (dihydrate) and disodium oxalate to provide pH4 and the second batch was prepared from disodium hydrogen phosphate and potassium dihydrogen phosphate to provide pH7. The third batch was prepared from sodium hydrogen carbonate and sodium carbonate to provide pH10. Every batch was homogenized by mechanical shaking for one night and bottled into 50 HDPE bottles, each is 250 mL. A number of bottles were systematically selected for homogeneity, stability and characterization studies of the buffer reference materials. These studies were carried out in accordance with the requirements of ISO 17034 and ISO Guide 35 using Baucke cell. The pH values 4, 7 and 10 of the secondary buffers were restandardized with regard to the pH values 4, 7 and 10 of the primary buffers produced by the Slovak National Metrology Institute, SMU. The results obtained showed that the produced buffer RMs were homogeneous and stable enough and their certified pH values were found 4.001±0.019, 7.005±0.015 and 10.002±0.023. These CRMs will be very useful as calibrants and as PT samples for analytical laboratories performing pH measurements in various fields.

Keywords: Buffer batch; homogeneity; stability; Baucke cell; characterization; uncertainty. © 2023 ACG Publications. All rights reserved.

1. Introduction

The measurement of pH is among the daily chemical measurements widely performed in various industrial and health applications [1]. These measurements are carried out routinely using glass electrode pH-meters, which measures the potential difference between two electrodes immersed in a solution [2,3]. The glass electrodes need periodic calibration to correct for systematic errors and to establish the metrological traceability of the pH measurement results [4-6]. Calibration is carried out using primary or secondary certified reference materials (CRMs). A CRM is defined as reference material, accompanied by documentation issued by an authoritative body and providing one or more

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[§]The study was presented in 2nd TCS Food Chemistry Congress, 16-19 March 2023, Kemer-Antalya-Türkiye.

The article was published by ACG Publications
http://www.acgpubs.org/journal/journal-of-chemical-metrology Month-Month 202x EISSN:1307-6133
DOI: http://doi.org/10.25135/rnp.87.2303.2773
Available online: May 19, 2023

specified property values with associated uncertainties and traceabilities, using valid procedures [7]. In case of pH measurements, the IUPAC Recommendation 2002 describes the procedures and the ways to establish traceability of the measurement results [4,7]. The primary buffer solutions are to be realized by Harned cell without transference using Pt/H_2 and Ag/AgCl electrodes immersed in a buffer solution to which chloride ions are added in at least three different molalities [4]. However, it has been reported that, the production of primary pH CRMs is carried out using complex equipment and takes long time with high cost [8,1]. Therefore, the calibration of glass electrodes by secondary buffer CRMs is more convenient [1,4,8]. These secondary buffer solutions can be certified with regard to primary buffer solutions of the same nominal composition using a differential potentiometric cell with single junction described by Baucke [8]. This cell is used for the restandardization of secondary buffer of pH(s) against a primary buffer of pH(p) in the range of pH between 3 and 11 in condition that the difference in pH is not more than 0.02. In this case, the liquid junction potential is mainly determined by ions other than hydrogen and hydroxyl, and is smaller than 10% of the measured e.m.f. The two buffer solutions are in contact with each other through a vertical sintered glass disk of a suitable porosity (40 μm). The potential is measured by two Pt/H_2 electrodes used at the same hydrogen pressure [4,8,9]. The Baucke cell is represented in the IUPAC Recommendation as: Pt | H_2 | buffer P ¦ ¦ buffer S | H_2 | Pt, and the half-cell reaction of the electrode is $2H^+ (aq) + 2e^- \rightarrow H_2 (g)$. It generally takes place on a platinum electrode while the pressure of the hydrogen gas present in the half-cell equals 1 bar. Hindayani and co-authors reported the development of phthalate buffer standard solution by Baucke cell method using potassium hydrogen phthalate NIST SRM 185i [2,10]. They have validated the method by successful participation in the key comparison, APMP.QM-k91 [11]. Koleva et al reported the development and optimization of a secondary pH measurement method for the production of phosphate buffer solution of pH7 at 25°C at the Bulgarian NMI with support by LNE, France. They have assessed the homogeneity and stability of the buffer and concluded that it can be used as PT samples [2]. Gonzaga et al reported a new differential potentiometric cell for the standardization of the pH buffer solutions [12]. This new cell was evaluated by means of a bilateral interlaboratory comparison, where one of the two laboratories used a traditional Baucke cell. In the present paper, oxalate, phosphate and carbonate buffer solutions were prepared and their homogeneity and stability were assessed. The pH of each buffer solution was characterized by Baucke cell and the results obtained were statistically analyzed. The certified pH values and their associated uncertainties were calculated in accordance with ISO 17034 and ISO guide 35 [13,14].

2. Materials and methods

2.1. Reagents

Potassium tetraoxalate dihydrate, disodium oxalate, disodium hydrogen phosphate, potassium dihydrogen phosphate, sodium hydrogen carbonate and sodium carbonate high pure salts (p>99.5%) were obtained from Alfa Acer, Germany. Ultrapure water used for buffer solutions preparations was produced by Melbourne water purification system. The primary buffers of pH 4.0018±0.0050, 7.0050±0.0050 and 10.0004±0.0050 were obtained from the national metrology institute of Slovakia, SMU. Lead acetate (≥99.99%) was obtained from PanReac AppliChem, Germany and chloroplatinic acid (99%) was purchased from Sigma-Aldrich, USA. Chromium oxide (≥99%) was obtained from Fisher, UK. Sulphoric, nitric and hydrochloric acids were obtained from PanReac AppliChem, Germany.

2.2. Equipment

A digital multimeter, 0.01 mV (34461A, Agilent Technologies) was used for potential measurements. The Baucke cell, the platinum wires (0.5mm,99.997%) and the Pt foil (0.1 mm, 99.99%) were purchased from Metrologia Holding AREKO, Slovakia. A water bath with calibrated thermostat was used to provide a water medium of 25°C. An analytical balance of weighing capacity 4100 g and resolution of 0.01g was used for weighing the salts required for buffer preparations and

clean glass beakers grade A were used for dissolving the weighed masses. Another balance of weighing capacity 60 kg and resolution 1 mg was used for weighing the batch buffer solutions. A Mittler Toledo calibrated pH-meter with glass electrode was used for the homogeneity study. The plastic container (15L) and the HDPE bottles were purchased from a local supplier.

2.3. Preparation of the Pt/Pt$_{black}$ Electrode

The Pt wire was welded to the Pt foil by oxyhydrogen welding machine and the combined wire was fitted into a soda glass tube (6mm) sealed just above the connection point [15]. The Pt electrodes were cleaned by dipping in a solution of HNO_3 + HCl (1:3 v/v) heated without moving until removal of the black color. The electrodes were then taken out of the solution and washed with ultrapure water. A second washing of the electrodes was carried out by dipping in a strong oxidizing solution prepared from CrO_3 in H_2SO_4 (5%:95% wt/wt) and heating at 60°C for 30 min to remove any other remaining precipitates. After that, the electrodes were washed with ultrapure water. An electroplating solution was prepared from 0.03% $Pb(CH_3COO)_2$ and 3% H_2PtCl_6 in water and the two electrodes were dipped in it. An electric current of 20-25 mA was applied in the electroplating cell for 30s until the Pt foils were coated with Pt black. The electrodes were taken out from the cell and kept in water until use.

2.4. Preparation of the Buffer Solutions

The plastic container and the HDPE bottles were washed with ultrapure water acidified with 5% nitric acid then rinsed with ultrapure water and left open under suction until complete dryness. Potassium tetraoxalate (dihydrate) was dried in air and disodium oxalate was dried for 1h in an oven at 120 °C. Since the buffer solution prepared from this pair of oxalate salts is not reported in the IUPAC Recommendation 2002, it is worthy to mention that the pH value of this buffer was attained at pKa2 equals 3.81 as reported in the handbook of chemistry and physics, 100th edition [16]. On the other hand, the buffer solutions prepared from the phosphate and carbonate salts for pH7, and pH10 respectively have been prepared in accordance with the IUPAC Recommendation 2002. The two phosphate salts were dried at 110°C for 1h before use. Sodium bicarbonate was dried at room temperature whereas sodium carbonate was ignited for 1h at 270°C before use. Each buffer batch was prepared as 13 liters using the masses shown in Table 1.

Table 1. Names and mass of salts required for buffer preparation

pH	Chemical	Formula	Mass (g/L)
4	Potassium tetraoxalate (dihydrate)	$KH_3(C_2O_4)_2.2H_2O$	1.4358
	+		+
	Disodium oxalate	$Na_2C_2O_4$	3.1031
7	Disodium hydrogen phosphate	Na_2HPO_4	4.1168
	+		+
	Potassium dihydrogen phosphate	KH_2PO_4	2.8578
10	Sodium hydrogen carbonate	$NaHCO_3$	2.092
	+		+
	Sodium carbonate	Na_2CO_3	2.640

In each batch preparation, the plastic container was weighed empty and about 4L of ultrapure water were added into it. Then, the weighed salts were completely dissolved in a clean beaker (2L) and added into the container. The beaker was rinsed three times with ultrapure water to ensure complete addition. The container was swirled to mix the solution well and the remaining water was added in it until the required mass of solution was reached. The container was closed, shacked well and left on a mechanical shaker for one night to homogenize the buffer solution.

2.5. Bottling

After mechanical shaking for one night, every batch solution was bottled into 50 HDPE bottles. Each bottle was tightly closed, sealed, and placed in strata in the filling order.

2.6. Bottle Selection for Certification Studies

Systematic sampling was applied to select bottles for homogeneity, short and long-term stability, characterization, and pH monitoring studies. The selection covered the top, middle and bottom areas of the container so that the results of each study represent the whole batch.

2.7. Potentiometric Measurements of pH Using Baucke Cell

The short-term stability, long-term stability, and characterization of pH values of the buffer solutions were carried out by Baucke cell shown in Figure 1. The cell allows the restandardization 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 [8]. 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/H_2 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.

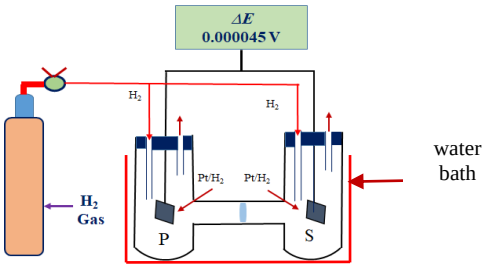

Figure 1. Schematic for the Baucke cell

3. Results and Discussions

3.1. The Homogeneity Study

The homogeneity study of the buffer RMs was carried out according to the requirements of ISO Guide 35 [13]. Since the number of the produced bottles of each buffer was fifty, 5 bottles (10%) were systematically selected to represent the different parts of the batch as shown in Figure 2.

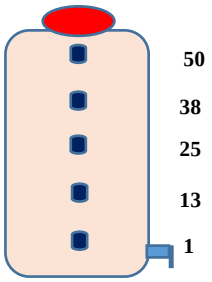

Figure 2. A schematic representation of the selected bottles for homogeneity study

To assess the between and the within bottle homogeneity, each of the selected bottles was divided into three portions. The pH of each portion was measured by a pH-meter calibrated by an SMU secondary buffer of ±0.020 uncertainty at 25°C. The measurements were performed in a random

order to avoid any trend that might have occurred by the filling order of buffer bottles and the obtained results were recorded in Table 2. They were tested for outliers by Grubbs test and no outliers were detected.

Table 2. Homogeneity measurement results at different pH values

	B1	B13	B25	B38	B50
pH 4	4.005	4.006	4.008	4.006	4.008
	4.006	4.004	4.009	4.007	4.003
	4.004	4.005	4.004	4.008	4.002
	4.008	4.006	4.007	4.005	4.009
	4.004	4.003	4.011	4.002	4.007
	4.003	4.007	4.009	4.003	4.008
pH 7	6.968	6.993	6.976	6.993	6.981
	6.972	6.975	6.974	6.973	6.972
	6.997	6.993	6.997	6.995	6.993
	6.987	6.989	6.985	6.988	6.989
	6.989	6.987	6.989	6.983	6.986
	6.987	6.982	6.984	6.981	6.982
pH 10	9.989	9.999	9.992	9.990	9.993
	9.988	10.002	9.991	9.994	9.986
	9.994	9.991	9.994	9.990	9.990
	9.991	9.995	9.989	9.991	9.991
	9.994	9.988	9.992	9.992	9.990
	9.986	9.996	9.991	9.988	9.998

The distribution of these results was found to follow the normal distribution model. After that, statistical analysis by ANOVA-single factor was performed to see if there are significant differences between bottles. The obtained ANOVA results given in Table 3 show that $F < F_{crit}$ and the p-value > 0.05. This means that the three buffer solutions are homogeneous enough and can be characterized as reference materials.

Table 3. ANOVA-single factor results for pH 4, 7 and 10

	Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
pH 4	Between Groups	3.82E-05	4	9.55E-06	1.917671	0.13874	2.75871
	Within Groups	0.000125	25	4.98E-06			
	Total	0.000163	29				
pH 7	Between Groups	4.07E-05	4	1.02E-05	0.140114	0.965696	2.75871
	Within Groups	0.001814	25	7.26E-05			
	Total	0.001855	29				
pH 10	Between Groups	8.83E-05	4	2.21E-05	1.853665	0.150138	2.75871
	Within Groups	0.000298	25	1.19E-05			
	Total	0.000386	29				

The uncertainty due to the material heterogeneity (σ_h) was calculated using equations 1 and 2 according to ISO Guide 35 and whichever, large value was considered.

$$\sigma_h = \sqrt{\frac{MS_{within} - MS_{within}}{n}} \quad (1) \qquad \sigma_{bb} = \sqrt{\frac{MS_{within}}{n}}\sqrt[4]{\frac{2}{\nu MS_{within}}} \quad (2)$$

where

$MS_{between}$ - mean square between groups

M_{within} - mean square within groups

νMS_{within} - degree of freedom

n - number of measurements per bottle

The obtained values of σ_h were found 0.00054, 0.0021 and 0.00075 for pH4, pH7 and pH10 respectively.

3.2. The Short-Term Stability

The short-term stability study was carried out using samples stored along 4 weeks to ensure that the buffer RMs can remain stable under transport conditions [13,17]. For this study, 9 bottles were systematically selected from each buffer batch. Four of them were stored in a refrigerator at 4°C for 4, 3, 2 and 1 weeks respectively and parallel to that, other 4 bottles were stored in an oven at 40°C for 4, 3, 2 and 1 weeks, respectively. Meanwhile, one bottle remained at room temperature, 21°C for 4 weeks. After the whole storage period was over, the 9 bottles were stored at a reference temperature (4°C) for one night and then conditioned to room temperature before the isochronous measurements. The measurements were carried out using Baucke cell with regard to the primary buffers. The cell potential, ΔE was measured 3 times for each bottle and the average was calculated. The corresponding pH values were calculated using Nernst equation 3,

$$pH_{(s)} = pH_{(p)} - \frac{\Delta E_{cell} \ x \ F}{RT \ln 10} \qquad (3)$$

where,

pH(s)	- pH of the characterized RM buffer
pH(p)	- pH of the primary CRM buffer
ΔE_{cell}	- measured potential in Volt
F	- Faraday constant
R	- universal gas constant
T	- thermodynamic temperature

The obtained pH results were recorded in Table 4.

Table 4. The pH results of the short-term stability

Storage temp, °C	Storage Time (W)	pH 4	pH 7	pH 10
RT	0	4.0123	7.0062	9.9979
4°C	1	4.0000	7.0041	10.0014
4°C	2	4.0011	7.0038	10.0025
4°C	3	4.0132	7.0043	9.9950
4°C	4	4.0131	7.0043	9.9990
40°C	5	4.0132	7.0060	9.9946
40°C	6	4.0125	7.0037	10.0032
40°C	7	4.0128	7.0035	10.0022
40°C	8	4.0130	7.0066	10.0004

The pH results in Table 4 were plotted against the storage time points at 4°C and 40°C within the certified uncertainty limits as it can be seen in Figure 3. From this figure, it is clear that the pH values measured at different storage conditions are stable enough within the uncertainty limits and did not encounter any trend.

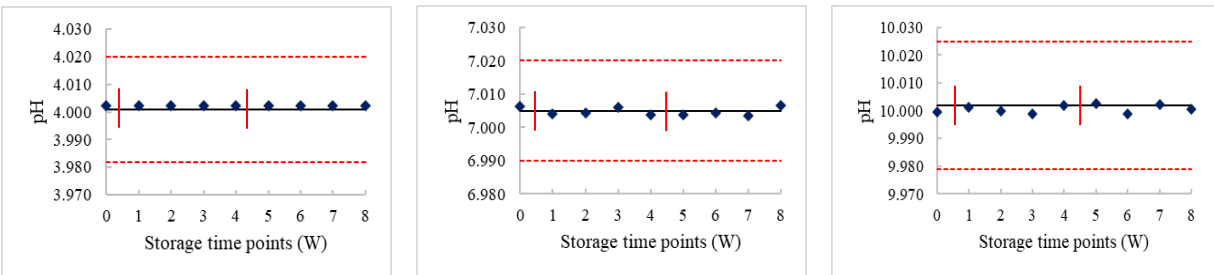

Figure 3. The pH results of the short-term stability within the certified uncertainty limits

This means that the buffer reference materials can be transported to customers at room temperature in a period of 4 weeks without being affected. The uncertainty in the measured pH values due to the short-term stability, u_{sts} was calculated by equation 4 [1].

$$u_{Sts} = \frac{SD}{\sqrt{\sum_{i=1}^{n}\left(t_i - \bar{t}\right)^2}}\, t \qquad (4)$$

where,

u_{Sts} - uncertainty of short-term stability

SD - standard deviation
t_i - the storage time (0,1, 2, 3 and 4 W)
$\bar{t}$ - average storage time (2 W)
t - number of storage weeks (4)

The u_{Sts} values were found 0.0069, 0.0016 and 0.004 for pH4, pH7 and pH10 respectively and these values will be part of the certified uncertainties.

3.3. Characterization of the pH of Buffer Solutions

The pH characterization measurements were performed over three different days (D1-D3) by Baucke cell using samples from three selected bottles. In each day, a sample from each bottle was measured three times, each was every 10 minutes. The pH values corresponding to the measured potentials were calculated using Nernst equation 3 and the results were recorded in Table 5. They seem to be stable along the three days, which ensures a good reproduceability of the measurement results. It also means that the pH was not affected by the multiple opening of the bottles along the days of study.

Table 5. the pH characterization results of the secondary buffer solutions

Days	Bottle	pH 4		pH 7		pH10	
		ΔE	pH	ΔE	pH	ΔE	pH
D 1	1	0.000034	4.0012	0.000041	7.0043	-0.000074	10.0017
	2	0.000033	4.0012	-0.000056	7.0059	-0.000086	10.0019
	3	0.000032	4.0013	-0.000059	7.0060	-0.000041	10.0011
D 2	1	0.000029	4.0013	0.000040	7.0043	-0.000073	10.0016
	2	0.000028	4.0013	-0.000056	7.0059	-0.000087	10.0018
	3	0.000027	4.0013	-0.000058	7.0059	-0.000041	10.0010
D 3	1	0.000013	4.0016	0.000042	7.0043	-0.000071	10.0016
	2	0.000014	4.0016	-0.000055	7.0059	-0.000086	10.0018
	3	0.000011	4.0016	-0.000060	7.0060	-0.000042	10.0011
Average			4.0014		7.0054		10.0015

3.3.1. Uncertainty of the pH Characterization

The uncertainty in the pH measurement results has been estimated based on ISO GUM and the EURACHEM/CITAC Guide [13,14]. The measurand was the $pH_{(x)}$ which has been calculated by Nernst equation 3. From this equation, the explicit sources of uncertainty can be identified as: cell potential ΔE, temperature T, and pH of the primary buffer, $pH_{(p)}$. In the meanwhile, there are three implicit sources of uncertainty, which can be identified from the Baucke cell measurement system, namely: the electrode stability, the signal stability and the difference in buffer solution levels in the half-cell. These three implicit sources of uncertainty have been incorporated into Nernst equation as f_1, f_2 *and* f_3 in condition that their pH values equal zero as shown in equation 5 [14,18,19]. All the uncertainty sources were shown as a fishbone structure given in Figure 4 and the estimation of them was made as described below.

$$pH_{(s)} = pH_{(p)} - \frac{\Delta E \; x \; F}{RT \ln 10} \cdot f_1 \cdot f_2 \cdot f_3 \qquad (5)$$

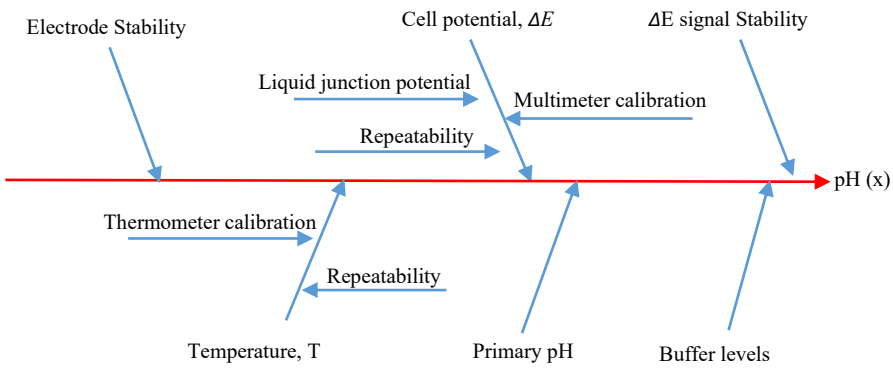

Figure 4. Fishbone structure showing the explicit and implicit uncertainty sources of pH characterization

3.3.1.1. The Cell Potential, ΔE

The uncertainty arising from the cell potential can be identified from three contributions, which are: calibration of the voltammeter, the liquid junction potential and the repeatability of measurements and can be estimated as below.

i) The uncertainty of the voltammeter calibration was calculated by taking the maximum error of the voltammeter divided by √3 in addition to the uncertainty from the calibration certificate divided by 2 according to equation 6.

$$u_{calb} = \sqrt{\left(\frac{\max error}{\sqrt{3}}\right)^2 + \left(\frac{U_{Cert}}{2}\right)^2} \qquad (6)$$

ii) The uncertainty of the liquid junction potential was estimated as 10% [4] of the measured potential divided by √3 according to equation 7.

$$u_{LJP} = \frac{10\%\ E}{\sqrt{3}} \qquad (7)$$

iii) The uncertainty of the repeatability of potential measurements was calculated by dividing the standard deviation of the average by the number of measurements according to equation 8.

$$u_{Rept} = \frac{SD}{\sqrt{n}} \qquad (8)$$

The combined standard uncertainty of the cell potential was calculated using equation 9 in which c_1, c_2 and c_3 are sensitivity coefficients and each of them equals 1 since the three uncertainties are in Volt.

$$u_{c\ \Delta E} = \sqrt{\left(c_1 . u_{calb}\right)^2 + \left(c_2 . u_{LJP}\right)^2 + \left(c_3 . u_{Rept}\right)^2} \qquad (9)$$

3.3.1.2. The Effect of Temperature

To estimate the uncertainty of this contribution, the temperature was measured in the four corners of the water bath and in the middle during the measurement. The difference between the largest and the smallest temperature reading (range) was calculated and divided by 2. The standard deviation (SD) of the average was also calculated. In addition, the uncertainty given in the calibration certificate of the thermometer was divided by 2 since it was reported at 95% confidence level. Hence, the combined standard uncertainty, u_{cT} was calculated using equation 10.

$$u_{c\,(T)} = \sqrt{\left(\frac{U_{Cert}}{2}\right)^2 + (SD)^2 + \left(\frac{Range}{2}\right)^2} \qquad (10)$$

3.3.1.3. The Primary Buffer Solution

The uncertainty reported in the certificates of the primary buffer solutions was divided by 2 according to equation 11.

$$u_{CRM} = \frac{U_{CRM}}{2} \qquad (11)$$

3.3.1.4. The Electrode Stability

This uncertainty contribution arises from the change of potential, *E* by time of measurements. Estimation was done by measuring potential of the same buffer solution in the half-cell (Z) then measuring potential of different buffer solutions (S) according to the following sequence: Z–S–S–Z–S-S–Z–S–S–Z. The number of Z samples was plotted against the corresponding measured potential, *E* values and the slope of the line was obtained. The uncertainty due to the electrode stability was then calculated using equation 12 in which E_1 - E_2 is the difference in potential between any two successive z points.

$$E = slope \times \frac{E_1 - E_2}{2} \qquad (12)$$

3.3.1.5. Signal Stability

Uncertainty due to instability of the potential signal has been estimated by monitoring the potential, *E* of buffer samples over time. It was noticed, that potential increases in the beginning of measurement and at some point it remains stable in a platu shape. The measurement results will be considered stable if it fulfils the following condition: t ≥ 5min, dV/dt ≤6μV. Therefore, the uncertainty of the signal stability was taken as 6 μV [8].

3.3.1.6. Buffer Solution Level Difference in the Half-cell

A difference in the levels of buffer solutions (l_1-l_2) was expected to occur because of the pressure difference in the half-cell. This level difference was taken as 1 mm and the uncertainty arising from it was calculated according to equation 13.

$$\Delta E = \frac{RT}{nF} \times \log\left(1 + \frac{(l_1 - l_2).\rho.g}{p_0}\right) / \sqrt{3} \qquad (13)$$

where,

ΔE - potential difference
R - universal gas constant (8.3144626 J $K^{-1}mol^{-1}$)
T - temperature in *K* (273.15 + t)
n - *n*umber of charges ($H^+ + 2e^- \longleftrightarrow H_2$)
F - Faraday constant (96 485.3321 sA/mol)
l_1-l_2 - difference in solution levels in the half-cell (*1mm*)
ρ - solution density (kg/m^3)
g - gravity (980 cm/s^2)
p_0 - atmospheric pressure (101.325 kPa)

Since the uncertainties of the electrode stability, signal stability and the solution level difference were in V, they have been transformed to pH by equation 14 in which ΔE is the uncertainty value in Volt.

$$pH = \frac{\Delta E.F}{RT \ln 10} \qquad (14)$$

3.3.1.7 The Combined Standard Uncertainty, u_c of Characterization

Due to the difference in uncertainty units of potential, temperature and primary pH, the sensitivity coefficients were obtained by differentiation of Nernst equation and were used to calculate the combined standard uncertainty according to equation 15.

$$u_{C\ char} = \sqrt{\left(\frac{\partial pH(x)}{\partial pH(p)} . u_{CRM}\right)^2 + \left(\frac{\partial pH(x)}{\partial \Delta E} . u_E\right)^2 + \left(\frac{\partial pH(x)}{\partial T} . u_T\right)^2 + \left(\frac{\partial pH(x)}{\partial f_1} . u_{f1}\right)^2 + \left(\frac{\partial pH(x)}{\partial f_2} . u_{f2}\right)^2 + \left(\frac{\partial pH(x)}{\partial f_3} . u_{f3}\right)^2} \quad (15)$$

The uncertainty components and the combined standard uncertainty, u_c are shown in Table 6.

Table 6. uncertainty budget of the pH characterization by Baucke cell

	Source of uncertainty	u_i	c_i	$c_i . u_i$
pH4	Cell potential	0.0001 V	-16.8988 V^{-1}	-0.0010
	Effect of temperature	0.0061 K	1.39 x 10^{-6} K^{-1}	8.43 x 10^{-9}
	Primary buffer	0.0025 pH	1	0.0025
	Electrode stability	1.69 x 10^{-9} pH	1	1.69 x 10^{-9}
	Potential signal stability	0.0001pH	1	0.0001
	Solution level difference	0.00055 pH	1	0.00055
	Combined standard uncertainty, u_c		0.0027	
pH7	Cell potential	0.003 V	-16.8988 V^{-1}	-0.0047
	Effect of temperature	0.0061 K	-1.39 $x10^{-6}$ K^{-1}	-8.43 x 10^{-9}
	Primary buffer	0.0025 pH	1	0.0025
	Electrode stability	1.69 x 10^{-9} pH	1	1.69 x 10^{-}
	Potential signal stability	0.0001pH	1	0.0001
	Solution level difference	0.00055 pH	1	0.00055
	Combined standard uncertainty, u_c		0.0054	
pH10	Cell potential	0.001 V	-16.8988 V^{-1}	-0.0014
	Effect of temperature	0.0061 K	-4.88 x 10^{-6} K^{-1}	-2.96 x 10^{-8}
	Primary buffer	0.0025 pH	1	0.0025
	Electrode stability	1.69 x 10^{-9} pH	1	1.69 x 10^{-9}
	Potential signal stability	0.0001pH	1	0.0001
	Solution level difference	0.00055 pH	1	0.00055
	Combined standard uncertainty, u_c		0.0029	

3.4. The Long-Term Stability

The study of the long-term stability was conducted using the samples stored at room temperature for 0, 1, 3 and 6 months. The potential measurements were carried out at 25°C using Baucke cell and the corresponding pH values were calculated using Nernst equation 3. The obtained pH results were plotted against the storage time and the regression lines were obtained as shown in Figure 5.

Using the slope of these regression lines, trend analysis was made in order to see if the certified pH values can remain stable within its associated uncertainty limits throughout the shelf life of the reference material. The slope of regression (b_1) was found: 0.0001, 0.00009 and 0.0002 for pH4, pH7 and pH10 respectively and the standard error of each the slope $s(b_1)$ was calculated by the regression test. The t-statistic was calculated as $|b_1|/s(b_1)$ according to ISO guide 35 [14] and the $t_{0.05,n-2}$ was obtained from the t-table using degrees of freedom, *df=3* at 95% confidence level since the time points were 4. All the obtained values were recorded in Table 7.

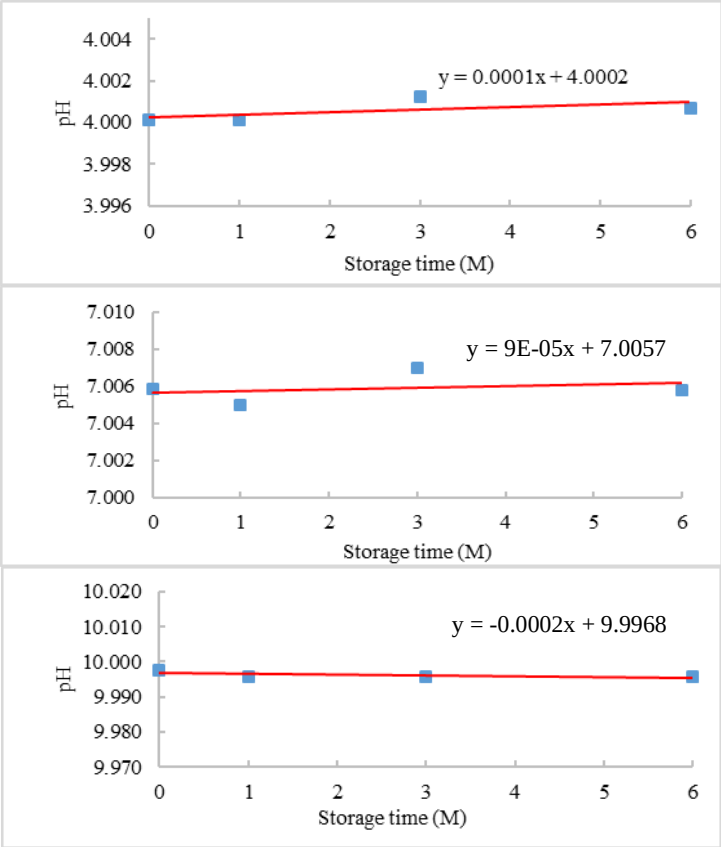

Figure 5. Regression lines of pH 4, pH 7and pH 10

Table 7. Results of the trend analysis for pH4, pH7 and pH10

Parameter	pH4	pH7	pH10
b_1	0.0001	0.00009	-0.0002
$s(b_1)$	0.00012	0.000215	0.0002
df	3	3	3
$t_{0.05,n-2}$	3.182	3.182	3.182
$t_{b1}= \lvert b_1 \rvert /s(b_1)$	0.838	0.419	1

From this table, it can be seen that the t_{b1} < t-tabulated, which means that the slope of each regression line did not deviate significantly from zero. Therefore, it can be concluded that no trend was observed in the measured pH4, pH 7 and pH 10 values during the long-term stability. This means that the pH of the buffer RMs can remain stable along the one-year validity.

3.4.1. Uncertainty Due to the Long-Term Stability

Uncertainty arising from the long-term stability (u_{lts}) was calculated by multiplying the slope of regression by time of the certificate validity using equation 16. The time of validity (t_{cert}) was taken as 52 weeks and the results obtained are given in Table 8.

$$u_{lts} = slope \times t_{cert} \qquad (16)$$

Table 8. Uncertainty results of the long-term stability

Buffer	Slope of regression	Certificate validity (W)	u_{lts}
pH4	0.0001	52	0.010
pH7	0.00009	52	0.005
pH10	-0.0002	52	0.010

3.5. The Certified Uncertainty

The uncertainty associated with each certified pH value was calculated according to ISO Guide 35 from the u_{char}, u_{homo}, u_{sts} and u_{lts} contributions at $k=2$ using equation 17. Table 9 shows these uncertainty components and the obtained certified uncertainty for each pH.

$$U_{CRM} = k\sqrt{u_{char}^2 + u_{\text{hom}}^2 + u_{sts}^2 + u_{lts}^2} \qquad (17)$$

Table 9. The certified uncertainty of the measured pH values

Source of uncertainty	pH4	pH7	pH10
Characterization	0.0038	0.0054	0.0029
Homogeneity	0.0005	0.0021	0.0008
Short term stability	0.0069	0.0016	0.0040
Long term stability	0.0052	0.0047	0.0104
Certified uncertainty	0.019	0.015	0.023

3.6. Compatibility of the Secondary pH Values with the Primary pH Values

The certified pH values and their uncertainties of the three buffer solutions were tested for compatibility with the pH values and uncertainties of the primary buffer solutions using The compatibility criterion shown in equation 18 [20].

$$\left|x_{obs} - x_{ref}\right| \le 2\sqrt{\left(u_{x_{obs}}\right)^2 + \left(u_{x_{ref}}\right)^2} \qquad (18)$$

Where,

x_{obs} - pH of the secondary buffer solution

x_{ref} - pH of the primary buffer solution

$u_{x\ obs}$ - standard uncertainty of the secondary buffer solution

$u_{x\ ref}$ - standard uncertainty of the pH of the primary buffer solution

From the results in Table 10, it can be seen that the absolute difference in pH between the secondary and the primary buffers fulfills the criterion in equation 21. This means that a strong traceability link of the pH of secondary buffer solutions to the pH of the primary buffer solutions was established.

Table 10. The compatibility of secondary pH with the primary pH values

x_{obs}	x_{ref}	x_{obs} - x_{ref}	$u_{x\ obs}$	$u_{x\ ref}$	$2\sqrt{\left(u_{x_{obs}}\right)^2 + \left(u_{x_{ref}}\right)^2}$
4.0014	4.0018	0.0004	0.0095	0.0025	0.0196
7.0054	7.0050	0.0004	0.0076	0.0025	0.0160
10.0015	10.0004	0.0011	0.0115	0.0025	0.0235

4. Conclusion

Three secondary buffer solution RMs of pH4, pH7, and pH10 were prepared and certified according to the IUPAC Recommendation 2002, ISO 17034 and ISO Guide 35 using Baucke cell. The certification studies showed that the buffer solutions were homogeneous and stable. The certified pH values and their associated uncertainties were found 4.001±0.019, 7.005±0.015 and 10.002±0.023. These certified pH values were found in very good compatibility with the pH values of the primary buffers and their uncertainties, which are 4.0018±0.0050, 7.0050±0.0050, 10.0004±0.0050. The produced pH CRMs are useful for analytical laboratories as calibrants of glass electrode pH-meters and as PT samples in laboratory accreditation schemes.

Acknowledgements

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