Production of Certified pH Buffer Solutions at National Metrology Institute of Turkey

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Abstract

pH, a thermodynamic function, is the negative logarithm of the activity of hydronium ions. It is well-known concept used in many different areas from science to industry. The widespread use of pH measurements has increased the need for certified reference solutions in this field. The primary pH measurement system that was established in Turkey as the first and only was used for production and certification of reference pH buffer solutions. The system consists of measurement cell named as Harned cell, Ag/AgCl electrodes, Pt/Pt$_{black}$ or Pt/Pd$_{black}$ electrodes, thermostatic bath, PT-100 probe and display unit, data acquisition unit and barometer. The software of primary system was developed and validated in TUBITAK UME. Moreover, high precision coulometry system has been used to determine the acid molality utilized at first step of primary level pH measurement system. Homogeneity, short and long term stability, characterization, certification and post-production studies were performed according to ISO Guide 34: 2009, ISO Guide 35: 2006 and ERM Application Note 1: 2010 for the production and evaluation of the results of certified pH buffer solutions. Thanks to this situation, traceability will be disseminated through TUBITAK UME directly. Moreover the foreign currency spent for these solutions, that are generally used for calibration of pH meters and used in many other areas, will be retained in the country.

Keywords: pH, primary level pH measurement system, Harned cell, certified pH buffer solution, uncertainty

Türkiye Ulusal Metroloji Enstitüsü'nde Sertifikalı pH Tampon Çözeltilerinin Üretimi

Öz

Termodinamik bir fonksiyon olan pH, hidronyum iyonlarının aktivitesinin eksi logaritması olarak tanımlanmaktadır. pH, bilimden endüstriye kadar çok farklı alanlarda kullanılan, iyi bilinen bir kavramdır. pH ölçümlerinin yaygın kullanımı bu alanda sertifikalı referans çözelti ihtiyacını arttırmıştır. Türkiye'de ilk ve tek olarak kurulan birincil seviye pH ölçüm sistemi referans pH tampon çözeltilerinin üretim ve sertifikasyonu için kullanılmıştır. Sistem, Harned hücresi olarak isimlendirilen bir ölçüm hücresi, Ag/AgCl elektrotları, Pt/Pt$_{siyah}$ veya Pt/Pd$_{siyah}$ elektrotları, termostatik banyo, PT-100 probu ve göstergesi, veri toplama ünitesi ve barometreden oluşmaktadır. Sistemin yazılımı TÜBİTAK UME'de geliştirilmiş ve valide edilmiştir. Ayrıca, birincil seviye pH ölçüm sisteminin ilk aşamasında kullanılan asitin molalitesinin tayini yüksek kesinlikte kulometri cihazı kullanılarak yapılmıştır. Sertifikalı pH tampon çözeltilerinin üretimi ve sonuçların değerlendirilmesi için homojenlik, kısa ve uzun dönem kararlılık, karakterizasyon, sertifikasyon ve sertifikasyon sonrası izleme çalışmaları ISO Rehberi 34: 2009, ISO Rehberi 35: 2006 ve ERM Uygulama Notu 1: 2010 dokümanlarına göre gerçekleştirilmiştir. Bu durum sayesinde izlenebilirlik TÜBİTAK UME üzerinden doğrudan sağlanacaktır. Ayrıca genellikle pH metrelerin kalibrasyonu için ve pek çok diğer alanda kullanılan bu çözeltiler için harcanan döviz ülkede kalacaktır.

Anahtar Kelimeler: pH, birincil seviye pH ölçüm sistemi, Harned hücresi, sertifikalı pH tampon çözelti, belirsizlik

1. Introduction

pH, a well-known concept, is the activity of hydronium ions. It was stated as below in Eq. (1).

$$pH = -\log a_H^+ = -\log \left(\frac{m_{H^+} \gamma_{H^+}}{m^0} \right) (1)$$

where a_{H^+} is the relative activity, γ_{H^+} is the molal activity coefficient and m_{H^+} is the molality of hydronium ions, and m^0 is the standard state molality of hydronium ions, which is generally 1 mol kg^{-1} (Buck et al., 2002; IUPAC, 1993; Milton and Wielgosz, 1999; Sørensen and Linderstrøm-Lang, 1924).

Primary Level pH Measurement System

Primary level pH measurements depend on the measure of potential difference between Ag/AgCl and Pt/Pt$_{black}$ or Pt/Pd$_{black}$ electrodes using Harned cell. Scheme representation of this cell is in Eq. (2) (Milton and Wielgosz, 1999; Buck et al., 2002).

$$Pt, Pt_{black} \, or \, Pt, Pd_{black} \mid H_2(gas, 101325 \, Pa)\mid$$

$$buffer \, solution, Cl^- \mid AgCl \mid Ag \quad (2)$$
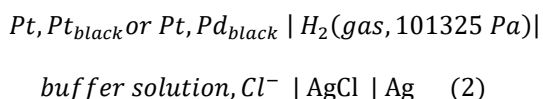
The measurement of pH using primary level pH measurement system consists of two steps: determination of standard potentials of Ag/AgCl electrodes and determination of acidity function and pH of the solution. The detailed procedure is as follows:

1. Calculation of pressure:

$$p_w = e^{\left(\frac{a}{T} + b + T \times (c + dT) + e \times \ln(T) \right)} (3)$$

where p_w, saturated vapour pressure of water at temperature T, T, temperature in K and a, b, c, d and e are the constants (Milton and Wielgosz, 1999) for calculation of p_w. a, -

6096.9385, b, 21.2409642, c, -0.02711193, d, 0.00001673952 and e, 2.433502.

2. Calculation of mean activity coefficient of HCl:

$$\gamma_{HCl} = e^{\left(\frac{1}{A + B \times T + C \times T^{\frac{3}{2}}} \right)} (4)$$

where γ_{HCl}, mean activity coefficient of HCl and A, B and C are the constants (Milton and Wielgosz, 1999) for calculation of γ_{HCl}. A, -7.725555, B, -0.06080444 and C, 0.00309226.

3. Calculation of corrected voltage for 101325 Pa:

$$U^* = -\frac{RT}{2F} \ln \left(\frac{p - p_w}{p_0} \right) (5)$$

where U^*, corrected voltage for 101325 Pa, U, voltage, R, gas constant (8.314472 J/mol.K), F, Faraday constant (96485.3415 C/mol), p, pressure and p_0, standard pressure (101325 Pa) (Milton and Wielgosz, 1999).

4. Calculation of Debye-Hückel constant:

$$A_T = j + T \times \left(k + T \times (m + T \times n) \right) (6)$$

where A_T, Debye-Hückel constant at temperature T and j, k, m and n are the constants (Milton and Wielgosz, 1999) for calculation of A_T. j, 0.4444505, k, 2.08171×10^{-5}, m, -7.33866×10^{-7} and n, 4.72830×10^{-9}.

5. Calculation of standard electrode potential:

$$E^0 = U^* + \frac{2RT}{F}\ln(m_{HCl} \times \gamma_{HCl}) \ (7)$$

where E^0, standard electrode potential and m_{HCl}, the exact molality of HCl (Milton and Wielgosz, 1999).

6. Calculation of acidity function:

$$-\log(a_{H^+}\gamma_{Cl^-}) = \frac{(U^* - E^0)F}{RTln10} + \log(m_{Cl^-}) \ (8)$$

where $-\log(a_{H^+}\gamma_{Cl^-})$, acidity function and m_{Cl^-}, molality of chloride (Milton and Wielgosz, 1999).

7. Calculation of logarithmic activity coefficient of Cl⁻:

$$\log(\gamma_{Cl^-}) = -\frac{A_T \times \sqrt{I}}{1 + 1.5 \times \sqrt{I}} \ (9)$$

where γ_{Cl^-}, activity coefficient of Cl⁻ and I, ionic strength (Milton and Wielgosz, 1999).

8. Calculation of pH:

$$pH = -\log(a_{H^+}\gamma_{Cl^-}) + \log(\gamma_{Cl^-}) \ (10)$$

Standard potentials of Ag/AgCl electrodes are determined by Eq. (7). After the acidity function is determined by Eq. (8), pH is found by summing the acidity function and logarithmic activity coefficient of chloride ions using Eq. (10).

Primary level pH measurement system used in TUBITAK UME is shown in Figure 1.
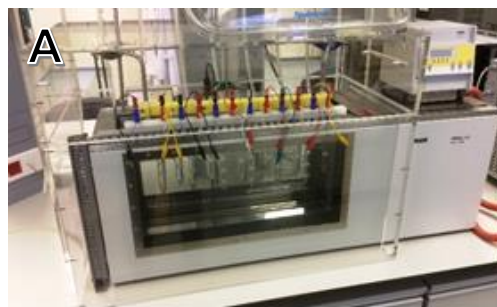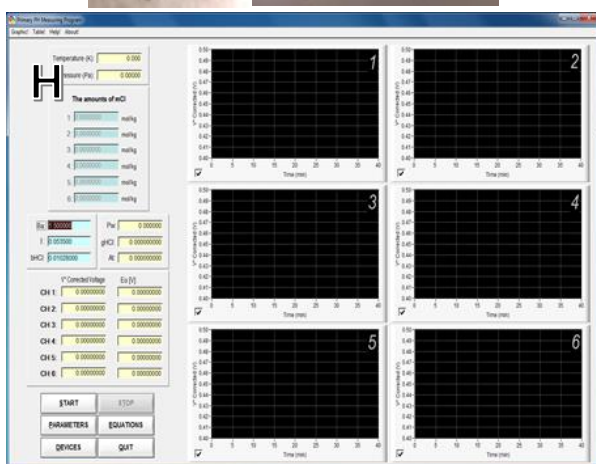
Figure 1. Water bath (A), gas distribution system (B), data acquisition unit (C), pressure gauge (D), temperature display unit (E) with 5626 platinum resistance thermometer (F), Harned cell (G) and software appearance (H) of primary level pH measurement system.

In this study, it was aimed to the production and certification of standard pH buffer solutions using primary level pH measurement system that was established in Turkey as the first and only. Thanks to this situation, the foreign currency spent for these solutions will be retained in the country.

2. Material and Methods

2.1. Chemicals

Potassium hydrogen phthalate ($KC_8H_5O_4$), disodium hydrogen orthophosphate (Na_2HPO_4), potassium dihydrogen orthophosphate (KH_2PO_4), sodium carbonate (Na_2CO_3) and sodium hydrogen carbonate ($NaHCO_3$) were obtained from Merck as Emsure. Platinum wire (0.5 mm, 99.997% metals basis) and platinum foil (0.1 mm, 99.99% metals basis) were obtained from Alfa Aesar. The other chemicals were used as analytical reagent grade.

2.2. Apparatus

Ultrapure water (18.2 MΩ) was procured from Milli-Q Integral 10 water purification system and this water was used for preparation of all solutions.

Agilent 34970A model data acquisition unit was used to collect the data. Fluke 1502A/5626 digital display unit with platinum resistance thermometer was used for temperature readings during the measurement. Digital pressure gage was used for open-air pressure readings during the measurement. Lauda Proline PV 36 water bath was used to create thermostatically stable media. GPIB-USB-HS instrument control cable and IEEE-488 GPIB bus interface cables were used to ensure the communication among the instruments. Specially constructed Harned cells were used for measurement.

Stinflame oxyhydrogen welding machine was used for the welding/production process of Pt/Pt$_{black}$, Pt/Pd$_{black}$ and Ag/AgCl electrodes. Chronopotentiometric electrode preparations were performed using a Metrohm Autolab PGSTAT 128N potentiostat/galvanostat instrument connected to a BASi C3 cell stand.

2×110 L high density poly ethylene (HDPE) tanks and circulating pump were used in pH certified reference material (CRM) production. 500 mL HDPE bottles were filled with related buffer solutions and labeled.

Mettler Toledo Seven Easy pH meter was used for homogeneity and short and long term stability studies.

Jeol JSM 6335-F scanning electron microscope was used for characterization of Pt/Pt$_{black}$ and Ag/AgCl electrodes.

Circulating pump system was used for homogenization of solutions.

2.3. *Preparation of Pt/Pt$_{black}$ or Pt/Pd$_{black}$ Electrode*

130×0.5 mm Pt wire and $10 \times 10 \times 0.1$ mm Pt foil were welded to each other and the combined wire is placed into the soda glass tube (6 mm) sealed just above of the connection point of the weld by oxyhydrogen welding machine.

The Pt plate was first cleaned in 6 M HNO$_3$ with boiling and washed with deionized water at least 3 times. Then same process was performed in deionized water and burned in the flame of the oxyhydrogen welding machine until it became a core. After this chemical cleaning step, an electrochemical cleaning was carried out. For this purpose, electrodes were placed in 0.1 M HNO$_3$ solution for 1 min. anode and then 4 min. as a cathode (Jakobsen, 2014).

Pt foil was dipped into the solution which contains of 3.4% H$_2$PtCl$_6$, 0.005% Pb(CH$_3$COO)$_2$ and 40 µL 37% HCl for Pt$_{black}$ coating. 100 mA was applied by potentiostat/galvanostat for 60 seconds and Pt foil was coated with Pt black. The figure of

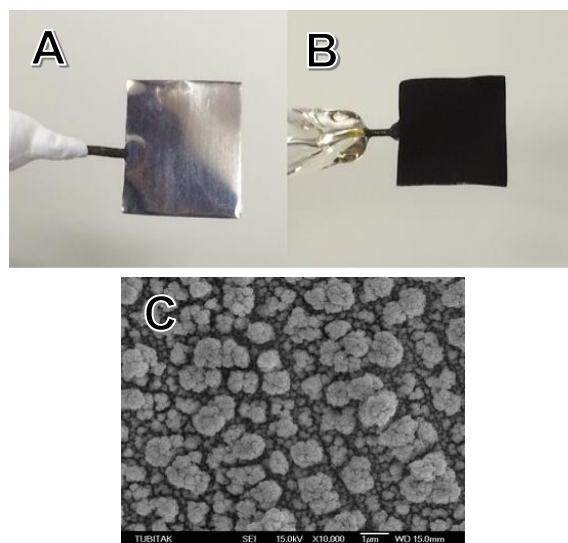bare Pt and Pt/Pt$_{black}$ and SEM image of Pt/Pt$_{black}$ are demonstrated in Figure 2.

Figure 2. (A) Bare Pt, (B) Pt/Pt$_{black}$ electrodes and (C) SEM image of Pt/Pt$_{black}$ electrode.

Pt foil was dipped into the solution which contains of 3% PdCl$_2$ and 1 M HCl for Pd$_{black}$ coating. 275 mA was applied by potentiostat/galvanostat for 100 seconds and Pt foil was coated with Pd black.

2.4. *Preparation of Ag/AgCl Electrode*

25×0.5 mm Pt wire was spirally shaped with pliers. 110×0.5 mm Pt wire and shaped Pt wire was welded to each other. The combined wire was placed into the soda glass tube (6 mm) sealed just below of the connection point of the weld with oxyhydrogen welding machine.

The Ag$_2$CO$_3$ paste preparation was made by precipitation reaction of silver nitrate with sodium hydrogen carbonate according to the following equation (Vyskočil et al., 2001):

$$2AgNO_3 + 2NaHCO_3 \rightarrow$$
$$Ag_2CO_3 + 2NaNO_3 + CO_2 + H_2O \quad (11)$$
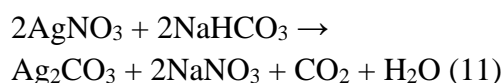
After this step, silver carbonate paste was coated onto the spiral Pt wire and reduced to silver oxide (black) and after silver (white) by heating 400 °C in a fused silica tube. The reactions can be seen in Eq. (12) and Eq. (13) (Vyskočil et al., 2001). This procedure was repeated until the desired thickness of cylindirical silver layer (~0.2 mm thickness) was obtained. The production steps and SEM image of Ag/AgCl electrode are shown in Figure 3.
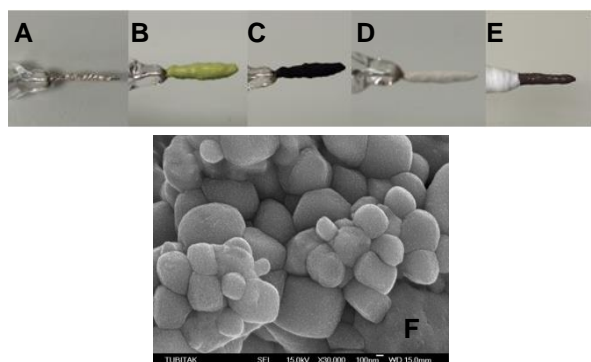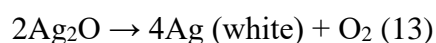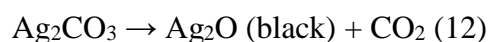
$$Ag_2CO_3 \rightarrow Ag_2O \text{ (black)} + CO_2 \quad (12)$$

$$2Ag_2O \rightarrow 4Ag \text{ (white)} + O_2 \quad (13)$$

Figure 3. (A) Spiral-Pt wire, (B) green-silver carbonate, (C) black-silver oxide, (D) white-silver and (E) brown-Ag/AgCl electrodes and (F) SEM image of Ag/AgCl electrode.

The prepared Ag electrode was dipped into 0.1 M HCl solution with vigorously stirring. The electrode was coated with AgCl layer by 7 mA/cm^2 current density. The coating process was stopped when the chronopotentiogram curve increased vertically.

2.5. Measurement Procedure

Harned cells are filled with the HCl solution which has known molality (m_{HCl}) determined by high precision constant current coulometry. Pt/Pt$_{black}$ or Pt/Pd$_{black}$ electrodes are attached to one site of the cells, Ag/AgCl

electrodes are attached to another site of the cells and H$_2$ gas is passed through the Pt/Pt$_{black}$ or Pt/Pd$_{black}$ electrodes, Ar gas is passed through the Ag/AgCl electrodes. Standard potentials of Ag/AgCl electrodes are determined in first step. Thereafter, HCl solution is emptied and the cells filled with buffer solution which has different amounts of chloride ions to be measured and acidity function is determined with extrapolating to zero chloride concentration. Finally, pH is found by summing the acidity function and logarithmic activity coefficient of chloride ions.

2.6. Production and Certification of Reference pH Buffer Solutions

2.6.1. Homogenization

Cleaning of all labwares were done by deionized water and checking cleanliness systematically. The chemical materials (KC$_8$H$_5$O$_4$ for pH 4, Na$_2$HPO$_4$ and KH$_2$PO$_4$ for pH 7 and Na$_2$CO$_3$ and NaHCO$_3$ for pH 10) were dissolved in a pre-cleaned tanks filled with 150 L deionized water and homogenized for 8 hours using a homogenizing equipment with a help of acid resistant pump as shown in Figure 4.

2.6.2. Filling and Storage

Candidate buffer solutions were prepared (300 units each) and transferred into pre-cleaned 500 mL HDPE bottles manually within a day. All the bottles were labeled in the filling order. The bottles were stored in reference temperature (4 °C) except the samples for long term and short term stability.

2.6.3. Homogeneity

Homogeneity test was performed according to ISO Guide 34: 2009 (ISO, 2009). Selection of

Figure 4. Circulating pump system for homogenization.

the samples was done by randomly stratified sampling software (TRaNS). Analysis of candidate pH buffer samples were grouped into three different pH values; 4, 7 and 10. The whole of the sample preparation process was performed gravimetrically. 10 samples from each buffer solution were used for homogeneity testing. Data evaluation was performed according to ISO Guide 35: 2006 (ISO, 2006).

2.6.4. *Short Term Stability*

Short term stability test is performed to determine the effects of environmental conditions at the certificate value during the transportation of the CRMs to the customer. This test was performed according to ISO Guide 34: 2009 (ISO, 2009). The samples for short term stability study were selected using TRaNS software. The temperatures to be tested for short term stability studies were 18 °C and 50 °C, and the periods were 1, 2, 3 and 4 weeks. Two units of UME CRM 1401, UME CRM 1402 and UME CRM 1403 were put in

test cabinet for each time interval to be tested at both temperatures. One each unit of CRM samples was reserved for the reference temperature and these units were placed directly to the reference temperature of 4 °C. At the end of each test period, 2 units from both test temperatures were transferred to the reference temperature. When the four-week test period was completed, all units transferred to the reference temperature were analysed at the same time as the units to be used as reference. Data evaluation was performed according to ISO Guide 35: 2006 (ISO, 2006).

2.6.5. *Long Term Stability*

Long term stability test is performed to determine the storage conditions of the CRMs. This test was performed according to ISO Guide 34: 2009 (ISO, 2009). The samples for long term stability study were selected using TRaNS software. The samples selected for long term stability were kept at 18 °C for 0, 3, 6, 9 months and they were transferred to the reference temperature as 4 °C from 18 °C at the end of 0th, 3th, 6th and 9th months. All of the samples were analysed at the same time at the end of 9th month. 2 samples from each buffer solution for each month were used for long term stability testing. Data evaluation was performed according to ISO Guide 35: 2006 (ISO, 2006).

2.6.6. *Characterization*

Characterization was performed according to ISO Guide 34: 2009 (ISO, 2009). The characterization studies was performed using primary level pH measurement system which its procedure was explained beforehand. The characterization measurements were performed as three analyzes for each pH and each temperature value (20 °C and 25 °C). The average of each measurement was used as

the certificate value. Data evaluation is performed according to ISO Guide 35: 2006 (ISO, 2006).

2.6.7. *Value Assignment and Uncertainties*

Measurement uncertainty was evaluated according to "Guide to the Expression of Uncertainty in Measurement" (GUM) principles. The certified values and the uncertainty values are traceable to International System of Units. The uncertainty of the certified values include characterization uncertainty (u_{char}), homogeneity uncertainty (u_{bb}), short term stability uncertainty (u_{sts}) and long term stability uncertainty (u_{lts}). These different parameters were combined to obtain the uncertainty of CRM. The expanded uncertainty of the certified value, U_{CRM}, was calculated with a coverage factor of $k = 2$, representing a confidence level of approximately 95%.

2.6.8. *Post-certification*

After the certification of the buffer solutions, post-certification monitoring analyses were carried out every year to determine whether the solutions deviated from the certification values or not according to European Reference Materials Application Note 1 (ERM Note 1) (Linsinger, 2010) named as "Comparison of a measurement result with the certified value".

3. Result and Discussion

The production consisted of 7 steps as homogenization, filling and storage, homogeneity measurements, short & long term stability measurements, characterization measurements and assigned a certified & uncertainty values. After the production, the certified values have been checked every year according to ERM Note 1 (Linsinger, 2010).

pH meter with combined glass electrode was used and also calibration and interim controls of the pH meter were carried out with Merck Certipur® 4.00, 7.00 and 10.00 standard buffer solutions, which can be traced to certified reference materials produced by National Institute of Standards and Technology (NIST) and Physikalisch-Technische Bundesanstalt (PTB) in homogeneity, short & long term stability and post-certification measurements.

3.1. *Homogeneity*

The results were evaluated using one-way ANOVA. Relative standard deviations of within ($s_{wb,rel}$) and between ($s_{bb,rel}$) bottles were calculated by the following equations.

$$s_{wb,rel}(\%) = \frac{\sqrt{MS_{within}}}{\bar{y}} \times 100 \quad (14)$$

$$s_{bb,rel}(\%) = \frac{\sqrt{\frac{MS_{between} - MS_{within}}{n}}}{\bar{y}} \times 100 \quad (15)$$

$$u_{bb,rel}^*(\%) = \frac{\sqrt{\frac{MS_{within}}{n}} \sqrt[4]{\frac{2}{v_{MSwithin}}}}{\bar{y}} \times 100 \quad (16)$$

where MS_{within} is the mean square within a unit from an ANOVA, $MS_{between}$ is the mean squares between-unit from an ANOVA, $\bar{y}$ is the average of all results of the homogeneity study, n is the average number of replicates per unit, $v_{MSwithin}$ is the degrees of freedom of MS_{within} and $u_{bb,rel}^*$ is the relative homogeneity uncertainty. The results of homogeneity study and homogeneity uncertainty (u_{bb}) are as in Table 1. The higher one between $s_{bb,rel}$ and $u_{bb,rel}^*$ is selected as final homogeneity uncertainty value (u_{bb}).

3.2. Short Term Stability

It was examined whether there was an outlier of 95% and 99% confidence level using Grubbs test and no outlier value was found. For the evaluation of the compatibility between the pH data plotted against the test time, an alignment line was drawn.

Table 1. The results of homogeneity study

CRMs	$s_{wb,rel}$ (%)	$s_{bb,rel}$ (%)	$u^*_{bb,rel}$ (%)	u_{bb} (%)
UME CRM 1401 (pH 4)	0.102	0.150	0.030	0.150
UME CRM 1402 (pH 7)	0.037	0.050	0.010	0.050
UME CRM 1403 (pH 10)	0.018	0.060	0.010	0.060

Table 2. The results of short term stability study

		UME CRM 1401	UME CRM 1402	UME CRM 1403
u_{sts} (%)	18 °C	0.074	0.014	0.009
	50 °C	0.067	0.013	0.014

As a result of the t-test applied for slope lines, it was found that the slopes were not different from zero within 95% and 99% confidence levels. As a result, it was concluded that the samples could be delivered to the end user without any cooling application provided that the temperature did not exceed 50 °C and the period did not exceed 4 weeks. The uncertainty values obtained in the short term stability studies are given in Table 2.

3.3. Long Term Stability

Similar to short term stability, it was examined whether there was an outlier of 95% and 99% confidence level using Grubbs test and no outlier value was found. For the evaluation of the compatibility between the pH data plotted against the test time, an alignment line was drawn. As a result of the t-test applied for slope lines, it was found that the slopes were not different from zero within 95% and 99% confidence levels. The measurements were made for 9 months, but the long term stability uncertainty was calculated for a 12 months shelf life. The uncertainty values obtained in the long term stability studies are given in Table 3.

Table 3. The results of long term stability study

		UME CRM		
		1401	1402	1403
u_{lts} (%)	18 °C	0.000	0.088	0.035

3.4. *Characterization, Value Assignment and Uncertainties*

Characterization uncertainty was calculated according to JCGM 100: 2008 (JCGM, 2008), Evaluation of measurement data – Guide to the expression of uncertainty in measurement. Characterization uncertainty was examined under two headings as standard potential and acidity function. Standard uncertainties of cell voltage, molality of HCl, partial pressure of H_2 and temperature under standard potential heading and standard uncertainties of cell voltage, standard potential, chloride molality, partial pressure of H_2 and temperature under acidity function heading were calculated and combined to obtain u_{char}.

Certificate values and expanded uncertainty values and their uncertainty components are as shown in Table 4 and Table 5. Expanded uncertainties were calculated by using characterization uncertainty (u_{char}), homogeneity uncertainty (u_{bb}), short term stability uncertainty (u_{sts}) and long term stability uncertainty (u_{lts}) values with coverage factor ($k = 2$) as seen in Eq. (17).

$$U_{CRM} = k\sqrt{u_{char}^2 + u_{bb}^2 + u_{sts}^2 + u_{lts}^2} \quad (17)$$

Table 4. Certificate values and uncertainties for 20 °C

UME CRM	pH	U_{CRM}	U_{CRM} (%)	u_{bb} (%)	u_{sts} (%)	u_{lts} (%)	u_{char} (%)
1401	4.034	0.014	0.360	0.150	0.074	0.000	0.066
1402	7.051	0.015	0.216	0.050	0.014	0.088	0.035
1403	10.021	0.015	0.150	0.060	0.014	0.035	0.024

Table 5. Certificate values and uncertainties for 25 °C

UME CRM	pH	U_{CRM}	U_{CRM} (%)	u_{bb} (%)	u_{sts} (%)	u_{lts} (%)	u_{char} (%)
1401	4.041	0.014	0.358	0.150	0.074	0.000	0.064
1402	7.043	0.015	0.217	0.050	0.014	0.088	0.036
1403	9.991	0.015	0.151	0.060	0.014	0.035	0.026

3.5. *Post-certification*

According to ERM Note 1, each buffer solution was measured (5 sample × 2 readings) at each temperature, then Eq. (18) was carried out (Linsinger, 2010).

$$\Delta_m = |c_m - c_{CRM}| \quad (18)$$

where Δ_m is absolute difference between mean measured value and certified value, c_m is mean measured value and c_{CRM} is certified value. Afterwards, combined uncertainty of result and certified value (u_Δ) was calculated from Eq. (19) (Linsinger, 2010).

$$u_\Delta = \sqrt{u_m^2 + u_{CRM}^2} \quad (19)$$

where u_m is uncertainty of the measurement result and u_{CRM} is uncertainty of the certified value. Then expanded uncertainty (U_Δ) was calculated by multiplication of u_Δ by 2 for 95% confidence level as seen in Eq. (20) (Linsinger, 2010).

$$U_\Delta = 2 \times u_\Delta \quad (20)$$

If $\Delta_m \leq U_\Delta$, it can be said that there is no significant difference between the certified value and the measurement result (Linsinger, 2010).

In the measurements carried out for 3 years, no significant difference was found between certified value and measurement result of the CRMs at 95% confidence level.

4. Conclusion

The hardware and software installation of the primary level pH system, which was established in Turkey as the first and only, and the production of standard hydrogen electrode and Ag/AgCl electrode were successfully carried out. Then, the production of certified pH buffer solutions and the evaluation of the results with this system were completed according to ISO Guide 34: 2009 (ISO, 2009) and ISO Guide 35: 2006 (ISO, 2006). At the same time, after the end of the project, there is full compliance with the new standards, ISO 17034: 2016 and ISO Guide 35: 2017, which are replaced by the documents released in the post-certification phase. The certificates and uncertainty values are traceable to the International System of Units (SI). Thanks to this situation, traceability will be disseminated through TUBITAK UME directly. The foreign currency spent for these solutions, that are generally used for calibration of pH meters and used in many other areas, will be retained in the country.

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