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To cite this article: H Torres and R O Cristancho 2018 *J. Phys.: Conf. Ser.* **1119** 012011

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# Implementation of the primary pH-measurement system and its uncertainty estimation

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**Abstract.** pH in aqueous solutions is one of the most frequent parameter that is measured in analysis laboratories. It is relatively simple, cheap, robust and for its determination is generally used a potentiometric method with glass pH-electrode, which must be calibrated with Certified Reference Material-CRM, and preferably not with dissolutions prepared in situ by laboratories. The assignment of pH value to these CRM, requires a measurement method of high metrological hierarchy such as the primary pH-measurement system. This system allows to ensure direct traceability to the international system of units-SI. The certification of these materials is done by national metrology institutes-NMI and their validity is accepted worldwide. In this way, it is necessary that analytical laboratory have access to CRM, in order to ensure the quality of its measurement results.

## 1. Introduction

The pH-measurement is routinely made in laboratory of analysis, industry and academy, due to the pH is a parameter of control of measurements. To guarantee the quality of measurement results and to ensure the traceability to SI, it is essential that equipments will be calibrated with CRMs which are produced by NMIs. These references are accepted in each part of world, independent if they are made by different people or teams, in different times [1,2].

The pH-magnitude is defined in terms of hydronium ion activity, this activity is difficult to determine individually, thus it is necessary to verify experimentally with a measuring method that is classified according to a metrological hierarchy, which allows to ensure the traceability [3]. The highest metrological method that exists for pH-measuring is the primary pH-measurement system, which made a link between theoretical pH-definition and its materialization. NMIs use the primary system to assign values to CRMs or reference buffer solutions. It allows production of these reference of level primary, which are required to provide traceability to others method of lower metrological hierarchy, e.g. pH-meters -the most frequently instruments used by laboratories and industries [4]. The certified pH-value of these reference buffer solutions, will be the reference for pH-meter calibrations.

The National Institute of Metrology of Colombia-INM is a governmental entity that coordinates scientific and industrial metrology in the country. The INM must establish, implement and maintain the highest metrological methods. Consequently, the aim of the this work is shows implementation of the primary pH-measurement system at INM, which will allow the production of primary buffer solutions, necessary to maintain the traceability of pH-measurements developed in Colombia.



### 1.1. Definition of pH

The concept of pH is unique among physicochemical magnitudes defined by International Union of Pure and Applied Chemistry-IUPAC. The pH term is a definition that only involves the activity of hydrogen ions in solution [5], equation 1.

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

Where  $a_{H^+}$  is relative activity,  $\gamma_{H^+}$  is the molal activity coefficient of the hydrogen ion at the molality  $m_{H^+}$ , and  $m^o$  is the standard molality that is equal to 1 mol·kg<sup>-1</sup>.

The  $-\log(a_{H^+})$  can only be defined conceptually, because there is not a thermodynamically valid method to measure the activity of a single ion. Considering that, the pH-measurement is made in relation to a pH standard solution-pH(PS) with declared uncertainty [5,6]. The pH assignment is carried out using a cell without transference known as Harned cells (the main component of the primary system), and involved a convention called Bates-Guggenheim for making of the pH(PS) a conventional magnitude that can be incorporated and accepted within the SI [3].

## 2. Metodology

### 2.1. pH-measurement with Harned cells

The primary pH-measurement system is based on determination of the potential into an electrochemical Harned cells [5,7]. These cells are used for assignment of pH-value of buffer solutions by means of the potential difference determination between platinum platinized electrodes (Pt/H<sub>2</sub>) and silver-silver chloride electrodes (Ag/AgCl).

The Harned cell contains the item under test with an addition to chloride ions necessary to operation of Ag/AgCl electrodes. This effect added is eliminated by a function called *acid function*, that depends on the  $pa_{(H^+)}$  measurements of at least three different concentrations of chloride ions and a subsequent extrapolation to zero concentration of chloride ions [8].

### 2.2. Experimental setup of the primary system

The primary pH-measurement system is shown in Figure 1 and consists of:

(1) *Harned cells set*, there are ten glass cells type Harned. If it is required to determine the Ag/AgCl standard potential, all cells are filled with HCl 0.01 mol·kg<sup>-1</sup>. If it is required to determine the acid function is necessary to fill cells with the item under test and addition of [Cl<sup>-</sup>] from 0.005 mol·kg<sup>-1</sup> to 0.02 mol·kg<sup>-1</sup>. These cells are organized in groups to obtained replicates.

(2) *Thermometer*, it is used for temperature measurement with a resolution of 0.001 K.

(3) *Thermostatic bath*, it is necessary to maintain the system at constant temperature, generally 25° C. Prior to measurement, the stability and homogeneity of bath is performed.

(4) *Hydrogen gas*, it is essential the hydrogen gas to operation of Pt/H<sub>2</sub> electrode, and its flow must be constant.

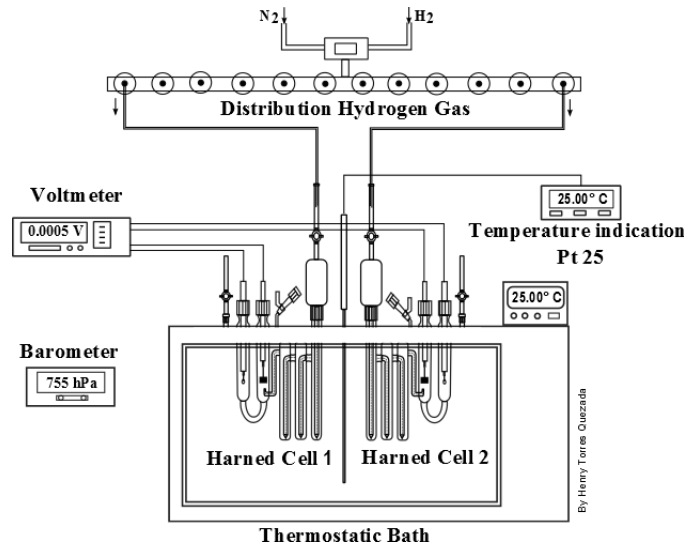
(5) *Voltmeter*, it is used a digital multimeter of 6.5 digits to determine the potential difference between Pt/H<sub>2</sub> and Ag/AgCl electrodes, in each cell.

(6) *Barometer*, it is required for recording of atmospheric pressure measurements. The data obtained allows to determine the partial pressure of hydrogen in each cell.

### 2.3. Measurement procedure

The cell potential difference- $E$  depends on the hydrogen ion activity- $a_{H^+}$ , and must be measured according to equation 2 (corrected to 101.325 kPa hydrogen partial pressure).

$$E = E^o - \left[ \frac{RT}{F} \ln 10 \right] \log \left[ \left( \frac{m_{H^+}\gamma_{H^+}}{m^o} \right) \left( \frac{m_{Cl^-}\gamma_{Cl^-}}{m^o} \right) \right] \quad (2)$$



**Figure 1.** Experimental setup of the primary pH-measurement system

Where  $E^\circ$  is the standard potential of the Ag/AgCl reference electrode,  $\gamma_{Cl^-}$  is the molal activity coefficient of chloride ion at the standard molality  $m^\circ$ ,  $R$  is the universal gas constant,  $T$  is temperature and  $F$  is the Faraday constant.

The measurement of pH with primary system consists of several steps defined below [1, 3, 6]:  
*Step 1.* The standard potential- $E^\circ$  is determined with HCl  $0.01 \text{ mol}\cdot\text{kg}^{-1}$  according to equation 3. The average activity coefficient of hydrochloric acid- $\gamma_{\pm HCl}$ , at various temperatures is extensively studied at this molality, for that reason this concentration is used as reference.

$$E^\circ = E + \left[ 2 \frac{RT}{F} \ln 10 \right] \left[ \log \left( \frac{m}{m^\circ} \right) + \log \gamma_{\pm HCl} + 0.25 \log \left( \frac{p^\circ}{p} \right) \right] \quad (3)$$

Where  $p^\circ$  is the standard pressure 101325 Pa and  $p$  is the hydrogen partial pressure in each cell.

*Step 2.* The equation 2 can be rearranged to give the acid function- $pa$  in equation 4. The  $pa$  is measured as a function of the molarity of chloride ions- $m_{Cl^-}$ .

$$pa = -\log \left( \frac{m_{H^+} \gamma_{Cl^-}}{m^\circ} \right) = \frac{E - E^\circ}{\left[ \frac{RT}{F} \ln 10 \right]} + \log \left( \frac{m_{Cl^-}}{m^\circ} \right) + 0.5 \log \left( \frac{p^\circ}{p} \right) \quad (4)$$

*Step 3.* The acid function allows to eliminate the effect of chloride ions addition by extrapolation to zero concentration of chloride ions, according to equations 5 and 6.

$$pa_0 = -\log \left( \frac{m_{H^+} \gamma_{Cl^-}}{m^\circ} \right)_{m_{Cl^-} \rightarrow 0} \quad (5)$$

$$pa = pa_0 + b m_{Cl^-} \quad (6)$$

Where  $b$  is an empirical constant that depends on temperature.

*Step 4.* The molal activity coefficient of chloride ion- $\gamma_{Cl^-}$  at ionic strength  $I$ , of a solution is obtained by consideration of the Bates-Guggenheim convention and it is obtained by equation 7.

$$\log \gamma_{Cl^-} = \frac{-A \left( \frac{I}{m^o} \right)^{1/2}}{1 + 1.5 \left( \frac{I}{m^o} \right)^{1/2}} \quad (7)$$

Where  $A$  is a constant that depends on temperature and it is obtained from the Debye-Huckel theory [9].

*Step 5.* From equations 1, 4, 5 and 7, the pH-value is obtained by equation 8.

$$pH = pa_0 + \log \gamma_{Cl^-} \quad (8)$$

#### 2.4. Uncertainty of primary pH-measurement system

If it is assumed that  $y$  is pH, it is possible to estimate uncertainty value from other quantities. In this way, as  $y = f(x_1, x_2, \dots, x_i)$ , the combined standard uncertainty- $u_c(y)$  is determined by equation 9.

$$u_c(y) = \left[ \sum_{i=1}^n \left( \frac{\partial f}{\partial x_i} \right)^2 \cdot u^2(x_i) \right]^{1/2} \quad (9)$$

The uncertainty can be expressed as an expanded uncertainty- $U$  multiplying  $u_c(y)$  by an appropriate coverage factor- $k$ , generally this factor is equal to two, which indicates 95.45% of confidence level of measurement. [10]

The  $U$  typical for the pH measure with primary system is around of 0.004 [1, 6, 11]. For the traceability to SI, it is necessary combined this uncertainty with the uncertainty defined in the Bates-Guggenheim convention, to known 0.01 ( $k = 2$ ). The majority of the NMIs to certify reference buffer solutions including all sources of uncertainty excepts uncertainty by the Bates-Guggenheim convention. In this case, these values are considered as conventional pH-values [1, 12].

### 3. Results

For validation of system, it was used a nominal pH-value of 6.86 (SRM 186g of NIST) with composition of 0.025 mol·kg<sup>-1</sup> of Na<sub>2</sub>HPO<sub>4</sub> and 0.025 mol·kg<sup>-1</sup> of KH<sub>2</sub>PO<sub>4</sub>. The results obtained with primary pH-measurement system are presented in Table 1.

#### 3.1. The standard potential- $E^o$ determination

$E^o$  was obtained by measurement of potential difference generated between Ag/AgCl electrodes in each cell along with the activity coefficient by literature,  $\gamma_{\pm HCl}$  is 0.9042 at 25° C [8, 13, 14]. The cells operated with 0.01 mol·kg<sup>-1</sup> of HCl at 25° C, the standard potential value obtained was 0.22280 V. This value is comparable to OIML R54, 0.22234 V at 25° C [9]. The combined uncertainty of the  $E^o$ -measurements is estimated in Table 1. The  $u_c(E^o)$  is 8.94 x 10<sup>-5</sup> V.

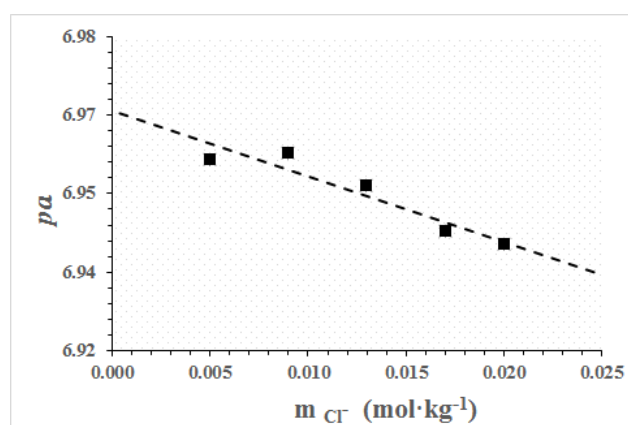
#### 3.2. Acid function and extrapolation

The cells were divided into five groups with two cells. Each group containing the item under test with different concentration of chloride ions (0.005, 0.009, 0.013, 0.017 and 0.020 mol·kg<sup>-1</sup>). The Figure 2 shows the acid function according to [Cl<sup>-</sup>]. The linear extrapolation to zero chloride molality, generated a  $pa^o$  value of 6.9728. With this value and logarithm of activity coefficient of ion chloride- $\log \gamma_{Cl^-}$ , equal to -0.1096 (from the Bates-Guggenheim convention), it is estimated a pH-value of 6.8633 by equation 8. This value is compared with SRM pH-value used, obtaining a bias of 0.00075. The  $u_c(pH)$  of SRM is 0.0008 at 25° C.

**Table 1.** The uncertainty budget of the standard potential  $E^o$  with  $0.01 \text{ mol}\cdot\text{kg}^{-1}$  of HCl

Quantity	Estimate $x_i$	Standard uncertainty $u(x_i)$	Sensitivity coefficient $ c_i $	Uncertainty contribution $u_c(y)$
Cell Potential(V)	0.460	$3.5 \times 10^{-6}$	1	$3.50 \times 10^{-6}$
m HCl ( $\text{mol}\cdot\text{kg}^{-1}$ )	0.010	$5.0 \times 10^{-6}$	5.12	$2.56 \times 10^{-5}$
$\text{pH}_2(Pa)$	71726.07	25.04	$1.79 \times 10^{-7}$	$4.49 \times 10^{-6}$
$\Delta E \text{ Ag/AgCl (V)}$	$8.19 \times 10^{-5}$	$8.2 \times 10^{-5}$	1	$8.19 \times 10^{-5}$
$\gamma_{\pm \text{HCl}}$	0.904	$2.9 \times 10^{-4}$	0.057	$1.65 \times 10^{-5}$
T thermometer (K)	298.25	0.02	$7.96 \times 10^{-4}$	$1.79 \times 10^{-5}$
T stability (K)	0.00225	$2.9 \times 10^{-3}$	$7.96 \times 10^{-4}$	$2.34 \times 10^{-6}$
T homogeneity (K)	298.25	0.02	$7.96 \times 10^{-4}$	$1.79 \times 10^{-5}$

$$u_c(E^o) = 8.94 \times 10^{-5} \text{ V}$$

**Figure 2.** The acid function ( $pa$ ) at different concentrations of chloride ions.

The uncertainty budget of the acid function is shown in Table 2, where  $u_c(pa)$  is 0.0022. This value together with the error of intercept obtained from figure 2, to know 0.00246, allows to estimate the combined uncertainty,  $u_c(pH)$  of 0.0033. This uncertainty has to be expressed as expanded uncertainty,  $U(pH)$  of 0.0066 ( $k=2$ ). For providing the traceability of measurement to SI, it is necessary to include the Bates-Guggenheim convention in the uncertainty estimation, thus the expanded uncertainty will be  $U(pH)$  of 0.012 ( $k=2$ ).

#### 4. Conclusions

The pH value obtained from the primary pH-measurement system implemented at INM of Colombia is  $6.863 \pm 0.012$  at  $25^\circ \text{C}$  ( $k=2$ ). The conventional pH value (without the Bates-Guggenheim convention) is  $6.8633 \pm 0.0066$  at  $25^\circ \text{C}$  ( $k=2$ ). This certification of reference buffer solutions will allow to give confidence and direct traceability to SI of pH-measurements developed in Colombia.

The combined uncertainty- $u_c(pH)$  obtained is 0.0033 at  $25^\circ \text{C}$ , this value is comparable to reported internationally for primary pH systems (between 0.003 and 0.004).

The bias between the pH-value obtained and the SRM used, indicates that the primary

**Table 2.** Estimation of the uncertainty of the acidic function  $pa$ 

Quantity	Estimate $x_i$	Standard uncertainty $u(x_i)$	Sensitivity coefficient $ c_i $	Uncertainty contribution $u_c(y)$
Cell Potential(V)	0.766	$3.50 \times 10^{-6}$	16.9	$5.91 \times 10^{-5}$
$m_{Cl^-}$ (mol·kg <sup>-1</sup> )	0.005	$2.20 \times 10^{-6}$	86.9	$1.91 \times 10^{-4}$
pH <sub>2</sub> ( $Pa$ )	71726.07	25.04	$3.03 \times 10^{-6}$	$7.58 \times 10^{-5}$
$\Delta E$ (V)	$8.19 \times 10^{-5}$	$8.19 \times 10^{-5}$	16.9	$1.38 \times 10^{-3}$
$E^o$ Ag/AgCl(V)	0.2228	$8.94 \times 10^{-5}$	16.9	$1.51 \times 10^{-3}$
T thermometer (K)	298.25	0.02	$3.76 \times 10^{-2}$	$8.45 \times 10^{-4}$
T stability (K)	0.00225	$2.94 \times 10^{-3}$	$3.76 \times 10^{-2}$	$1.11 \times 10^{-4}$
T homogeneity (K)	298.25	0.02	$3.76 \times 10^{-2}$	$4.35 \times 10^{-5}$

$$u_c(pa) = 0.0022$$

pH-measurement system implemented at INM of Colombia is reproducible.

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