Uncertainty estimation of primary pH-measurement system by Monte-Carlo simulation method

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Abstract. As fundamental part to assess traceability and quality of pH-measurements carried out in various sectors of industry and academy in Colombia, National Metrology Institute-INM has developed and implemented a primary pH-measurement system that will allow to certification of reference materials. In this work, it is showed according to Guide for the Expression of Measurement Uncertainty ISO/IEC GUM, the uncertainty estimation of the primary system by Monte-Carlo simulation method.

1. Introduction

In many industries, such as food, cosmetic, textile, chemical, etc., there is a remarkable parameter of control called pH, which determines the acidity or alkalinity of substances that are involved in various chemical and biological processes. Thus, it is necessary that pH-measurement results be traceable to International System of Units-SI by means of an associated uncertainty, in order to obtain quality assurance of measurements results. International Organization of Standards-ISO had developed and published the Guide to the expression of Uncertainty in Measurement -GUM, [1] which is widely used and accepted for uncertainty estimation; however, there are any limitations in this estimation due to any difficult generated when it is required to use a complex mathematical model. In consequently, The ISO had developed the Evaluation of measurement data — Supplement 1 to the “Guide to the expression of uncertainty in measurement” [2]; which had proposed to use Monte Carlo method algorithm computer simulation to estimate uncertainty. This estimation by the Monte Carlo method is applied in various national metrology institutes to strengthen the measurement knowledge [3,4].

The uncertainty estimation by Monte Carlo simulation to the primary pH-measurement system implemented at INM-Colombia is presented in this paper.

2. Measurement process

The primary pH-measurement system is shown in figure 1. It consists in a barometer (a), a voltmeter (b), a multiplexer (c), a thermometer (d) and a thermostatic bath (e); the system is complemented with a set of 12 Harned-type glass cells, which were divided in four groups of three cells to obtain measurements by triplicate. One group serves to determine standard potential group 1. and the others were classified as group 2., group 3. and group 4.; which have three different chloride concentrations to determine a lineal regression called acid function, figure 2. Each cell to determine a potential difference (in volts) between silver-silver chloride...
electrode -Ag/AgCl and platinized electrode activated with hydrogen gas -Pt/H₂. Cells were put into a thermostatic bath to obtain a measuring-temperature constant. Measurements were carried out under automatic control software developed in LabVIEW [5], which commands data of barometer, voltmeter, multiplexer and thermometer, and performing a sweep in each cell to record the potential difference between electrodes.

3. Mathematical model
Measuring of the pH involves several steps to be followed. First, it is necessary to obtain a correction of hydrogen partial pressure used as part of Pt/H₂ electrode in each cell. This correction was calculated by equation 1.

\[ p_{H_2} = p + 4.2556h_H - 133.3225e^{20.84-(\frac{5268}{T})} \]  

(1)

Where \( p \) is the atmospheric pressure in pascal, \( h_H \) is the immersed distance of electrode in meters and \( T \) is the measuring temperature in kelvin. After having obtained \( p_{H_2} \), second step involves to calculate the standard potential \(-E^\Theta\) of group 1. by equation 2.

\[ E^\Theta = E + \frac{2RT\ln10}{F} \log(m_{HCl}) + \log(y_{\pm HCl}) + 0.25\log\left(\frac{p^\Theta}{p_{H_2}}\right) \]  

(2)

where:

- \( E \) = Potential difference average of group 1. in volts
- \( R \) = Gas constant, 8.31451 J mol\(^{-1}\)K\(^{-1}\)
- \( T \) = Measuring temperature in kelvin
- \( F \) = Faraday constant, 96485.33289 C mol\(^{-1}\)
- \( m_{HCl} \) = Hydrochloric acid concentration, in mol kg\(^{-1}\)
- \( y_{\pm HCl} \) = Hydrochloric acid activity coefficient
- \( p^\Theta \) = Reference pressure, 101325 Pa

Third step is developed with \( E^\Theta \) previously obtained and equation 3., to calculate the acid function in each \( E_n \) group 2, 3, and 4. These are points of the function obtained with different concentrations of KCl. The potential difference average of each group it is represented as \( E_n \) (in volts) and \( m_{HCl_n} \) is KCl concentration, table 1.

\[-\log(a_{HCl})_{mx} = \frac{F(E_n - E^\Theta)}{(RT\ln10)} + \log(m_{HCl_n}) + 0.5\log\left(\frac{p^\Theta}{p_{H_2}}\right) \]  

(3)
Table 1. Cells-group used to pH-measurements.

| Group | Cells number | Solution and purpose          |
|-------|--------------|-------------------------------|
| 1     | 1 2 3        | HCl 0.001 mol kg$^{-1}$ -- $E^Θ$ determination |
| 2     | 4 5 6        | KCl 0.005 mol kg$^{-1}$ -- $E_2$ determination |
| 3     | 7 8 9        | KCl 0.010 mol kg$^{-1}$ -- $E_3$ determination |
| 4     | 10 11 12     | KCl 0.015 mol kg$^{-1}$ -- $E_4$ determination |

In figure 2 is shown the acid function generated by $E_2$, $E_3$ and $E_4$ values obtained with equation 3. The function $-\log(a_{H\gamma Cl})_{mx}$ and chloride ion-concentration was conducted for the purpose of obtaining the intercept of the regression.

![Acid Function](image)

Figure 2. Acid function, $[Cl^-]$ vs $-\log(a_{H\gamma Cl})_{mx}$

With fourth step is determined the chloride ion activity coefficient in the intercept by equation 4. Where $A$ is the coefficient Debye–Hückel and $I/m^Θ$ is the ionic strength of dissolution according to OIML R 54 [5].

\[
\log[\gamma Cl]_{mCl\rightarrow 0} = \frac{(-A\sqrt{I/m^Θ})}{(1 + 1.5\sqrt{I/m^Θ})} \tag{4}
\]

Final step is calculated the pH-value by equation 5 with the results previously obtained in equations 3 and 4.

\[
pH = -\log[a_{H\gamma Cl}]_{mCl\rightarrow 0} + \log[\gamma Cl]_{mCl\rightarrow 0} \tag{5}
\]

4. Application of Monte-Carlo method to estimate uncertainty

The guide ISO-GUM [1] and Supplement 1 [2] were followed to estimate uncertainty of primary pH-measurement system according to mathematical model. The uncertainty sources are defined in a cause-effect diagram, figure 3. The uncertainty estimated is performed in LabVIEW software-National Instruments [5].
Figure 3. Diagram cause-effect E: the potential difference of cell; T: temperature; Rep.: repeatability; Trac.: traceability; $p_{H2}$: hydrogen-partial pressure; mCl: chlorides mass; disso. mass: dissolution mass; NaCl mass: sodium chloride mass, R: gas constant; F: Faraday constant. In the box, $E^\Theta$: standard potential; HCl mass: hydrochloric acid mass and $\gamma_{\pm HCl}$: the ionic activity coefficient.

4.1. Propagation of PDF (probability density function) with the mathematical model

This is done by pseudo-random numbers generated with its respective PDF of input quantities, whereby it is obtained M number of experiment replicas (two million for this simulation).

As a result of this data analysis is obtained an output PDF, that is evaluated with statistical parameters such as median, average and asymmetry coefficient to evaluate asymmetry of the output distribution. In addition, an adjustment function is performed to PDF obtained. Table 2 presents an example of the input quantities and Figure 4. shows algorithm flow chart developed.

Table 2. Input quantities used for Monte-Carlo simulation

| Input Quantity   | Estimated value | Standard deviation | Units       | PDF     |
|------------------|-----------------|--------------------|-------------|---------|
| $E_2$            | 0.900857        | 3.70 x 10^{-5}     | volts       | Normal  |
| $E_3$            | 0.882926        | 4.10 x 10^{-5}     | volts       | Normal  |
| $E_4$            | 0.872077        | 4.10 x 10^{-5}     | volts       | Normal  |
| Pressure         | 75052.04        | 25.04              | pascal      | Normal  |
| Temperature      | 298.15          | 4.80 x 10^{-3}     | K           | Normal  |
| $m_{HCl}$ 2      | 0.005           | 2.20 x 10^{-6}     | mol/kg      | Normal  |
| $m_{HCl}$ 3      | 0.010           | 2.20 x 10^{-6}     | mol/kg      | Normal  |
| $m_{HCl}$ 4      | 0.015           | 2.20 x 10^{-6}     | mol/kg      | Normal  |
| $E_1$ or $E^\Theta$ | 0.46929     | 1.00 x 10^{-5}     | volts       | Normal  |
| $m_{HCl}$ 1      | 0.01            | 1.00 x 10^{-5}     | mol/kg      | Normal  |
| Faraday constant | 96485.33289     | 5.90 x 10^{-4}     | C/mol       | Normal  |
| Gas constant     | 8.3144598       | 4.80 x 10^{-6}     | J mol/K     | Normal  |
| Immersed distance| 0.01            | 0.001              | meter       | Uniform |
| Ionic activity coefficient at 25°C $\gamma_{HCl}$ | 0.9042 | 0.0003 | — | Normal |
5. Analysis of results

Once the output quantity PDF is obtained a histogram is generated by simulation, table 3 shows the output quantities-PDF parameters obtained. The close coincidence between the mode, the average and the asymmetry coefficient close to zero confirm the normal distribution without asymmetries. By means of the Sub Virtual Instrument function of LabVIEW [5] called “normal distribution adjustment” function, it is applied to adjusts PDF to a normal distribution by graphical method. This is done to evaluate experimental normal distribution quality. Figure 2. shows confidence interval and extrapolation at concentration zero from acid function. This interval is established according to considerations from the Monte Carlo-simulation.

| Parameter                  | Value                  |
|----------------------------|------------------------|
| Mean                       | 8.98600674             |
| Median                     | 8.98600688             |
| Asymmetry coefficient      | 0.00338558             |
| Standard deviation         | 0.00148399             |
| 95% Confidence interval    | 8.9830982 - 8.9889153  |

6. Discussion

A comparison between parameters obtained by Monte-Carlo and the GUM-methodology is showed in table 4. The pH-values obtained with a 95.45% confidence interval are very similar using the two methodologies mentioned.

| Parameter                  | GUM estimation | Monte-Carlo estimation | Variation  \
|----------------------------|----------------|------------------------|------------|
| Expanded uncertainty       | 0.007098       | 0.007148               | 5×10⁻⁴     |
| pH value                   | 8.9857         | 8.9860                 | 3×10⁻⁴     |
Figure 5: show adjust of function to normal distribution and experimental function tests performed with different M-number of repetitions.

![Figure 5](image)

**Figure 5.** Comparison of experimental (red) and adjustment functions (blue) with a. M = 1000 and b. M = 2000000 for Monte Carlo simulation.

It is important to select a number of replicas suitable, due to a low number will not offer a precise simulation and generates an unclear output distribution. In this study, two million iterations are recommended as the M-number for obtaining a good distribution.

The simulation helps to define better the uncertainty because LabVIEW [6] permits internal access to create control points, intermediate data validation, graphically analysis and errors detection.

7. Conclusions
The Monte-Carlo method offers a very good alternative to limitations of uncertainty estimation generates with GUM-methodology due to use of complex or non-linear models.

With this simulation is obtained a better approximation to uncertainty because it is possible to control and to improve input variables that affect the behavior of process.

References
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