Evaluation of Ag/AgCl-electrode standard potential uncertainty used in primary pH measurements by Monte Carlo simulation

J.C. Damasceno, R.M.H. Borges, A.P. Ordine, M.A. Getrouw, I.C.S. Fraga, P.P. Borges, V. Souza

Divisão de Metrologia Química, Instituto Nacional de Metrologia, Normalização e Qualidade Industrial – Inmetro, R. N. S^{ra}. das Graças, 50, Xerém, Duque de Caxias, RJ, CEP 25250-020, Brazil, E-mail: jcdamasceno@inmetro.gov.br

Abstract. *The chemical quantity pH is a quality control parameter used in several industrial processes. Therefore, its proper determination and uncertainty estimation are extremely important to provide reliability and traceability to pH measurements. The uncertainty estimation procedures recommended in ISO-GUM are largely used by several laboratories and institutes. This work compares the ISO-GUM approach and the Monte Carlo simulation method for the Ag/AgCl electrode potential uncertainty (UE^o) determination used in pH uncertainty estimation in a phosphate solution at 25°C. The Monte Carlo simulation showed very similar results in comparison to the ISO-GUM approach. It can be concluded that both methods are applicable for UE^o determination and give reliable results.*

Keywords: Monte Carlo simulation, primary pH measurement, ISO-GUM, uncertainty estimation

1. Introduction

pH is an important quality control parameter used in several industrial processes, such as food processing, metallurgical extractions, pharmaceutical production and environmental control. It is commonly measured by calibrated pH meters. The use of Certified Reference Materials (CRM) [1], necessary for the calibration of pH meters, is essential to guarantee pH measurement reliability. At Inmetro, the Brazilian National Metrology Institute (NMI), a primary system for pH measurement was set up in 2003, so far unique in South America. Ever since, this system has been improved in order to certify Reference Materials (RM), thus providing traceability to secondary certification measurements of standards produced and used by many national laboratories and industries.

International trade, environmental protection and science demand reliable measurements, which can be achieved by measurement traceability and uncertainty estimation. Currently, most analytical laboratories adopt the ISO-GUM approach [2] when calculating measurement uncertainties. However, when the model equation presents a strong non-linear nature, the overall uncertainty may be underestimated due to limitations of the ISO-GUM method, such as linear approximation, assumption of normality on the parameter being studied and analytical evaluation of the effective degrees of freedom [3]. In this way, Monte Carlo simulation is raising interest as a more reliable tool for evaluation of measurement uncertainties, because it uses random number generation for simulating the values of the random variables rather than analytic calculations [3].

In this work, Monte Carlo and ISO-GUM methods were used to determine the Ag/AgCl electrode potential uncertainty (UE^o) used in pH uncertainty estimation for a given primary pH measurement at Inmetro.

2. Subject and Methods

Primary pH measurements for primary reference material certification were carried out using twelve Harned cells [4], silver-silver chloride (Ag/AgCl) electrodes, platinum electrodes and pure hydrogen (99.99%). The cells were placed in high precision thermostatic baths (thermal stability of 0.003K), which temperature was monitored by resistance thermometers (PT100). The hydrogen pressured in the cells was monitored by measuring the atmospheric pressure with a barometer (resolution of 1Pa). The cells were divided in four groups containing three Harned cells each. One group contained a 0.01 mol kg^{-1} hydrochloric acid (HCl) solution, in which the standard potential of the Ag/AgCl electrodes (E^o) was determined. In the other three groups, the buffer solution to be certified – a 0.025 mol kg^{-1} phosphate solution with a nominal pH value of 6.865 at 25^{o}C – was analyzed. pH values were calculated considering all measured cell potentials using a 8.5-digit multimeter [5].

Calculation of E^o in a primary pH system using Harned cells is given by Eqs. 1 to 3 [3], where E is the potential difference between Ag/AgCl and Pt/H_2 electrodes; R, the molar gas constant; T, the system temperature; F, the Faraday constant; m_{Cl}, the chloride molality; $\gamma^{\pm}$, the activity coefficient of the HCl solution at molality 0.01 mol kg^{-1}; pH_2, the hydrogen partial pressure inside the cell; p^o, the standard atmospheric pressure (101325 Pa); p_{atm}, the measured atmospheric pressure; p_{hid}, the hydrostatic pressure inside the Harned cell; ρ_{H2O}, the water density at system temperature; g, the local gravity acceleration and h, the height of solution in which the electrodes are immersed.

$$E^o = E + \frac{2RT\ln 10}{F}\log(m_{Cl}\gamma^{\pm}) - \frac{RT\ln 10}{2F}\log(\frac{pH_2}{p^o}) \tag{1}$$

$$pH_2 = p_{atm} - p_{H_2O} + p_{hid} \tag{2}$$

$$p_{hid} = 0.4\rho_{H_2O}\, g\, h \tag{3}$$

Estimation of E^o uncertainty using the ISO-GUM approach considered the contributions suggested by IUPAC [4], with some additional uncertainty sources, as described below for each parameter and shown in Table 1.

(1) Cell potential (E): the uncertainty influences were due to repeatability (uE_A) and calibration of the multimeter (uE_B).

(2) Molar gas constant (R): the standard uncertainty for R was given by CODATA [6].

(3) Temperature (T): five contributions were considered: repeatability (uT_A); calibration of the multimeter (uT_{Mult}) used to acquire data from the PT100; thermal gradient of the baths (uT_{TG}); calibration of the PT100 (uT_{PT100}) and the bath temperature stability (uT_{Bath}).

(4) Faraday constant (F): the standard uncertainty for F was given by CODATA [6].

(5) Chloride molality (m_{Cl}): the uncertainty was obtained from coulometric titrimetry carried out at Inmetro.

(6) Bias potential (ΔE): this contribution, attributed to the quality of the Ag/AgCl electrodes, was expressed as the maximum admitted potential between the used electrodes and a reference Ag/AgCl electrode.

(7) Activity coefficient ($\gamma^{\pm}$): the uncertainty was considered to be 0.00029 [7 "incluir esta no final"].

(8) Hydrogen partial pressure (pH_2): the uncertainty was determined considering p_{atm}, p_{H2O} and p_{hid} uncertainties (refer to Eq. 2). The uncertainty of p_{atm} has two contributions:

repeatability (up_{atmA}) and resolution of the barometer (up_{atmB}). The uncertainty of p_{H2O} is estimated as being 0.01/√3 Pa. The uncertainty of p_{hid} involves contributions from ρ_{H2O}, g and h uncertainties.

Table 1. Parameters and uncertainty contributions used for E^o uncertainty estimation.

Quantity	Units	Distribution	Estimate	Standard uncertainty	Dispersion
E					
E_A	V	Normal	0.46429907	5.1606E-11	6.5684E-10
E_B	V	Normal	0	2.89E-6	2.89E-6
R	J mol^{-1} K^{-1}	Normal	8.314472	5E-6	5E-6
T					
T_A	K	Normal	298.154	8.4625E-5	8.7945E-4
T_{Mult}	K	Normal	0	7.0508E-4	7.0508E-4
T_{TG}	K	Normal	0	0.0004	0.0004
T_{PT100}	K	Normal	0	0.0092195	0.0092195
T_{Banho}	K	Uniform	0	1.7321E-3	0.003
F	C mol^{-1}	Normal	96485.3383	0.0083	0.0083
m_{Cl}	mol kg^{-1}	Normal	0.009902	1.1334E-5	1.1334E-5
ΔE	V	Uniform	0	2.8868E-5	0.00005
$\gamma^{\pm}$	-	Normal	0.90425	2.9E-4	2.9E-4
pH_2					
p_{atmA}	Pa	Normal	100711	16.6021	122
p_{atmB}	Pa	Uniform	0	0.57735	1
p_{H2O}	Pa	Uniform	3169.6441	1.02155	1.7694
p_{hid}	Pa				
ρ_{H2O}	kg L^{-1}	Uniform	996.5354	5.7735E-3	0.01
g	m s^{-1}	Uniform	9.787487	5.7735E-7	0.000001
h	m	Uniform	0.01	2.8868E-3	0.005

Evaluation of E^o uncertainty using Monte Carlo simulation was carried out using Crystal Ball® version 4.0g software [8]. This package uses Microsoft® Excel-based applications for Monte Carlo calculations. Each Excel® cell can represent a random variable featured by its expected value (the value of the cell) and its assumed probability density function (normal, uniform, triangular, etc) together with a given dispersion measurement (standard deviation or interval). After having defined all parameters that affect the measurand and their probability density functions (one Excel® cell for each parameter), the measurand value was computed in another Excel® cell by applying the corresponding mathematical operations with the parameters cells, according to the measurand determination formula, and that cell was chosen as a forecast cell. Then, the number of trials (M = 100000) was chosen and the simulation was started. Table 1 shows the dispersion values used for each parameter in Monte Carlo simulation. The measurand (E^o) formula was computed according to Eqs. 1 to 3, adding also the contribution for ΔE.

3. Results and Discussion

The obtained expanded uncertainty for E^o measurement using the ISO-GUM approach was 0.00013621 V, while the estimate obtained analytically was 0.22246361 V. On the other hand, statistics obtained by Monte Carlo simulation are presented in Table 2. Considering that the value obtained for distribution skewness is sufficiently near zero to assume a symmetrical distribution for E^o, its expanded uncertainty can be calculated as UE^o = (0.22260143 – 0.22232731)/2 = 0.00013706 V.

Table 2. Statistics obtained by Monte Carlo simulation.

Mean (V)	Median (V)	Standard deviation (V)	Skewness	Confidence interval for 95%
0.22246360	0.22246345	0.00007014 V	-0.01114217	[0.22232731 to 0.22260143] V

A comparison between both methods of uncertainty estimation is shown in Table 3. As one can see, there is a good agreement between the estimation methods for both E^o and UE^o values. Estimated values of E^o are practically identical and values of UE^o differ each other by only 0.6%.

When working with Monte Carlo simulations, it is necessary to emphasize that the analyst should be very careful in order to properly identify the main uncertainty contributions and their respective distributions. On the contrary, erroneous uncertainty estimates could be obtained for the parameter under analysis. It should be observed that the use of a computer program and a high speed computer are also required.

Table 3. Comparison between ISO-GUM and Monte Carlo simulation uncertainty estimation methods.

	ISO-GUM	Monte Carlo simulation
Estimate (E^o)	0.22246361 V	0.22246360 V
Expanded uncertainty (UE^o)	0.00013621 V	0.00013706 V

4. Conclusions

ISO-GUM and Monte Carlo uncertainty estimation methods showed very similar results when used for Ag/AgCl electrode potential uncertainty (UE^o) estimation in primary pH measurements. Monte Carlo simulation may be successfully used to estimate UE^o given that the main uncertainty contributions and their respective distributions are correctly identified.

The measurement uncertainty estimation of the standard potential of the Ag/AgCl electrodes used in primary pH measurement has been investigated at Inmetro. This work was the first step to study the pH primary measurement uncertainty itself.

5. References

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