Determinación de pureza de ácido fórmico potasio por sistema de titulación culemética: Estudio de validación y estimación de incertidumbre

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Abstract. Este trabajo describe el sistema de Coulometría implementado en el Instituto Nacional de Metrología (NMI) de Colombia para la certificación de pureza de ácido fórmico potasio (KHP). El sistema se propone convertirse en un sistema de medición primaria. Este estudio incluye un análisis de precisión en términos de desviación estándar relativa (%RSD), y su asociada incertidumbre por repetibilidad y detección de punto terminal como incertidumbre tipo-A; y por resistencia eléctrica, tiempo, diferencia potencial y masa del muestreo como incertidumbre tipo-B. La implementación de este sistema permitirá la certificación de pureza de diferentes materiales referenciales.

1. Introducción
La titulación culemética es un método analítico que utiliza una cantidad de carga durante los experimentos para generar alguna especie química o reactivante, en la superficie del electrodo de trabajo [1]. En este método es necesario que cada corriente eléctrica que circula a través de la celda electroquímica produzca un reactivante sin presencia de reacciones secundarias durante el proceso de electrolysis. Esta especie química debe reaccionar cuantitativamente con la sustancia a ser titulada. Por lo tanto, la cantidad de sustancia (n) se relaciona con la carga eléctrica generada durante el proceso de electrolysis y depende del comportamiento del intensidad de corriente (I vs t) que se aplica a la celda electroquímica. La ecuación 1 describe esta situación de acuerdo con la ley de Faraday [2].

\[ n = \frac{Q}{zF} = \int \frac{I \, dt}{zF} \]  

Donde Q es la carga eléctrica, I es la intensidad de corriente, t es el tiempo de electrolysis, z es el número de carga de la reacción, F es la constante de Faraday y n es la cantidad de sustancia. De manera similar, la carga eléctrica generada durante el proceso de electrolysis se puede relacionar con la resistencia eléctrica (R), el tiempo (t) y la diferencia potencial (V) por la ecuación 2, lo que permite determinar la cantidad de sustancia por kilogramo \( \nu \) (mol kg\(^{-1}\)). De esta manera, es posible obtener \( \nu \)-traceabilidad al SI (Sistema Internacional de unidades) a través de la medida de la resistencia eléctrica, el tiempo y la diferencia potencial.

\[ \nu = \frac{V \, t}{zF \, Rm} \]
In accordance with the Faraday's law and the relationship of the current function vs time, may be present two forms of coulometry: (i) the controlled-potential whereby the electric current decreases exponentially with the time; and (ii) the controlled-current whereby the electrical current is constant. The controlled-potential method is most selective for each reaction but an exponential failure of the current intensity generated limitations in the electric charge measurement accuracy. In addition, the controlled-current method is less selective but to allow to obtain a better electric current efficiency in an adequate range of measurements [3]. The coulometry is classified as a potential primary method for determination of the amount of substance with direct mole traceability, a SI base unit [4]. Thus, different national metrology institutes- NMIs have been developed these methods for certification of reference materials according to analyte requires for acidimetry, alkalimetry, argentometry, oxidimetry and complexometry, among others [5].

This paper shows the main aspects related with to preliminary studies of 32 measurements developed to determine purity of a commercial potassium hydrogen phthalate (KHP); the purity is expressed as the amount of substance per kilogram. This value and its associated uncertainty were estimated by the Coulometric titration system at current constant that had been developed at Electrochemical Analysis Working Group of Instituto Nacional de Metrologia de Colombia. The implementation of this analytical technique opens the door to production and certification of primary reference materials in magnitude of the amount of substance according to ISO 17034:2016 [6].

2. Methods
2.1. Coulometry Measurement System
Coulometric system implemented by Colombian-NMI consists in, Figure 1, an electrochemical glass cell type-vertical (128 cm×68.3 cm of diameter) with two independent compartments (A), one is called cathodic and another anodic. The cathodic-compartment (B) is filled with 250 mL of KCl 1.0 mol kg$^{-1}$ (Merck Emsure- 99.5% purity) prepared with ultrapure water and stirred.

The anodic-compartment (D) contains a spiral Ag-wire (Alfa Aesar- 99.999% purity and 100 cm×1.0 mm of diameter) as counter electrode (E) whose inner part is filled with agar-agar (F) (Merck ultrapure) prepared in KCl 1.0 mol kg$^{-1}$ (Merck Emsure- 99.5% purity) and the mixture is heated to 150$^\circ$C for 10 minutes. The working electrode was a Pt-wire (G) (Alfa Aesar- 99.95% purity and 25 cm×1.0 mm of diameter) and the indicating electrode was a pH-unitrode Pt1000 (H) (combined glass pH-electrode with temperature sensor). The supporting electrolyte into the cathodic-compartment is bubbled with 400 mL min$^{-1}$ of high purity argon gas (99.999%) and it...
Figure 2. Experimental procedure applied to amount substance determination of KHP by Coulometric titration

Figure 3. Precision diagrams (A and B) test of first experimentalist.

is stirred during all assays (C-K). Metrohm Autolab potentiostat/galvanostat PGSTAT128N is used such as a current source and end-point indication detection (J). Frequency Counter/Timer is used to follow the titration time (L), Keithley multimeter 2002 is used to potentiometric measurements (M), Guildline 9345/100K decade box is used to control the electric resistance (N). For data acquisition system is used Metrohm Autolab Nova 2.1 software (O), and for reagents weighting is used a microbalance (P) (resolution 0.1 mg). Finally, it is used ultrapure water with electrolytic conductivity around of 0.1 $\mu$S cm$^{-1}$ and temperature control is achieved by thermostatic bath.

2.2. Coulometric titration of Potassium hydrogen phthalate

Figure 2 represented the experimental procedure which begin with a cleaning process of electrochemical cell, it is realized with consecutive washes of soap phosphate-free to 5%, ultrapure water and ethanol (96% purity). Then, cell is dried with argon gas and purged during five minutes. Second, 500 mg of KHP dried (Carlo Erba- 99.5% purity) is putted into cathodic-compartment of the clean cell. Third, carefully it is added 150 mL of KCl 1.0 mol kg$^{-1}$ previously bubbled with argon gas. The mixture is stirred for 15 minutes in presence of 400 mL min$^{-1}$ argon gas flow and then, it is added again 100 mL of KCl 1.0 mol kg$^{-1}$ to complete 250 mL in the cathodic-compartment. Fourth, the anodic-compartment (Ag-wire), the Pt-wire and pH-electrode are putted into the electrochemical cell and that is sealed to be submerged into thermostatic bath. Finally, the Coulometric titration starts when is applied 75 mA for 4000 seconds with constant stirring. Data acquisition of electrical charge, time, potential difference, electric resistance, pH and temperature are recorded each 0.22 seconds.
3. Results

3.1. Precision Study

Two experimentalists made 16 measurements in duplicate to evaluate measurement precision, a standard deviation ($\sigma$) parameter is established with values of $\pm \sigma$, $\pm 2\sigma$ and $\pm 3\sigma$ by each eight-measurement group. Figure 3 and 4 showed precision diagram by first experimentalist. Figure 3A shows the first-measurements group obtained, the standard deviation value ($\sigma$) is 0.1646 mol kg$^{-1}$ and seven out of eight replicates are located between $\pm \sigma$ (4.8052 to 5.1344 mol kg$^{-1}$), in this interval the relative standard deviation-RSD correspond to 3.31%; the test N$^5$ has an atypical value, it is defined how the value outside of $\pm \sigma$ interval, which is located between $\pm 3\sigma$ (4.4759 to 5.4637 mol kg$^{-1}$). This deviation is attributed to random factors in the measurement system. Figure 3B shows the second-measurement group obtained, the standard deviation value ($\sigma$) is 0.0491 mol kg$^{-1}$ and seven out of eight replicates are located between $\pm \sigma$ (4.9010 to 4.9993 mol kg$^{-1}$) in this interval RSD correspond to 0.99%; the test N$^8$ has an atypical value located between $\pm 3\sigma$ (4.8027 to 5.0975 mol kg$^{-1}$), this is also associated with random factors in the measurement system. According to the two measurement groups, the intermediate precision condition evaluated with $\sigma$, is decreased of three times between these experiments by the experimentalist; this variation could be attributed to measurement-time and expertise of the first experimentalist.

Figure 4A shows the third-measurements group obtained, the standard deviation value ($\sigma$) is 0.0202 mol kg$^{-1}$ and six out of eight replicates are located between $\pm \sigma$ (4.9351 to 4.9755 mol kg$^{-1}$), in this interval RSD correspond to 0.41%; the tests N$^3$ and N$^7$ have atypical values located between $\pm 2\sigma$ (4.9148 to 4.9958 mol kg$^{-1}$), which is also attributed to random factors on the measurement system. Figure 4B shows the fourth-measurement obtained, the standard deviation value ($\sigma$) is 0.1527 mol kg$^{-1}$ and five out of eight replicates are located between $\pm \sigma$ (4.8607 to 5.1660 mol kg$^{-1}$) in this interval RSD correspond to 3.05%; the tests N$^2$, N$^7$ and N$^8$ have atypical values located between $\pm 2\sigma$ (4.7080 to 5.3186 mol kg$^{-1}$).

According to the two measurement groups, the intermediate precision condition evaluated with $\sigma$, is increased significant of seven times between these experiments by the experimentalist; this variation could be attributed to loss of control of measurement conditions and expertise to the second experimentalist. With regard to the all measurements groups exists any atypical values that indicates a loss of control of any experimental factors such as (a). sample introduction into cell, (b). mass-loss in cell container by bubbled with argon gas and (c). sample-loss by diffusion between compartments due to inefficient separation. These undesirable conditions generated random errors in the Coulometric system which affected measurement precision [7]. For this study, the intermediate precision average is 1.94%. The better precision condition is obtained in the third-measurements group with repeatability of 0.41%.

3.2. Uncertainty Estimation

Equation 3 shows the mathematical model used for amount content determination by the Coulometric system implemented at Colombian-INM. The variables, its units and associated sensibility coefficients are presented in Table 1.

$$\nu = \frac{V_l \times t_t}{zFRm} + A + k$$

The uncertainty is estimated according to Guide for the Expression of Uncertainty in Measurement-GUM [8]; the guide indicates that each sensitivity coefficient ($c_i$) is multiplied by typical uncertainty ($u_i$) of result to each variable measured, in order to obtain a combined uncertainty ($u_c$). Equation 4 shows the $u_c$ associated to the mathematical model described in equation 3.
Figure 4. Precision diagrams (A and B) test of second experimentalist.

\[ u_c(KHP) = \sqrt{(c_u u_t)^2 + (c_v u_v)^2 + (c_F u_F)^2 + (c_R u_R)^2 + (c_m u_m)^2 + (c_A u_A)^2 + (c_k u_k)^2} \]  \tag{4}

In this way, the \( u_c(KHP) \) is estimated from one group of uncertainty sources such as electric resistance (\( u_R \)), sample weighing (\( u_m \)), Faraday constant (\( u_F \)), the potential difference (\( u_v \)) and titration time (\( u_t \)), that are taken as type B uncertainties; likewise, a second group of uncertainty sources such as end-point detection (\( u_A \)) and repeatability (\( u_k \)) are taken such as type A uncertainties to complete uncertainty estimation.

Table 1. Variable description of the mathematical model

| Symbol | Units         | Description                        | Expression (\( c_i \)) | Value (\( c_i \)) | Units (\( c_i \)) |
|--------|---------------|------------------------------------|------------------------|------------------|-------------------|
| Vt     | V             | Applied potential in              | \( \frac{\partial\nu}{\partial V} = \frac{V_t}{zRFm} \)       | 65.75            | mol (kg V)\(^{-1}\) |
| t_t    | s             | Coulometric titration time         | \( \frac{\partial\nu}{\partial t} = \frac{V_t}{zRFm} \)       | 1.5 \times 10^{-3} | mol (kg s)\(^{-1}\) |
| z      | -             | Electrons exchanged in titration   |                        | -                | -                 |
| F      | C mol\(^{-1}\) | Faraday constant according to CODATA [9] | \( \frac{\partial\nu}{\partial F} = -\frac{V_t t_t}{zRFm^2} \) | -5.1 \times 10^{-5} | mol (kg C)\(^{-1}\) |
| R      | \( \Omega \)  | Electrical resistance measured     | \( \frac{\partial\nu}{\partial R} = -\frac{V_t t_t}{zFR^2m} \) | -4.9653          | mol (kg \( \Omega \))^{-1} |
| m      | kg            | Sample-mass corrected by air buoyancy | \( \frac{\partial\nu}{\partial m} = -\frac{V_t t_t}{zFRm^2} \) | -9728            | mol (kg)\(^{-2}\)  |
| A      | mol kg\(^{-1}\) | Correction by end-point detection | \( \frac{\partial\nu}{\partial A} = 1 \)                         | 1                | mol (kg)\(^{-1}\)  |
| k      | mol kg\(^{-1}\) | Repeatability                      | \( \frac{\partial\nu}{\partial k} = 1 \)                        | 1                | mol (kg)\(^{-1}\)  |

Table 2 presents uncertainty budget, here it is observed that significant uncertainty correspond to repeatability -close to 99% of \( u_c(KHP) \), the evidence is coherent according to previous precision study and suggests that the precision conditions must be improved.
Table 2. Uncertainty Budget for KHP-purity measurements

| Uncertainty Source   | Measure Value | Type | Distribution  | Typical uncertainty value | \( u_i \) |
|----------------------|---------------|------|---------------|---------------------------|------|
| Potential difference | 0.075519      | B    | Rectangular   | 3.5 \times 10^{-1}        | 2.3 \times 10^{-3} |
| Time                 | 3238.12231    | B    | Rectangular   | 3.4 \times 10^{-9}        | 5.2 \times 10^{-12} |
| Faraday constant     | 96485.33289   | B    | Rectangular   | 5.9 \times 10^{-4}        | -3.0 \times 10^{-8} |
| Electric resistance  | 1.00000342    | B    | Rectangular   | 4.5 \times 10^{-6}        | -2.2 \times 10^{-5} |
| Mass-sample weight   | 0.000509      | B    | Rectangular   | 4.3 \times 10^{-8}        | -4.1 \times 10^{-4} |
| End-point detection  | -             | A    | Normal        | 8.8 \times 10^{-5}        | 8.8 \times 10^{-5} |
| Repeatability        | -             | A    | Normal        | 2.0 \times 10^{-2}        | 2.0 \times 10^{-2} |

\( u_c \) Type B mol (kg)^{-1} 4.1 \times 10^{-4} \\
\( u_c \) Type A mol (kg)^{-1} 2.0 \times 10^{-2} \\
\( u_c \) Total mol (kg)^{-1} 2.0 \times 10^{-2} \\
U(k=2) mol (kg)^{-1} 0.0404 \\
U (Relative %) 0.81

It is possible that exist an over-estimation in repeatability uncertainty condition due to the Coulometric system is founded in preliminary stages, thus the study will be continued to avoid the presence of unwanted conditions such as KHP-diffusion between compartments and mass-loss during measurement, as well as it is necessary to control the contaminants presence such as O\(_2\) and CO\(_2\), or traces of reducing agents inside of the supporting electrolyte [10, 12].

4. Conclusion
The work is a good start by implementation of the Coulometric system for future certification in purity of substances; the system requires improvements in instrumental procedures to improve the system control in terms of the precision due to relative uncertainty value of 0.81%, it is significant influenced by repeatability condition. The variables such as the sample weighing, the potential difference, the electric resistance, the time and the end-point detection are not be significant, however the idea will be consolidate it with future improvements.

5. References
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