Constant-Current Coulometry Studies for Assay of Primary Reference Materials to Develop Standards for Titrimetric Analysis

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ABSTRACT

Coulometry is a primary method for measuring the amount of substance of high-purity compounds and its solutions. Coulometric titration is used to determine the purity of primary reference materials for acid/base, precipitation, redox and complexometric titrations. This work aims at presenting the primary system of coulometry from Inmetro, which was used for the characterization of hydrochloric acid solutions from nominal values of 1.0 mol·kg^{-1} and 0.01 mol·kg^{-1}, as well as the preliminary studies and the results of the key comparison CCQM-K48, which Inmetro has recently participated to determine the purity of potassium chloride (KCl).The reference materials characterized by the Inmetro's primary system of coulometry will be used to guarantee the traceability and reliability to the measurement results from titrimetric analysis carried out by the Brazilian chemical analysis laboratories.

1. INTRODUCTION

Metrology in chemistry has been currently acknowledged as a relevant area in researches of analytical and measuring chemistry. Its importance comes from the need to produce reliable and uniform measurements in science, technology and international trade.

In the analytical chemistry area, a great number of methods use titration as the main technique to determine the concentration of a substance in a specific analyte. To carry out this analysis with accuracy, the laboratories need to use primary standard.

Coulometry has the potential to become a primary method [1] by the Consultative Committee for Amount of Substance (CCQM). Its main function in the National Metrology Institutes (NMI) is to characterize primary standards, e.g., to determine the purity of primary reference materials. After being certified, these reference materials can be used as primary standards in acid/base, precipitation, redox and complexometric titration techniques [2] to determine the concentration of diverse chemical substances.

Inmetro, the NMI of Brazil has established its primary system of coulometry [3] to characterize and certify high-purity reference materials such as primary standards to guarantee the reliability of the chemical analysis performed by Brazilian laboratories.

This work aims to present the studies which have been developed in the Electrochemical Laboratory of Inmetro using the primary system of coulometry to characterize primary standards. Initially, the characterization of hydrochloric acid solutions from nominal values of 1.0 mol·kg^{-1} and 0.01 mol·kg^{-1} will be shown and afterwards the preliminary studies to determine the purity of potassium chloride (KCl) from NIST and the results of the key comparison CCQM-K48, which Inmetro has recently participated in will be focused.

2. EXPERIMENTAL

2.1. Primary System of Coulometry
Fig. 1 shows the primary system of coulometry from Inmetro [3]. It consists of a coulometer (current source, indication unity and valve unit), argon gas unit, burette (dispenser), microbalance, water bath, magnetic stirrer, glass cells, electrodes and a microcomputer. The coulometric system is similar to the one in Slovak Institute of Metrology (SMU).
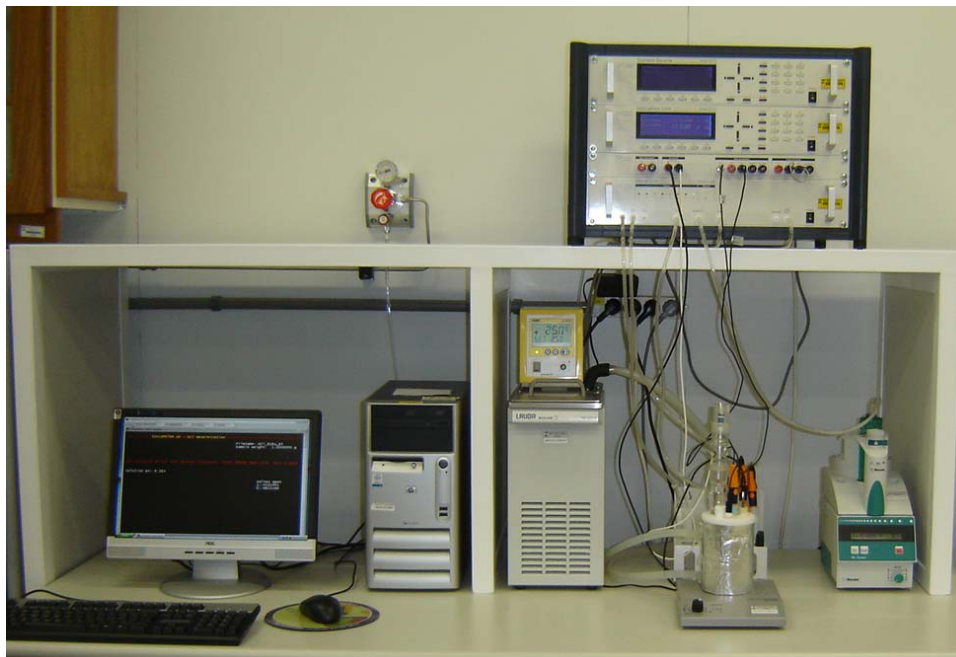
Fig. 1. Inmetro's primary system of coulometry.

2.2. Coulometric Titration Procedure

The coulometric titration procedure used in all assays is as followed. In the constant-current coulometric titration, the charge is added in three different stages [2, 3], as in Eq. (1).

$$\nu = \frac{I_1 \cdot (t_1 - cor_1) + I_2 \cdot t_2 + I_3 \cdot t_3}{z \cdot F \cdot m \cdot cor}, \qquad (1)$$

where, ν is the amount content; I_1 is the current during the initial titration; I_2 is the current during the main titration; I_3 is the current during the final titration; t_1 is the total time of initial titration from the initial end-point; t_2 is the time of the main titration; t_3 is the total time of final titration up to the final end-point; z is the charge number of the analyte; F is the Faraday constant (96 485,338 3 $C \cdot mol^{-1}$); m is the sample weight; *cor* is the sample weight to air buoyancy correction; cor_1 is the correction of the difference between the end point and time of filling the Intermediate Compartment (IC) of the cell.

At the initial titration with small charge increments, the electrolyte is prepared for the second titration called main titration, where 99.5 % of the electrochemistry reaction is carried out by using higher current than the initial titration and the process is ended with the final titration, using small charge increments again.

2.3. Coulometric Titration for HCl

To determine the concentration of HCl solution of nominal value of 0.01 $mol \cdot kg^{-1}$, high-purity HCl acid solution from Merck (HCl Suprapur 30 %) was used. The solutions were prepared by using deionized water purified by the Milli-Q$^{\circledR}$ system, whose electrolytic conductivity was approximately 0.06 $\mu S \cdot cm^{-1}$. During the measurement, an electrochemical glass cell (600 mL) was used encased by another glass beaker to maintain the temperature which comes from a water bath (Lauda RE 204) at 23.0 °C. The cell has the anodic compartment separated by a cathodic one and an agar-agar plug. The supporting electrolyte used (250 mL) was 1.0 $mol \cdot L^{-1}$ KCl and argon gas bubbles (99.999 %) were applied during the entire assay. The cathode was a platinum electrode (5 mm × 5 mm × 0.25 mm) and the anode was a spiral wire of silver (99.99 %) with dimensions of 50 mm × 55 mm × 5 mm. In the initial titration, it was passed a current of 2 mA; in the main titration, it was passed 100 mA and for the final titration, it was passed 2 mA. The end-point was potentiometrically determined using a combined pH electrode. For each assay, it was used about 10 g of HCl of nominal value of 0.01 $mol \cdot kg^{-1}$ and 5 g to determine the concentration of a 1.0 $mol \cdot kg^{-1}$ HCl. Both were weighted in an analytic balance (Mettler Toledo AG 285, resolution 0.01 mg), by using a syringe. The solution in the cathodic compartment was stirred by a magnetic stirrer.

2.4. Coulometric Titration for KCl

The coulometric titration with constant-current and potentiometric end-point were detected by using two electrodes: one silver electrode with a layer of silver chloride deposited in it and a separated glass electrode. The sample of KCl was dried in mufla furnace at the temperature of 500 ^{o}C during 6 h. The coulometric cell was made of glass and had a vertical design with two separate compartments: a cathodic and an anodic one. The cathodic compartment was inside an IC which was separated from the anodic one through a silicate plug. The supporting electrolyte (250 mL) was a solution of 3.5 M of perchloric acid (Merck, 70 % to 72 %). A high purity silver rod (99.999 %) was the anode with an initial area of aproximately 8 cm^2. Pt electrode (1 cm^2 area) was the cathode. The necessary current to the coulometric titration of KCl sample (weighing on the range of 300 mg by using a microbalance, Mettler Toledo, UMX 5, resolution 0.1 μg) was passed through 3 different stages: in the initial titration, it was passed a current of 10 mA; in the main titration, it was passed 200 mA and for the final titration, it was passed 10 mA. All the weighing was corrected for buoyancy and the coulometric cell was maintained at the temperature of 23.0 ^{o}C during the experiment. Argon gas of high purity (99.999 %) was passed through the anodic compartment for deaeration or maintained above it during the titrations. All the titrations were carried out without the presence of light and the solution was stirred with magnetic stirrer.

3. RESULTS

3.1. HCl Solutions

Table 1 presents the results of the coulometric titrations for HCl solution of nominal concentration value of 1.0 mol·kg^{-1}. These characterization results will be used to develop certified reference material (CRM) of HCl acid solutions, such as 0.1 and 0.01 mol·kg^{-1}.

Table 1. Coulometric titration results for 1.0 mol·kg^{-1} HCl.

n^*	Assay (mol kg^{-1})
1	0.99957
2	0.99977
3	0.99988
4	0.99965
5	0.99993
Mean (mol kg^{-1})	0.99976
RSD (%)	0.015

* n= measurement.

The coulometric titration results for HCl solution of nominal concentration value of 0.01 mol kg^{-1} are shown in Table 2. The characterization of this solution by constant-current coulometry was used at Inmetro to develop CRM of pH buffer by using the primary pH system [4].

Table 2. Coulometric titration results for 0.01 mol·kg^{-1} HCl.

n^*	Assay (mol kg^{-1})
1	0.0099972
2	0.0099955
3	0.0099980
Mean (mol kg^{-1})	0.0099969
RSD (%)	0.013

* n= measurement.

3.2. KCl Purity

In Table 3, the preliminary studies related to the measurement results of the purity of the KCl in mass fraction by coulometric titrations using the SRM 999b are shown.

Table 3. Purity of the KCl determined by coulometric titration (SRM 999b).

n^*	Assay (mol kg^{-1})	Mass Fraction (%)
1	13.40705	99.951
2	13.40694	99.951
3	13.40695	99.951
4	13.40769	99.956
Mean [mass fraction (%)]		99.952
RSD (%)		0.003

* n = measurement.

3.3. Key Comparison CCQM-K48

Inmetro has participated in the key comparison CCQM-K48 using the primary system of coulometry for the first time. This exercise was coordinated by the National Institute of Metrology P. R. China (NIM) for the determination of the purity of KCl. The uncertainty budget [5] for this comparison is shown in Table 4. According to this table, the main source of uncertainty has come from the current.

There was comparability among the participant Institutes, denominated as laboratories (Inmetro, A, B, C, D, E and F) as shown in Fig. 2.

The KCl purity, after bromide correction, determined by Inmetro in this exercise was 99.978 7 %, which is

equivalent to an amount content of $(13.410\,77 \pm 0.002\,9)$ mol·kg^{-1} ($k=2$).

In Fig. 2, the results are shown with bromide correction, since it is the major contaminant in the KCl. The bromide assay was determined by ionic chromatography technique performed by Inorganic Laboratory from Inmetro which is part of the Chemical Metrology Division. The bromide assay was 0.00039 mol kg^{-1} $\pm$ 1.3% ($k=2$), for a confidence level of 95% [6].

Table 4. Uncertainty budget for key comparison CCQM-K48.

Effect	Probability distribution*	Sensitivity coefficient		Uncertainty		Product	
		c_i	units	u_i	units	$c_i u_i$	units
Weighing	N	44316.7287	mol/kg^2	5.50E-10	kg	2.44E-05	mol/kg
Buoyancy correction	N	13.4005	mol/kg	2.28E-07		3.06E-06	mol/kg
Time	N	0.0068	mol/kgs	7.50E-08	s	5.14E-10	mol/kg
Current	N	66.8490	mol/kgA	1.70E-05	A	1.14E-03	mol/kg
Faraday constant	R	0.0001	mol^2/kgC	4.79E-03	C/mol	6.66E-07	mol/kg
End-point det'n	N	1		1.34E-04	mol/kg	1.34E-04	mol/kg
Rinse correction	N	1		6.71E-05	mol/kg	6.71E-05	mol/kg
Current efficiency	N	1		8.33E-05	mol/kg	8.33E-05	mol/kg
Adsorption on AgCl	N	1		3.66E-05	mol/kg	3.66E-05	mol/kg
u_A (Type A uncertainty)						0.0009	mol/kg
u_B (Type B uncertainty)						0.0012	mol/kg
u_C						0.0015	mol/kg
U ($k=2$; 95%)						0.0029	mol/kg

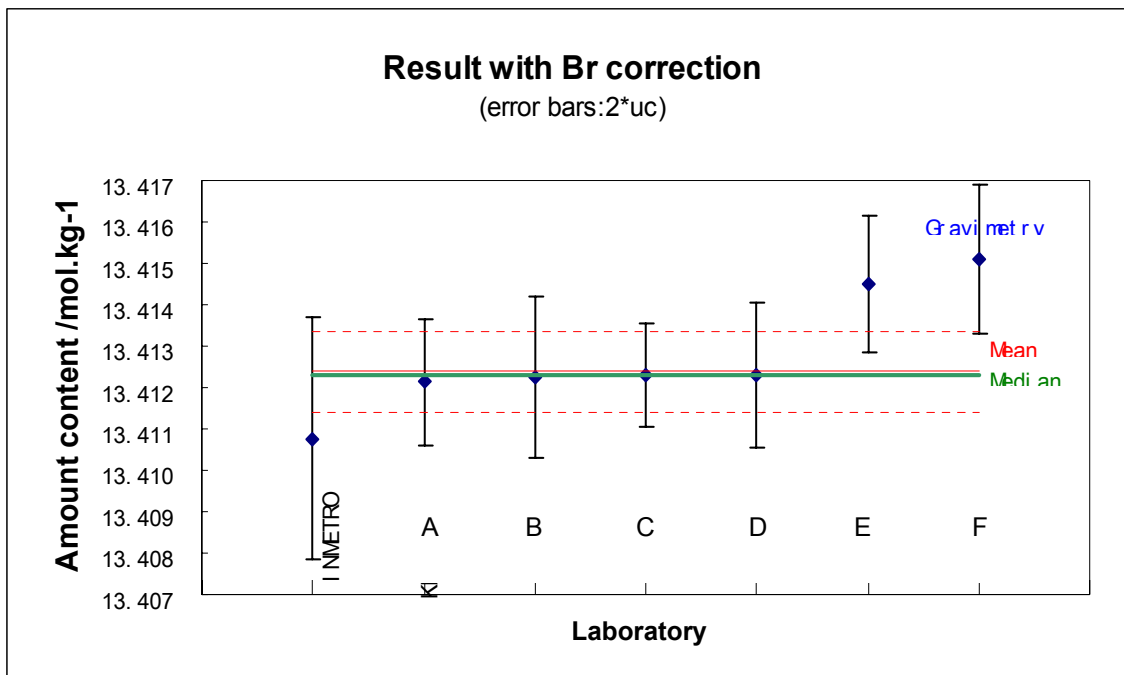N for Normal; R, rectangular.

Fig. 2. Key-comparison results, CCQM-K48, to determine the purity of KCl (adapted) [5].

4. DISCUSSION

The primary system of coulometry from Inmetro can be used either for the certification of primary reference materials or for the determination of the concentration of HCl solution with nominal value of 0.01 mol kg^{-1} (Table 2). This solution is important to the measurement of the standard potential, E^o, in

the primary pH system from Inmetro to characterize pH buffer solutions [4]. Dilute acid solutions should be prepared from a more concentrated HCl solution whose concentration was accurately determined by coulometric titration as shown in Table 1.

In order to evaluate the accuracy of the measurement results using the primary system of coulometry from Inmetro, constant-current coulometric titration was applied to determine the purity of potassium chloride (KCl) from NIST (SRM 999b). In Table 3, the result showed good agreement with the certified value [7]. However, considering the certified value of SRM 999b (99,977 %), the measurement presented good precision (RSD 0,003 %), but it was 0,025 % biased (Table 3). Therefore, this result shows that the measurement needs to be improved in order to increase its sensibility as well as its accuracy. One possibility is to use a silver electrode with high purity, because at the time the assays were carried out a silver electrode with only 99.99 % purity was used, which may have influenced the current efficiency.

According to the uncertainty budget (Table 4), the contribution of the current to the combined uncertainty was very high, which demands better evaluation in future works.

Inmetro has obtained good performance in the key comparison CCQM-K48. Although the results from Inmetro were comparable with other National Institutes of Metrology, as shown in Fig. 2, the measurements to determine the purity of KCl need more improvements. One possible improvement could be by making assay with increased sample weighs to select the best weigh which can reach better current efficiency and, consequently, more accuracy.

5. CONCLUSIONS

The characterization results of primary reference materials using the primary system of coulometry from Inmetro, after being optimised, will guarantee to Inmetro the competence of measuring amount content with accuracy and reliability which is needed to develop CRM for acid, bases and salts. These CRMs can be used to provide traceability and realibility to the measurements carried out by chemical laboratories in Brazil.

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