

Implementation of Coulometric Titration System at Constant Current for Certification of Primary Reference Materials

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Abstract. Coulometry is a primary method for measuring high purity substances. This is used to certify the primary reference materials required in a chemical analysis process. This paper describes the coulometric titration system developed by the National Metrology Institute (NMI) of Colombia for the certification of hydrochloric acid 0,1 mol·kg⁻¹. In addition, it also shows preliminary studies for future development of and ethylenediaminetetraacetic acid disodium salt (EDTA-Na₂) certification.

Introduction

Coulometry is a high-level electroanalytical technique for measuring the amount of substance in compounds and solutions. This technique has been used to determine the purity of primary reference materials required by industry and in chemical testing laboratories [1]. Coulometry is one of the most widely used analytical techniques in research laboratories and National Metrology Institutes (NMI) worldwide due to its high precision and accuracy for measuring the trace level or purity of different materials [2]. Coulometric analysis uses electrolysis to generate a titrant that reacts stoichiometrically with an analyte, thus making possible a determination of the amount of substance. For this reason, The Consultative Committee for Amount of Substance (CCQM) of the International Bureau of Weights and Measures-(BIPM) has considered coulometry to be a primary method that can be used to determine the purity of primary reference materials.

Electroanalytical methods for analyzing compounds are supported by current, potential and charge measurements of a system. When an analyte is reduced or oxidized, these electrical signals are directly related to the amount of analyzed substance present in the system, which has a direct relation to the mole unit of the International system-SI. With coulometry, this relation consists of a determination of the amount of substance with electric charge added to the electrochemical system described by Faraday's law:

$$n = \frac{Q}{zF} = \frac{\int I dt}{zF} \quad (1)$$

Where n is the amount of substance, Q is electric charge, I is electric current, t is electrolysis time, z is the charge number of reaction and F is Faraday constant.

In accordance with Faraday's law, there are two forms of coulometry: (i) controlled-potential, in which electric current decreases exponentially over time; and (ii) controlled-current, in which electric current is constant. The latest form is used for determining analyte content in the matrix, such as salts or metals in solution. Coulometry provides high selectivity and good sensitivity for the identification and quantification of trace-level, which is hard to determine by other electroanalytical methods [3,4]. Additionally, it is able to provide good results with low uncertainty and has been implemented in a larger number of NMIs [5].

The goal of this paper is to provide constant current coulometry studies as developed for the Electrochemical Analysis Working Group at the National Metrology Institute (NMI) of Colombia. First, characterization studies of aqueous hydrochloric acid solutions 0,1 mol·kg⁻¹ will be presented. Then, preliminary studies to determine the purity of EDTA-Na₂ will be presented.

1. Method

Coulometry system development for the NMI of Colombia is similar to the system used by Ural Scientific and Research Institute for Metrology of Russia [6]. This coulometry system consists of: (i) a titration vessel with two independent compartments (these compartments

are separated by agar gel) (ii) A Metrohm Autolab potentiostat/galvanostat PGSTAT128N (Metrohm AG Switzerland, Inc.) is used as a source of current, as a potentiometric endpoint indicator and for time control; (iii) argon UHP grade; (iv) a microbalance (Mettler Toledo XP56, resolution 0,001 mg); (v) a magnetic stirrer; (vi) a pH unitrode electrode, Ag/AgCl reference electrode, platinum (Pt-) and copper (Cu-) electrodes; (vii) and Metrohm Autolab Nova 2.0 software. Water used has electrolytic conductivity $\approx 0,08 \mu\text{s}\cdot\text{cm}^{-1}$.

1.1. Coulometric Titration of HCl

An aqueous solution of HCl ($0,1000 \text{ mol}\cdot\text{kg}^{-1}$) was prepared for diluting high-purity hydrochloric acid solution (Merck Titripur – 1,0 N) in ultrapure water. Approximately 5 g of HCl dissolution, weighed in microbalance, was transferred to a titration vessel and KCl ($2,0 \text{ mol}\cdot\text{kg}^{-1}$) as electrolyte. The Pt-electrode (AlfaAesar – 99,997% purity and 5 mm \times 0,5 mm of diameter) was used as cathode and Ag-electrode (AlfaAesar – 99,99% purity and 80 cm \times 1,0 mm of diameter) in spiral shape was used as anode. The electric current value is kept for 1800 s at 30 mA. The endpoint was determined by pH-measure. Systems have been bubbling using argon (99,999% purity UHP).

1.2. Coulometric Titration of EDTA [7]

An aqueous solution of EDTA ($0,0958 \text{ mol}\cdot\text{kg}^{-1}$) was prepared for diluting EDTA- Na_2 (Merck - 99% purity) in ultrapure water. Approximately 1 g of this dissolution, weighed in microbalance, was titrated with Cu^{2+} electrochemically generated at 30 mA from a Cu-electrode. Since Cu^{2+} is captured as soon as it is formed, it was not necessary to separate electrode compartments. An electrochemical reaction was performed with phthalate buffer solution of 4,00 pH-units (20°C), where the EDTA predominate species is $[\text{H}_2\text{EDTA}]^{2-}$. The endpoint was determined by measuring the increase in absorbance of the $[\text{CuEDTA}]^{2-}$ product using a Cary 4000 UV-visible spectrophotometer at 320 and 730nm.

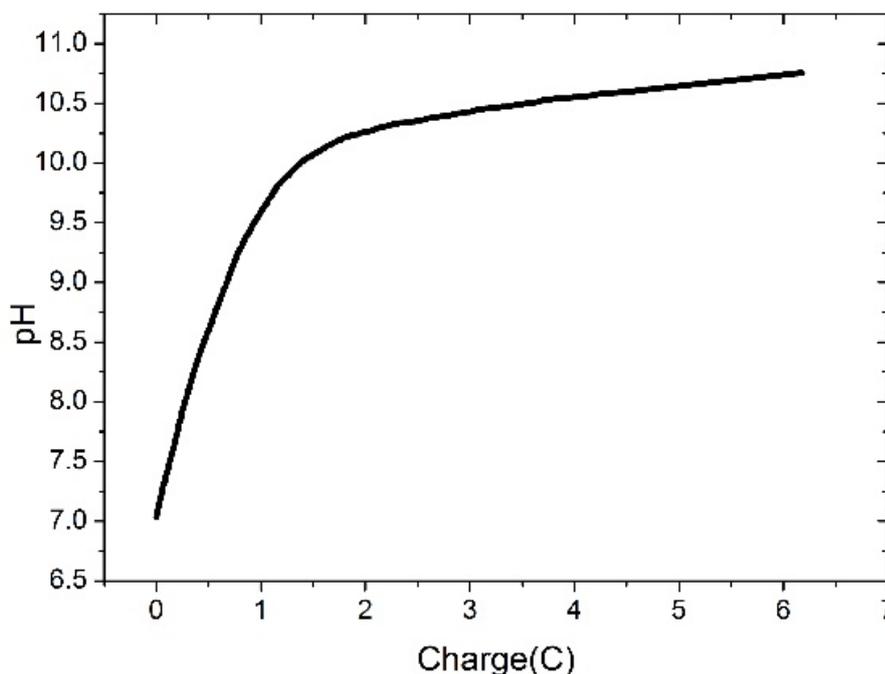


Figure 1. Coulometric titration for a typical blank solution.

2. Results

2.1. HCl Dissolution

The hydronium ions (H_3O^+) derived from HCl dissociation reacted with hydroxide ions (OH^-) to produce water. The experimental procedure developed in this step consists of the electrochemical generation of hydroxide ions for determining hydrochloric acid concentration; thus, calibration curves were taken from 7 to 10 pH units to determine the charge quantity required (1,5 C) and to evaluate the negative presence of species that interfered with the

titration process (Fig. 1). Due to this, resistivity increases with an increment in potential difference at low-concentration which could cause redox effects in water.

To determine hydrochloride acid concentration ($0,1 \text{ mol}\cdot\text{kg}^{-1}$), coulometric titration was brought into contact with argon (Fig. 2). The degasification process was efficient because measurements do not exceed expected value ($0,1000 \text{ mol}\cdot\text{kg}^{-1}$). The presence of CO_2 gas affects this measure [8]. The average value of HCl concentration was $0,099639 \text{ mol}\cdot\text{kg}^{-1}$ with 0,36% of error and 0,11% of RSD (percent relative standard deviation). The value found was comparable with the literature [6,9], but this measurement was not sufficiently accurate to consider for standard use. Due to diffusion problems that generate a decrease in accuracy when acid diffusion is too high between anodic and cathodic compartments, it is not possible to titrate the H_3O^+ ions located in anodic compartment. Thus, it is necessary to reduce diffusion rates with an extreme control of temperature [10].

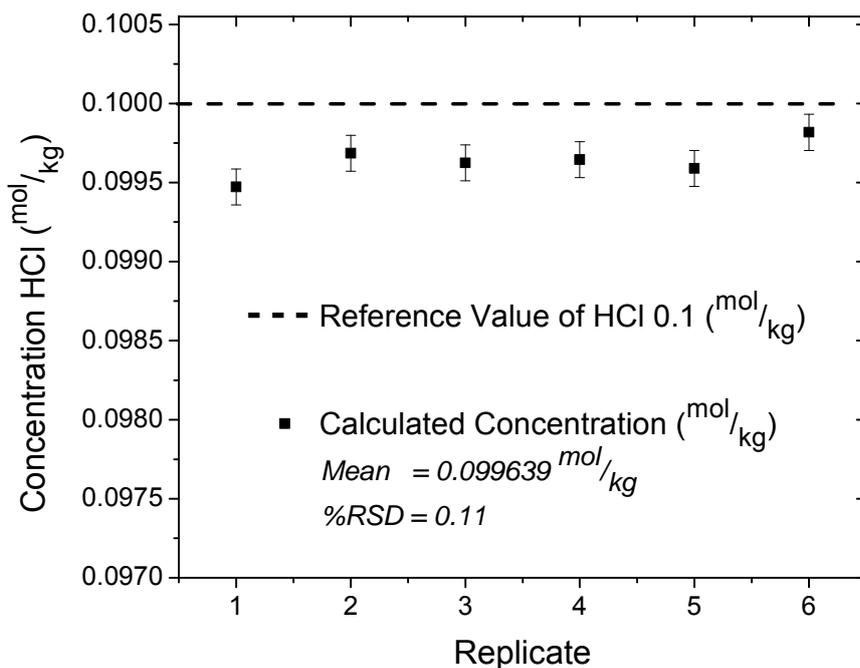


Figure 2. HCl concentration determination by coulometric titration at constant current.

2.2. EDTA Dissolution

The reaction mechanism of EDTA- Na_2 titration was similar to that of previous studies [7], with the difference being that copper cations were produced by ionic complex $[\text{Cu}(\text{EDTA})]^{2-}$. The reaction was followed by spectrophotometric measurements and the endpoint was detected when ionic specie $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ appeared after that ionic specie $[\text{H}_2(\text{EDTA})]^{2-}$ was completely consumed. The relation between absorbance and charge data obtained at 320 nm and 730 nm determined the point of species consumption and generation (Fig. 4).

In EDTA- Na_2 titration, absorbance increases sharply as the $[\text{Cu}(\text{EDTA})]^{2-}$ ion is formed. However, at the intercept point between lines, this increment changes because there are not more $[\text{H}_2(\text{EDTA})]^{2-}$ and Cu^{2+} generated electrochemically. $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ complex starts to form with water. To determine the exact value of charge, it was necessary to find intercept between lines. One is taken at 320 nm ($L=1$, $L=2$) and the other at 730 nm ($L=3$, $L=4$). The value of this intercept was 9,10 C. This value is obtained through mathematical interpolation between lines: $L1=0,0205x+0,0152$; $L2=0,0087x+0,12289$; $L3=0,0042x+0,001$; $L4=0,002x+0,0209$ and it corresponds to a concentration of $0,0943 \text{ mol}\cdot\text{kg}^{-1}$ (Error= 1,56%).

This obtained concentration was close to real value ($0,0958 \text{ mol}\cdot\text{kg}^{-1}$). Therefore, it was necessary to conduct more tests to obtain clear results.

3. Conclusion

The coulometric titration system developed at NMI of Colombia will allow for certification of Reference Materials of HCl ($0,1 \text{ mol}\cdot\text{kg}^{-1}$) because of the homogeneous and reproducible measurements obtained. On the other hand, the preliminary studies for certification of KCl and EDTA- Na_2 were successful.

Although the coulometry system is in an early stage of implementation, the results obtained indicate that the measurement system has been properly implemented.

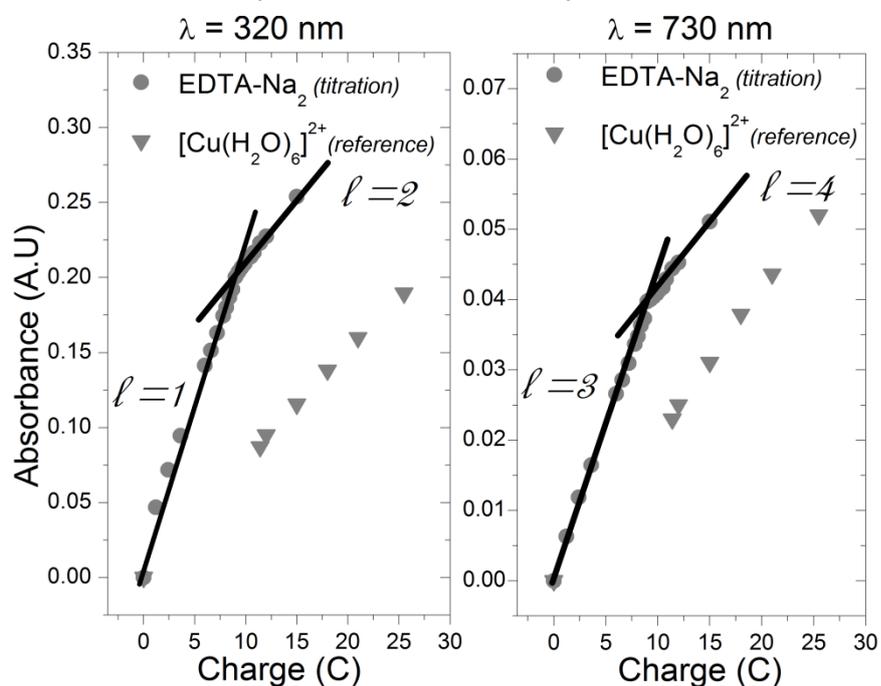


Figure 4. Comparison between EDTA- Na_2 curve titration with Cu^{2+} and $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ electrochemical formation at 320 nm and 730 nm.

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