

POTENTIOMETRIC TITRATION OF HYDROCHLORIC ACID DILUTE SOLUTION USING A METROLOGICAL APPROACH

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Abstract: Primary methods of measurement are essential in the realization of the SI units. In 1995, the CCQM (Comité Consultatif pour la Quantité de Matière) identified titrimetry as a primary method of measurement. Titrimetry is a method that has wide range of applications for amount of substance measurements and can be applied at primary level and at working level depending on the uncertainty values. The aim of this work is to present the results of potentiometric titration of a dilute solution of hydrochloric acid (HCl). The potentiometric titration method was carried out with the solution addition controlled gravimetrically. The results were accurate and HCl concentration of (0.010042 ± 0.000112) mol kg⁻¹, $k = 2$ for approximately 95% confidence level was obtained. The molality determination of HCl solution is a prerequisite for the use of a Harned cell, the primary method for the realization of pH measurement. The HCl solution is used in the pH primary system at Inmetro to obtain accurate value of the silver-silver chloride electrode potential. This standard potential is very important for the correct measurement of pH to certificate pH buffer.

Keywords: Potentiometric titration, gravimetry, hydrochloric acid.

1. INTRODUCTION

Titration is a process which involves determination of the quantity of an analyte by adding measured increments of substance with which it reacts. This substance is called the titrant and is usually a standardized solution, but it can also be a standardized amount of ions generated at an electrode by an electric current of known magnitude (coulometric titration). When the amount of added titrant is chemically equivalent to the amount of analyte in the sample, the equivalence point is reached. Its position can be estimated by observing some physical or chemical change associated with the condition of equivalence. This practical estimate is called the titration end-point. Indicators are often added to the analyte solution in order to provide an observable physico-chemical change (the end-point) at or near to the equivalence point. Potentiometric titration is one of the most important method used to monitor the titration end-point. Titration has been applied since the 18th century and is one of the oldest method of chemical analysis [1-3]. It has been further developed a great variety of procedures, but the basic principles are still the same. Titrimetric methods allow

simple, accurate and relatively fast determination of the concentration of a large number of analytes. Depending on the chemical reaction in progress, it is possible to identify precipitation, complexometric, redox and neutralization titrations. All titrimetric methods depend on the availability of high purity reagents that can be standardized with a known degree of uncertainty [2-3].

2. PURPOSE

The purpose of this work is to present the results of HCl concentration of a nominally 0.01 mol kg⁻¹ HCl solution using the potentiometric titration method in a metrological approach, e.g. when all the volumetric operations is replaced by weighing.

3. METHODS

The method used for the determination of the concentration of HCl dilute solution in molality was potentiometric titration where each added titrant was weighed and recorded. Molality is defined as the amount (number of moles) of solute per kilogram of solvent. The method is as follows: firstly, it was prepared a standard solution of nominal value of 0.01 mol kg⁻¹ potassium hydrogen phthalate (KHP, NIST 84k) and a solution of about 0.01 mol kg⁻¹ sodium hydroxide (NaOH, Merck, P.A.). All solid substances were weighed using an AG 285 Mettler Toledo analytical balance, with a resolution of 0,01 mg. The water ($0.054 \mu\text{S cm}^{-1}$ from Millipore system) was weighed on a PR1203 Mettler Toledo balance, with a resolution of 1 mg. In addition, the NaOH solution was titrated against a KHP standard solution. After the standardization of the NaOH, the HCl solution, with a nominal concentration of 0.01 mol kg⁻¹, was titrated by the just standardized NaOH solution. The end-point was indicated by the secondary derivative of a third degree equation that was obtained by the best line which passed on the dots at the graph of pH versus mass of titrant added.

4. RESULTS

There are several uncertainty contributions which have to be added to those associated with the quantities in the basic titration equation [4-5]. The basic titration equation to

sodium hydroxide standardization can be seen in Equation (1). The Table 1 shows the uncertainty budget for the NaOH standardization where m_{KHP} is the mass of KHP used to prepare the standard solution, r_{KHP} is the buoyancy correction for mass of KHP, P_{KHP} is the purity of KHP, M_{KHP} is the molar mass of KHP, m_{KHPsol} is the mass of KHP solution which was titrated, r_{KHPsol} is the buoyancy correction for KHP titrated solution, v_{KHP} is the concentration in molality of KHP solution, m_{KHPeq} is the mass of KHP titrated solution at the end point, r_{KHPeq} is the buoyancy correction for mass of KHP titrated solution at the end point, m_{NaOHeq} is the mass of NaOH titrated solution at the end point, and r_{NaOHeq} is the buoyancy correction for mass of NaOH titrated solution at the end point.

$$v_{\text{NaOH}} = \left(\frac{m_{\text{KHP}} \times r_{\text{KHP}} \times P_{\text{KHP}}}{M_{\text{KHP}} \times m_{\text{KHPsol}} \times r_{\text{KHPsol}}} \right) + \left(\frac{v_{\text{KHP}} \times m_{\text{KHPeq}} \times r_{\text{KHPeq}}}{m_{\text{NaOHeq}} \times r_{\text{NaOHeq}}} \right) \quad (1)$$

Table 1 – Experimental data and uncertainty budget for the NaOH standardization.

Quantity/unity	Estimate, x_i	Standard uncertainty, u_i	Sensitivity coefficient, /c/	Contribution, u (y)
m_{KHP} (g)	0.7493	0.000015	1.33E-5	2.00E-10
r_{KHP}	1.000578	7.7096E-6	9.97E-6	7.69E-11
P_{KHP} (g/g)	0.999911	5.1384E-5	9.98E-6	5.13E-10
M_{KHP} (g/mol)	204.2212	0.0038	4.88E-8	1.84E-10
m_{KHPsol} (g)	367.6412	0.0005	2.71E-8	1.36E-11
r_{KHPsol}	1.001045	2.3635E-6	9.96E-6	2.35E-11
v_{KHP} (mol kg ⁻¹)	0.009979	5.87E-7	9.75E-1	5.72E-7
m_{KHPeq} (g)	20.004	0.000015	4.86E-4	7.29E-9
r_{KHPeq}	1.001057	5.7680E-6	9.72E-3	5.61E-8
m_{NaOHeq} (g)	20.51947	0.000015	4.74E-4	7.11E-9
r_{NaOHeq}	1.001041	2.0199E-6	9.72E-3	1.96E-8
v_{NaOH} (mol kg ⁻¹)	0.009739			
Mean results (n = 3);				
v_{NaOH} (mol kg ⁻¹)				
Type B	0.009743			
SD	0.000001			
Type A	0.000033			
Combined uncertainty	0.000033			
Expanded uncertainty	0.000065	(k = 2; 95%)		

The results for concentration of HCl solution in amount content (number of moles of solute per kilogram of solution) and its uncertainty budget are showed in Table 2 and the titration equation which was used for calculation is showed in Equation (2) where v_{NaOH} is the NaOH molality, m_{NaOHtit} is the mass of NaOH solution at the end point, m_{NaOHeq} is the mass of NaOH in the equivalence point, r_{NaOHtit} is the buoyancy correction for mass of NaOH titrated solution at the end point, m_{HCl} is the mass of HCl titrated solution and

r_{HCl} is the buoyancy correction for mass of HCl titrated solution.

$$v_{\text{HCl}} = \frac{v_{\text{NaOH}} \times (m_{\text{NaOHtit}} - m_{\text{NaOHeq}}) \times r_{\text{NaOHtit}}}{m_{\text{HCl}} \times r_{\text{HCl}}} \quad (2)$$

Table 2 – Experimental data and uncertainty budget for the HCl determination.

Quantity/unity	Estimate, x_i	Standard uncertainty, u_i	Sensitivity coefficient, /c/	Contribution, u (y)
v_{NaOH} (mol kg ⁻¹)	0.009743	0.000001	1.03E+0	5.93E-7
m_{NaOHtit} (g)	20.61929	0.000015	4.87E-4	7.31E-9
r_{NaOHtit}	1.001043	2.7014E-6	1.00E-2	2.71E-8
m_{HCl} (g)	20.00533	0.0005	5.02E-4	2.51E-7
r_{HCl}	1.001046	2.0611E-6	1.00E-2	2.07E-8
m_{NaOHeq} (g)	0	0.09	4.87E-4	4.38E-5
v_{HCl} (mol kg ⁻¹)	0.010042			
Mean results (n = 3);				
v_{HCl} (mol kg ⁻¹)				
Type B	0.010042			
SD	0.000044			
Type A	0.000035			
Combined uncertainty	0.000056			
Expanded uncertainty	0.000112	(k = 2; 95%)		

The important source of error in titrimetric analysis comes from the end-point detection and has to be taken into account [1,6]. Contributions coming from the weighing operations, the air buoyancy corrections and the purity of the substances have also to be considered. The greatest uncertainty contribution to the potentiometric titration of the HCl solution by NaOH solution in this work, almost 100%, came from the uncertainty associated with end-point detection.

5. DISCUSSION

The metrological approach used in the potentiometric titration for reducing uncertainty was done by replacing all the volumetric operations by weighing and proper mass determination. In fact, using this approach, the uncertainty obtained was in the range of 10⁻⁵, 100 times lower than once considered for working-level measurements [3]. Table 1 shows that the greatest contribution of uncertainty came from the uncertainty associated with the molality of KHP. On the other hand, the highest uncertainty contribution on Table 2 came from the end-point detection because of the sample dilution as potentiometric titration is limited by the error imposed by the dilution effect, which is most pronounced in lower concentrated solutions, as in the case of the HCl solution used in this work [3]. This fact agrees with the literature data [1-4], since the measured end point

does not represent the real equivalence point even for strong acid-strong base titrations. In fact the equivalence point precedes the point of maximum slope in all acid-base titrations. This error increases as the reactants become more dilute, the extent of dilution increases and the reaction becomes weaker, what makes harder to determine the point of maximum gradient [6].

6. CONCLUSIONS

The technique of potentiometric titration used in a metrological approach to determine the HCl concentration was very accurate.

The analysis of hydrochloric acid dilute solution whose nominal value was 0.01 mol kg^{-1} has reached a concentration of $(0.010042 \pm 0.000112) \text{ mol kg}^{-1}$, $k = 2$ for approximately 95% confidence level.

Therefore, the potentiometric titration method used in the Chemical Metrology Division/INMETRO using a metrological approach allows to determine the concentration of HCl dilute solution with an uncertainty level adequate to be used in the Harned cell for measuring with accuracy the pH of buffer solutions at a primary level.

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REFERENCES

- [1] H. Felber, S. Rezzonico, M. Máriássy, "Titrimetry at a metrological level", *Metrologia* Vol. 40, pp. 249-254, 2003.
- [2] D.A. Skoog, D.M. West, F.J. Holler, "Analytical Chemistry, an Introduction", Saunders College Publishing, 6th ed., Philadelphia, 1994.
- [3] B. King, "Review of the potential of titrimetry as a primary method", *Metrologia*, Vol. 34, pp 77-82, 1997.
- [4] M. Pueyo, J. Obiols, E. Vilalta, "Expression of Uncertainty of an Acid-base Titration", *Analytical Communications*, Vol. 33, June, pp. 205-208, 1996.
- [5] *Quantifying Uncertainty in Analytical Measurement*, EURACHEM, 1995.
- [6] Brown, R., Milton, M., Brewer, P., "High Accuracy Titrimetry with application to HCl", NPL Report COAM 5, November 2001.