

KJ 2051**Coulometric titration of hydrochloric acid**

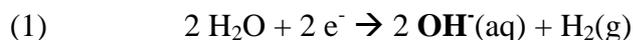
By F.G. Banica, 22 September 2006

This document includes a short theory of this experiment. See Ref. [1] for experimental procedure and Ref. [2] for theory details.

Many chemical methods of analysis are based on reactions among the analyte and a titration reagent that is added to the sample in a measurable form. For example, in a volumetric method (titration), the reagent is added in the form of a solution with an accurately known concentration. The amount of analyte is finally calculated by means of the volume of reagent solution that was necessary to convert the analyte into a stable product.

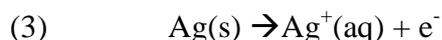
In a coulometric titration, the reagent is generated by an electrochemical reaction that occurs in the sample itself. To this end, an electrochemical cell is build-up [1]; it contains the sample solution (with some suitable additives) as electrolyte, and a pair of electrodes that convey electricity to the system. In addition, the experimental set-up includes a system for monitoring the progress of the reaction in order to detect the end point.

In this experiment, a sample of HCl is titrated by OH⁻ ions produced by electrolysis at the Pt cathode according to the following reactions:



Due to the above reactions, solution pH varies and allows monitoring the progress of the titration.

The anode consists of a silver thread and the anode reaction occurs as follows:

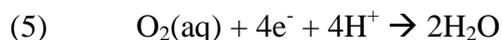


A halogen ion (e.g. Br⁻) should be added to the sample in order to form a sparingly soluble compound that prevents Ag⁺ from reaching the cathode:



If **no Br⁻** is present in the solution, Ag⁺ can reach the cathode and get reduced (according to the reverse of reaction No. 3). This reaction would compete with OH⁻ production (reaction 1) that is the single cathode reaction expected to occur.

Dissolved oxygen should be removed from the sample by a stream of pure nitrogen. Otherwise, oxygen undergoes a cathode reaction (No. 5) which consumes electrons in addition to reaction No. (1) and leads to a positive error.



The nitrogen stream also removes dissolved carbon dioxide which imparts the solution some acidity in addition to the sample hydrochloric acid.

KNO_3 should be added in order to impart the sample solution a good electric conductivity.

The titration proceeds at a constant electric current (constant current coulometry). OH^- ions (that are produced according to reaction (1)) diffuse rapidly into the solution and reacts with H^+ ions arising from the sample. The amount of HCl (n_{HCl} , in mole) is the same as the amount of OH^- produced by electrolysis. This one (n_{OH}) results from the laws of electrolysis (Faraday) applied to reaction (1):

$$n_{\text{OH}} = \frac{it}{\nu F}$$

Here, i is the current (in A), t is the electrolysis time (in seconds), ν is the number of electrons per OH^- ion in the cathode reaction (1), and F is the Faraday constant (in coulombs per mole of electrons). In order to monitor the progress of the titration, pH is recorded and plotted as a function of electrolysis time (Fig. 1). The end point is indicated by a abrupt increase in pH and the time corresponding to $\text{pH} = 7$ (t_e) indicates the end of the neutralization process. The amount of HCl in the **titrated aliquot** (in moles) is:

$$n_{\text{HCL}} = \frac{it_e}{\nu F}$$

Clearly, the **accuracy** of the final result depends on the accuracy in t_e determination.

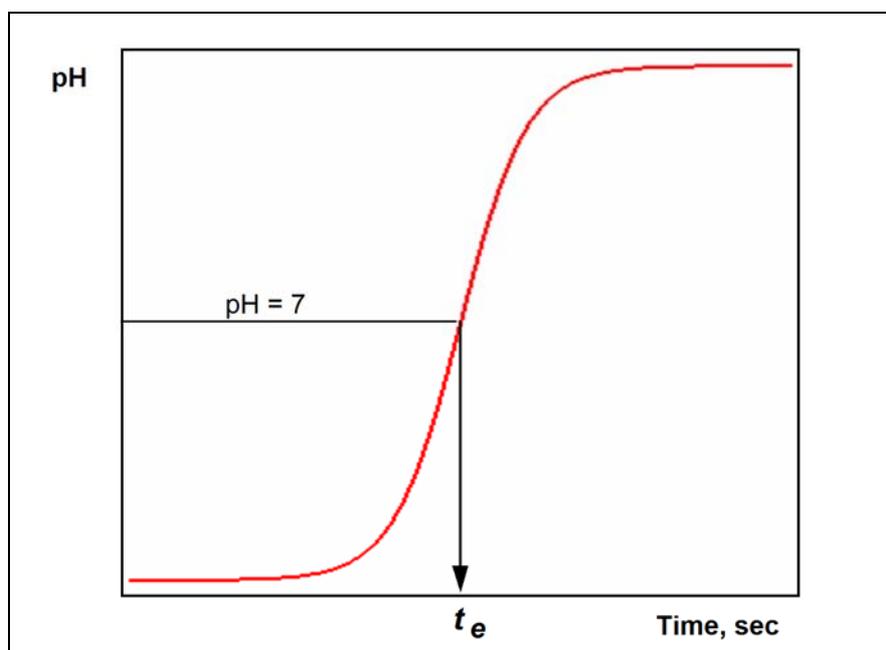


Fig. 1. Schematics of the coulometric titration curve.

Experimental set-up

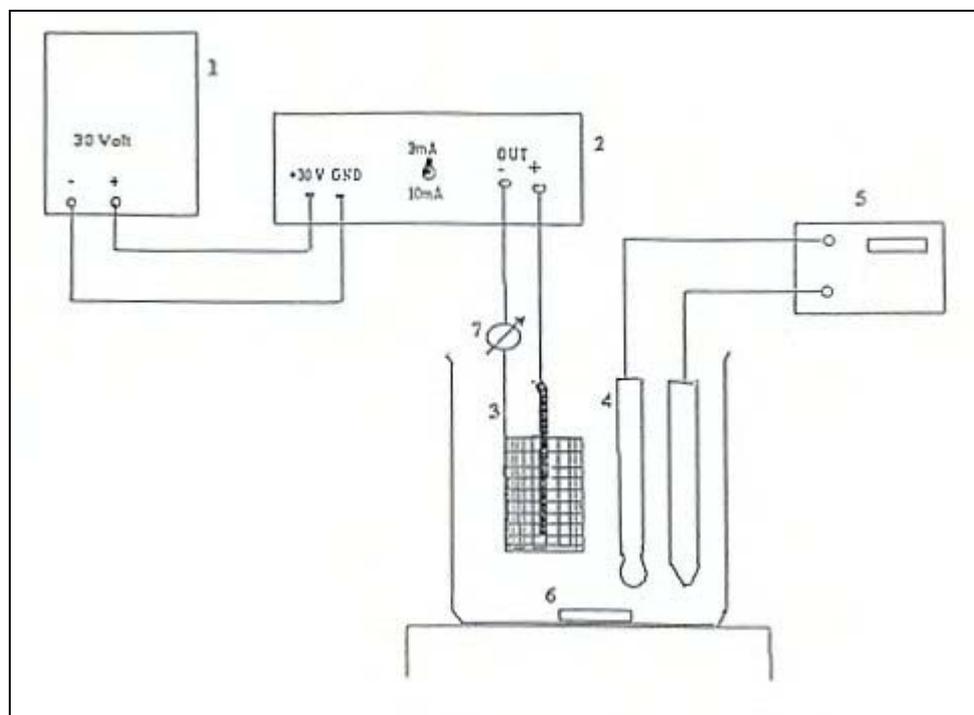


Fig. 2. Schematics of the experimental setup. 1) Regulated power supply (30 V DC); 2) Current regulator (3.000 mA); 3) Platinum mesh cathode (connected to -) and silver anode (connected to +); 4) Glass electrode and reference electrode (or a combination glass electrode); 5) pH-meter; 6) Magnetic stirrer. 7) mA-meter. 8) Stop-watch (not displayed).

The experimental setup is shown in Fig. 2. The cathode (-) should be in the form of a Pt plate, spiral or mesh, in order to secure a large enough surface. The anode (+) is a silver spiral or rod. The pH meter, which is used to monitor pH variation during the titration, should be calibrated prior to the titration by means of suitable pH standards. Phenolphthalein can also be used to detect the end-point by color change.

Procedure

Following solutions should be added to a 150 ml beaker glass (low form):

1. 25 ml of the unknown HCl sample;
2. Approx. 50 ml of an electrolyte solution containing 0.05 M NaBr and 0.1 M KNO₃;
3. 2-3 drops of phenolphthalein solution.

The experimental setup is assembled according to Fig. 2. Before starting the experiment, the experimental setup should be checked by the instructor.

In order to start up the titration, shut on the power supply and start up the stop-watch at the same moment. Check out the current value by means of the mA-meter (it could be slightly different of 3.000 mA due to the instrument error, but it provides an indication of current flow across the cell). Record the pH as a function of time.

Data processing

Plot the titration curve (as in Fig. 1), find out the equivalence time (t_e) and calculate the amount of HCl in the **whole** sample (in grams).

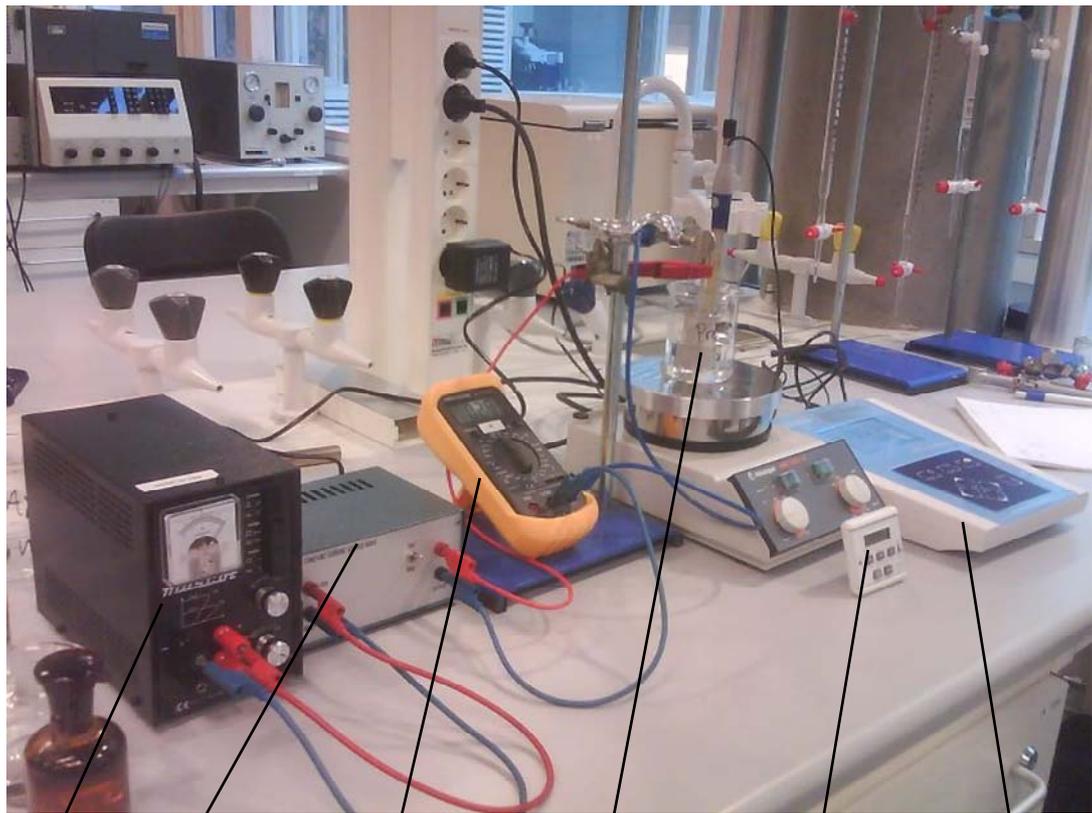
Results to be reported:

- Amount of HCl in the delivered sample solution (grams).
- Deviation (avvik) from the expected value (fasit), in % (error limit: 1.0%).

References

1. KJ 2051: Pensum og laboratoriekurs.
2. D.A. Skoog, D.M. West, F.J. Holler and S.R. Crouch, Fundamentals of Analytical Chemistry, Brooks/Cole, 2004, Section 22.D-5

IMPORTANT: Do not limit yourself to this document when writing the theory part of your report! Go to the recommended literature and try to make a personalized presentation of this matter.



Voltage source

Constant current source

Amperometer

Electrolysis cell

Stopwatch

pH-meter

Fig. 3, Experimental set-up for coulometric titration

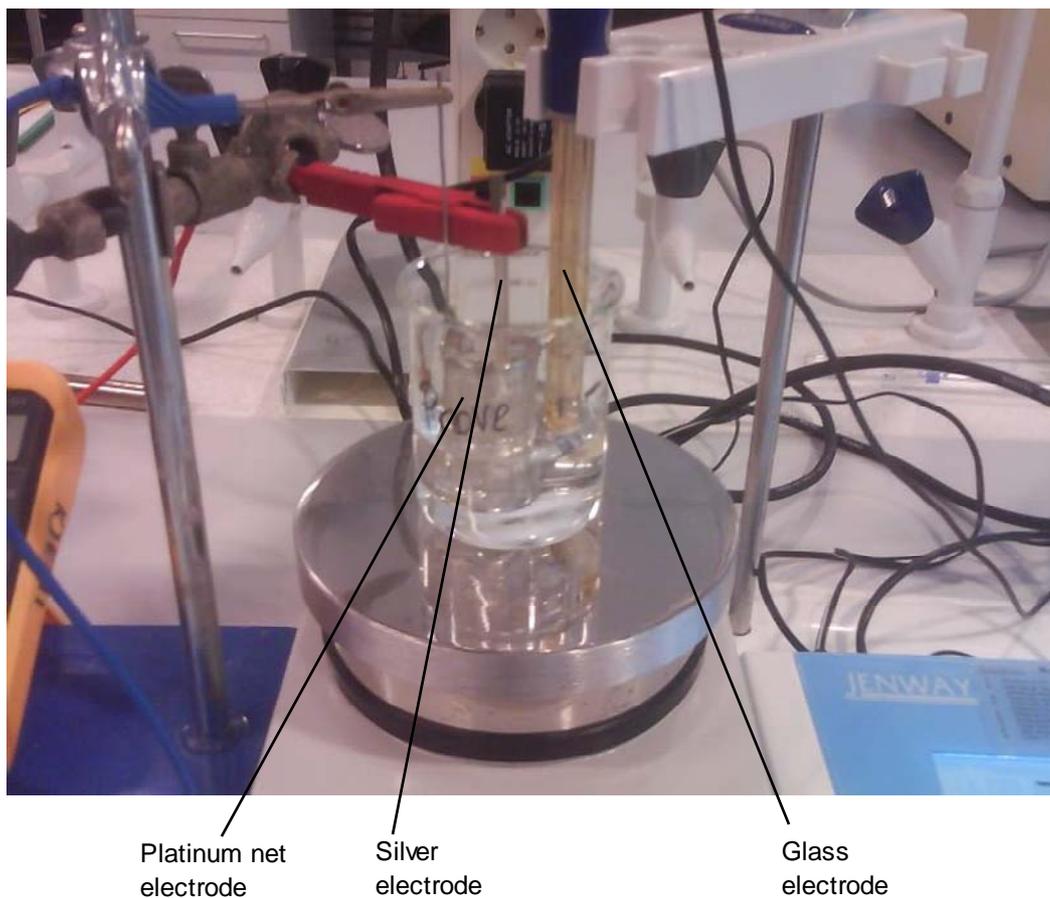


Fig. 4. Details of the electrolysis cell.