CHEM 334 Quantitative Analysis Laboratory

Determination of Chloride by Potentiometric Titrimetry

Introduction

Indicators used in volumetric titrations to signal end-points can take on many forms but the all share the common property that they reveal the increase in concentration of a particular chemical species that occurs when the analyte has been completely consumed by the titrant. The more sensitive the indicator is the closer the observed end-point is to the equivalence-point.

Precipitation titrations are based upon reactions that yield ionic compounds of limited solubility. Silver ion (Ag^+) is a very important and common precipitating reagent. Titrimetric methods based on Ag^+ are termed *argentometric* methods. In this experiment, chloride ion (Cl^-) is determined by reaction with Ag^+ to produce an insoluble, white precipitate of silver chloride.

$$Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)} \qquad K_{sp} = 1.8 \times 10^{-10}\ (M^2) \qquad (1)$$

The indicator used in this method is an electrochemical cell which permits measurement of the concentration of silver ion, $[Ag^+]$, continuously during the titration. This measurement reveals the equivalence point of the titration. The cell consists of a reference electrode made up of a $Cu|Cu^{2+}$ half-cell with a $CuSO_4$ electrolyte including a $CuSO_4$ salt bridge and an indicator electrode consisting of a $Ag|Ag^+$ half-cell with the electrolyte made up by the analyte itself. The cell is represented by the *line diagram*

$$Cu_{(s)}|Cu^{2+}_{(aq)}||Ag^+_{(aq)}|Ag_{(s)} \qquad (2)$$

The cell potential (under the condition of zero current) is given by the difference between the potentials of the two electrodes:

$$E_{cell} = E_+ - E_- \qquad (3)$$

The potentials for the half-reactions are given by the Nernst equation for the two half-cells

$$E_+ = E_{0,Ag} - 0.0592 \log([Ag^+]) \qquad (4)$$

$$E_- = E_{0,Cu} - (0.0592 / 2) \log([Cu^{2+}]) \qquad (5)$$

Here the simplification of unity activity is assumed. The standard potentials ($E_{0,Ag}$, $E_{0,Cu}$) are constants and the $[Cu^{2+}]$ is held constant in this experiment. The only variable in equations (3) through (5) is $[Ag^+]$ and the cell potential can be written in simplified form

$$E_{cell} = constant - 0.0592 \log([Ag^+]) \qquad (6)$$

The measured cell potential, related to $[Ag^+]$, can be plotted against the added titrant volume to generate a titration curve. Because $[Ag^+]$ in a titration varies over several orders of magnitude it is helpful to plot $\log([Ag^+])$ and it is convenient that the measured cell potential is directly proportional to this parameter. In order to obtain absolute values for $[Ag^+]$ it is necessary to calibrate the cell using one or more known standards but this is not necessary to determine the equivalence-point. The equivalence-point can be determined from the titration curve by standard methods, that is, evaluation of the first and second derivatives.

Procedures

Electrode Assembly: Pull a 4 mm outside diameter soft glass tube to a 1 mm constriction, break the tube at the constriction and fire-polish all tube ends. After the glass is thoroughly cool, draw up 2-3 cm of salt bridge solution (30 g L^{-1} agar and 0.1 M $CuSO_4$, held at ~100°C in a water bath). Maintain a finger seal at the top of the tube to prevent escape of the solution as it solidifies. After cooling (this will take no more than a few minutes), add 2-3 cm of electrolyte (0.1 M $CuSO_4$) and a 10 cm long piece of 0.5 mm diameter copper wire into the solution. Secure the wire with a piece of tape. Secure a length of combination wire (a 3 cm silver wire electrode soldered to a 10 cm copper wire connection) to the side of the glass tube with a piece of tape. Adjust the height so that the silver/copper junction remains dry for the entire titration. Ensure that the two copper wires are not in contact with each other or the combination electrode will short out and not operate. Store the combination electrode between uses with the salt bridge immersed in distilled water to prevent it from drying out.

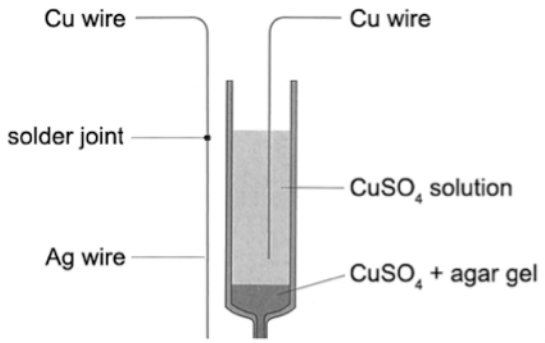

Figure 1. Schematic depiction of the combination electrode used in this method. The $Ag|Ag^+$ indicator appears on the left and the $Cu|Cu^{2+}$ reference electrode with an integral salt bridge is on the right. A cell is completed by immersing this combination electrode in the analyte.

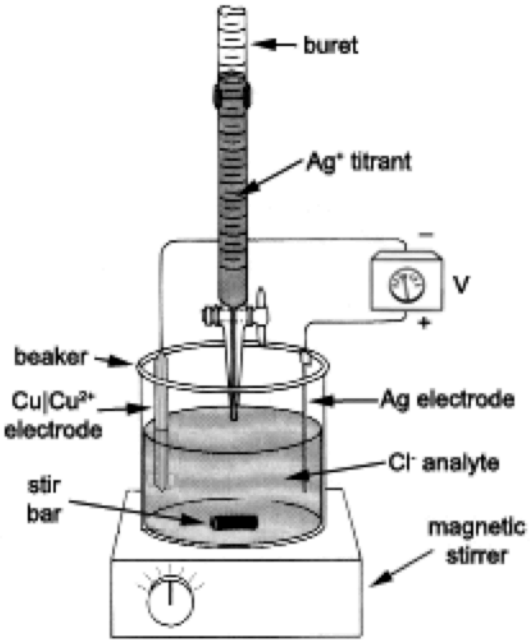

Figure 2. Apparatus for measuring the argentometric titration profile in the determination of chloride ion by volumetric titration. The silver electrode responds to $[Ag^+]$ and the copper half-cell provides a constant reference potential. The titrant & analyte are maintained at pH 2.0 using 10 mM potassium bisulfate buffer.

Apparatus Assembly: Set up the apparatus as shown in the Figure 2. The electrodes are shown separated in the figure but, in fact, are sandwiched together as an electrode combination. Affix the electrode combination to the side of the beaker with a clip or piece of tape. Ensure that the electrode ends are submersed in the analyte, the solder joint of the indicator electrode is high enough to remain dry for the entire titration and the entire assembly is clear of the stir bar. Attach the electrodes to a millivoltmeter with the copper half-cell connected to the reference connector (the negative input) and the silver half-cell connected to the sense connector (the positive input) of the meter.

Titration Measurement: Load a 25-mL burette 4.0 mM silver nitrate in 10 mM potassium bisulfate (pH 2.0) titrant solution. Place an aliquot (with a volume no more than 72 mL) of an analyte containing approximately 5 x 10^{-5} mol of Cl^- in a clean 150-mL beaker. (A rough or "quick and dirty" titration can be performed if the approximate concentration of Cl^- in the analyte is unknown.) Add 8 mL of 0.1 M potassium bisulfate buffer (pH 2.0). Make up the solution volume to 80 mL with distilled water and begin stirring at a rate where a small vortex forms at the surface of the solution but no splashing occurs. Titrate with 1-mL aliquots of the titrant with constant stirring until a total of 25 mL of the titrant have been added or until both sides of the equivalence-point is clearly defined. Read the cell potential at each addition to the nearest millivolt after approximately 20 seconds.

Results

Plot the measured cell potential of the analyzed solution as a function of added titrant. Compute the first and second derivatives and determine all equivalence-point.

Report the concentration of the chloride ion in the sample as molarity, percent (by weight) and ppm. Include a suitable error analysis.

Discussion

Discuss the strengths and weaknesses of using a potentiometric detection of equivalence-point in a volumetric titration. Why is equivalence-point of the titration measured in this method rather than the end-point?

A student of quantitative analysis once wrote "Volumetric titration is universally applicable. If the crude analyte is too concentrated for the titrant concentration, then it is diluted appropriately and a suitable aliquot is analyzed. If the analyte is too dilute then either a larger aliquot is used or the titrant concentration reduced to provide for a convenient titrant volume or both." Explain why this statement is logically unsound. Provide a crisp, valid substitute statement.

References

- Harris, D.C., "Quantitative Chemical Analysis" (2010) eighth edition, Freeman & Co., NY, Chapter 13 & Section 26-5.
- Lisensky, G. and Reynolds, K. "Chloride in Natural Waters." *J. Chem. Edu.* **1991**, *68*, 334-335.