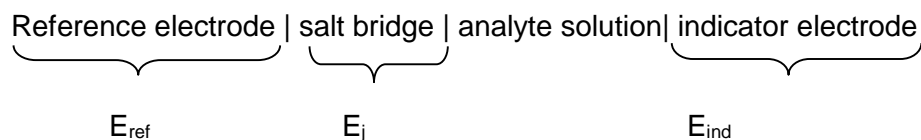


POTENTIOMETRIC TITRATIONS**INTRODUCTION**

General Principle

A typical cell for potentiometric analysis consists of a reference electrode, an indicator electrode and a salt bridge. This cell can be represented as



A **reference electrode**, E_{ref} , is a half-cell having a known potential that remains constant at constant temperature and independent of the composition of the analyte solution. The reference electrode is always treated as the left-hand electrode in potentiometric measurements. Calomel electrodes and silver/silver chloride electrodes are types of reference electrodes.

An **indicator electrode** has a potential that varies with variations in the concentration of an analyte. Most indicator electrodes used in potentiometry are selective in their responses. Metallic indicator electrode and membrane electrodes are types of indicator electrodes.

The third component of a potentiometric cell is a **salt bridge** that prevents the components of the analyte solution from mixing with those reference electrode. A potential develops across the liquid junctions at each end of the salt bridge. The junctions potential across the salt bridge, E_j , is small enough to be neglected.

The potential of the cell is given by the equation;

$$E_{\text{cell}} = E_{\text{ind}} - E_{\text{ref}} + E_j$$

The Glass Electrode for pH Measurements

Typical cell for measuring pH consist of a glass indicator electrode and a saturated calomel reference electrode immersed in the solution whose pH is unknown. The indicator electrode consists of a thin, pH sensitive glass membrane sealed onto one end of a heavy-walled glass or plastic tube. A small volume of hydrochloric acid saturated with silver chloride is contained in the tube. A silver wire in this solution forms a silver/silver chloride inner-reference electrode, which is connected to one of the terminals of the potential-measuring device, pH-meter. The calomel electrode is connected to the other terminal.

The electric potential created between the glass electrode, and the inner-reference electrode is a function of the pH value (activity of hydronium ion, $a_{\text{H}_3\text{O}^+}$) of the measured solution. So once

the potential difference between glass electrode and outer-reference calomel electrode has been measured the pH value can be calculated.

Modern pH electrodes are usually of the "combination" type, meaning that a single cylinder contains both a glass membrane electrode and the outer-reference calomel electrode, (Figure 1).

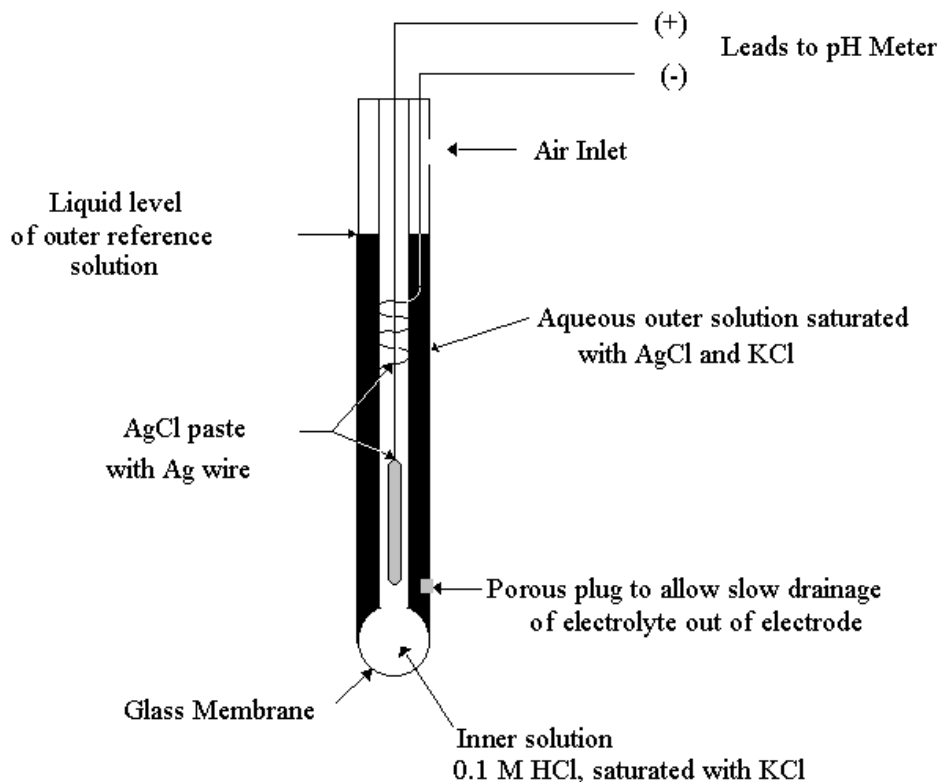


Figure 1. Combination glass electrode

A change in hydronium ion concentration causes a change in composition of the glass membrane due to an ion exchange process involving the solution and the membrane. A corresponding change in membrane potential, proportional to pH, is what is measured. All other potentials are constant. In effect the membrane potential (variable) is measured against two fixed potentials, the external reference and the internal reference, both Ag/AgCl reference electrodes. Potential difference is measured using a high impedance (internal resistance) potentiometer.

Potentiometric Titrations

Potentiometric titrations involves the measurement of the potential of a suitable indicator electrode with respect to a reference electrode as a function of titrant volume. Potentiometric titrations provide more reliable data than data from titrations that use chemical indicators and are particularly useful with colored or turbid solutions and for detecting the presence of unsuspected species.

A typical set up for potentiometric titrations is given in Figure 2. Titration involves measuring and recording the cell potential (in units of millivolts or pH) after each addition of titrant. The titrant is

added in large increments at the outset and in smaller and smaller increments as the end point is approached (as indicated by larger changes in response per unit volume). Sufficient time must be allowed for the attainment of equilibrium after each addition of the reagent by continuous stirring. For this a magnetic stirrer with a stirring magnet bar is used.

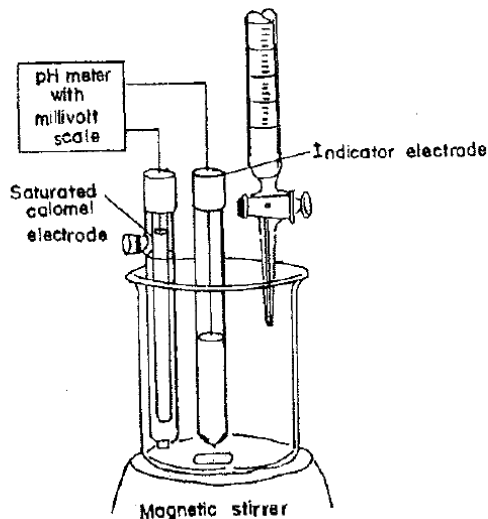


Figure 2. Apparatus for potentiometric titrations

Potentiometric titrations can be classified as precipitation titrations, complex formation titrations, neutralization titrations and oxidation/reduction titrations.

End-Point Detection with Potentiometric Titrations

Several methods can be used to determine the end point of a potentiometric titration. The most straightforward one involves a direct plot of potential as a function of reagent volume, as a Figure 3.

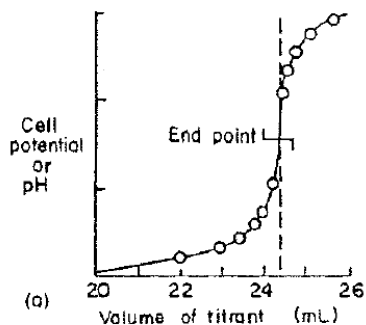


Figure 3. Titration curve

The midpoint in the steeply rising portion of the curve is estimated visually and taken as the end point.

The second approach to end-point detection is to plot the derivative curves:

1. Plotting first derivative curve by calculating the change in potential or pH per unit volume of titrant (that is, $\Delta E/\Delta V$ or $\Delta \text{pH}/\Delta V$). A plot of $\Delta E/\Delta V$ or $\Delta \text{pH}/\Delta V$ as a function of corresponding reagent volume produces a curve with a maximum that corresponds to the point of inflection (Figure 4).

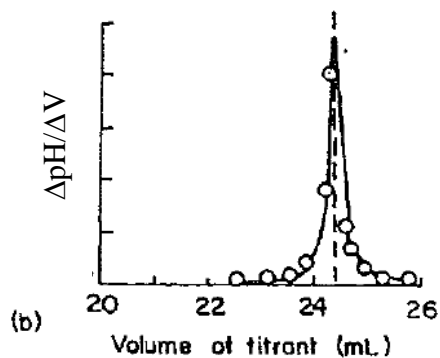


Figure 4. First-derivative curve

2. Plotting the second derivative curve by calculating change in potential-change or pH – change per volume change. Then their ratios, $\Delta^2 E/\Delta V^2$ or $\Delta^2 \text{pH}/\Delta V^2$ values, are plotted against corresponding volume of the titrant. As shown in Figure 5, the data changes sign from (+) to (-) at the inflection point. Second derivative curve gives the end point more precisely.

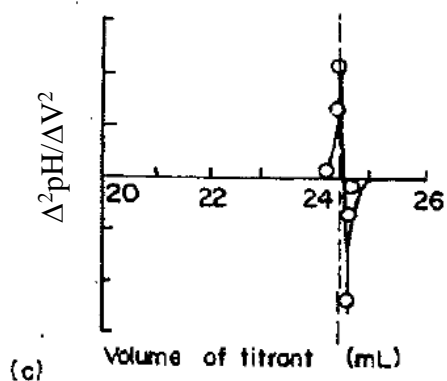


Figure 5. Second derivative curve

REAGENTS AND APPARATUS

- 250 mL of 0.1 M NaOH (for each group)
- Phosphoric Acid solution (already prepared)
- Potassium hydrogen phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$) (primary standard)
- pH 4.0 and 7.0 buffer solutions.
- Buret
- 250 mL beaker
- 100 mL graduated cylinder
- Stirring rod
- Combination glass electrode
- pH meter

PROCEDURE

A) Standardization of Sodium Hydroxide

- 1) Boil 250 mL of distilled water and then cool it. Use this distilled water to prepare 250 mL of 0.1 M NaOH solution for **each group**.
- 2) Transfer 0.20 g (± 1 mg) of potassium hydrogen phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$) into a 250 ml beaker. Dissolve the salt in 200 mL of distilled water. Titrate with 0.1 M NaOH solution prepared. Use the following increments:

Increments, mL	Volume of NaOH, mL
1	0-8
0.1	8-12
1	12-18

- 3) Calibrate pH meter using pH 4.0 and 7.0 buffer solutions.
- 4) Plot the pH vs. volume of NaOH required and then draw 1st and 2nd derivation of the titration curve and from 2nd derivative curve determine the end point.
- 5) Calculate the molarity of NaOH solution.

B) Potentiometric Titration of Phosphoric Acid

- 1) Take your unknown sample into a 400 mL beaker and add 100 mL distilled water.

- 2) Titrate analyte solution with standard NaOH solution. Add small increments of titrant and record pH for corresponding volume of titrant.

Increments, mL	Volume of NaOH, mL
1	0-8
0.1	8-12
1	12-18
0.1	18-22
1	22-28

- 3) Plot the data and establish the end points. (Note: How many end points will be obtained? Discuss with your instructor)
- 4) Calculate experimental K_a values from the titration curve

PRE-LAB STUDIES

Read the introduction from the manual.

- 1) What are the function(s) of reference electrode?
- 2) Write the working principle of calomel and silver/silver chloride reference electrodes?
- 3) Draw the apparatus for a potentiometric titration and name the each component? Explain their functions.
- 4) How is end point determination performed in potentiometric titrations?

POST-LAB STUDIES

- 1) Draw schematic diagram of experimental set up and write the name of each component of experimental set up you used?
- 2) How many end points were you observed in the titration of H_3PO_4 ? Explain by using K_a values.
- 3) Compare experimental and theoretical K_a values of H_3PO_4 ?

