Scholarly Research Journal for Interdisciplinary Studies,
Online ISSN 2278-8808, SJIF 2019 = 6.380, www.srjis.com
PEER REVIEWED & REFEREED JOURNAL, MAY-JUNE, 2020, VOL- 7/59

BASICS OF AMPEROMETRY

Anjanaba J. Khuman
M.Sc. (Chemistry)

I. INTRODUCTION

Amperometry in chemistry is detection of ions in a solution based on electric current or changes in electric current.

Amperometry is used in electrophysiology to study vesicle release events using a carbon fibre electrode. The electrode used for amperometry is not inserted into or attached to the cell, but brought in close proximity of the cell.

The measurements from the electrode originate from an oxidizing reaction of a vesicle cargo released into the cell. Amperometric titration refers to a class of titrations in which the equivalence point is determined through measurements of the electric current produced by the titration reaction. It is a form of quantitative analysis.

II. ORIGIN OF AMPEROMETRY

Electrochemical or amperometric detection as it was first used in ion chromatography was single potential or DC amperometry, useful for certain electrochemically active ions such as cyanide, sulfite and iodide.

The development of pulsed amperometric detection (PAD) for analytes that fouled electrode surfaces when detected eventually helped create a new category of ion chromatography for the detection of carbohydrates.

It was established that neurotransmitters could be electrochemically detected by placing a carbon electrode into tissue and recording the current from neurotransmitters.

One of the first measurements was made using an implanted carbon fiber electrode in the neostriatum of rats. Further work was done in chromaffin cells to investigate catecholamine release from large dense core vesicles.

III. PRINCIPLE

The amperometric titrations rely on the principle that the diffused current (id) is proportional to the concentration. Thus, when an electroactive material (metal ion) is removed from a solution using some reagent (ligand), a decrease in the diffused current is observed.

IV. DETECTION METHODS

1. Single Potential Amperometry:

Any analyte that can be oxidized or reduced is a candidate for amperometric detection. The simplest form of amperometric detection is a single sweep or DC Amperometry. A voltage is applied between two electrodes positioned in the coloum effluent. The measured current changes as an electroactive analyte is oxidized at the anode or reduced at the cathode. Another possible more advantage of amperometry over other detection methods for these and other ions such as iodide, sulfite and hydrazine is specificity.

2. Pulsed Amperometry:

An extension of single-potential amperometry is pulsed amperometry, most commonly used for analytes that tend to foul the electrodes. In pulsed amperometric detection (PAD), a working potential is applied for a short time, followed by higher or lower potentials that are used for cleaning the electrode.

The current is measured only while the working potential is applied, then sequential current measurements are processed by the detector to produce a smooth output. PAD is most often used for detection of carbohydrates after an anion exchange separation, but further development of related techniques show promise for amines, reduced sulfur species, and other electroactive compounds.

V. AMPEROMETRIC TITRATIONS

- **Introduction:**

  Amperometric titrations are otherwise called as polarographic or polarometric titration because of the similarity in principle.

- **Principle:**

  The principle is that, the potential applied between polarisable and non-polarisable electrode is constant and the diffusion current is measured during the titration. During the titrations, the concentration of the reducible ion changes and hence current also changes. The current voltage curve of different concentration of same ion shows that at low concentration there

is less current and at high concentration there is more current. During the titration the concentration of ion changes and hence current also changes.

- **Conditions for performing titration:**
  1. Both should be reducible
  2. The potential applied should limiting current
- **Apparatus for Amperometric titration:**

Rotating platinum micro electrode (RPME):

It consists of a glass rod with platinum wire at about 600rpm wire made through mercury so that the potential can be applied and current is measured.

VI. TYPES OF AMPEROMETRIC TITRATION

1. Titration of reducible ions vs non-reducible
   Eg. Lead (Pb) vs Sulphate ions (SO_4)

2. Titration of non-reducible vs reducible ions
   Eg. Chloride (Cl) vs Silver (Ag)

3. Titration of reducible ion vs reducible ion
   Eg. Lead (Pb) vs Dichromate ion

4. Redox Titration (oxidant and reductant)
   Eg. Ferric (Fe^3) ions vs titanous ions (Ti)

5. End point techniques (Karl Fischer)
   (Determination of water using Karl Fischer reagent)

1. Titration of reducible ion vs non-reducible ions:

Here, lead ion is titrated against sulphate ions. Current is observed due to lead only. Current decreases due to decreased concentration of lead ions in solution due to ppts as lead sulphate by sulphate ions.

2. Titration of non reducible ions vs reducible ions:

In this titration of chloride ions with silver chloride ions are electro reducible, then current is minimum.

3. **Titration of reducible ions vs reducible ions:**

   It is titration of lead ions with dichromate ions. Current decreases due to decrease in the concentration of lead ions and gradually ppt as lead chromate. After end point, addition of dichromate ions in solution, then current increases and V-shaped curve is obtained.

4. **Redox titration:**

   Oxidant and reductant gives different current, for example titration of ferric ions against titanous ions. In the first part of the curve, current decreases due to decrease in concentration of ferric ions. When ferric ions are reduced, the diffusion current is minimum. In the second part of the curve, current set up by oxidation of titanous ions is added. The end point shown by two lines is intersection by difference in slope.

5. **End point techniques (Karl Fischer):**

   The method is applicable when redox system is present before and after the end points for example, water using Karl Fischer reagent. In this method, small potential is applied between two similar platinum electrodes.

   When water is present, both electrodes are depolarized and then addition of Karl Fischer A and B till end point is done. When current is decreased at the end point and only one electrode is depolarized and then current becomes zero.

VII. ADVANTAGES OF AMPEROMETRIC TITRATION

- Both reducible as well as non-reducible ions groups can be determined.
- Dilute solutions can be analyzed.
- The reaction carried out can be reversible or irreversible can be known.
- The apparatus is simple and temperature needs not to be provided constantly.

VIII. APPLICATIONS

1. Amperometric titration-
   - Quantitative in nature
   - Used to determine the end point
2. Determination of water by using Karl Fischer reagent

3. Amperometric detector-
    - They can detect very low concentration of reducible ions and can be easily determined.
4. Quantification of ion or mixture of ions.

IX. REFERENCES

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