

A Review on Introduction to Electroanalytical Chemistry and its Advancements in Pharmaceutical Industries

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Abstract: *Electrochemical detection provides an essential technique in the analysis of pharmaceuticals. Electro analytical chemistry is a subfield of electrochemistry focused on the development of new techniques, methods, and modified electrodes for quantitative analytical investigations. Electrochemical analysis often offers advantages over other analytical methods such as a high degree of accuracy, precision, selectivity and also low cost of operation.*

Keywords: Potentiometry, Voltammetry, Conductometry, Amperometry, Redox Potential, Electrogravimetry

1. Introduction

Electrochemistry is a branch of chemistry concern with the interaction of electrical and chemical effects. A large part of this field deals with the study of chemical changes caused by the passage of an electrical current and the production of electrical energy by chemical reaction. It is named electrochemistry because its originated from the study of the movement of electrons in an oxidation - reduction reaction. Electrochemical methods are analytical techniques that use a measurement of potential, charge or current to determine an analytes concentration or to characterize an analytes chemical reactivity. It is a qualitative and quantitative methods of analysis based on electrochemical phenomena occurring within a medium or at the phase boundary and related to changes in the structure, chemical composition or concentration of the compound being analysed.

The applications are as follows:

- Obtaining thermodynamic data about a reaction.
- To generate an unstable intermediate such as radical ion and study its rate of decay or its spectroscopic properties.
- They use to analyse a solution for trace amount of metal ions or organic species.
- The electrochemical properties of the system themselves are of primary interest, for example, in the design of a new power source or for the electrochemical methods have been developed.^[1]

Electro analytical methods are a class of techniques in analytical chemistry, which study an analyte by measuring the potential (volts) and or current (amperes) in an electrochemical cell containing the analyte. These methods can be broken down in to several categories depending on which aspects of the cell are controlled and which are measured.

A variety of electrochemical methods have been developed, out of which we are as follows:

- Potentiometry
- Conductometry
- Coulombmetry
- Electrogravimetry
- Voltammetry (Polarography / Amperometry).

The discussion of the electrochemical methods assumes the knowledge of Redox reactions, the Nernst equation, galvanic cells and electrodes.

Electrodes:

Electrodes are the interfaces between metallic and electrolyte conductors of electricity. Electrical conduction in metal means the transportation of electrons, where as cations and anions are the mobile charge carriers in electrolytes. Thus, any instrumental set up, which measures current and or voltage signals, necessarily will have an interface between metallic conductors (wires) and electrolytes.

Electrochemical cells:

Electrochemical cells consist of two electrodes: an anode (the electrode at which the oxidation reaction occurs) and a cathode (the electrode at which the reduction reaction occurs).^[2]

Types of Electrochemical Techniques

- 1) Bulk techniques, in which we measure a property of solution in the electrochemical cell. An example is the measurement of a solutions conductivity, which is proportional to the total concentration of dissolved ions,
- 2) Interfacial techniques, in which the potential, charge, or current depends on the species present at the interface between an electrode and the solution in which it sits. An example is the determination of P^H using a P^H electrode.

Despite the difference in instrumentation, all electrochemical techniques share several common features.

- The electrodes potential determines the analytes form at the electrodes surface.
- The concentration of analyte at the electrodes surface may not be same as its concentration in bulk solution.
- Current is a measure of the rate of the analytes oxidation or reduction, and
- We cannot simultaneously control current and potential.

Type of Electrochemical Methods

1) Potentiometry methods

It measures the potential of a solution between two electrodes. The potential is then related to the concentration

of one or more analytes. The cell structure used is often referred to as an electrode even though it actually contains two electrodes: an indicator electrode and a reference electrode.

Potentiometry usually uses electrodes made selectively sensitive to the ion of interest, such as fluoride - sensitive electrode. The most common potentiometric electrode is the glass - membrane electrode used in a P^H meter.

2) Voltammetry method:

It is based on the applies a constant and / or varying potential at an electrodes surface and measures the resulting current with a three electrode system. Voltammetry, with its variety of methods, constitutes the largest group of electrochemical methods of analysis and is commonly used for the determination of compounds in solutions. (for example, Polarography and Amperometry)

3) Coulometry methods

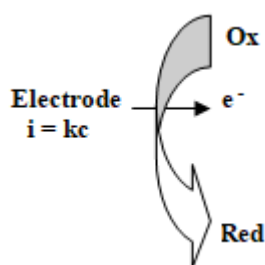
It is based on the measurement of the amount of material deposited on an electrode in the course of an electrochemical reaction in accordance with Faradays laws. A distinction is made between coulometry at constant potential and coulometry at constant current.

4) Conductometry methods

It is the method in which the electrical conductivity of electrolytes (aqueous and non - aqueous solutions, colloid systems and solids) is measured. It is based on the change in the concentration of a compound or the chemical composition of a medium in the inter electrode space. [3]

Electroanalytical Measurements

Electrochemical (analytical measurements) are heterogeneous in nature.



Current is also a direct measure of reaction rate.

Important Factors: Electrode material, Electrolyte solution, Surface cleanliness and Surface chemistry.

Potentiometric Measurements:

Potentiometry passively measures the potential of a solution between two electrodes, affecting the solution very little in the process. The potential is then related to the concentration of one or more analytes.

$$E_{\text{ind (v s. ref)}} = L + \frac{0.0592}{Z} \text{Log [Ox]}$$

Examples: P^H measurements, Ion selective electrodes, Gas sensing electrodes.

Voltammetric Measurements

Voltammetry applies a constant and / or varying potential at an electrodes surface and measures the resulting current with a three electrode system. This method can reveal the reduction potential of an analyte and its electrochemical reactivity. This method in practical terms is non-destructive since only a very small amount of the analyte is consumed at the two-dimensional surface of the working and counter electrodes.

Various electrochemical sensors can be used to measure important analytes in blood. They tend to be inexpensive, robust, sensitive and selective with proper surface modification. [4]

Electroanalytical Methods in Pharmaceutical Analysis and their Validation

Electrochemical detection provides an essential technique in the analysis of pharmaceuticals. Electrochemical analysis of active drugs is based on redox reactions depending on electron transfer pathways. So, there is a close relationship between electrochemical and biological reactions.

Electrochemical analysis often offers advantages over other analytical methods such as a high degree of accuracy, precision, selectivity and also low cost of operation.

It deals a linear relationship with sweep voltammetry, cyclic voltammetry and pulse voltammetric methods and their applications in pharmaceutical analysis. Electrochemical analysis plays an important role in drug development, metabolite determination, oxidative stress and electrochemical therapy. [5]

Advances in Electroanalytical Chemistry:

- Electro analytical chemistry is a subfield of electrochemistry focused on the development of new techniques, methods, and modified electrodes for quantitative analytical investigations.
- In some instances, those quantitative analytical investigations are used for sensing and detecting an analyte (glucose concentrations in blood), but in recent years, there has been considerable technique development for studying electro catalysis in fuel cells and electrolyzers, investigating intercalation in batteries, interrogating the electrode interface.
- Analytical chemists have been improving single molecule and single entity detection methods for several decades. Single molecule detection is difficult in electrochemistry, but several researchers have improved the signal from a single redox event by potentiostatic redox cycling in the gap between a tip and macro electrodes in scanning electrochemical microscopy.
- Scanning probe electroanalytical techniques have also made significant advances over the past decade with the enhanced abilities of scanning electrochemical microscopy (SECM), Scanning ion conductance microscopy (SICM), scanning electrochemical cell microscopy (SECCM). [6]

References

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