



Ministry of higher education and scientific research
AL-Mustaqbal University college
Department of medical physics



Analytical chemistry

Lecture 5

Voltammetric and Conductmetric analysis

By

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Electroanalysis

Measuring transport properties of ion in phases

Conductometry

-Electrophoresis

Measuring of electrochemical equilibria and charge transfer reactions and interfaces

Static methods

-Potentiometry (pH electrodes and other ion-sensitive electrodes)

Dynamic methods

Controlled potential methods

Controlled potential coulometry

Voltammetry

$(I = f(E))$

Chronoamperometry

Amperometry

Impedance spectroscopy

Controlled current methods

Current controlled coulometry

Chronopotentiometry

What are voltammetric techniques? •

The term voltammetry is derived from •
voltamperometry, and it expresses that the current is
measured as a function of voltage, i.e., electrode
potential. Since any electrochemical cell needs two
electrodes, it would be impossible to extract
unambiguous analytical information, if both electrodes
would determine the magnitude of the flowing
current. Therefore, one electrode is made much
smaller than the other, so that the flowing current is
limited by this electrode only. This electrode is called
the working electrode, and the other (larger) electrode
is called the auxiliary electrode.

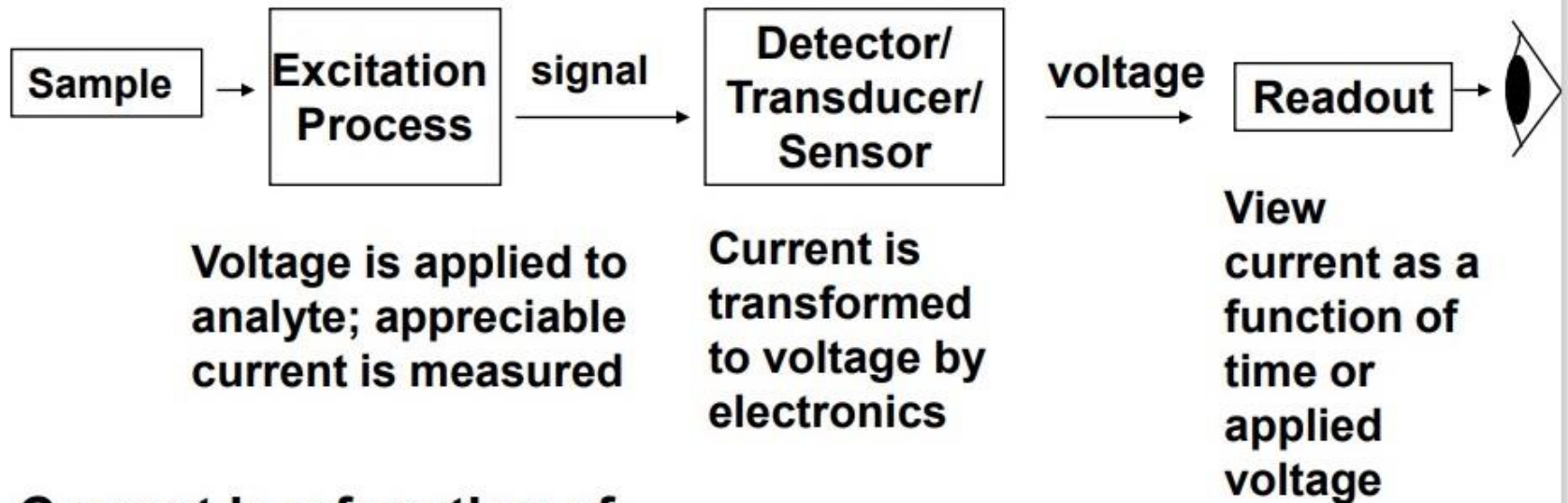
Characteristics

- ❑ **Voltammetry** is based upon the measurement of a current that develops in an electrochemical cell under conditions of complete concentration polarization.
- ❑ **Potentiometric** measurements are made at currents that approach zero and where polarization is absent.
- ❑ **Furthermore**, in voltammetry a minimal consumption of analyte takes place, whereas in electrogravimetry and coulometry essentially all of the analyte is converted to another state
- ❑ **Voltammetry** (particularly classical polarography) was an important tool used by chemists for the determination of inorganic ions and certain organic species in aqueous solutions.

What is the principle of voltammetry?

In voltammetry, information about an analyte •
is obtained by measuring the current as the
potential is varied. The analytical data for a
voltammetric experiment comes in the form
of a voltammogram which plots the current
produced by the analyte versus the potential
of the working electrode.

Concept



Current is a function of

- **analyte concentration**
- **how fast analyte moves to electrode surface**
- **rate of electron transfer to sample**
- **voltage, time...**

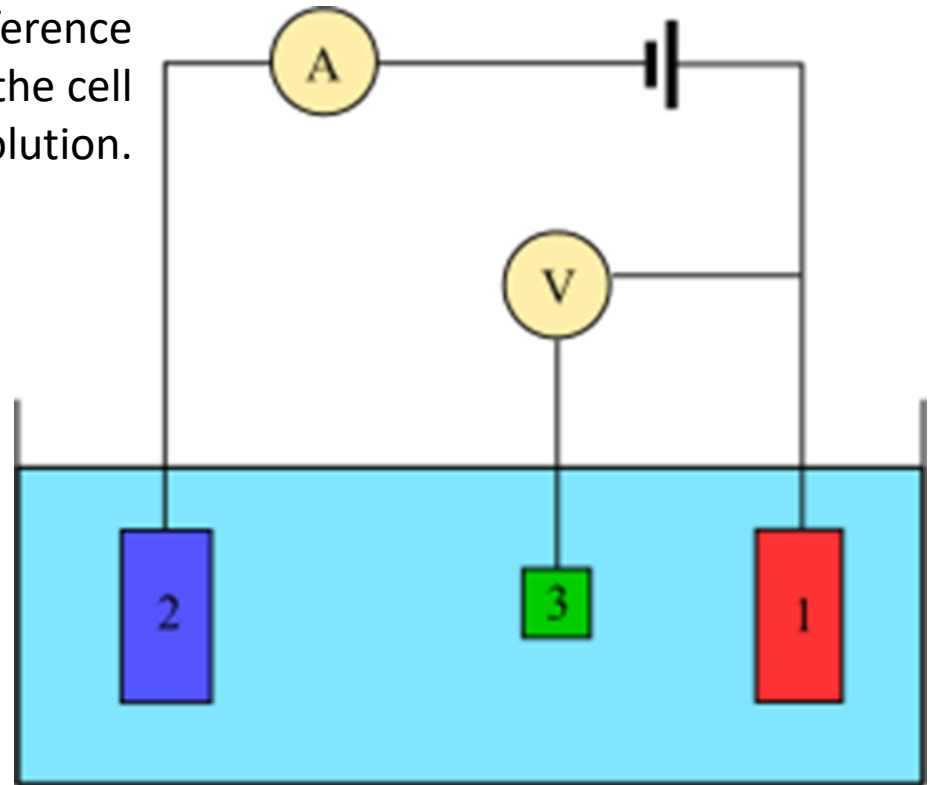
Solutions and electrodes

- 1. Solutions: redox couple + solvent + supporting electrolyte**
 - **supporting electrolyte: salt that migrates and carries current, and doesn't do redox in your potential window of interest**
 - **a wide potential window is desirable**
 - **water - good for oxidations, not reductions except on Hg**
 - **supporting electrolytes: lots of salts**
 - **nonaqueous solvents: acetonitrile, dimethylformamide, etc.**
 - **supporting electrolytes: tetraalkylammonium BF₄, PF₆, ClO₄**
 - **Oxygen is fairly easily reduced - we remove it by deoxygenating with an inert gas (N₂, Ar).**

How many electrodes are used in voltammetry?

three electrodes are used. The physical setup of an electrochemical cell is relatively simple. The working and counter electrodes sit in an electrochemical solution, and the reference electrode sits in a separate tube within the cell containing the reference solution.

These electrodes, the working, reference, and auxiliary make up the modern three-electrode system.



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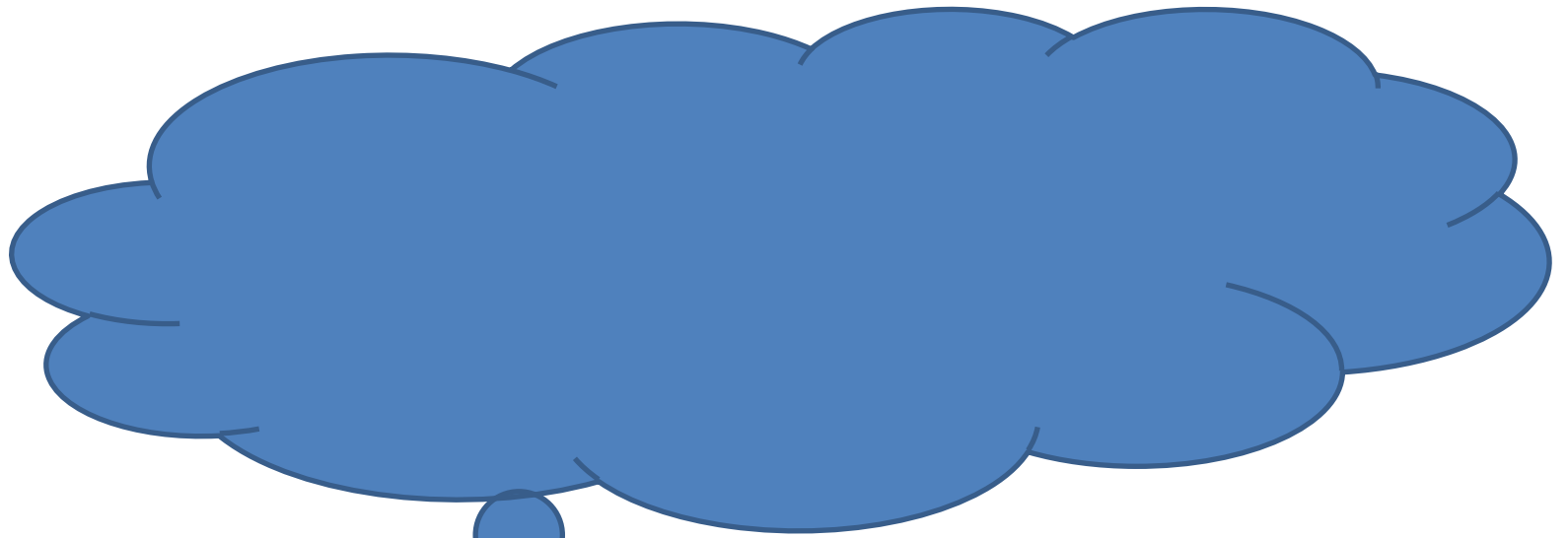
Three-electrode setup:

(1) working electrode: is the electrode in an electrochemical system on which the reaction of interest is occurring.[1][2][3] The working electrode is often used in conjunction with an auxiliary electrode, and a reference electrode in a three electrode system.

(2) auxiliary electrode: is an electrode used in a three electrode electrochemical cell for voltammetric analysis or other reactions in which an electric current is expected to flow

:(3) reference electrode :is a half cell with a known reduction potential. Its only role is to act as reference in measuring and controlling the working electrode's potential and at no point does it pass any current.

- Types of voltammetry •
- Voltammetric Techniques •
 - Polarography •
- Square Wave Voltammetry •
 - Cyclic Voltammetry •
 - LSV •
 - Differential Pulse •
 - Normal Pulse •
 - Sampled DC •
- Stripping Analysis •





Thank You
For Your
Attention

