ELECTRO-ANALYTICAL TECHNIQUES

POTENTIOMETRIC TECHNIQUES

Principle

Electrochemical techniques/ Electrochemical methods are generally used for determination of analytes in ionic forms. The solution containing the analyte in ionic form behaves like an electrochemical cell having both cations and anions in the solution. An electrochemical cell can be compared with an electrical circuit when electrodes are applied with voltmeter/galvanometer connected. When electrodes are connected and inserted into the electrolyte, there is flow of electrons (current flow) as the cations flow towards cathodes and anions flow towards anode.

For a voltage (electrical potential/electromotive force) to be generated by a chemical reaction, a chemical transformation must involve charged species. The magnitude of the voltage associated with an equation involving charge transfer is described quantitatively by the Nernst Equation.

$E = E^o - RT/nF \ln K_{ac}$

where

E = the electrochemical potential (EMF) and is related to free energy for the reaction by the equation

E^o = standard potential. This is the EMF for the reaction under standard state conditions

R = Gas constant (8.3145joules/K/mol)

T = Temperature in K

n= number of moles of charges transferred in reaction per mole of reactants.

F = Faraday constant which represents the number of coulombs in a mole of electron (F=96485Coulombs/mol of joules/V/mol)

Numerical substitution for T = 298 (25 ^{o}C)

R and F can be made along with a conversion for natural base-10 logarithm.

$E = E^{o} – 0.059/n \log K$ at 298K.

$E = E^{o}$ when all species in standard states

$K_{act} = 1$ also at the standard state

The Nernst equation applied to two types of chemical processes that involve the motion of electrical charges

- Oxidation-reduction reactions
- Transfer of ionic charges by diffusion of ions from a region where they are more concentrated to a region where they are more dilute.

Ion Selective Electrodes

Ion selective electrodes make use of the principles elucidate by the Nerst Equation (the principle of potentiometric methods). Whenever an interface forms between two phases that do not mix freely, an electrochemical potential is generated which is called interface potential. This interface potential forms the basis of the measurement made with ion selective electrodes

Example is the pH electrode which is used to the activity of H^+ in in the presence of any other ions..

Advantages

1. Saves time (speed of determination)
2. Relatively inexpensive
3. Simple to operate

Disadvantages

1. Interferences can occur if concentration of the interfering ionic species are substantially greater than the ion of interest. This requires that the method of extraction has to be such that only ions are substantially extracted in the measuring solution.
2. Electrodes are very fragile and need much care

COULOMETRIC TECHNIQUES

Principle

This involves measurement of quantity of electric charges. It could be direct coulometry or coulometric titration.

The electrical current in a coulometric titration is carefully maintained at a constant and accurately known level. The product of this current in amperes, and the time in seconds required to reach an end point equals the number of coulombs which is proportional to the quantity of analyte involved. The end-point is detected amperometrically (e. g chloride titrators).

Chloride titrator

In the chloride titrator, a constant direct current is passed between a pair of Ag generator electrodes (Ag wire) in a coulometric circuit, causing release of Ag ions into the titration solution at a constant rate. The Ag^{2+} reacts with Cl^- in the sample to form precipitate. The end point is reached when all the Cl^- in the sample has been precipitated. At the end point, there will be a sudden increase in concentration of Ag^{2+} which leads to a rise in current flow through the pair of Ag electrodes. The amperometric circuit senses the increase in current and stops the timer which runs concurrently with the generation of $Ag^{2+.}$ Since the rate of Ag^{2+} generation is constant, the amount of Cl^- precipitated is proportional to the elapsed time.

Advantages: Lack of interfering except iron sulphide at very low concentration; sensitivity to low analyte concentration.

Disadvantage: It takes time with samples high in Cl^- concentration

Other use of coulometric techniques include carbon and sulphur, and Ca and Mg

SEPARATION TECHNIQUES

QUANTITATIVE SOLID-LIQUID EXTRACTION

Generally, in quantitative solid-liquid extraction, a weighed solid is placed in a closable container, and some solvent is added. The solid and liquid are mixed well, and the liquid is separated from the solid. The procedure involves using a liquid to dissolve the analytes that are part of the solid (but not covalently bound within it).

In soil science, extraction involves the transfer of analytes from the soil matrix into solution which is then separated from the soil either through centrifugation of filtration. The process of soil extraction is based on the ion exchange phenomenon. During extraction, ions in solution referred to as the *extractant* exchange for ions that are electrovalently bonded to the charged sites on the surfaces of soil particles.

CHROMATOGRAPHY

Chromatography can be defined as the science and art of separating the components of materials from each other. Such separation are achieved using variety of techniques based on diverse molecular differences such as molecular charge, molecular size, molecular mass, bond polarity, redox potential, ionization constants, and arrangement of bonds such as isomer structure. However, separation methods that use electric fields to drive charged molecules so that they separate are not generally included in chromatographic techniques. Such techniques are referred to as electroseparation, electromigration and electroporesis.

ION EXCHANGE CHROMATOGRAPHY

Ion-exchange chromatography is a process that allows the separation of ions and polar molecules based on the charge properties.

Principle of Ion-exchange chromatography (IEC)

Separation in ion exchange chromatography depends upon the reversible adsorption of charged solute molecules to immobilized ion exchange groups of opposite charge. The process of IEC is in five main stages.

1. The first stage is equilibration in which the ion exchanger is brought to a starting state, in terms of pH and ionic strength, which allows the binding of the desired solute molecules. The exchanger groups are associated at this time with exchangeable counter-ions (usually simple anions or cations, such as chloride or sodium).

2. The second stage is sample application and adsorption, in which solute molecules carrying the appropriate charge displace counter-ions and bind reversibly to the gel. Unbound substances can be washed out from the exchanger bed using starting buffer.

3. In the third stage, substances are removed from the column by changing to elution conditions unfavourable for ionic bonding of the solute molecules. This normally involves increasing the ionic strength of the eluting buffer or changing its pH.

4. The fourth the removal from the column of substances not eluted under the previous experimental conditions and

5. The fifth stage is re-equilibration at the starting conditions for the next purification.

Separation is obtained since different substances have different degrees of interaction with the ion exchanger due to differences in their charges, charge densities and distribution of charge on their surfaces. These interactions can be controlled by varying conditions such as ionic strength and pH.

There are two types: Cation chromatography, and Ion chromatography