Chapter 1

INRODUCTION

OVERVEW

The objective of analytical chemistry is essentially to develop and apply new methodology and instrumentation with the goal of providing information on the nature and composition of matter. Analytical chemistry also allows the determination of a compound's structure in a sample of differing complexity. Finally, part of the role of analytical chemistry is to provide an interpretation of the results obtained. It plays a vital role in the medical, biochemical, environmental, and pharmaceutical sciences, and in numerous industrial areas.

In contrast to the traditional qualitative and quantitative analysis, the present view of analytical chemistry depends mainly on the instrumental techniques, such as gas chromatography, liquid chromatography, mass spectrometry, IR, UV/VIS spectrometry, X-ray emission and absorption spectrometry, atomic absorption spectroscopy and electrochemical methods. Electrochemical techniques, which include voltammetric, amperometric, conductometric, potentiometric, and coulometric methods, offer powerful tools for solving variety of analytical problems. Ion-selective electrodes represent an important division of the potentiometric analysis that offers the advantage of sensitivity, selectivity, low cost, simplicity, instant results, and ability to measure in the field.

ION SELECTIVE ELECTRODES

Ion selective electrodes (ISE's) are membrane electrodes that respond selectively to ions in the presence of others by measuring the potential of the specific ion in solution. This potential is measured against a stable reference electrode of constant potential. The potential difference depends, mainly upon the activity of the specific ion in solution,[1-3] therefore, allowing the user to make an analytical measurement of that specific ion. Several ISE 's have been developed for a variety of different ions.

1.1. Theory of ISE's

The basic theory of ISE 's was developed many decades ago.[4-8] ISE's work on the basic principals of the galvanic cell. By measuring the electric potential generated across a membrane by "selected" ions, and comparing it to a reference electrode, a net charge is determined. The strength of this charge is directly proportional to the concentration of the selected ion. The basic formula for the galvanic cell is given as :

$$E_{cell} = E_{ISE} - E_{ref}$$

If ions can penetrate the boundary between two phases, then electrochemical equilibrium will be reached, in which different potentials in the two phases are formed.[9] If only one type of an ion can be exchanged between the two phases, then the potential difference formed between the phases is governed only by the activity of this target ion in these phases. When the membrane separates two solutions of different ionic activities (a_1 and a_2) and the provided membrane is only permeable to this single type of ions, the potential difference (E) across the membrane is described by Nernst equation.[10,11]

$$E = \frac{RT}{zF} \ln \left(\frac{a_2}{a_1} \right)$$

If the activity of the target ion in phase 1 is kept constant, the unknown activity in phase 2 ($a_2 = a_x$) is related to (E) by the flowing equation:

$$E = \frac{RT}{z_X F} \ln \left(\frac{a_X}{a_1} \right) = const + S.\log(a_X)$$

Where the constant is the standard potential for $a_x = 1$ mol/l, R is the gas constant (8.314 j k^{-1} mol^{-1}), F is Faraday's constant (9.6485x104 C mol^{-1}), T is the absolute temperature and z_x is the charge of the analyte ion. The potential difference can be measured between two identical reference electrodes placed in the two phases. In practice the potential difference i.e. the electromotive force is measured between an ion selective electrode and a reference electrode, placed in the sample solution. An exemplary set-up for the measurement of electromotive force is presented in Fig 1.1