CHAPTER 1

INTRODUCTION

Electroanalytical technique is a branch of chemical analysis that employs electrochemical methods to obtain information related to the amounts, properties, and environments of chemical species. It can be used to study anything that directly or indirectly undergoes a reaction involving electron transfer. The significant limitation of electroanalytical techniques is the fact that there must always be at least two electrodes, and hence one must consider not only what is going on at a single probe electrode but also what is going on at the second electrode, even if the second electrode is not of direct interest and is present only to complete the circuit. In practice, we usually want to consider only one electrode at a time; in principle, both must always be considered at the same time [1]. An electrode can be as simple as a wire, eg. copper, silver, or as complex as some ion-selectives electrodes [2]. Many ion-selective interfaces have been studied, and several different types of electrode have been marked commercially [3]. The commercially available electrode assemblies are fairly bulky and, because of their fairly complex structures, rather expensive. Coated wire ion-selective electrode (CWISE) demonstrates the possibility of developing a wide variety of miniaturized, inexpensive, sturdy, and reliable electrodes. Preliminary works in the laboratory dealing with various inorganic and organic anion selective electrodes have proved that the coated wire electrodes are effective for many ions and those the internal reference solutions are not needed [4].

1.1Principle [1,2,5,6,]

A typical electrochemical reaction is given in reaction 1. In this model, the oxidized and reduced forms of the redox couple, Ox and Red, respectively are interrelated by a transfer of n electrons at the electrode surface.

$$Ox + ne^- \underset{}{\overset{k_s}{\rightleftharpoons}} Red \overset{k_c}{\rightleftharpoons} Z \qquad (1)$$

The primary electrode product, Red, may not be stable, and may undergo follow-up homogeneous chemical reaction in solution to give another product(s) Z. There may also be chemical reactions coupled to Ox, not shown in (1) which determine the availability of Ox to undergo the reduction. The rate constants of the heterogeneous reactions and homogeneous coupled reactions determine the reversibility of the redox couple. The standard heterogeneous electron-transfer rate constant, k_s or K_c is the value of this quantity of the standard potential, E^o. By this idea and the fact that electric current is caused by the flow of electrons in conductors, the system of electrochemical cell consists of two electrodes dipping into an electrolyte solution. When a chemical reaction occurs within the cell, the chemical reactions occuring at an electrode will be observed along with the consequences when equilibrium prevails at the electrode. The electrochemical cell itself developes a potential difference between the electrodes. In general, the two electrodes in the electrochemical cell consist of

1) indicator (working) electrode at which the redox process of interest occurs

2) reference electrode, which carries no cell current and to which the potential of the working electrode is referred. The cell potential is as the equation below:

$$E_{cell} = E_{IND} + E_j - E_{ref} \qquad (2)$$

when

E_{cell} = the potential difference between electrodes

E_{IND} = the potential of indicator (working) electrode

E_{ref} = the potential of reference electrode

E_j = the potential of liquid junction

E_j and E_{ref} are supposed to be constant, thus the cell potential is obtained in the form of Nernst equation as :

$$E_{cell} = E^o + \frac{RT}{nF} \ln \frac{a_{ox}}{a_{red}} \qquad (3)$$

when

E^o = standard electrode potential

R = gas constant

T = temperature (K)

n = the actual number of electrons involved in the electrode reaction

F = Faraday constant

a_{ox} = activities of the oxidized forms

a_{red} = activities of the reduced form

1.2 Ion-selective electrodes [1,5]

Ion-selective electrodes can be used in any aqueous or partially aqueous medium. Ion-selective electrodes have many advantages over other methods of analysis. They are specific for certain ions or compounds, selecting for them against all others. They are comparatively low in cost, non-destructive sensors, reasonably portable, and can be used in the field. Finally, they are very useful for ions where analysis by other procedures are difficult, such as Na^+, K^+, F^-, Ca^{2+}, and for ion-ionic materials as well as by indirect methods. On the other hand, ion-selective electrodes have certain disadvantages that are inherent in the electrodes themselves. One of these is the drift, a slow change of potential with time in a solution of constant composition and temperature. Drift is a characteristic of the electrode itself and little effective remedial action can be taken. A more serious problem is hysteresis; a phenomenon occurring when some electrodes are immersed in a standard solution followed by placing in an unknown solution, and then restored to the standard again, this will not give the same potential as originally observed in the standard solution. This error is systematic, being in the direction of the concentration of the solution in which the electrode was previously immersed, and cannot be effectively remedied. Other problems may arise from the specific electrode or medium being studied.

The range of an ion-selective electrode is usually given as the range over which the concentration of principal ion can be measured with an essentially Nernstian response from electrodes. The high end of the range is due to the effect of activity coefficient changes at high concentrations and is not a serious limitation since it can be avoided by dilution with an inert electrolyte of fixed ionic-strength. The low end of the range is imposed by the electrode seeing itself, as the loss of ions from the electrode controls the concentration of ions being sensed. The detection limit of electrode is given by the point of intersection of the horizontal and

Nernstian portion of the potential logarithm of concentration response curve as shown in Fig 1.

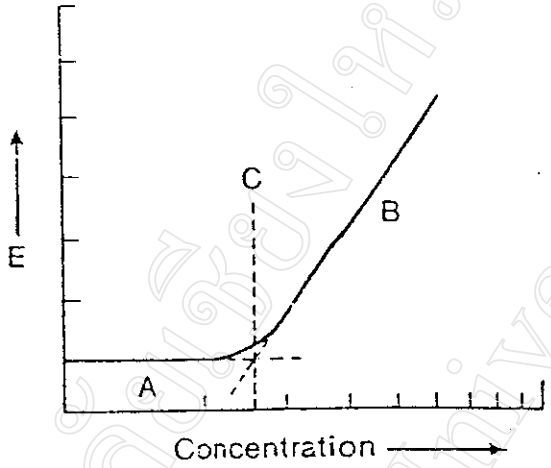

Fig. 1 Detection limit of ion-selective electrode.[1]
A, horizontal region; B, Nernstian region;
C, detection limit.

The measured potential of ion-selective electrodes is the sum of the potential of electrodes, potential of liquid junctions, and potential difference across the membrane:

$$E = \Delta E_{membrane} + E_1 - E_2 + \Sigma E_j \quad (4)$$

where E_1 is the potential of the electrode inside the membrane, E_2 is the potential of the electrode outside the membrane, and the E_j values are the liquid junction potentials of the cell. If the potentials of the liquid junctions and the electrodes are constant, as is generally the case, then

$$E = E' + \Delta E_{membrane} \quad (5)$$

where

$$\Delta E_{membrane} = \frac{RT}{ZF} \ln \left(\frac{a^+_{outside}}{a^+_{inside}} \right) \quad (6)$$

The notation a^+ is a summary notation for all of the ionic activities outside or inside the membrane. It is characteristic of membranes in general that they respond to a concentration difference in the activities of any one or more ions across them by

establishing a potential difference. It is the purpose of the development of ion-selective membrane to ensure that the response in terms of potential is very much greater for some ions than for others so that variations in the activities of certain ions will be sensed while variations in the activities of others are not. In other words,if the value of RT/ZF ln (a^{+}_{inside}) is incorporated into the potential E′, which is legitimate because the composition of the solution on one side (usually inside) of electrode does not change, then the summarized notation of the Nernst equation for univalent ions is

$$E = E' + \frac{RT}{F} \ln \left[\sum_i K_i a_i \right] \qquad (7)$$

For multivalent ions, the charge becomes important:

$$E = E' + 2.303 \frac{RT}{FZ_A} \log \sum_i K(A,i)\, a_i^{z_A/z_i} \qquad (8)$$

where

E = the measurable or experimentally observed potential of a cell

a_i = activity of the ith ion (taken to the power Z_A/Z_i in order to compensate for the appearance of Z_A in the prelogarithmic term)

A = principle ion to which the electrode response is related

K(A,i) = selectivity coefficient for the ith ion over the principle ion A

Z_A,Z_i = integer corresponding in sign and in magnitude to the charge of the principle ion A and of the ith ion i,respectively.

The ion-selective electrode can be used in any formats depicted in Fig 2.

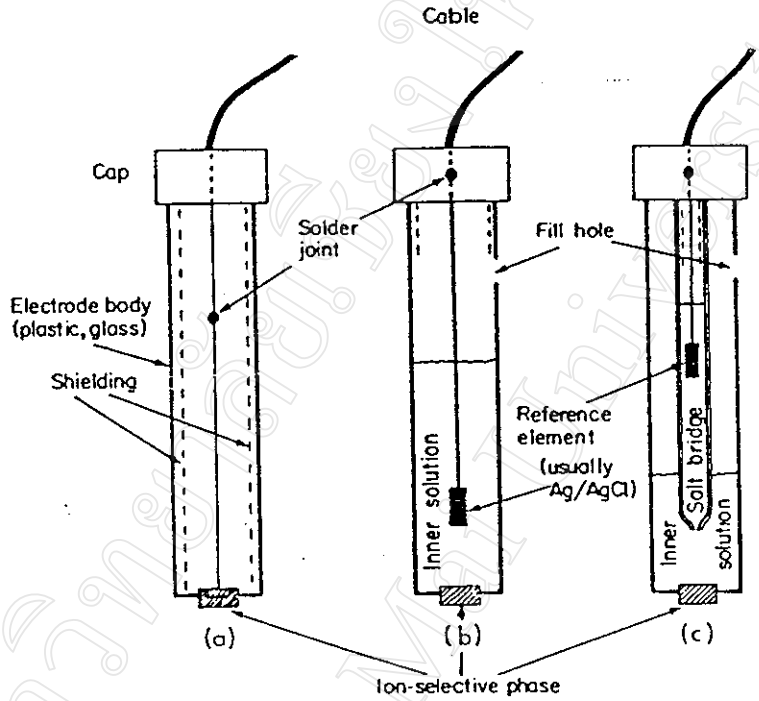

Fig. 2 Possible construction of ion-selective electrode with ion-selective phases: (a) direct contact of the metallic conductor with the active phase, (b) contact through an inner reference solution and an internal reference element, (c) contact through an inner solution and an internal reference element with salt bridge. Fill hole often omitted in (b)[5].

An ordered classification of all ion-selective electrode type is a formidable task because electrode distinctions tend to blur across membrane, format, and response characteristics. The suggested IUPAC grouping is followed in Table 1.

Table 1 Classification of ion-selective electrodes [5]

Electrode class	Active membrane material	Examples
Primary electrodes		
solid membrane electrode	**Crystalline** (single, mixed, or poly)	
	-Homogeneous	LaF_3, $AgCl/Ag_2S$, (no inert matrix)
	-Heterogeneous	AgI in silicone rubber (has inert matrix)
	Noncrystalline	
	-Glass	Na, K glass electrode
	-SiO_2, Si_3N_4	Gateless ISFET*
	-Organic	Ion-exchange resin electrode
Liquid membrane electrode	(May be unsupported or supported with an inert solid matrix)	
	-Neutral carrier	Valinomycin/PVC K^+ ISE
	-Charged carrier	Ph_4B^-, R_4N^+ in cellulose filters
Sensitized electrode		
Gas-sensing electrode	-Gas-permeable membrane (with electrolyte, ISE)	pCO_2, pNH_3 ISE
	-Air gap (with electrolyte, ISE)	same
Biosensitive electrode	-Enzyme(s) in matrix on ISE	Enzyme electrode for urea, glucose

*= insulated silicon field-effect-transistor

1.3 Coated wire ion selective electrode; CWISE

Coated wire ion selective electrode (CWISE) introduced by Freiser in the mid-1970 s, has also attracted attention as a means of easily miniaturizing ion-selective electrode[7]. In the course of a study of a serie of liquid membrane ion-selective electrodes, Freiser and his co-worker became intrigued by the solution developed by two Japanese scientists for the failure of Cu_2S plated copper to act as a sulfide-responsive electrode. Hirata and Date[8] developed a well-behaved electrode by embedding a Cu conductor in a disc made by incorporating finely divided Cu_2S in a polymeric matrix. Inspired by this, Freiser and his co-worker attempted to prepare electrodes by dipping the tip of a platinum wire in a solution of poly(vinyl chloride) (PVC) in cyclohexanone or tetrahydrofuran (THF) containing also a suitable soluble electroactive material and allowing the resulting thin film to air dry overnight. The electrodes were founded to give Nernstain potential response to the change in activities of the designated ions.

CWISE consists of ion-selective chemistries in a polymer matrix coated directly over a metallic wire conductor. No attempt is made to define a thermodynamic, ion-reversible internal reference by the usual solution or solid salt means. Many metals have been used as internal conductors, but Ag, Cu, and especially Pt are favored. Polymers of choice are poly(vinyl chloride) (PVC), poly(methylmethacrylate) (PMMA), epoxy resin, or other hydrophobic solvent-soluble matrices. Unless the ion-selective chemistry processes plasticizing ability (like the liquid exchanger, Aliquat),a plasticizer solvent is also included in the fomulation. The coating "recipe" of chemistry, plasticizer, and polymer matrix dissolved in an evaporable coating solvent like tetrahydrofuran, cyclohexanone is virtually identical with that used to fabricate PVC liquid membrane for traditional barrel formats[4,5].

Electrode preparation processes are : [5]

1) cleaning the wire with mechanical polishing and washing solution such as deionized water, laboratory detergent, and acetone[8].

2) cleaned, exposed end of the wire is then dipped into, or sprayed or coated with the coating solution

3) air drying followed by repeated coating then follows, thickness of 0.1-1.0 mm usually satifactory.

4) uncoated-wire portions are then masked with teflon tape, parafilm, or non-conductive and water-impermeable material

5) normally a preconditioning step for several hours or more in a dilute solution of intended analyte must be provided

6) storage is either in conditioning solution or in air if a conditioning step is performed after each long drying period.

The unique feature of CWISE is that it does not require the internal reference solution and electrode present in conventional ion-selective electrode of liquid or polymer membrane type. While from a theoretical view point this presents some problems in interpreting the mechanism of operating of CWISE. As a result, lack of internal reference components give CWISE some interesting advantages over conventional type ion-selective electrodes. Firstly, CWISE is easier to construct and require less construction time than conventional polymer membrane ion-selective electrodes. Secondly, CWISE is far less expensive than conventional ion-selective electrodes. This difference is particularly true when the cost of CWISE is compared to that of commercially available ion-selective electrodes. In addition, CWISE may be easily miniaturized, making possible intercellular or other in vivo electrochemical measurements[8]. In general, CWISE response characteristics as detection limit, selectivity coefficients, and lifetimes are similar to the PVC-membrane barrel-format electrodes with internal solution[5].

The advantages of CWISE technology are low cost and simplicity. Any test ion-selective, liquid-membrane chemistry can be quickly evaluated in this format.

The several CWISE containing an electroactive materials ion-association compounds formed between negatively charged halide complexes of the metal ions to be determined and strong hydrophobic cations, have been reported. Antimony[9], iron[10], copper[11], mercury[12], zinc[13], cobalt[14],gold[15] and thallium[16] have been determined as their chloro complexes. Aliquat 336[10-14], 1,2,4,6-tetraphenylpyridimium [9,15,16] have been used as counter-ions. CWISE based on bidentate neutral carrier, 4,4′ - di(5-nonyl) -2,2′-bipyridine, was developed for the determination of divalent cadmium[17]. An antibacterial agent, Ciprofloxacin (CF), has been determined by CWISE based on a molecular dispersion of certain 4-quinolones and dioctylphthalate as a plasticizing solvent mediator in an inert poly (vinyl chloride) support[18]. CWISE has been suggested as a useful transducer for developing micro-biosensor. An acetylcholine sensor was constructed with

acetylcholinesterase which was immobilized on a hydrogen-CWISE[19]. Tridodecylamine- and carboxyl- substituted for micro-biosensor[20]. CWISE can be applied adventageously in titration based on ion-pair to the determination of cationic and anionic surfactants[21], and arenediazonium salts in analytical control of azo dyestuff production[22]. The cationic CWISE based on dinonylnaphthalene has been applied to determine the compounds of pharmaceutical and clinical interest[23].

1.4 Aims of the research

1) To construct the iodide coated wire ion selective electrode (Iodide CWISE).
2) To study the properties of the Iodide CWISE.