Chemical sensors for some clinically and environmentally relevant species

A thesis presented

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Chapter 1
Introduction

1.1. General introduction

Ion-selective electrodes (ISEs) are an important class of chemical sensors that has found widespread use today in a wide number of routine applications and more over in handheld bedside testing applications. A key driving force for the development of ISEs was their implication in automated clinical analyzers for the high throughput determination of blood gas and electrolytes in physiological samples. Indeed, developed ISEs are today used in many worldwide clinical analyzers. They are integrated in the state-of-the-art multifunction capital instruments housed in centralized laboratories of hospitals. They also incorporated in many compact bench top systems that have become available in recent years. The success story of ISEs is largely attributed to the creativity and efforts of scientists over the past few decades, at a time when ion-selective electrodes research captured the fascination of a generation of scientists and was displayed as lead articles in top Journals and prestigious books **(Frant and Ross, 1966; Covington, 1980; Ma and Hassan, 1982; Arnold and**

Meyerhoff, 1984; Koryta, 1984; Koryta, 1990; Meyerhoff *et al*., 1996; Bakker, 1997a; Bakker *et al*., 1997b). The commercialization success of the technology was based on extensive research activities. This lead to the development of new ideas (**Baker Review *et al*., 2008**).

1.1.1. Historical background of ISEs

In 1906 Cremer, introduced a novel and simple approach for pH measurement based on the glass electrode (**Cremer, 1906**). This finding was followed by extensive studies on the Nernstian response of the glass electrode **(Haber and Klemensiewicz, 1909)** as well as comparing its response with that of the conventional hydrogen electrode (**Hughes, 1922**). Later, many theories have been described to explain the origin of the glass electrode response to hydrogen ion. The same sensing approach was extended for the selective detection of other cations such as Na^+, K^+, Ag^+, NH_4^+, Tl^+, Li^+ and Cs^+ **(Dole, 1941; Eisenman. et al., 1957; Eisenman, 1962 and 1965; Garrels, 1967)**. All these approaches didn't attain the success that the glass electrode had gained, which enabled it to be considered as the most reliable ion-selective electrode. The first trial for the fabrication of a cation selective electrode based on non-

glass membrane was described by Tendeloo and coworkers (**Tendeloo and Krips, 1957; 1959; Tendeloo and Van der Voort, 1960**). The sensitive membrane was made of calcium oxalate or calcium sorbate supported on paraffin membrane and was sensitive for Ca^{2+} ion. On the other hand, the work for the development of anion selective membrane electrodes was first described in 1937 (**Kolthoff and Sanders, 1937**). Then, Pungor and coworkers had made their analytically useful anion sensitive membrane electrodes for the measurement of chloride (**Pungor, *et al.*, 1964**) and iodide ions (**Pungor, *et al.*, 1965**). The membrane they formulated was prepared by dispersing silver salts in graphite or silicon-rubber inert matrices. In the year 1966, Frant and Ross had introduced their highly selective solid state fluoride electrode based on LaF_3 single crystal doped with europium (**Frant and Ross, 1966**). After that many electrode systems for anions, cations, gases, and compounds have been developed and find a wide spread applications in manual and automated systems of analyses. Every year, a lot of publications appeared in this dynamic field of research.

1.1.2. Sensors

There are three general types of sensors:

(I) Physical sensors: These are sensitive for some physical parameters such as pressure, temperature, force, distance,…etc.

(II) Chemical sensor: (see definition below) these are sensitive to inorganic and organic species.

(III) Biosensor: These measure biological species or utilize such species in their construction.

One of the main interesting areas in analytical chemistry over the last few decades is chemical sensors because of their sensitivity, selectivity and automation feasibility. Chemical sensors are defined by IUPAC recommendation [**Hulancki, *et al*., 1989**] as miniaturized transducers that selectively and reversibly respond to chemical compounds or ions and yield electrical signals which depend on the concentration. The chemical sensors are composed of three basic components: recognizer, transducer and electronic units as shown in Fig. (1.1).The most important component is the recognition unit, since the development of a sensor with high selectivity is dependent primarily on the recognition process. The recognition makes

use of specific chemical reactions such as complexation, ion association, addition, or redox reactions of the analyte species **[Camman, *et al*., 1991].** The chemical recognition step can be transduced by a wide variety of signals including all five forms of energies: electrical, optical, thermal, magnetic and mechanical energies. The third component is the electronic unit (a preamplifier, analogue/digital converter…etc.) which is directly connected to the transducer to suppress electrical noise or external influences caused by the interference of electronics or magnetic fields.

Chemical sensors can be classified according to the type of energy of transduced signal into four groups, electrochemical, optical, thermal and mass sensors. Electrochemical sensors are further classified into, potentiometric (ion selective electrodes), amperometric, voltammetric and conductometric based sensors. The focus of this thesis is on the development of novel polymer membrane ion-selective electrodes for pharmaceutical and food industry applications.

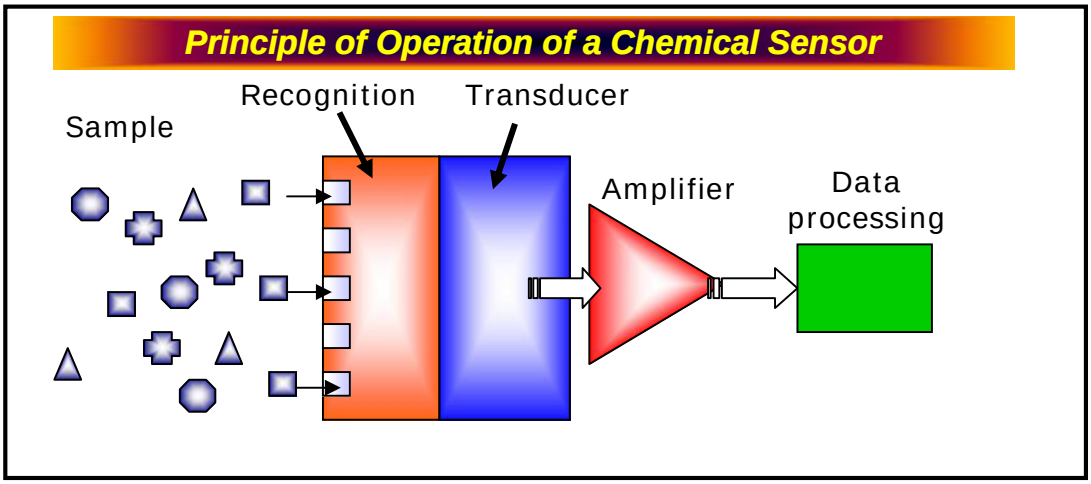


Fig. (1.1): The basic construction and the principle of operation of chemical sensors.

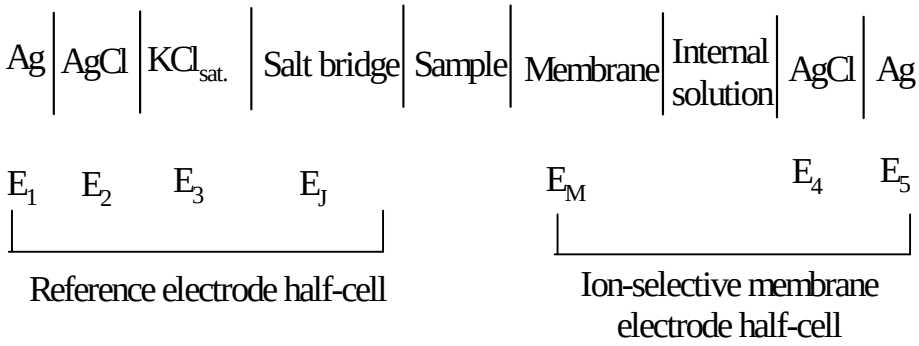
1.2. Ion selective electrodes

Ion-selective electrodes (ISEs) are chemical sensors selective for analyte ions in the presence of various interfering ions from the sample. ISEs include probes that measure specific ions or gases in solution. The basic ISE setup includes a high input impedance voltammeter (capable of reading millvolts), a probe (selective for each analyte of interest), and various consumables used for pH or ionic strength adjustments. The expenses of ISEs are considerably less than other methods, such as atomic adsorption spectrometry or ion chromatography. ISE determinations are not subject to interferences such as

color or turbidity in the sample. Ion-selective electrodes have found wide spread uses especially for the direct determination of ionic species in whole and diluted blood, serum, urine, tissue, and intracellular samples [**Meyerhoff, 1993**]. If ISEs are used in direct potentiometry, they have unique response characteristics compared with other analytical methods and allow the assessment of so called free ion activities. Construction and then application of ion-selective electrode as a potentiometric sensor offers interesting advantages such as simplicity, speed, low cost, and wide linear range **[Ardakani*, et al*., 2002].**

1.2.1. Principle of ion selective electrodes

A measurement in potentiometry is conducted in a two electrode galvanic cell (see Fig 1.2) under zero current conditions. With ion-selective electrodes, one electrode is the reference electrode and the other is the indicator electrode:



When ion-selective electrode is placed in a solution containing the primary ions to which the membrane is selective (due to the interaction of analyte ion with the ion selective membrane) a charge separation at the boundary of the membrane/sample interface is developed. This potential is measured against standard external reference electrode. The electromotive force (EMF) of this galvanic cell is a sum of number of local potential differences, arising at the boundaries [**Bakker, *et al.*, 1997**].

$$EMF = E_{-} + E_{M} + E_{J} \tag{1.1}$$

Where

E_{-} is the external reference electrode potential

E_{J} is the liquid junction potential

E_{M} is the membrane potential

The reference electrode potential is constant at a fixed temperature. The liquid junction potential (E_J) is diminished to zero by using an electrolyte in which the mobilites of cation and anion are nearly equal. Therefore, the measured EMF of the cell can be correlated only to the membrane potential developed at the membrane sample interface, which in turn reflects the activity of the analyte ion (a_i) according to Nernst equation [**Nernst, 1889**]:

$$EMF = E^{-} + \frac{2.303R\ T}{Z_i F}\log a_i \qquad (1.2)$$

Where:

a_i is the activity (mol L^{-1}) of the primary ion of charge Z_i

E^{-} is the standard cell potential

R is the molar gas constant (8.314 JK^{-1} mol^{-1})

T is the absolute temperature

F is the Faraday's constant (96487 C mol^{-1})

In the presence of interfering ions, j, and analyte ion i, the cell potential is given by Nicolsky-Eisenman equation [**Eisenman, 1957; Nicolsky, 1937**]:

$$EMF = E_i^{-} + \frac{2.303RT}{Z_i F}\log(a_i + \sum_i K_{ij}^{pot} a_j^{z_i/z_j}) \qquad (1.3)$$

Where a_i, a_j activity of primary ion of charge Z_i and interfering ion of charge Z_i respectively (mol L^{-1}).

E_i^- standard potential of the cell.

K_{ij}^{pot} potentiometric selectivity coefficient.

Ideal selective membrane electrode responds only to analyte ion without significant influence of interfering ions ($K_{ij}^{pot} = Zero$).

However, in most cases ISEs respond to interfering ions and K_{ij}^{pot} value provide information on how significant is the interference The separate solution method (SSM) is most commonly used for determination of K_{ij}^{pot} which involves the measurements of the cell potential for interfering ion *(ΔE_j)* and analyte ion *(ΔE_i)* solutions with the same concentration **[Zhanget, *et al.*, 1998; Umezawa, *et al.*, 1995].** These values can be used to calculate the selectivity coefficient by substitution in equation (1.3).

$$\log K_{ij}^{pot} = \frac{(\Delta E_j - \Delta E_i)Z_i F}{2.303RT} - \log a_j^{Z_i/Z_j} + \log a_i \qquad (1.4)$$

If the activity and the valance of the primary and interfering ions are the same, the above equation becomes:

$$\log K_{ij}^{pot} = \frac{\Delta E_j - \Delta E_i}{S} \qquad (1.5)$$

Where: *S* is the slope of the calibration curve of the primary ion.

In fixed interference method (FIM), the membrane electrode is calibrated for the analyte in the presence of fixed concentration of the interfering ion. The response curve obtained under these conditions might show a loss of sensitivity at lower (a_i) values. The interaction of the extrapolated linear segments of the response curve gives the activity of the analyte ion. Insertion of the obtained (a_i) value and the known activity of the interfering, ion (a_j), in equation (1.6) gives the selectivity coefficient.

$$\log K_{ij}^{pot} = \log a_i - \log a_j^{Zi/Zj} \qquad (1.6)$$