Ain Shams University
College of Women
For Arts, Science and Education
Chemistry Department

Updating Microanalytical Methods for the Determination of Some Heterocyclic Compounds

A Thesis Submitted for the Degree of Master
In
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Presented
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Approval of Chemistry Department Council / /2009

Approval of Faculty Council / /2009

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جامعة عين شمس
كلية البنات للأداب والعلوم والتربية
قسم الكيمياء

طرق تحليلية ميكروئية حديثة لتقدير بعض المركبات غير متجانسة الحلقة

رسالة مقدمة إلى
كلية البنات للأداب والعلوم والتربية
جامعة عين شمس

من
عبدالله علي عبدالله احمد
بكالوريوس علوم (كيمياء)

للحصول على
درجة الماجستير فى العلوم
(الكيمياء غير العضوية و التحليلية)

تحت إشراف

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٢٠٠٩

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Abdallah Ali Abdallah

DEDICATION

To

My distinguished parents

I do appreciate my God

For giving me wonderful parents

Who are always supporting me

in all my life .

I also thank my family

For continuous encouragement and help.

And many thanks to my wife, son and daughters

Chapter I

General introduction

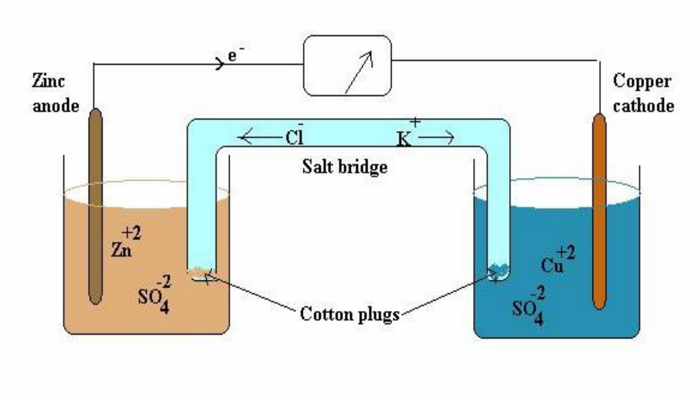
I.1 Introduction

Chemical sensors are miniaturized analytical devices, which can deliver real-time and on-line information on the presence of specific compounds or ions in complex samples. 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. Usually an analyte recognition process takes place followed by the conversion of chemical information into an electrical or optical signal. Among various classes of chemical sensors ion-selective electrodes (ISE) are one of the most frequently used potentiometric sensors during laboratory analysis as well as in industry, process control, physiological measurements, and environmental monitoring. The principle of ion-selective electrodes operation is quite well investigated and understood.

An ion-selective membrane is the key component of all potentiometric ion sensors. It establishes the preference with which the sensor responds to the analyte in the presence of various interfering ions from the sample. If ions can penetrate the boundary between two phases, then an electrochemical equilibrium will be reached, in which different potentials in the two phases are formed. 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 activities of this target ion in these phases. 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 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, fast response, low cost, and wide linearity range. **[Ardakani, et al., 2002].**

I.2 Principle of Potentiometry

Potentiometry is a method of analysis developed from galvanic cell basis, it is a technique that uses electrode to measure potential difference that provide chemical information. In the simplest case an analyte participates in the chemical reaction of a galvanic cell. Fig.(I.1). Imagine a solution containing an electroactive species(the analyte) whose activity (concentration) we wish to measure. An electroactive species is one that can donate or accept electrons from an electrode. we can turn the unknown into a half-cell by inserting an electrode (such as a Pt-wire)into the solution to transfer electrons to or from the analyte. Because this electrode responds directly to the analyte ,it is called the indicator electrode . we then connect this half-cell to a second half-cell via a salt bridge. The second half-cell has a fixed composition that it will have a constant potential, the second half-cell is called a reference electrode. The cell voltage is the difference between the variable potential that responds to analyte activity and the constant potential of the reference electrode.



Figure(I.1) Galvanic Cell Diagram

I.2.1Reference Electrodes

A reference electrode must have a potential that is independent of the solution concentration in which it is immersed and that does not change significantly when a small amount of current is passed through it .the large majority of electrochemical measurement are made with three different reference electrodes

I.2.1.1 SHE(Standard Hydrogen Electrode)

This is the ultimate reference agent which the potential of all other electrodes are measured either directly or indirectly. It is extremely reproducible and develops a potential that is very close to that predicted theoretically but it isn’t very convenient. The actual electrode surface is quite fragile and should not be touched, scraped or allowed to dry out, H_2 gas and associated pressure and flow regulators are required, so most routine measurement is made with one of the next two electrodes.

I.2.1.2 Saturated Calomel Electrode

The working part of the electrode consists of a Pt wire immersed in a slurry of solid mercurous chloride (i.e calomel),liquid Hg ,and aqueous saturated KCl contained in an inner tube, the outer tube is merely a saturated KCl salt bridge that permits the entire assembly to be placed directly in the solution to be measured . The salt bridge tube has a small porous asbestos thread or ceramic fiber at the bottom that permits electrode contact to be made between one side of the salt bridge and the tested solution without allowing any appreciable flow of liquid between the two solutions. The opening near the top of the outside tube is for addition or replacement of the KCl solution. mercurous chloride is reduced and mercury element is oxidized in the reversible electrode half-reaction.

$$Hg_2Cl_2(s) + 2e \rightleftharpoons 2Cl^- + 2Hg$$

Since the activity of the liquid Hg and solid Hg_2Cl_2 are both unity, the potential of the electrode is described by Nernst equation as

$E=E^o{}_{Hg2Cl2}$ -0.0592/ log (1)$[Cl^-]^2$/1

The concentration of Cl^- is fixed (i.e saturated KCl is 4.2M), so the electrode potential remains constant as long as the salt bridge solution is not permitted to mix with the test solution.

I.2.1.3 Silver-Silver Chloride Electrode

Consists of a Ag wire coated with AgCl that is immersed in a KCl solution saturated with AgCl

AgCl(s) +e(half-reaction) $\rightleftharpoons$ Ag(s) + Cl^-

$E=E^o{}_{AgCl/Ag+}$ -0.0592/2 log (1) $[Cl^-]$/1

The potential of the electrode depends only on the concentration of Cl^-, the advantages of this electrode over the calomel electrode are that it can be made very small and can be used at somewhat higher temperatures.

I.2.2 Indicator Electrode

Indicator electrodes for potentiometric measurements are classified according to the mechanism by which the electrode potential is produced into

I.2.2.1 Metal Indicator Electrodes

Based on the development of an electrical potential in response to a redox reaction at the metal surface. The most common metal indicator electrodes are the most widely used electrodes, a metal electrode works best when its surface is large and clean. A brief dip in concentrated nitric acid, followed by a rinse with distillated water, is often effective for cleaning an electrode.

I.2.2.2 Ion Selective Electrodes (Membrane Indicator Electrodes)

Based on selective migration of one type of ions across the electrode membrane, it generates an electrical potential due to difference in concentration of ions, there isn’t redox reaction.

I.3 Principle of Ion Selective Electrodes.

Ion-selective membrane electrodes are investigated under zero-current conditions in a galvanic cell see Fig(I.2) such as the following:

$$\xrightarrow[\text{Reference electrode half cell}]{\text{Ag/AgCl /KCl (sat)/ salt bridge/sample}}$$

$$\xrightarrow[\text{Ion-selective membrane electrode half cell}]{\text{/membrane/internal solution/AgCl/Ag}}$$

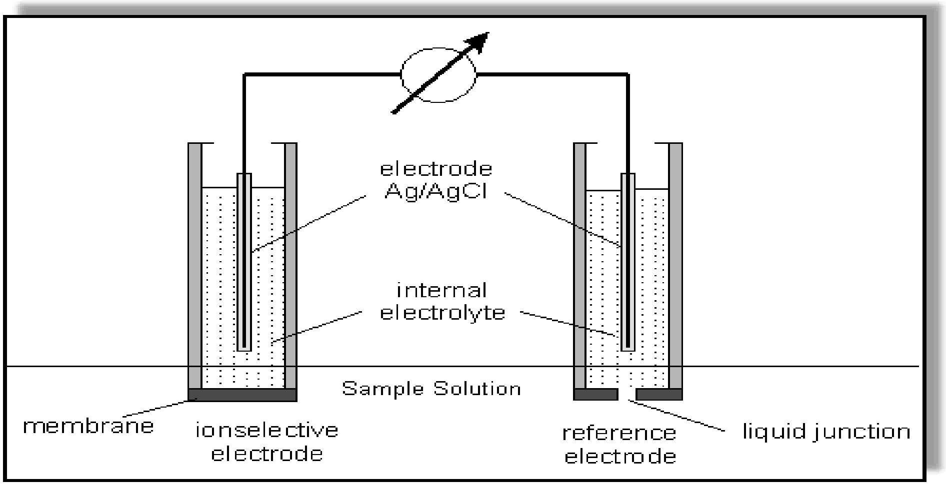


Fig. (I.2) Schematic Diagram of Membrane Electrode Measuring Circuit and Cell Assembly.

When the ion-selective electrode is placed in a solution containing the primary particular 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 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**]

$$EMF = E_O + E_M + E_J \qquad (I.1)$$

Where E_o 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 the cation and the anions have nearly equal values. 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**]:

$$\text{EMF} = E^o + \frac{2.303RT}{Z_i F} \log a_i \qquad (I.2)$$