



**Shiraz University
Faculty of Sciences**

M.Sc. Thesis in Analytical Chemistry

**Carbon nanotube composite coated stainless steel disk electrode
with polypyrrole film as ion-to-electron transducer for
determination of Hg(II)**

AND

**A simple and sensitive bioassay based on scanner spectroscopy
for detection of glucose by using silver nanoparticles as
colorimetric probes**

By

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In The Name Of God

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ELECTRODE WITH POLYPYRROLE FILM AS ION-TO-ELECTRON TRANSDUCER
FOR DETERMINATION OF Hg(II)**

AND

**A SIMPLE AND SENSITIVE BIOASSAY BASED ON SCANNER SPECTROSCOPY
FOR DETECTION OF GLUCOSE BY USING SILVER NANOPARTICLES AS
COLORIMETRIC PROBES**

BY

Mohammad Reza Shahriyari

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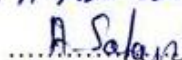
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In the name of GOD

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Dedicated to:

My Father and My Mother

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In the Name of God, the Compassionate the Merciful

Thanks GOD for awarding me the chance of thoughts.

I would like to express my deepest sense of gratitude to my supervisors Prof. A. Abbaspour and Dr. M. Akhond for his patient guidance, constant support, encouragement and excellent advice throughout this study and thanks are due to the committee members, Prof. A. Safavi, Prof. G. Absalan and Dr. M. M. Doroodmand, for their careful review of the manuscript and helpful suggestions and corrections.

I should express my special thanks to my family for their help in my life.

ABSTRACT

Carbon nanotube composite coated stainless steel disk electrode with polypyrrole film as ion-to-electron transducer for determination of Hg(II)

AND

A simple and sensitive bioassay based on scanner spectroscopy for detection of glucose by using silver nanoparticles as colorimetric probes

BY

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An ion-selective electrode for mercury(II) ion is fabricated based on primary surface electrodeposition of polypyrrole on stainless steel, followed by coating multiwall carbon nanotubes (MWCNTs), poly(vinyl chloride) (PVC) composite membrane modified with a new Enamine ionophore. Polypyrrole film was prepared as an intermediate layer of solid contact electrode, because of its stability and conductivity. The combination of conducting polymers with those of MWCNTs leads to an improved performance of the resulting sensing devices. The electrode showed a Nernstian slope of 29.34 ± 0.25 mV decade⁻¹ over a wide concentration range of 5.0×10^{-7} to 1.0×10^{-2} mol L⁻¹ of Hg(NO₃)₂ with detection limit of 1.4×10^{-7} mol L⁻¹. The prepared electrode exhibited a very good selectivity toward Hg(II) ion over a wide variety of other metal ions. This nanocomposite membrane electrode operates well in the pH range of 3.7 – 8.8 and can be used for at least two months without observing any considerable deviation. The practical applicability of this sensor as an indicator electrode in potentiometric titration of Hg(II) ions with EDTA and in titration of mixed halides are demonstrated. This electrode also was successfully applied for determination of mercury in river water sample.

A novel biosensor based on silver nanoparticles decolorizing for the photometric determination of glucose was developed. The method is based on change in the chemical properties of silver nanoparticles, used here as chromogenic indicators, in response to the analyte. In the presence of glucose, the enzymatically generated hydrogen peroxide induces a visual color change in the silver nanoparticles immobilized onto the bioactive sensing paper, from yellow to colorless, in the redox manner. The results showed that this bioassay is sufficiently sensitive to allow for detection of glucose over the concentration range of 5.0×10^{-6} to 1.0×10^{-1} M with a detection limit of 8.6×10^{-7} M at pH 7.5. Examples of analytical application were demonstrated for the detection of glucose in urine.

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GLOSSARY OF ABBREVIATIONS

(a) General abbreviations:

CDEs	Coated disk electrodes
CSSDs	Coated solid-state devices
CNTs	Carbon nanotubes
CCD	Charged coupled device
Const.	Constant
DL	Detection limit
FID	Fix interference method
ISFETs	Ion-selective field effect transistors
ISE	Ion-selective electrode
IUPAC	International union of pure and applied chemistry
MPM	Matched potential method
Sat'd	Saturated
SSM	Separate solution method
SWCNTs	Singlewall carbon nanotubes
TLC	Thin layer chromatography

(b) Abbreviations used for chemicals:

DBP	Dibutyl phthalate
DBS	Dibutyl sebacate
DMS	Dimethyl sebacate
GO _x	Glucose oxidase
MWCNT	Multi wall carbon nanotube
o-NPOE	orto- nitrophenyl octyl ether
ppy	Poly pyrrole
PVC	Poly(vinyl chloride)
Ag-NPs	Silver nanoparticles
THF	Tetrahydrofuran

CHAPTER ONE

INTRODUCTION

1.1 Potentiometry

Since the membrane is usually interposed between the sample and an inner reference electrolyte, it is common to divide the membrane potential into three separate potential contributions, namely the phase boundary potential at both interfaces and the diffusion potential within the ion-selective membrane [1-3]. While the potential at the membrane/inner filling solution interface can usually be assumed to be independent of the sample, the diffusion potential within the membrane may become significant if considerable concentration gradients of ions with different motilities arise in the membrane. Historically, there have been some debates about the relevance of the membrane diffusion potential [4]. While one reason was that no obvious explanation could be found for the observed permselectivity, another was the excellent correlation between the potentiometric and transport selectivity of such membranes. As a consequence rather complex models have been used [5] that often make an intuitive understanding difficult.

The theory of ion-selective electrode (ISE) response is well-established especially owing to the pioneering work of Eisenman's group [5] and others [6]. As mentioned before, the membrane potentials can be described as the sum of the two-phase boundary potentials and the diffusion potential within the membrane [1, 2]. The latter being negligible in electrodes of practical relevance [7, 8].

1.2 Ion-selective electrodes (ISE)

The basic theory of the response of solvent polymeric membrane electrodes was developed many decades ago [1, 9-11]. However, the relevance of the various contributions to the membrane potential has been the subject of long-lasting debates [3, 4]. Only since it had been fully recognized that, such membranes have intrinsic cation-exchanger properties very intuitive models could be developed. Indeed, neutral-carrier based membranes with poly(vinyl chloride) as membrane matrix without the addition of lipophilic ionic sites have been shown to give cationic response only because of anionic impurities present in the membrane [4, 12, 13].

In fact, membranes based on rigorously purified membrane components yielded ISEs that, even with the extremely selective valinomycin as neutral ionophore, had completely lost their cation permselectivity [14, 15] showing that the present of ion-exchanger sites is crucial for the functioning of these sensors.

1.3 Types and characteristics of ion-selective electrodes

Electrodes containing membranes having a specific response for a particular ion is known as ion-selective electrodes.

These membranes can conveniently be classified as follows:

- 1) Homogeneous solid-state membrane electrodes.
- 2) Heterogeneous solid state membrane electrodes [16].
- 3) Glass membrane electrodes.
- 4) Gas-sensing membrane electrodes [17].
- 5) Liquid and polymer-matrix membrane electrodes.

1.3.1 Homogeneous solid-state membrane electrodes [17, 18]

The membranes of these electrodes are based on various crystalline materials, the forms include single crystals [19, 20], cast or sintered materials, pressed polycrystalline pellets [21, 22] as well as heterogeneous combinations of precipitates held in hydrophobic polymer binders.

1.3.2 Heterogeneous solid state membrane electrodes

The membranes of these electrodes consist of electrochemically active materials in the form of organics and inorganic salts of ion exchangers, embedded in an inert supporting material which acts as a binder [23-25]. These binders are usually polymeric substances.

1.3.3 Glass membrane electrodes

Glass electrodes are relatively well understood in terms of their function and response [26]. The membrane of these electrodes is made by melting mixtures of some elements oxides of group III and IV (e.g. Al, Si) with the oxides of some elements of group I and II (e.g. Na, Ca).

The pH glass electrode was the first ion-selective electrode discovered and is still one of the most important standard laboratory devices. Its unsurpassed specificity for hydrogen ions is due to the strongly basic nature of the charged silica groups residing in the glass network.

The response of the glass membrane is determined by the composition of the glass. Corning O15 glass has been used for many years in pH electrodes.

The glass consists of approximately 22% Na_2O , 6% CaO and 72% SiO_2 . Pure SiO_2 is essentially an insulator that is unresponsive to pH. The addition of Na_2O to the glass formulation disrupts the silica surface so that negatively charged oxide sites are paired with Na ions.

In an ion-selective glass electrode the glass membrane is viewed as consisting of at least three distinct regions:

Test solution // Hydrated glass layer / Dry glass layer / Hydrated glass layer // Internal solution

A considered glass electrode contains protons that have replaced sodium or other ions in the hydrated surface, and this reservoir of protons can exchange with cations in solution. The potential at a glass-solution interface is regarded as arising from the cation transfers going on continuously at this interface.

Special high pH electrodes are constructed of glasses containing Li_2O , which give better selectivity coefficients in favor of hydrogen ions and less interference from alkali metal ions at high pH. For glass electrodes generally, the value of $K_{\text{H}^+, \text{Na}^+}$ is small. Varying the composition of glass can alter the response to various univalent cations [27].

1.3.4 Liquid and polymer-matrix membrane electrodes

Liquid membrane selective electrodes are those in which the membranes are composed of water-immiscible organic solvents. This type of membranes is very important because they permit the direct potentiometric determination of the activities. Neutral carrier ionophore may also be used as the membrane material. So the compositions of membrane are formed from ion exchanger, ion pair compounds and neutral carriers. And the solvent with which the membrane is saturated must be quite insoluble in water; it must have a low vapor pressure and must have a sufficiently high viscosity. Furthermore if the dielectric constant of the liquid with high molecular weight is low, it must be available in sufficiently pure form at a reasonable price, and should be high stable. Liquid membrane electrodes are divided into two categories:

A. Organic ion exchangers

B. Neutral carrier based ISEs

The organic ion exchanger membranes can be classified to cationic [28-37] and anionic [38-44] ion exchangers, the membranes of these electrodes consist of an organic, water immiscible liquid phase incorporating mobile ionic or ionogenic compounds, such as hydrophobic acids, bases, and salts. The liquid ion exchanger and poly(vinyl chloride) are dissolved in a solvent such as tetrahydrofuran. Evaporation of the solvent leaves a flexible membrane, which can be cut and cemented to the end of a glass or plastic tube [45].

Neutral carrier liquid membrane electrodes [46], where the membrane is usually formed from an organic solution of electrically neutral, ion-specific complexing agents (ion carriers, ionophores) held in an inert polymer matrix.

The schematic diagram of the membrane portion of a liquid membrane ISEs that is in contact with internal and sample aqueous solution of analyte I^+ and its counter anion A^- is shown in Fig. 1.1. [47]

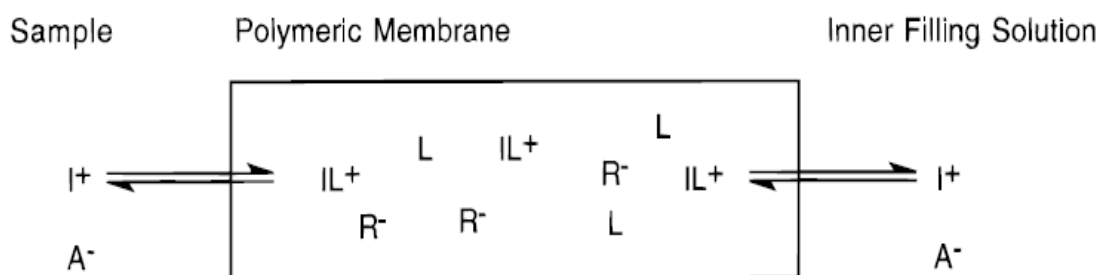


Figure 1.1 Schematic view of the equilibria between sample, ion-selective membrane and inner filling solution. Electrically neutral carrier (L), anionic sites (R^-), analyte (I^+) and its counter anion (A^-).

The neutral carrier ionophore (L) can react with I^+ at each membrane-solution interface and can extract I^+ into the membrane as IL^+ . The hydrophobicity of R restricts R and IL^+ to the membrane phase. The extraction of I^+ into the membrane occurs a positive membrane potential at each interface due to the charge separation when i) I^+ is extracted into the membrane in the form of IL^+