Novel Electrochemical Sensors for Quantification of Some Industrial Products and Environmental Pollutants

A Thesis Submitted in Partial Fulfillment of the Requirements of the M.Sc. Degree In Analytical Chemistry

Presented by

Heba Abd El- Naby Marzouk
B.Sc. (2007)

Chemistry Department Faculty of Science Ain Shams University



Ain Shams University Faculty of Science Chemistry Department

Novel Electrochemical Sensors for Quantification of Some Industrial Products and Environmental Pollutants

Supervised by:

Prof. Dr. Saad S. M. Hassan (D. Sc.)

Professor of Analytical Chemistry, Chemistry Department Faculty of Science, Ain Shams University

Dr. Ayman Helmy Kamel

Assistant Professor of Analytical Chemistry, Chemistry Department Faculty of Science, Ain Shams University

Chemistry Department
Faculty of Science
Ain Shams University
2013



Ain Shams University Faculty of Science Chemistry Department

Novel Electrochemical Sensors for Quantification of Some Industrial Products and Environmental Pollutants

By Heba Abd El- Naby Marzouk

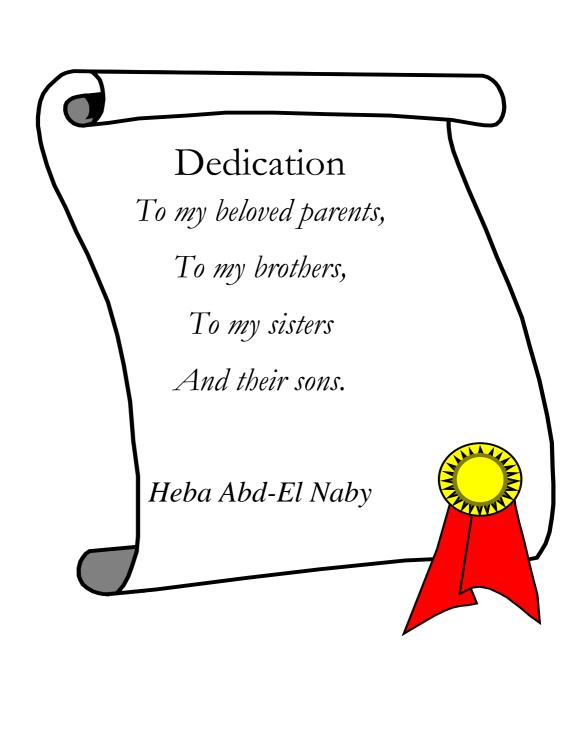
Approved
(D. Sc.)
nistry Department, Faculty of
••••••

Assistant Professor of Analytical Chemistry, Chemistry Department Faculty of Science, Ain Shams University

Head of Chemistry Department

Prof. Dr. Maged Shafik Antonious Nakhla

2013



ACKNOWLEDGEMENT

I would like to express my sincere gratitude and my hearty appreciation to **Prof. Dr. Saad S. M. Hassan, Ph.D., D.Sc.** Prof. of Analytical Chemistry, Chemistry Department, Faculty of Science, Ain Shams University for all facilities and for fruitful discussions. Prof. Dr. Saad S. M. Hassan was always so kind to follow up the progress of the work with keen interest, guidance and valuable criticism. It is great honor to work under his direct supervision.

Also, I wish to acknowledge my sincere gratitude and indebted to **Dr. Ayman Helmy Kamel** Associate Prof. of Analytical Chemistry, Department of Chemistry, Faculty of Science, Ain Shams University, for his devoted efforts and continuous guidance. He was always giving me valuable advice, encouragement and continuous helps during this research work.

Finally, my great and deep gratitude for all my colleagues in the lab for their kind help and valuable discussions.

Contents

Chapter (I) Principles and Characterization of

Ion-Selective Electrodes

	Page
1.1. Introduction.	1
1.2. Principles of ISEs Response and Componants.	3
1.2.1 Ion-selective membrane components.	5
1.2.2. Ionophores(recognition element).	6
1.3.Response Mechanism of ISE.	9
1.4. Characterization of an Ion-Selective Electrode.	18
1.4.1. Detection limit.	18
1.4.2. Lower detection limit.	18
1.4.3. Upper detection limit.	19
1.4.4.Selectivity of ion –selective electrodes.	20
1.5. Measurements of Selectivity Coefficients.	21
1.5.1. Mixed solution methods.	21
1.5.1.1. Fixed interference method (FIM).	21
1.5.1.2. Fixed primary ion method (FPM).	22
1.5.1.3. Two solutions method (TSM).	22
1.5.1.4. Matched potential method (MPM).	23
1.5.2. Separate solution methods.	23
1.5.2.1. Separate solutions method $(a_i=a_j)$ (SSM).	23
1.5.2.2. Separate solutions method $(E_i = E_j)$ SSM.	24
1.6. Classification of ISEs.	24
1.6.1. Homogeneous solid membrane electrodes	

(fixed ion-exchange Sites).	26
1.6.1.1. Glass Electrode.	26
1.6.1.2. Crystalline and polycrystalline membrane electrodes.	28
1.6.1.2.1 Single Crystal Membrane: The Fluoride electrode.	29
1.6.1.2.2. Compact Polycrystalline Membranes.	31
1.6. 2. Heterogeneous solid state membrane electrode.	31
1.6.3. Liquid membrane sensors.	33
1.6.4 Modified ISEs.	36
1.6.4.1. Enzyme electrodes.	36
1.6.4.2. Coated wire sensors (CW).	36
1.7. Advantages of ion selective electrode.	38
1.8. References.	41
Chapter (II)	
New Potentiometric Sensors Based on Selective Recognition	n Sites
for Determination of Ephedrine in Some Pharmaceuticals	s and
Biological Fluids	
2.1 Introduction	48
2.1.1Chromatographic methods.	49
2.1.2 Capillary electrophoresis.	52
2.1.3 Spectrophotometry.	54
2.1.4 Electrchemical methods.	54
2.2.Experimental.	58
2.2.1 Equipment.	58
2.2.2 Reagents and materials.	60
2.2.3. Sensor and detector preparation.	60

2.2.4. EMF measurement and sensor calibration.	62
2.2.5. Determination of ephedrine in pharmaceutical dregs.	63
2.2.6 Determination of ephedrine in biological fluids.	64
2.3 Results and discussion.	65
2.3.1 Performance characteristics of ephedrine sensors.	65
2.3.2. Origin of sensor response.	67
2.3.3. Method validation.	69
2.3.3.1. Linear range, sensitivity and lower detection limit.	69
2.3.3.2. Accuracy and precision.	70
2.3.3.3. Effect of pH.	73
2.3.3.4. The influence of response time.	75
2.3.3.5. Sensors selectivity.	76
2.3.4. Determination of ephedrine (EPD ⁺).	81
2.3.5. Flow injection measurement (FIA) of ephedrine.	83
2.3.6.Determination of ephedrine (EPD ⁺) in biological fluids.	85
2.4. Conclusions.	87
2.5. References.	89
Chapter III	
Flow Through Potentiometric Sensors for Cetrizine Assess	ement
in Pharmaceutical Products	
3.1. Introduction.	93
3.2. Experimental.	105
3.2.1. Equipments.	105
3.2.2. Reagents and materials.	105
3.2.3 Sensor preparation and EME measurements	106

3.2.4. Flow injection setup and measurements.	108
3.2.5. Analytical application.	110
3.3. Results and discussion.	111
3.3.1. Characterization of cetirizine ion –pair complexes.	111
3.3.2. Response characteristics of the electrode system.	116
3.3.3. Effect of pH and response time.	119
3.3.4. Selectivity.	121
3.3.5. Hydrodynamic monitoring of citirizine.	123
3.3.6. Assessment of cetirizine in Dosage forms.	128
3.4. Conclusions.	132
3.5. References.	133
Chapter IV	
Novel Potentiometric Sensors for Batch and Continuous	
Monitoring of Alizarin Red S Dye and Their Application t	0
Aluminum Assessment	
4.1. Introduction.	136
4.2. Experimental.	145
4.2.1. Apparatus.	145
4.2.2. Chemicals and reagents.	146
4.2.3. Sensors fabrication and EMF measurements.	146
4.2.4. Flow injection set up for alizarin determination.	147
4.2.5. Aluminum determination.	148
4.3. Results and discussion.	149
4.3.1. Performance characteristics of the sensors.	
	149

4.5. References.	167	
4.4 Conclusions.	166	
4.3.7. Analytical assessment of aluminum.	164	
4.3.6. Potentiodynamic monitoring of aluminum.	159	
4.3.5. Flow injection measurement (FIA).	157	
4.3.4. Selectivity.	155	
4.3.3. Membrane conditioning and Response time.	154	

List of Tables

Chapter(II)	page
Table (2.1) Potentiometric response characteristics of	71
EPD membrane sensor based on triacetyl-β-CD/PVC	
ionophore and carboxylated PVC membrane sensor.	
Table (2.2) Potentiometric selectivity coefficients	80
(Log $K^{pot}_{EPD,B}$) of ephedrine PVC membrane sensors.	
Table(2.3) Determination of ephedrine in some	82
pharmaceutical preparations using triacetyl β -CD/DOS-	
TPB membrane based sensor.	
Table (2.4)Determination of ephedrine in some biological	86
samples using triacetyl β-CD/DOS-TPBmembrane based	
sensor.	
Chapter (III)	
Table (3.1) General performance characteristics of	104
some potentiometric cetirizine membrane sensors.	
Table (3.2) Potentiometric response characteristics of	118
cetirizine membrane based sensors .	
Table (3.3) Selectivity coefficient values for cetirizin	123
selective electrodes as calculated by separate solution	
method.	

Table (3.4) Potentiometric response characteristics of	124
cetirizine membrane sensors based on Cet/PMA,	
Cet/TPB and Cet/Ren ion pairs using FI operation	
Table (3.5) Static determination of cetirizine in some pharmaceutical formulations using the proposed sensors.	130
Table (3.6) Hydrodynamic determination of cetirizin.	131
in some pharmaceutical formulations using the proposed	
sensor.	
Chapter (IV)	
Table(4.1) Potentiometric response characteristics of	151
alizarin dye membrane based sensors.	
Table(4.2) Potentiometric selectivity coefficients	156
(Log K ^{pot} AR, B) of alizarin PVC membrane sensors.	
Table (4.3) Potentiometric determination of aluminum	165
in some pharmaceutical and water samples using the	
proposed method and ICP technique.	

List of Figures

Chapter (I)	Page
Fig.(1.1) The basic construction and the principle of operation	4
of chemical sensors.	
Fig.(1.2) Chemical structures of some well-known	9
cation selective ionophores.	
Fig.(1.3)Schematic representation of a typical potentimetric	11
cell. The diaphragm depicted on the left electrode (Ion-	
Selective Electrode) is recommened for modern ISEs optimized	d
for measurements of trace levels.	
Fig. (1.4) Simple structure of the membrane mechanism	13
where β sample side, α the internal solution side and σ	
interior the membrane.	
Fig.(1.5) Typical response curve of an ion selective	17
electrode for a monovalent ion.	
Fig. (1.6) Sodium ions associated with fixed silicate.	27
groups at the surface of the glass electrode.	
Fig. (1.7) Hydrated surface layers of glass membrane.	28
Fig.(1.8) Structure of poly(vinyl chloride)(PVC) ,Tecoflex	34
polyurethane (PU),dioctylsebacate(DOS), o-nitrophenyl	
octylether (o-NPOE) and o-nitrophenyl phenylether (o-NPPE).	
Fig. (1.9) Different kinds of anion-selective species that can	35
be doped in conventional polymer membrane anion electrodes	

Chapter (II	hapter (II)
-------------	-------------

• ` '	
Fig(2.1)Chemical structure of Ephedrine hydrochloride.	58
Fig. (2.2)Manifold of the two channel FIA set up used	59
for the determination of EPD,A, tris buffer carrier solution	
of pH4.7; B, peristaltic pump; C, pulse damper; D,sample	
injection valve; E, flow injection detector; coated	
wire iodide membrane; F, reference electrode; G, data	
acquisition system; H, laptop computer.	
Fig.(2.3) Chemical structures of α, β, γ -cyclodextrin.	67
Fig.(2.4) Effect of membrane plasticizers on the potentiometric	72
response of EPD+ sensors: (A) Triacetyl-β-CD/PVC and	
(B) PVC-COOH based membranes in 10-2 mol L-1 tris buffer	
of pH 7.4.	
Fig (2.5) Effect of pH on the potentiometric response of EPD ⁺	74
sensors: (A) Triacetyl-β-CD/PVC and (B) PVC-COOH based	
membranes.	
Fig.(2.6) (■) Time response of carboxylated PVC membrane	76
based sensor, (•) time response of triacetyl-β-CD/PVC	
membrane based sensor.	
Fig. (2.7): Transient potentiometric signals of ephedrine using	84
triacetyl- β -CD/PVC+DOS based membrane detector.	
Conditions: carrier solution, 10 ⁻² mol L ⁻¹ tris buffer of	
pH 7.4; flow rate, 3 mL min $^{-1}$; injection valve100 μ L. Inset:	
calibration graph obtained under hydrodynamic mode.	
Fig. (2.8): Effect of the flow rate on the response of triacetyl	84
-β-CD/PVC membrane in FIA system.	

Chapter	III
---------	-----

Fig.(3.1) chemical structure of cetirizine hydrochloride.	103
Fig. (3.1) Schematic diagram of the flow injection system.	110
P: peristaltic pump, S:sample, C:buffer carrier solution,	
I:injection valve, GE:grounding electrode, ISE:Cetirizine	
selective electrode, RE: reference electrode, W:waste,	
mV: deci/milli-voltammeter, R:data acquisition system	
connected to a compute.	
Fig. (3.4)FTIR of PMA.	113
Fig. (3.5)FTIR of Cet /PMA complex.	113
Fig. (3.6) Chemical structure of Cet/PMA ion pair complexe.	113
Fig. (3.7)FTIR of TPB.	114
Fig. (3.8)FTIR of Cet/TPB complex.	114
Fig. (3.9) Chemical structure of Cet/TPB ion pair Complexe.	114
Fig. (3.10)FTIR of Ren.	115
Fig. (3.11)FTIR of Cet/Ren complex.	115
Fig. (3.12) Chemical structure of Cet/Ren ion pair Complexe.	115
Fig. (3.13) Potentiometric response of cetirizine membrane	117
based sensors plasticized in DOP.	
Fig.(3.14) Influence of pH on potentiometric respons of (A)	120
Cet/PMA; (B) Cet/TPBand(C) Cet/Ren membrane based sensors.	
Fig. (3.15) Influence of response time on potentiometric	121
response of (A) Cet/PMA; (B) Cet/TPB (C) Cet/Ren	
membrane based sensors.	