

Ain Shams University
Faculty of Science
Chemistry Department



New Nano Optical Sensors for the assessment of Some Materials of biological Activities in Human Body.

Presented by
Ibrahim Atfi Ibrahim
A Thesis Submitted

To
Faculty of Science
In Partial Fulfillment of the Requirements for
The Degree of Master of Science
(Analytical Chemistry)

Chemistry Department
Faculty of Science
Ain Shams University
(2018)



APPROVAL SHEET FOR SUBMISSION

Title of M.Sc. Thesis

**New Nano Optical Sensors for the assessment of Some
Materials of biological Activities in Human Body.**

By

Ibrahim Atfi Ibrahim

B.Sc.in major chemistry, Faculty of science

Ain Shams University

2005

The thesis has been approved for submission by the supervisors:

Prof.Dr. Mohamed Said Attia

Professor of Analytical Chemistry,

Faculty of Science,

Ain Shams University

Dr. Ahmed Osman Youssef

Associate Professor of Analytical Chemistry,

Faculty of Science,

Ain Shams University

Prof.Dr./Ibrahim H.A.Badr
Chairman of Chemistry Department

Outlines

Chapter one

Introduction

Chapter Two

Studying of Eu^{3+} sensor for different Cyclines at optimum conditions to select the best sensor for the determination of alpha fucosidase enzyme .

Chapter Three.

Highly sensitive and selective spectrofluorimetric determination of Activity of Alpha Fucosidase in serum samples using Eu^{3+} -Tetracycline doped in sol-gel matrix.

Chapter Four.

Gatifloxacin assessment by the Enhancement of the Green Emission of Optical Sensor Tb^{3+} Doped in Sol-Gel Matrix.

Contents

Title	Page No.
Acknowledgement	i
Aim of the work	ii
List of Abbreviations.	iii
List of Figures.	iv
List of Tables.	v

Chapter (I) Introduction.

Title	Page No.
1.1. Nanotechnology.	1
1.2. Optical Sensors.	2
1.2.1. Optical Sensing Schemes.	3
1.2.2. Materials for Optical Chemical Sensors and Biosensors	3
1.2.3. Enzyme-Based Biosensors.	5
1.2.4. Introduction of Lanthanide.	6
1.2.4.1. Basis for Lanthanide Single-Molecule Magnets	8
1.2.4.2. Magnetism of Lanthanides.	9
1.2.4.3. Magnetism of Free Lanthanide Ions.	10
1.2.4.4 Spin–Orbital Coupling and Anisotropy of Free Lanthanide Ions	11
1.2.4.5. The electronic shielding of the f-orbitals of lanthanides is quite weak.	15
1.2.4.6. Energy levels and f–f absorption spectra of lanthanides	17

Title	Page No.
1.2.4.7. Intraconfigurational 4fN→4fN Transitions	17
1.2.5. Radiative and non-Radiative transitions in trivalent lanthanide ions.	22
1.2.5.1. Energy-Level Structures of Free Lanthanide Ions	22
1. 2.5.2. Radiative transitions.	27
1.2.5.3. Non-Radiative relaxation of excited lanthanide ions	29
1.2.6. Energy Transfer and Migration	31
1.2.7. Luminescence	32
1.2.8. luminescent Lanthanide Complex	35
1.2.8.1. Energy transfer in lanthanide complexes (antenna effect)	38
1.2.8.2. Size Effect on the Luminescence of Lanthanide Ions in Nano particles	39
1.2.9. Properties of Cyclines.	40
1.2.10. Solvent effect	41
1.2.10.1. Influence of the solvent on the intensity of absorption spectra	42
1.2.11. Analytical probes	43
1.2. 12. Fluorescence Quenching	46
1.2.12.1. Types of Fluorescence Quenching	47
1.2.13. Advantages of fluorescence spectroscopy	52
1.2.14. Literature review	52
1.2.15. References	56

Chapter (2).

Spectrofluorimetric Determination of different Cyclines by using Eu^{3+} ion in pharmaceutical and Serum Samples.

Title	Page No.
2.1. Introduction.	64
2.2. Experimental.	65
2.2.1. Apparatus.	65
2.2.2. Materials and reagents.	65
2.2.3. General procedures	67
2.2.3.1. Preparation of Different –Cycline complexes in the Solution.	67
2.2.3.2 Calibration Curves of (Eu (III)-Cyclines) Complexes $1 \times 10^{-4} \text{M}$.	68
2.3. Determination of different Cyclines in Pharmaceutical Preparations.	68
2.4. Result And Discussion.	71
2.4.1. Spectral Characteristic of the ligend and Complex.	71
2.4.1.1. Absorption Spectra	71
2.4.1.2. Emission Spectra	72
2.4.2. Molar ratio	73
2.4.3 Effect of Experimental Variables	75
2.4.3.1 Effect of Solvent	75
2.4.3.2. Effect of pH on Eu (III)-Cycline Complexes at the same solvent, Molar Ratio and the same Volume.	78
2.5. Analytical Performance.	82
2.5.1. Method Validation	82
2.5.1.1. Dynamic Range	82
2.5.2. Selectivity	87
2.5.3. Recovery Study	88
2.5.4. Accuracy and Precision of The method.	89
2.6. Conclusion	91
2.7. Reference	92

Chapter (3).

A spectrofluorimetric method for measuring the activity of the enzyme α -L-fucosidase using the nano optical sensor Eu(III) –Tetracycline complex doped in sol- gel matrix.

Title	Page No.
3.1. Introduction	95
3.2. Experimental	98
3.2.1. Chemicals and reagents	98
3.2.2. Apparatus	98
3.2.3. Collection of the samples	99
3.3. Method	99
3.3.1. Preparation of Eu (III) Tetracycline Complex.	99
3.3.2. Preparation of Eu (III) Tetracycline Complex in sol gel.	100
3.3.3. Preparation of 2-chloro-4-nitro phenol (2-CNP) solutions	101
3.3.4. Recommended procedure	101
3.3.5. Standard method	102
3.3.5.1. Assay Principle	102
3.4. Analytical application	104
3.5. Results and Discussion	105
3.5.1. Spectral characteristics	105
3.5.1.1. Absorption spectra	105
3.5.1.2. Excitation and emission spectra	106
3.6. Analytical performance	109

Title	Page No.
3.6.1. Selectivity	113
3.7. Effect of the reaction time between enzyme and substrate on The released 2-CNP.	113
3.8. Effect of the reaction time between enzyme and substrate On the luminescence intensity of Eu^{3+} -TC sensor doped In sol-matrix in Acetonitrile.	114
3.9. Conclusion	115
3.10. Reference	116

Chapter (4)

Gatifloxacin assessment by the Enhancement of the Green Emission of Optical Sensor Tb^{3+} Doped In Sol-Gel Matrix

Title	Page No.
4.1. Introduction	120
4.2. Experimental	121
4.2.1. Materials	121
4.2.2. Reagents	121
4.2.3. Apparatus	122
4.2.4. Synthesis of Tb- (GFX) complex-Doped in sol gel	122
4.2.5. General procedure	123
4.2.6. Determination of Gatifloxacin in pharmaceutical preparations	123
4.2.7. preparation of serum samples	124
4.3. Result and Discussion	124
4.3.1. Absorption and Emission Spectra	124
4.3.2. Effect of experimental variables	126
4.3.2.1. Effect of the amount of (GFX) and Tb^{3+}	126
4.3.2.2. Effect of PH	126

Title	Page No.
4.3.3. Linearity and validation parameters	127
4.3.3.1. linearity and range	127
4.3.3.2. Detection and quantification limits	127
4.3.3.3. Accuracy and precision	128
4.3.3.4. Selectivity	130
4.4. Conclusion	131
4.5. References	132

Acknowledgement

ACKNOWLEDGMENT

Words are not enough to describe my deep thanks to **Prof.Dr. Mohamed Said Attia**, Professor of Analytical chemistry, Faculty of Science, Ain Shams University, for suggesting the point of the research and management of this work of this work, his guidance and supervision in the course of the work, and for his stimulating criticisms and help in the preparation of the thesis. Who taught me how I can be a student seeks to research and knowledge, was supportive and did not spare something.

I would like to express my deep thanks and gratitude to Dr.Ahmed **Osman Youssef** Associate Professor of Analytical Chemistry, Faculty of Science, Ain Shams University for his valuable help and support throughout the course of this work. Also, I offer my thanks and appreciations to all of those who supported me in any respect in the Chemistry Department during the completion of this thesis. Last but not Least, my thanks are due to my family, especially my mother. For support and encouragement which gave me the strength to finish this work and a presence next to me in my life.

Ibrahim Atfi Ibrahim

Aim of the Work

Aim of the Work

The Aim of the present work is the development and introduction of the modern analytical methods with high sensitivity, selectivity and low cost for the determination of some industrial products by spectrofluorimetric technique to detect important enzymes in human body such as alpha fucosidase

This method includes

1-Anovel optical sensor for the determination of alpha fucosidase in human liver serum samples was established and approved the optimal experimental conditions such as solvent, pH and also the concentration of Eu^{3+} -TC matrix. Under optimal conditions the luminescence intensity of Eu^{3+} -TC matrix is inversely proportional to the concentration of 2CNP. With low cost determine some liver enzymes such as alpha L-fucosidase enzyme in different serum samples of liver patient by Photo analytical methods using nanoptical sensor Eu^{3+} -TC.

List of Abbreviations

List of Abbreviations

ACN	Acetonitrile
aPTT	activated partial thromboplastin time
Arab Caps	Arab Company for Gelatin and pharmaceuticals.
ADCO	Arab Drug Company for pharmaceutical and Chemical.
API	Active pharmaceutical ingredient
AFU	Alphafucosidase
AuNPs	Gold nanoparticles
2-CNP	2-chloro-4-nitrophenol
CNPF	2-chloro-4-nitrophenyl- α -L-fucocidase
B.P	British pharmacopeia
BSE	Bovine spongiform encephalopathy, or mad cow disease
CL.	Confidence limits
CTC	Chlortetracycline
CRAB	Cetyltrimethylammonium bromide
CV	Cyclic voltammetry
Copad pharma	Copad Egypt for Trade and pharmaceutical Industries.
CID	Chemical Industries Development .
DELFA	Dissociation enhanced lanthanide fluorescence immunoassay
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
DC	Doxycycline
DNA	Deoxyribonucleic acid
dpa	2,6-dipicolinate
ED	Electric dipole
EDFA's	Erbium(III) doped fiber amplifiers