



Ain Shams University

Faculty of Science

**“New Analytical Method Based on Lanthanide Luminescence for
Assessment of Activity of Some Glands in Human Body”**

Presented by

Mostafa Mohamed Mohamed Ahmed Elsaady

(B.Sc., Major Chemistry 2017)

For the Degree of

**Master of Science
(Analytical Chemistry)**

Department of Chemistry

Faculty of Science

Ain Shams University

(2020)



Ain Shams University
Faculty of Science

**New Analytical Method Based on Lanthanide Luminescence for
Assessment of Activity of Some Glands in Human Body**

A Master Thesis Submitted

To

Chemistry Department
Faculty of Science-Ain Shams University

For

Degree Master of Science
(Analytical Chemistry)

By

Mostafa Mohamed Mohamed Ahmed Elsaady
B. Sc. (Major Chemistry), 2017

Supervised By

Prof. Dr. Mohamed Said Attia
Professor of Analytical Chemistry-
Faculty of Science- Ain Shams
University

Prof. Dr. Mohamed Sabry Abdel-Mottaleb
Professor of Inorganic Chemistry –
Faculty of Science- Ain Shams University

Prof. Dr. Ahmed Osman Youssef
Professor of Analytical Chemistry-
Faculty of Science- Ain Shams University
(2020)



Ain Shams University
Faculty of Science

Approval Sheet for Submission

A Thesis Title

**New Analytical Method Based on Lanthanide Luminescence
for Assessment of Activity of Some Glands in Human Body**

Submitted by

Mostafa Mohamed Mohamed Ahmed Elsaady

B. Sc. (Major Chemistry), 2017

For the Degree of Master of Science (Analytical Chemistry)

This thesis has been approved by supervisor committee

Supervisors

Prof. Dr. Mohamed Said Attia

Prof. of Analytical Chemistry-
Faculty of Science -Ain Shams University

.....

Prof. Dr. Mohamed Sabry Abdel-Mottaleb

Professor of Inorganic Chemistry –
Faculty of Science- Ain Shams University

.....

Prof. Dr. Ahmed Osman Youssef

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

.....

Date of Examination: / /2020

Head of Chemistry Department
Prof. Dr. Ayman Ayoub Abdel-shafi

.....



Ain Shams University
Faculty of Science

**New Analytical Method Based on Lanthanide Luminescence
for Assessment of Activity of Some Glands in Human Body**

By
Mostafa Mohamed Mohamed Ahmed Elsaady

B. Sc. (Major Chemistry), 2017

This thesis for a Master degree has been approved by:

DATE OF EXAMINATION: / /2020

Prof. Dr. Mohamed Sabry Abdel-Mottaleb

Professor of Inorganic Chemistry –
Faculty of Science- Ain Shams University

Prof. Dr. Mohamed Said Attia

Prof. of Analytical Chemistry-
Faculty of Science - Ain Shams University

Prof. Dr. Ragaa El-Sheikh Shohaib

Prof. of Analytical Chemistry-
Faculty of Science - Al-Zagazig University

Prof. Dr. Alaa El-Sayed Amin

Prof. of Analytical Chemistry-
Faculty of Science - Banha University

Out lines

Chapter one:

Introduction

Chapter two:

A novel photoprobe based on nano tris(3-acetylindole) terbium (III) complex: molecular modeling investigations and application in quantitative determination of epinephrine in blood samples.

Chapter three:

Employing of $\text{Eu}(\text{TTA})_3\text{Phen}$ photoprobe for quantitative determination of Cortisol Hermon in human blood.

Chapter Four:

A novel photoprobe based on $\text{Eu}(\text{oxytetracycline})_2$ complex of high sensitivity and selectivity for TSH Hermon in blood serum samples

Contents

<i>Acknowledgment</i>	VI
<i>Aim of the work</i>	VIII
<i>List of abbreviation</i>	XI
<i>List of figures</i>	XVIII
<i>List of tables</i>	XXVI
Abstract:	XXVIII
1-Introduction.	1
1.1. History of Fluorescence:.....	1
1.2. Electronic states model.....	3
1.3. Absorption and emission spectra.....	10
1.4. The advantage of fluorometric technique.	14
1.5. Quenching of Fluorescence.....	16
1.6. Theory of collisional quenching.	18
1.7. Fluorescent Probe.	20
1.8. Luminescent lanthanides.	21
1.9. Mechanism of Lanthanide Luminescence.....	22
1.10. Sol-gel process.....	25
1.10.1. Mechanism of sol-gel formation.	26
2- Chapter Two.....	29
Abstract:.....	30
Part one:.....	31
2.1. Introduction	31
2.2. Experimental.	33
2.2.1. Apparatus.....	33
2.2.2. Materials and reagents.	33
2.2.3. Preparation of TbACl nano-optical sensor doped in PEG.....	34

2.2.4. Recommended Procedure.....	36
2.2.5. Proposed Method for Epinephrine.	36
2.3. Results and discussion.....	37
2.3.1. Absorption spectra.....	37
2.3.2 –Molar ratio, Solvent, and pH effect.....	38
2.3.3. Characterization of sol-gel nano TbAcI/PEG complex.....	42
2.3.4. Emission spectra.....	43
2.3.5. Calibration curve.	44
2.3.6. Method validation.....	46
Part Two	50
2.4. Experimental.	51
2.4.1. Computational methods.	51
2.5. Result and discussion.	53
2.5.1. Structure and electrostatic potential maps (ESP).	53
2.5.2. Absorption spectra.....	59
2.5.3. Excitation/emission mechanism	60
2.5.4. Emission quenching.....	63
2.5.5. AIMD in the S_1 state.	65
2.6. Conclusion.	68
3-Chapter Three	70
3.1. Introduction.	71
3.2. Experimental.	73
3.2.1. Apparatus.....	73
3.2.2. Materials and reagents.	73
3.2.3. The Preparation of Eu(TTA) ₃ Phen.....	74
3.2.4. Recommended Procedure.....	74
3.2.5. Proposed Method for CRT in blood plasma.	75
3.3. Results and discussion.....	75

3.3.1. Absorption spectra	75
3.3.2. Solvent and pH effect	77
3.3.3. Excitation / emission mechanism.....	79
3.3.4. Emission quenching.....	81
3.3.5. Calibration curve.	83
3.3.6. Method validation.....	84
3.4. conclusion.	88
4- Chapter Four	89
4.1. Introduction.	90
4.2. experimental.	96
4.2.1. Apparatus.	96
4.2.2. Materials and reagents.	96
4.2.3. The Preparation of Eu(Oxytetracycline) ₂	97
4.2.4. Recommended Procedure.....	97
4.2.5. Proposed Method for TSH in blood serum.	98
4.3. Results and discussion.....	98
4.3.1. Absorption spectra.....	98
4.3.2. Solvent, molar ratio and pH effects	100
4.3.3. Excitation / emission spectra.	104
4.3.4. Emission enhancement.	105
4.3.5. Calibration curve.	106
4.3.6. Method validation.....	107
4.4. conclusion.	110
5- References	111
<i>English Summary</i>	137

Acknowledgment

Acknowledgment

I would like to express my sincere gratitude and profound thanks to **Professors Dr. Mohamed Said Attia, Dr. M. Sabry Abdel-Mottaleb, and Dr. Ahmed Osman Youssef** for suggesting the research as well as the continuous support of my scientific work, for their patience, motivation, enthusiasm, and immense knowledge. Their guidance helped me in all the time of research and during writing the Master thesis. Their valuable instructions motivate and taught me how to be a student who seeks scientific study and knowledge. I would also like to thank them all for their friendship.

Mostafa Elsaady

Aim of the work

Aim of the work

In this work, we aim to assess the activity of some glands in the human body by determining the concentrations of some hormones that are released by these glands.

Epinephrine (EPI) or Adrenaline is one of the essential Catecholamine, which plays a critical role in motivating several actions of the sympathetic nervous system (SNS) known as "flight or fight response", also play a crucial role during physical or mental tension of the human body. Any change of EPI concentration in the blood plasma in the range [90–690 $\mu\text{g mL}^{-1}$] may cause several diseases. So, the establishment of an analytical method for the quantitative determination of the concentration of EPI in serum with high sensitivity and selectivity is an essential mission for developing nerve physiological researches, especially to remove the current defects in the traditional methods. Therefore, developing a simple method for accurate determination of EPI is still of great significance. Today, the research field with lanthanide complexes get great interest. Tb(3-acetylindole)₃ complex was established as a highly sensitive and selective optical sensor for the quantitative determination of ultra-trace concentrations of epinephrine in human serum samples, that may aid in assessing the activity of adrenal gland and then a diagnosis of optimal diseases that may be raised due to the abnormal ranges in human blood. Luminescent nano-optical sensor TbAcI doped in the sol-gel matrix has many advantages over the traditional methods.

Also, in this work, simulation and experimental investigations of molecular structures and interactions leading to luminescence quenching of TbAcI by EPI are assumed by applying DFT, TD-DFT, and ab initio

molecular dynamic (AIMD) methods. The molecules will be allowed to interact for a fixed time to visualize the dynamic evolution during molecular collisions that lead to luminescence quenching. The results reported in this thesis indicate the viability of the AIMD method for luminescence quenching research.

Also, we used $\text{Eu}(\text{TTA})_3\text{phen}$ for the quantitative determination of cortisol hormone in blood plasma. Finally, we used $\text{Eu}(\text{oxytetracycline})_2$ complex for assessment of TSH hormone in blood serum samples. The assessment of these hormones participates with a critical role in assessment of the activity of the above-mentioned glands.

List of abbreviation

List of abbreviation

% RE	Percent relative error
% RSD	percent relative standard deviation
(N)	Nucleophilicity
(η)	Chemical hardness
(μ)	Electronic chemical potential
(ω)	Electrophilicity
[Q]	The concentration of the quencher
μg	Micro gram
$^{\circ}\text{C}$	degree Celsius
a	Intercept
\bar{X}	The average value for three readings
\AA	Angstrom
AC	Acetonitrile
AIMD	Ab Initio molecular dynamic
b	Slope
BE	Binding energy
CA 125	Cancer antigen 125
CA15-3	Carcinoma antigen 15-3