

SPECTROSCOPIC METHOD FOR DETERMINING RARE EARTHS IN LOCAL MINERALS

THESIS

Submitted for Degree of
DOCTOR OF PHILOSOPHY

in
PHYSICS

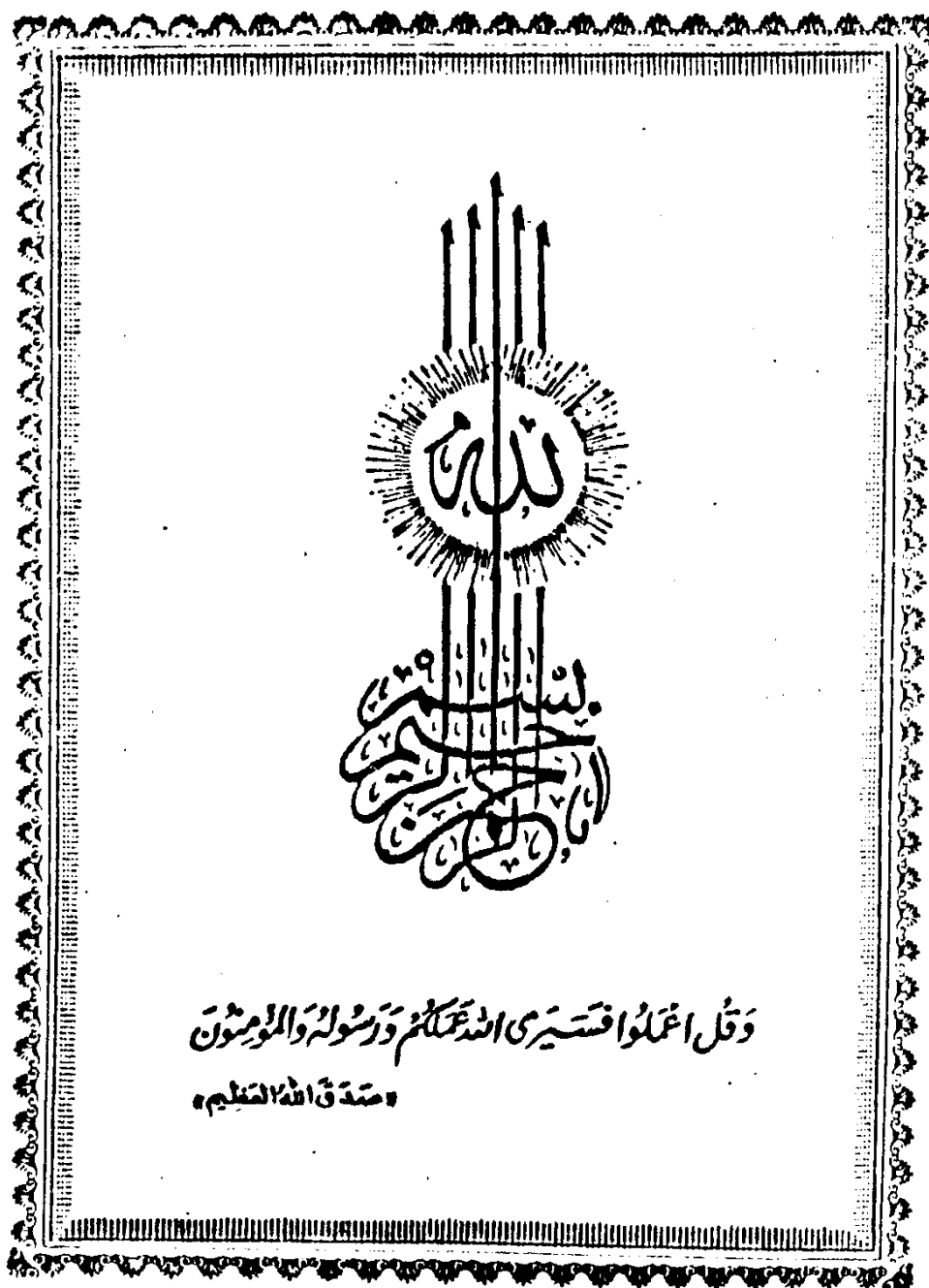
By

SOAD IBRAHIM MAHMOUD SOLIMAN

(B. Sc. ; M. Sc.)

Department of Physics
University College for Girls
Ain Shams University

1988





SPECTROSCOPIC METHOD FOR DETERMINING
RARE EARTHS IN LOCAL MINERALS

Thesis Advisors

Approved

1- Prof. Dr. A.El-Bialy,

...Aida El Bialy

Prof. of Physics, University

College for Girls (Ain Shams University)

2- Prof. Dr. M.A. Eid,

...M. Eid

Physics Department,

National Research Centre.

3- Prof. Dr. A.A. Fakhry,

...A. Fakhry

Head of Spectroscopy Lab.,

National Research Centre.

Head of Physics Department

M. A. Elwan

ACKNOWLEDGEMENT

I would like to express my sincere thanks to Prof. Dr. M. El Din Kinawy. Head of Physics Department, Faculty of Girls, Ain Shams University for his continuous encouragment and help.

My deep gratitude is due to Prof. Dr. Aida El Bialy. Physics Department, Faculty of Girls, Ain Shams University for her kind supervision and valuable discussions during the progress of the work.

My sincere thanks to Prof. Dr. Ahmed Fakhry Head of Spectroscopy Lab., National Research Centre, for valuable discussions, continuous help and supervising this work.

I am indepted to Prof. Dr. Mohamed Eid Spectroscopy Lab., N.R.C., for suggesting the point of research, continuous supervision, help, encouragement and fruitful discussions.

My thanks also to Dr. Monir M. Aly, Nuclear Materials Corporation, Egypt, for helpful discussions and continuous interest.

I would like to thank Dr. K.M. El Behery, Assistant Prof. Spectroscopy Lab., N.R.C., for fruitful discussions and encouragement.

This work has been carried out at the pectroscopy Lab., N.R.C., I wish to express my sincere thanks and gratitude to all the staff members of the Laboratory for their kind help and fruitful cooperation.

CONTENTS

	Page
Summary	i
<u>CHAPTER I</u>	
INTRODUCTION	1
AIM OF THE PRESENT WORK	8
<u>CHAPTER II</u>	
REVIEW ON THE PHYSICAL TECHNIQUES FOR DETERMINATION OF REE IN GEOLOGICAL MATERIALS	10
2.1. Conventional D.C. arc technique	11
2.2. Neutron activation method	13
2.3. Mass spectrometry method	18
2.4. X-ray fluorescence spectrometry,.....	22
2.5. Inductively coupled plasma atomic emission spectrometry.	26
2.6. Review on the REE determination in Egyptian phosphates	30
<u>CHAPTER III</u>	
FUNDAMENTAL THEORETICAL BASIS OF OPTICAL EMISSION SPECTROSCOPY.....	35
3.1. Energy levels of an atom and statistical weights	35
3.2. The emission of spectral lines.....	36
3.3. Transition probabilities.	37

	Page
3.4. The intensity of spectral line	40
3.5. Plasma models	41
3.5.1. Thermal equilibrium (TE)	41
3.5.2. Local thermal equilibrium	46
3.5.3. Partial thermal equilibrium	48
3.5.4. The corona model	48
3.6. Broadening of spectral lines	50
3.6.1. Natural line broadening	50
3.6.2. Doppler broadening	51
3.6.3. Stark broadening or pressure broadening.	53
3.6.4. Convolution of profiles	54

CHAPTER IV

EXPERIMENTAL WORK

RESULTS AND DISCUSSIONS.....	55
4.1. Apparatus and measuring technique	56
4.1.1. The excitation source	56
4.1.2. The nebulizer	57
4.1.3. Argon humidification.....	58
4.1.4. Ignition of the arc.....	59
4.1.5. Illumination of the spectrograph	60
4.1.6. The spectrograph	62
4.1.7. Measurement of intensity of spectral lines.	63
4.1.7.1. Emulsion calibration curve	63
4.1.7.2. Methods of obtaining emulsion calibration data	65

	Page
4.1.7.3. The preliminary curve	66
4.1.7.3.a. Transmittance preliminary curve	67
4.1.7.3.b. Blackening (Density) preliminary curve	68
4.1.7.3.c. Seidel preliminary curve.....	68
4.1.7.4. Emulsion calibration (present work).....	69
4.1.7.4.a. The blackening calibration curve.....	70
4.1.7.4.b. Emulsion calibration using Kaiser transformation function	72
4.1.7.4.c. Determination of spectral intensity from the knowledge of γ and K.	76
4.1.7.5. Background correction	76
4.2. Sample preparation and selection of analysis lines	78
4.2.1. The phosphate samples	78
4.2.2. Methods of dissolution of phosphate samples	78
4.2.3. Preparation of solution of phosphate samples (present work).....	80
4.2.4. Preparation of standard solutions	80
4.2.5. The plasma of the wall-stabilized arc and its spectrum.....	81
4.2.5.1. Effect of easily ionizable elements for analysis using the plasma arc.....	81
4.2.6. Optimal excitation conditions for analysis using the plasma arc.....	83
4.2.6.1. Effect of the concentration of KCl on the intensity of the spectral lines ...	85

	Pages
4.2.6.2. Effect of arc current on the intensity of spectral lines.....	86
4.2.6.3. Effect of aerosol flow rate on the inten- sity of spectral lines	88
4.2.6.4. Effect of argon flow rate at cathode on the intensity of spectral lines	89
4.2.7. Selection of spectral lines of REE for analy- tical application	90
4.2.7.1. Sources of spectral interference	90
4.2.7.2. Choice of analytical lines of REE for the present work	94
4.3. Effect of sample matrix on the excitation conditions and the radiation out-put in the wall-stabilized arc.....	97
4.3.1. Matrix effect in analytical plasmas.....	97
4.3.2. Effect of sample matrix on excitation tempe- ratures.....	99
4.3.2.1. Measurement of excitation temperature.	99
4.3.2.2. Effect of sample matrix on atom-excita- tion temperature	101
4.3.2.3. Effect of sample matrix on ion-excitation temperature.....	105
4.3.3. Influence of matrix on the intensity of spectral lines.....	110

	Page
4.4. Analytical calibration curves	113
4.4.1. The analytical calibration function	113
4.4.2. Limit of detection	118
4.4.3. Precision	123
4.4.4. Analysis of the phosphate samples	124
 <u>CHAPTER V</u>	
CONCLUSIONS	128
APPENDIX	131
REFERENCES	140
ARABIC SUMMARY .	

S U M M A R Y

SUMMARY

The present work has been devoted for the development of a spectroscopic technique for the determination of the group of rare earth elements in local phosphate deposits. The developed technique uses a home-made plasma excitation source, that is the wall-stabilized argon arc constructed at the Spectroscopy Laboratory, National Research Centre. This arc has many features which makes it a suitable source for such a task. Its spectrum shows very low background emission and no molecular bands are observed except the OH-band spectrum at 306.4 nm. At the optimal operating conditions used for the analytical application of the arc, the intensity of the argon lines is highly reduced and depending on the current may completely disappear. Moreover at these conditions the arc emits a simple spectrum. With these properties of the present source spectral interference is at minimum. This is a favourable advantage of the arc specially for the rare earth elements with its complex spectra. For this reason a considerable part of the work has been dedicated for achieving the optimal excitation conditions and studying the effect of the matrix of the phosphate samples on the plasma temperature as well as on the intensity of the emitted spectral lines.

The thesis is divided into five chapters:-

The first chapter, the introduction, describes the requirements which should be fulfilled in an analytical technique applied for elemental determination. It gives a brief account on the efforts that had been devoted to excitation sources for optical emission spectroscopy which resulted in the development of plasma sources like inductively coupled plasma (ICP) and the direct current plasma (DCP). The introduction discusses also the importance of developing analytical techniques for the rare earth elements in geological samples specially those techniques which require no pretreatment of the samples for enrichment. At the end of this chapter the need of a spectroscopic technique for the determination of REE in local phosphate samples is discussed and therefore, the aim of the present thesis is given.

The second chapter gives a review on the physical techniques used for the determination of REE in geological materials. These techniques are, the optical emission spectroscopy using d.c. carbon arc, neutron activation, mass spectrometry, X-ray fluorescence, and the inductively coupled plasma atomic emission spectrometry. For each technique a review on the published work is also given. This chapter reviews also the previous

efforts carried out for the determination of REE in Egyptian phosphates.

Chapter III is devoted to review briefly the fundamental theories related to the emission of spectral lines. It gives the important mathematical equations which relate the line intensity and the plasma temperature. This is necessary for the study of the effect of sample matrix on the plasma conditions. Also the factors influencing the line width are discussed.

Chapter IV is devoted for the experimental work and the obtained results. It is divided into four parts. The first part describes the experimental set-up, including the wall-stabilized arc which was used as an excitation source, the plane grating spectrograph PGS2 (Carl Zeiss Jena) and its illumination as well as the methods used for the emission calibration. The second part describes the phosphate samples and standard solutions preparation for nebulization and the selection of interference-free spectral lines for the analytical application. The effect of sample matrix on the plasma temperature and the intensity of the analysis lines is described in the third part of this chapter. For this purpose, atom-excitation temperature was measured using

the intensity distribution over a group of FeI lines in the wavelength region between 371.99 nm and 376.3 nm. Also ion-excitation temperature was measured using a group of TiII lines in the wavelength region from 321.7 nm to 324.2 nm. This study revealed that the sample matrix has a slight and insignificant effect on the excitation temperatures and consequently on the intensity of spectral lines. This is explained to be due to the presence of relatively high concentration of the easily ionizable element, potassium. The last part of this chapter describes the construction of the analytical calibration function, the determination of the limits of detection for REE (which was found to be $0.008 \mu\text{g ml}^{-1}$ for Yb and $0.374 \mu\text{g ml}^{-1}$ for Er), as well as the precision of determination. The obtained values of the precision of the REE spectral lines was found to be 0.02 for Eu and 0.097 for Tm. Finally the result of the application of the developed technique for the determination of REE in twelve phosphate samples collected from Abu-Tartur plateau is given. The significance of these results in the field of exploration geochemistry is given as an appendix.

In the conclusion, chapter V the most important characteristics of the developed technique are summarized.

The results obtained in this work reveal that the technique is available for similar studies in any minerals or solution samples.