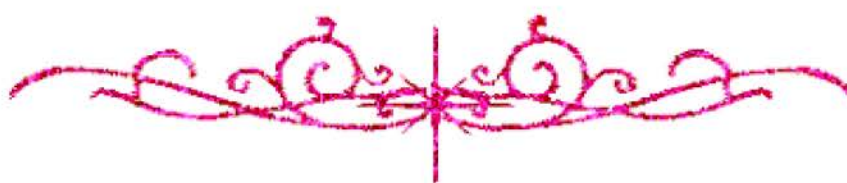


سامية محمد مصطفى



شبكة المعلومات الجامعية

بسم الله الرحمن الرحيم



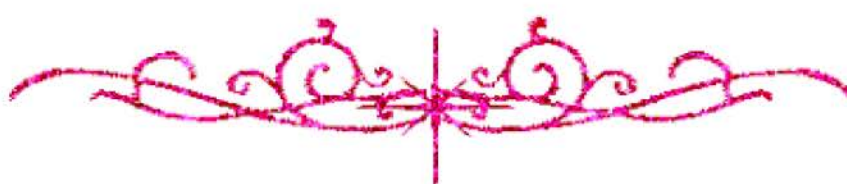
سامية محمد مصطفى



شبكة المعلومات الجامعية



شبكة المعلومات الجامعية التوثيق الالكتروني والميكروفيلم



سامية محمد مصطفى



شبكة المعلومات الجامعية

جامعة عين شمس

التوثيق الإلكتروني والميكروفيلم

قسم

نقسم بالله العظيم أن المادة التي تم توثيقها وتسجيلها
علي هذه الأقراص المدمجة قد أعدت دون أية تغيرات



يجب أن

تحفظ هذه الأقراص المدمجة بعيدا عن الغبار



سامية محمد مصطفى



شبكة المعلومات الجامعية



بعض الوثائق الأصلية تالفة



سامية محمد مصطفى



شبكة المعلومات الجامعية



بالرسالة صفحات لم ترد بالأصل



**Trace Elements and Isotopic Analysis of Some Rare Earth Elements
by Inductively Coupled Plasma Mass Spectrometry and Ion
Chromatography**

By

Hazem Hassan Mahmoud Mansour

B.Sc.

**Central Laboratory for Elemental and Isotopic Analysis,
Nuclear Research Center, Atomic Energy Authority**

A Thesis Submitted

To

**Department of Chemistry, Faculty of Science,
Cairo University**

For

**The Degree of Master of Science
in Chemistry**

Supervised by

Prof. Dr. N. F. Zahran
*Head of Basic Nuclear
Sciences Division, Atomic
Energy Authority*

Prof. Dr. M. Waheed. A. Badawy
*Prof. of Physical Chemistry
Faculty of Science
Cairo University*

2006

B
15/11

APPROVAL SHEET FOR SUBMISSION

Title of (M.Sc.) Thesis:

"Trace Elements and Isotopic Analysis of Some Rare Earth Elements by Inductively Coupled Plasma Mass Spectrometry and Ion Chromatography"

Name of the candidate: Hazem Hassan Mahmoud Mansour

This thesis has been approved for submission by the supervisors:

1- Prof. Dr. M. Waheed A. Badawy

Signature W. Badawy

2- Prof. Dr. Nagwa F. Zahran

Signature Nagwa Zahran

Prof. Dr. Rifaat Hassan Helal



Chairman of Chemistry Department
Faculty of Science, Cairo University

ABSTRACT

Name: Hazem Hassan Mahmoud Mansour

Title of thesis:

"Trace Elements and Isotopic Analysis of Some Rare Earth Elements by Inductively Coupled Plasma Mass Spectrometry and Ion Chromatography"

Degree : (M.Sc.) thesis , Faculty of Science, Cairo University , 2005/2006

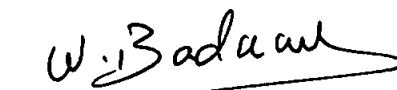
This work has been carried out to :-

- Optimize the sample preparation methods used for the ion chromatography (IC) and inductively coupled plasma mass spectrometer techniques (ICP-MS) in analysis of rare earth elements in rocks samples.
- Optimize the operational parameters of inductively coupled plasma (ICP-MS) and ion chromatograph (IC) for analysis of rare earth elements (REEs).
- Develop reproducible and accurate methods for Rare Earth Elements analysis of rocks and minerals, using inductively coupled plasma mass spectrometry (ICP-MS) and ion chromatography (IC).
- Investigate the possibility of using the inductively coupled plasma mass spectrometer in isotopic analysis .

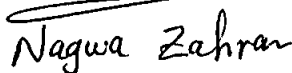
Keyword : Trace Elements , Isotopic Analysis , Rare Earth Elements, Inductively Coupled Plasma Mass Spectrometry, Chromatographic Separation ,Interference Elimination,Ion Chromatography.

Supervisors :

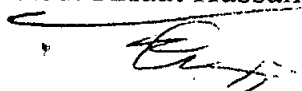
1- Prof. Dr. M.Waheed A. Badawy



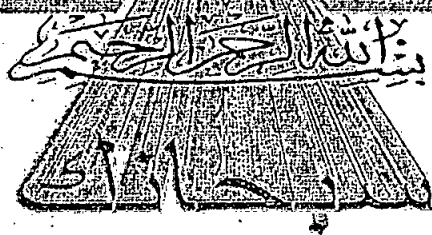
2- Prof. Dr. Nagwa F. Zahran



Prof. Dr. Rifaat Hassan Helal



Chairman of Chemistry Department
Faculty of Science, Cairo University



لَا عِلْمَ لَنَا إِلَّا مَا عَلَّمْتَنَا

إِنَّكَ أَنْتَ الْعَلِيمُ الْحَكِيمُ

صَلَّى عَلَى النَّبِيِّ الْعَظِيمِ

ACKNOWLEDGMENT

I would like to express my gratitude and appreciation to Prof. **Dr. N. F. Zahran** head of Basic Nuclear Sciences Division, Nuclear Research Center, Atomic Energy Authority for her sincere advice, helpful guidance and valuable discussions throughout this work.

I wish to express my deepest thanks to **Prof. Dr. M. Waheed A. Badawy** Prof. of physical chemistry faculty of science, Cairo University for his continuous support, encouragement and constructive discussions.

Special thanks also expressed to **Prof. Dr. A. H. Hashad** and **Mr. M. Farid** Nuclear Materials Authority, for providing the geological samples.

Many thanks are also to my colleagues in the Central Lab. for Elemental and Isotopic Analysis, Nuclear Research Center, Atomic Energy Authority for their help and collaboration.

I wish also to thank head and the staff of the accelerators and ion sources department for their great help.

CONTENTS

Chapters	Subjects	Pages
	Acknowledgments	
	List of tables	IV
	List of figures	VI
	List of abbreviations	VIII
	Abstract	1
Chapter (I)	Introduction and Aim of the Work	
1.1.	Introduction	2
1.2.	Rare Earth Elements	3
1.2.1.	Abundance and Occurrence	4
1.2.2.	The Position of Rare Earth Elements in Periodic Table	7
1.2.3.	Lanthanide Contraction	7
1.2.4.	Properties of Rare Earth Elements	8
1.2.4.1.	Physical Properties	8
1.2.4.2.	Chemical Properties	9
1.2.5.	Application of Rare Earth Elements	10
1.3.	Rare Earth Elements in Geological samples	11
1.4.	Aim of the Work	12
Chapter (II)	Theoretical Considerations	
2.1.	The Microwave Digestion System	14
2.1.1.	Absorption of Microwave Energy and Heating	14
2.1.2.	Laboratory Microwave Design	15
2.1.3.1.	Understanding Chemical Reaction Profiles in the Closed Vessels	16
2.1.3.2.	Features of Closed Vessel Digestion	17
2.1.4.	Microwave Reaction Control	17
2.2.	Stepwise Development of Microwave Dissolution Procedures	19
2.2.1.	Data Quality Objectives	19
2.2.2.	The matrix	20
2.2.3.	The Analyte	21
2.2.4.	Reaction Properties Defined by the Matrix, Analyte, and Reagent Selected	22
2.2.5.	Methodology and Instrumentation	22
2.3.	Acid chemistry	22
2.3.1.	Introduction to the Primary Dissolution Reagents	22
2.3.2.	Reaction with Nitric Acid	23
2.3.3.	Reaction with Hydrochloric Acid	23
2.3.4.	Reaction with Hydrofluoric Acid	25
2.3.5.	Reaction with Sulphuric Acid	26
2.3.6.	Reaction with Perchloric Acid	26
2.3.7.	Reaction with Hydrogen Peroxide	27
2.4.	The ICP as an Ion Source for MS	27
2.5.	Detection limit	31
2.6.	Accuracy, precision and reproducibility	32

2.7.	Types of Analysis	32
2.7.1.	Qualitative Analysis	32
2.7.2.	Semi quantitative Analysis	33
2.7.3.	Quantitative Analysis	34
2.7.3.1.	Relative Sensitivity Coefficient Method	34
2.7.3.2.	Direct Calibration Curves Method	35
2.8.	Isotope Ratio Measurements	37
2.9.	Interferences	39
2.9.1.	Isobaric Overlap	39
2.9.2.	Polyatomic Ions	41
2.9.3.	Refractory Oxides	42
2.9.4.	Doubly Charged Ions	43
2.10.	Principles of Ion Chromatographic Separation and Detection	44
2.10.1.	Introduction	44
2.10.2.	Requirements for Separation	44
2.10.3.	Performing separation	45
2.10.4.	Migration of Sample Ions	45
2.10.5.	Detection	48
2.10.6.	Basis of separation	48

Chapter (III)

APPARATUS AND EXPERIMENTAL CONDITIONS

3.1.	JMS-PLASMAX2 Mass Spectrometer	50
3.1.1.	General Features of the ICP-MS	50
3.1.2.	Vacuum System	51
3.1.2.1.	Interface Evacuation Subsystem	52
3.1.2.2.	Mass Analyzer Evacuation Subsystem	53
3.1.3.	Sample Inlet System	54
3.1.3.1.	Meinhard Concentric Nebulizer	55
3.1.3.2.	Ultrasonic Nebulizer	57
3.1.4.	ICP Ion Source	58
3.1.5.	Mass Analyzer	61
3.2.1.	Sample Introduction System	63
3.2.1.1.	Introduction of Liquid Samples	63
3.2.2.	ICP Ion Source	64
	-ICP Torch	64
	-RF Generator	65
3.3.	Ion Chromatograph System	65
3.3.1.	Components of an Ion Chromatographic Instrument	65
3.3.2.	Dead Volume	66
3.3.3.	Degassing the Eluent	67
3.3.4.	Pumps	68
3.3.5.	Gradient Formation	70
3.3.6.	Pressure	72
3.3.7.	Injector	72
3.3.8.	Column Oven	74
3.3.9.	Column Hardware	74
3.3.10.	Column Protection	75
3.3.11.	Detection and Data System	76

Chapter (IV)

Experimental Results and Discussion

4.1.1.	Optimization of ICP-MS	78
	Measuring Conditions of ICP-MS	80
4.2.1.	Optimization of IC	81
	Measuring Conditions of IC	82
4.3.	The Desolvating System	85
4.3.1	Effect of Sweep gas flow rate	85
4.3.2	Effect of RF power	86
4.3.3.	Accuracy and Precision	87
4.4.	Optimization of IC	90
4.4.1	Effect of the concentrations of the Eluents	90
4.4.1.1.	Effect of the concentrations of oxalic acid solution	91
4.4.1.2.	Effect of the concentrations of diglycolic acid	92
4.4.2.	Effect of the pH of the Eluents	93
4.4.2.1.	pH of Oxalic acid	93
4.4.2.2.	pH of Diglycolic acid	95
4.4.3.	Effect of the flow rate of the Eluents	96
4.4.4.	Post Column Reaction	97
4.4.4.1.	Effect of the Concentrations of PAR	98
4.4.4.2.	Effect of the Flow Rate of PAR	98
4.5.	Ion exchange and ion chromatographic separation of the REEs from geological samples	99
4.5.1.	Analytical Procedure	99
4.5.1.	Sample dissolution and matrix removal	99
4.5.1.2.	Standardizations	102
4.5.1.3.	Ion exchange separation	104
4.5.1.4.	Interference from polyatomic ions	107
4.5.1.5.	Algebraic correction scheme of the interference	108
4.5.1.6.	Validity of Analytical Procedure	110
4.6.	Analysis of the rare earth elements in some geological sample	114
4.6.1.	Younger granite chondrite normalized REEs Pattern	115
4.6.2.	Allanite chondrite normalized REEs Pattern	120
4.6.3.	Amphibolites chondrite normalized REEs Pattern	122
4.7.	Final conclusions	124
	References	125
	Arabic Summary	132

List of Tables

Table	Title	Page
(1-1)	Natural abundance in the earth crust of the rare earth elements.	6
(1-2)	List of standards and Samples used in this work.	12
(2-1)	Considerations in Selecting Decomposition Protocols.	20
(2-2)	Distribution of ionization energies among the elements for singly and doubly charged ions at 1eV interval.	30
(4-1)	The optimum experimental conditions for high resolution ICP-MS	80
(4-2a)	Analytical conditions for the analysis of REEs by anion-exchange chromatograph.	83
(4-2b)	Analytical conditions for the elimination of transition metals and the analysis of REEs by anion-exchange chromatography.	84
(4-3)	The accuracy of analysis of REEs in BCR-2(CRM) by ICP-MS.	88
(4-4)	The accuracy of analysis of REEs in AGV-2(CRM) by ICP-MS.	89
(4-5)	Logarithms of formation constant of transition metals complex with oxalic acid and PDCA.	91
(4-6)	Distribution coefficient of some metals between Dowex 50W –X8 and different concentration of hydrochloric acid.	105
(4-7)	The formation yield of mono-oxide ions of REEs, Ba and their contribution to metallic ions of REEs and interference errors in andesite (AGV-2).	109
(4-8)	Isotope ratios of some REEs in AGV-2 (CRM) before and after separation and algebraic corrections for oxides and isobaric interference.	111
(4-9)	Concentration of REEs (ppm) in BCR-2 (CRM) by ICP-MS and ion chromatography (Dionex Ion CS5A).	112
(4-10)	Concentration of REEs (ppm) in AGV-2 (CRM) by ICP-MS and ion chromatography (Dionex Ion CS5A).	113
(4-11)	Average concentrations (ppm) in chondritic meteorites.	115
(4-12a)	REEs concentration (ppm) of the granite samples by ICP-MS and Ion Chromatography.	116

(4-12b)	REEs concentration (ppm) of the granite samples by ICP-MS and Ion Chromatography.	117
(4-13a)	REEs concentration (ppm) of the granite samples by ICP-MS and Ion Chromatography.	118
(4-13b)	REEs concentration (ppm) of the granite samples by ICP-MS and Ion Chromatography.	119
(4-14)	REEs concentration (ppm) of the three allanite samples by ICP-MS and Ion Chromatography.	121
(4-15)	REEs concentration (ppm) of the amphibolite samples by ICP-MS and Ion Chromatography.	123