



**UNIVERSITI PUTRA MALAYSIA**

**ELEMENTAL DISTRIBUTIONS IN MARINE SEDIMENTS IN THE  
STRAITS OF MELAKA USING NEUTRON ACTIVATION AND  
MASS SPECTROSCOPIC ANALYSES**

**AWAD AHMED AL-ZAHRANY**

**FS 2007 2**



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UNIVERSITI PUTRA MALAYSIA**

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**By**

**AWAD AHMED AL-ZAHRANY**

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,  
in Fulfilment of the Requirement for the Degree of Doctor of Philosophy**

**March 2007**



## DEDICATION

*I would like to dedicate this thesis to my parents, brothers, and sisters. I am especially dedicating this thesis to my ever supportive wife Mrs. Fatima Saleh. Finally, I would like to dedicate this thesis to my daughters Rawabi, lamya, my sons Abdul-Allah, Zead and Osama.*

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of requirement for the degree of Doctor of Philosophy

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**AWAD AHMED AL-ZAHRANY**

**March 2007**

**Chairman: Professor Elias Saion, PhD**

**Faculty: Science**

The horizontal and vertical distributions of concentrations of major, minor, and trace elements from the grab and core marine sediment samples along the West Coast of Peninsular Malaysia were investigated. All together there are 35 elements including the following 27 elements namely Al, As, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Mg, Mn, Na, Rb, Sb, Sc, Sm, Ta, Th, U, V, Yb, and Zn were studied by using Instrumental Neutron Activation Analysis (INAA) and the following 8 elements namely Cd, Cu, Mo, Pb, Ni, Sr, Ba, and Ti were studied by using Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) technique. The obtained elemental concentrations were evaluated by various methods including by comparing the



concentrations to that of the mean crustal materials and average shales, the national studies, and the international guidelines for marine sediments of Canada, Netherlands and USA-New York State. The enrichment factor method was used to determine whether the elements belong to anthropogenic and non-anthropogenic sources. In addition, different statistical analysis methods including the linear regression analysis and the cluster analysis were used to determine the correlation of concentrations between the measured elements. To ensure the accuracy and precision of the generated data, proper quality control and quality assurance procedures have been incorporated in the INAA analysis including 'blank', duplicate sample analysis, application of certified reference materials, and quantification using  $K_0$ -NAA procedure. The data generated using ICP-MS were subject to the same quality control and quality assurance procedures as the INAA analysis without  $K_0$ -NAA procedure.

For the horizontal elemental distributions the grab sediment samples were used. The non-anthropogenic elements identified by the enrichment factor calculation were Al, Ba, Ca, Cd, Co, Cr, Cu, K, Mg, Mn, Mo, Na, Ni, Rb, Sr, Ta, Ti, V, and Zn. The concentrations of Al, Ba, Cd, Co, Cr, Cu, K, Mn, Mo, Ni, Sr, Ta, Ti, V, and Zn are lower than those of the average shales and the mean crustal materials. This may be due to high solubility of these elements in the tropical weathering. The concentrations of Ca, Mg and Na are lower than the mean crustal materials but higher than the average shales. The concentration of Rb is slightly greater than that of the mean crustal materials but lower than the average shales. Also, this may be due to high solubility of Ca, Mg, Na, and Rb in the tropical weathering. The anthropogenic elements in the grab sediment samples were As, Br, Cs, Fe, Hf, Pb,

Sb, Th, and U. The concentrations of As, Br, Cs, Hf, Pb, and Sb are greater than those of the mean crustal materials. This indicates that there were external inputs of anthropogenic sources such as industrial and mining activities at the inland area along the Straits of Melaka. The concentration of Pb is approximately twice of the average shales and three times than the mean crustal materials. Higher concentration of Pb in the grab sediment samples may be due to industrial activities such as manufacture of batteries and automotive emissions from cities along the rivers flowing into the Straits of Melaka.

For the vertical elemental distributions the core sediment samples were used. The non-anthropogenic elements Al, Ba, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Rb, Sr, Ta, Ti, V, and Zn in the core sediment samples are lower than the concentrations of the mean crustal materials and average shales. The anthropogenic elements in the core sediment samples were As, Br, Ca, Cs, Hf, Pb, Sb, Th, and U, where the concentrations of Br, Ca, Cs, Hf, Th, and U are greater than the concentrations of the mean crustal materials and average shales. This indicates that there were external inputs of anthropogenic sources such as industrial and mining activities at the inland area along the Straits of Melaka. The concentration of Pb is greater than the concentration of the mean crustal materials but lower than the average shales. For toxic elements such as As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, and Zn the mean concentrations are either lower than or equal to the mean concentrations for the Straits of Johor and the Penang Island. Moreover, the mean concentrations of most elements were found lower than the international guidelines for marine sediments from Canada, Netherland and USA-New York State, except for the concentrations of Cr and Ni, which are greater than the international guidelines.

The depth profile of As/Al, Cd/Al, Cr/Al, Cu/Al, Fe/Al, Mn/Al, Sb/Al, and U/Al of the core sediment samples normalized to aluminum metal revealed the general trends that the concentration level in the upper layer is higher than the bottom layer. The explanation for the higher concentrations of As, Cd, Cr, Cu, Fe, Mn, Sb, and U in the upper layers may be due to the lower oxygen level in an anoxic sediment which caused diagenesis process in which the multi-oxidations state in those elements tend to be higher for concentration level at the surface sediment layer. This indicates that the core marine sediments in the Straits of Melaka are having enough oxygen level and remain healthy for marine ecosystem.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**TABURAN KEPEKATAN UNSUR DALAM SEDIMEN MARIN DI SELAT  
MELAKA DENGAN MENGGUNAKAN KAEDAH ANALISIS  
PENGAKTIFAN NEUTRON DAN SPEKTROMETRI JISIM.**

OLEH

**AWAD AHMED AL-ZAHRANY**

**March 2007**

**PENGERUSI:            Profesor Elias Saion, PhD**

**FAKULTI:             Sains**

Taburan kepekatan mengufuk dan mencancang bagi unsur major, minor dan surih dalam sedimen marin secara pesampelan cekup dan teras di sepanjang perairan Selat Melaka, Pantai Barat Semenanjung Malaysia telah diselidiki. Kesemuanya 37 unsur termasuk 27 unsur berikut Al, As, Ba, Br, Ca, Cd, Ce, Co, Cr, Cs, Cu, Eu, Fe, Hf, K, La, Lu, Mg, Mn, Mo, Ni, Pb, Rb, Sb, Sc, Sm, Sr, Ta, Th, Ti, U, V, Yb and Zn telah dikaji dengan menggunakan kaedah instrumentasi analisis pengaktifan neutron (INAA) dan 8 unsur berikut Cd, Cu, Mo, Pb, Ni, Sr, Ba, and Ti telah dikaji dengan menggunakan teknik aruhan gandingan plasma-jisim spektroskopi (ICP-MS). Keputusan analisis kepekatan diinterpretasikan dengan pelbagai kaedah, termasuklah membandingkan keputusan dengan nilai purata bahan kerak bumi dan purata kepekatan dalam batuan, membandingkan dengan kajian peringkat kebangsaan, dan

membandingkan dengan penunjuk antarabangsa untuk penilaian tahap pencemaran sedimen marin daripada Kanada, Netherlands dan USA-Negeri New York. Kaedah factor pengayaan telah digunakan untuk menentukan sama ada sesuatu unsur itu berasal daripada kegiatan manusia iaitu antropogenik atau sebaliknya bukan antropogenik. Di samping itu pelbagai kaedah statistik seperti kaedah analisis regresi linear dan analisis kelompok telah juga digunakan untuk menentukan korelasi kepekatan antara unsur-unsur yang dikaji. Untuk memastikan ketepatan dan kejituan data yang dijana dalam kajian ini, beberapa kaedah kawalan kualiti dan ketentuan kualiti telah disertakan dalam analisis  $K_0$ -INAA termasuk penggunaan sampel kosong atau 'blank, analisis penduaan sampel, menggunakan penilaian kepekatan unsur rujukan piawai dan menggunakan kaedah  $K_0$ -NAA. Data yang dijana dengan kaedah ICP-MS juga telah dipastikan kualitinya dengan cara yang sama tetapi tanpa menggunakan kaedah  $K_0$ -NAA.

Untuk taburan kepekatan mengufuk pesampelan cukup telah digunakan. Unsur bukan antropogenik yang dikenal pasti menggunakan factor pengayaan ialah Al, Ba, Cd, Co, Cr, Cu, K, Mg, Mn, Mo, Ni, Rb, Sr, Ta, Ti, V, and Zn yang mempunyai kepekatan lebih rendah berbanding dengan kepekatan kedua-dua bahan dalam batuan dan kerak bumi. Kepekatan Mg lebih rendah berbanding purata kepekatan dalam batuan tetapi lebih tinggi sedikit berbanding purata kepekatan dalam kerak bumi. Sementara kepekatan Rb lebih tinggi sedikit berbanding purata kepekatan kerak bumi tetapi lebih rendah berbanding purata kepekatan dalam batuan. Keadaan ini mungkin disebabkan oleh Mg, Na, and Rb lebih mudah larut dalam cuaca panas iklim tropika seperti di kawasan perairan Selat Melaka. Unsur antropogenik yang telah di kenal pasti dalam sampel sedimen cukup ialah As, Br, Cs, Fe, Hf, Pb, Sb, Th,

dan U. Kepekatan As, Br, Cs, Hf, Pb, dan Sb lebih besar daripada purata kepekatan bahan kerak bumi. Ini mungkin disebabkan terdapatnya input bahan pencemaran daripada aktiviti perindustrian dan perlombongan di kawasan daratan sepanjang Selat Melaka. Kepekatan Pb didapati menghampiri dua kali kepekatan dalam batuan dan tiga kali lebih tinggi daripada bahan kerak bumi. Kepekatan Pb yang tinggi dalam sampel cukup mungkin disebabkan aktiviti industri seperti kilang bateri dan pencemaran kenderaan di bandar-bandar sepanjang sungai yang mengalirkan airnya ke Selat Melaka.

Untuk taburan kepekatan mencacang pesampelan teras telah digunakan. Unsur bukan antropogenik yang dikenal pasti menggunakan factor pengayaan ialah Al, Ba, Cd, Co, Cr, Cu, K, Mg, Mn, Mo, Ni, Rb, Sr, Ta, Ti, V and Zn yang didapati lebih rendah berbanding purata kepekatan dalam bahan kerak bumi begitu juga berbanding dengan purata dalam batuan. Unsur antropogenik yang di kenal pasti dalam sample sedimen teras pula ialah As, Br, Ca, Cs, Hf, Pb, Sb, Th and U yang mana kepekatan Br, Ca, Cs, Hf, Th and U adalah lebih besar daripada purata kepekatan dalam bahan kerak bumi dan juga berbanding purata dalam batuan. Ini mungkin disebabkan terdapatnya input bahan pencemaran daripada aktiviti perindustrian dan perlombongan di kawasan daratan sepanjang Selat Melaka. Di samping itu kepekatan Pb di dapati lebih besar berbanding purata dalam kerak bumi tetapi lebih rendah berbanding dengan kepekatan dalam batuan. Untuk unsur toksik seperti As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb dan Zn, menunjukkan purata kepekatan sama ada lebih rendah atau setara dengan purata kepekatan dalam sedimen daripada perairan Johor dan Pulau Pinang. Dalam pada itu juga, kepekatan purata untuk semua unsur berkenaan didapati kepekataannya lebih rendah berbanding dengan nilai penunjuk

pencemaran antarabangsa daripada Canada, Netherlands dan USA-Negeri New York kecuali bagi kepekatan Cr dan Ni dimana kepekataannya lebih tinggi daripada penunjuk pencemaran antarabangsa.

Profil kepekatan unsur As/Al, Cd/Al, Cr/Al, Cu/Al, Fe/Al, Mn/Al, Sb/Al dan U/Al yang dinormalisasikan terhadap kepekatan logam aluminium menurut kedalaman teras sampel sedimen menunjukkan bahagian lapisan teratas lebih tinggi kepekataannya berbanding lapisan bawah. Tingginya kepekatan As, Cd, Cr, Cu, Fe, Mn, Sb, and U mungkin boleh dijelaskan oleh kurangnya kepekatan oksigen di antara lapisan sedimen dan kolom air, menyebabkan terbentuknya sedimen permukaan yang anoksik. Ini mengakibatkan berlakunya proses diagenesis yang menyebabkan unsur-unsur multi-oksidaan berhijrah daripada sedimen bahagin bawah ke permukaan. Ini menunjukkan bahawa dalam sedimen marin teras kandungan paras oksigen adalah mencukupi dan masih sesuai untuk ekosistem marin.

## ACKNOWLEDGEMENTS

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

In the Name of God, the Most Gracious, the Most Merciful

First of all, all praises due to Allah, Lord of the universe. Only by His grace and mercy this thesis has been completed.

I would like to take this opportunity to express my most grateful and deep appreciation to my supervisor and Chairman of the Supervisory Committee Professor Dr. Elias Saion for his sincere and invaluable guidance, honest encouragement, and patience throughout my research.

I would like to extend my heartfelt gratitude to the member of my Supervisory Committee, Dr. Abdul Khalik Wood for his continuous follow up, invaluable contribution, and generous support. I wish to express my very much thankful to the member of my Supervisory Committee, Assoc. Prof. Dr. Zainal Abidin Sulaiman for his guidance and honest encouragement.

I am grateful to my government of Saudi Arabia - the King Abdul-Aziz City for Science and Technology (KACST), Institute of Atomic Energy Research for approving the leave to pursue my PhD study.

Thanks are expressed to the Malaysian Nuclear Agency (MNA) for their continuous supporting and the usage of their facilities. I extend my words of thanks to the RAS staff, namely Mr. Hj Halim, Mrs. Shamsiah Abdul-Raham, Dr. Mohammed Suhaimi

and Mr. Wee Siong for their support and assistance. I am very much thankful and especial thanks to Mr. Md Suhaimi Elias and Mr. Ariffin Talib for their help in collecting data in the laboratories. Especial thanks to the staff of MNA research reactor in particular En. Adnan Bokhari for his help.

I would like to extend my great thanks to the staff of the Department of Physics, Universiti Putra Malaysia.

Special thanks are extended to my research group namely, Mr. Iskandar , Mr. Azhar, Mr. Yusuf, Mr. Zain and Mrs. Shifa. My great thanks go to the invaluable colleagues and good friends ever since Mr. Mohammad Ahmed Omer and Mr. Khalid Rabiah.

I would like to express my deepest gratitude to my parents, brothers and sisters for their prayers and unending encouragement. Finally, I would like to express my sincere gratitude to my wife, my daughters and sons for their patience and prayers.

I certify that an Examination Committee has met on 28 March 2007 to conduct the final examination of Awad Ahmed Al-Zahrany on his Doctor of Philosophy thesis entitled “Elemental Distributions in Marine Sediments in the Straits of Melaka Using Neutron Activation and Mass Spectroscopic Analyses” in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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## **DECLARATION**

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

---

**AWAD AMED AL-ZAHRANY**

Date: 2007

## TABLE OF CONTENTS

	<b>Page</b>
<b>DEDICATION</b>	2
<b>ABSTRACT</b>	3
<b>ABSTRAK</b>	7
<b>ACKNOWLEDGEMENTS</b>	11
<b>APPROVAL</b>	13
<b>DECLARATION</b>	15
<b>LIST OF TABLES</b>	20
<b>LIST OF FIGURES</b>	34
<b>LIST OF ABBREVIATIONS</b>	45

### CHAPTER

<b>1</b>	<b>INTRODUCTION</b>	
	1.1 General Introduction	49
	1.2 Sources of Heavy Metals in the Marine Sediments	50
	1.3 General View and the Importance of Trace Elements	53
	1.4 Definition of the Study Area	54
	1.5 Significance of the Study	58
	1.6 Problem Statement	60
	1.7 The Scope of the Present Study	61
	1.8 Objectives of the Study	61
	1.9 Outline of the Thesis	62
<b>2</b>	<b>LITERATURE REVIEW</b>	
	2.1 Introduction	64
	2.2 Elemental Pollution in the West Coast of Peninsular Malaysia	64
	2.3 Elemental Pollution in other Regions of Peninsular Malaysia	67
	2.4 Studies of Elemental Pollution in Different Regions over the World	74
<b>3</b>	<b>THEORETICAL</b>	
	3.1 Introduction	79
	3.2 Neutron Energy Classification	80
	3.3 Sources of Neutrons	82
	3.3.1 Nuclear Reactors	82
	3.3.2 Spontaneous Fission Sources	83
	3.3.3 Neutron Generators	84
	3.3.4 Alpha Particle-Neutron Reactions	84



3.3.5	Photo-Neutron Sources	85
3.4	Interaction of Neutrons with Matter	86
3.4.1	Elastic Scattering	87
3.4.2	Inelastic Scattering	87
3.4.3	Radiative Capture Reaction	88
3.4.4	Charged Particle Reaction	88
3.4.5	Fission Reaction	89
3.5	Neutron Cross Sections	89
3.6	Principles of Neutron Activation Analysis Technique	91
3.7	Neutron Activation Analysis Categorizations	93
3.7.1	Prompt Gamma-Ray Neutron Activation Analysis (PGNAA)	94
3.7.2	Instrumental Neutron Activation Analysis (INAA)	94
3.7.3	Epithermal neutron activation analysis (ENAA)	94
3.7.4	Radiochemical neutron activation analysis (RNAA)	96
3.8	Advantages of Instrumental Neutron Activation Analysis	97
3.9	Disadvantages of Neutron Activation Analysis	98
3.10	Interaction of Gamma-Rays with Matter	98
3.10.1	Introduction	98
3.11	Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)	106
3.11.1	Principles Operation of ICP-MS System	107
3.11.2	Sample Introduction System and Radio-Frequency (RF) Generator	109
3.11.3	Interface Region and Vacuum System	110
3.11.4	Quadrupole Mass Spectrometer and Detector	111

## 4

### **MATERIALS AND METHODS**

4.1	Procedure for Collection of the Grab Sediment Samples	112
4.2	Procedure for Collection of the Core Sediment Samples	115
4.3	Preparation of Sediment Samples for INAA	121
4.4	Preparation of Sediment Samples for ICP-MS Analysis	122
4.5	Irradiation Facility	124
4.6	Reactor Components	126
4.6.1	The Reactor Core	126
4.6.2	Reflector	126
4.6.3	Fuel-Moderator Elements	127
4.6.4	Graphite Dummy Elements	127
4.6.5	Control System	127
4.6.6	Reactor Water System	127
4.6.7	Neutron sources	128

4.7	Experimental and Irradiation Facilities	130
4.8	Characteristics of the Gamma-Ray Spectrometry System	131
4.8.1	Introduction	131
4.8.2	Energy Calibration of the Gamma-Ray Spectroscopy System	136
4.8.3	Efficiency Calibration of the Gamma-Ray Spectroscopy System	138
4.9	Lower Limit of Detection (LLD)	145
4.10	The Concentration Calculation	147
4.11	Preparation of Standards used for Calculating the Elements Concentrations	153
4.12	Preparation of Standards used for ICP-MS	154
4.13	Elemental Analysis Methods for INAA	160
4.13.1	Relative Method	160
4.13.2	Single Comparator Standardization by K <sub>0</sub> Method	163
4.14	Instrumental Neutron Activation Analysis Procedure	164
4.15	Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) Analysis Procedure	166

## 5

### RESULTS AND DISCUSSION

5.1	Applicability of the INAA Technique for Analysis of Marine Sediment	167
5.1.1	Investigation of the Applicability by Using the CRM	167
5.1.2	Comparison of INAA and ICP-MS Analysis for As, Mn, and Zn	174
5.1.3	K <sub>0</sub> -INAA Results of Analysis of the CRM	175
5.2	Quality Assurance and Quality Control of INAA Technique	177
5.2.1	Precision determination by duplication the samples	178
5.2.2	Blank Samples	179
5.2.3	Certified Reference Materials (CRM)	179
5.3	Quality Control for ICP-MS Analysis Technique	185
5.3.1	Precision determination by duplication the samples	185
5.3.2	Blank Samples	185
5.3.3	Certified Reference Materials (CRM)	186
5.4	Results and Data Analysis for the Grab Sediment Samples	190
5.4.1	Comparison the Average Concentrations in the Grab Sediment Samples to the Concentration of Mean Crustal Materials and Average Shales	192

5.4.2	Comparative the Most Toxic Elements to National Studies and the International Guideline for Marine Sediments	194
5.4.3	Using Enrichment Factor for Evaluation the Anthropogenic Sources	210
5.4.4	Statistical Analysis	259
5.5	Results and Data Analysis for the Core Sediments Samples	275
5.5.1	Comparison the Average Concentrations in the Core Sediment Samples to the Concentration of Mean Crustal Materials and Average Shales	281
5.5.2	Comparative the Most Toxic Elements to National Studies and International Guideline for Marine Sediment	304
<b>6</b>	<b>CONCLUSION</b>	
6.1	Spatial Distribution of Elemental Pollution in the Straits of Melaka	325
6.2	Vertical Distribution of Elemental Pollution in the Straits of Melaka	328
6.3	Future Work and Recommendations	330
	<b>REFERENCES</b>	333
	<b>APPENDICES</b>	342
	<b>BIODATA OF THE AUTHOR</b>	448

## LIST OF TABLES

Table		Page
1.1	Total marine fish landings by fishing areas in Peninsular of Malaysia in 1997	60
2.1	The range of the Cu and Pb concentrations ( $\mu\text{g/g}$ ) in offshore and Intertidal sediments of the West Coast of Peninsular Malaysia	66
2.2	The range of the Cd and Zn concentrations ( $\mu\text{g/g}$ ) in offshore and intertidal sediments of the West Coast of Peninsular Malaysia	67
2.3	Range and mean of elemental concentrations in surface sediments of Straits of Johor	70
2.4	Mean concentrations in 0-2 layer of the coastal sediments of Penang Island and the range, mean for grab sediments samples of the Penang Island	73
3.1	Neutron sources from ( $\alpha$ , n) reactions	85
3.2	Neutron sources from ( $\gamma$ , n) reactions	86
4.1	Geographic coordinates, distance from the offshore and water depth of garb marine sediment samples from the Straits of Melaka	113
4.2	Geographic coordinates, distance from the offshore and water depth of core marine sediments samples for station WC01 from the Straits of Melaka	117
4.3	Geographic coordinates, distance from the offshore and water depth of core marine sediment samples for station WC02 from the Straits of Melaka	118

4.4	Geographic coordinates, distance from the offshore and water depth of core marine sediment samples for station WC03 from the Straits of Melaka	119
4.5	Geographic coordinates, distance from the offshore and water depth of core marine sediment samples for station WC04 from the Straits of Melaka	120
4.6	Gamma energies used for gamma energy calibration	137
4.7	Lower limit of detection in ppm for (INAA) using decay gamma-rays	146
4.8	gamma-ray energy lines used for analysis, half-life, abundance of gamma-ray energy, nuclear reaction and thermal cross section of reaction for short-lived radio-nuclides	150
4.9	gamma-ray energy lines used for analysis, half-life, abundance of gamma-ray energy, nuclear reaction and thermal cross section of reaction for medium-lived radio-nuclides	151
4.10	gamma-ray energy lines used for analysis, half-life, abundance of gamma-ray energy, nuclear reaction and thermal cross section of reaction for long-lived radio-nuclides	152
4.11	Standard sources that used for determination of short-lived isotopes	156
4.12	Standard sources that used for determination of medium- lived isotopes	157
4.13	Standard sources that used for determination of long-lived isotopes	158
4.14	The detection limit for some elements in water solution measured by ICP-MS	159
5.1	Comparison of concentrations determined in the IAEA-SOIL7 with the certified and the recommended values by INAA in	169

	the comparative method	
5.2	Comparison of concentrations determined in the NIST-SRM 1646a Estuarine Sediment with the certified and the recommended values by INAA in the comparative method	171
5.3	Comparison of concentrations determined in the IAEA-SL-1 with the certified and the recommended values by INAA in the comparative method	173
5.4	Comparison of concentrations determined in the IAEA-SOIL7 with the certified and the recommended values by INAA and ICP-MS methods	174
5.5	Comparison of concentrations determined in the IAEA-SOIL7 with the certified and the recommended values by INAA in the $K_0$ -method	176
5.6	Comparison of concentrations determined in the certified reference material (IAEA-SOIL7) between the certified and the recommended values for INAA by comparative method and $K_0$ -method for analysis of the grab samples	182
5.7	Comparison of concentrations determined in the certified reference material (IAEA-SOIL7) with the certified and the recommended values for INAA by comparative method and $K_0$ -method for the core samples	184
5.8	Comparison of concentrations determined in the certified reference material (IAEA-SOIL-7) with the certified and the recommended values for ICP-MS results for analysis of the grab samples	188
5.9	Comparison of concentrations determined in the certified reference material (IAEA-SOIL-7) with the certified and the recommended values for ICP-MS results for analysis of the core samples	189
5.10A	Concentrations of non-anthropogenic elements (ppm dry-weight) in the grab sediment samples from the Straits of Melaka	202



5.10B	Concentrations of non-anthropogenic elements (ppm dry-weight) in the grab sediment samples from the Straits of Melaka	203
5.10C	Concentrations of non-anthropogenic elements (ppm dry-weight) in the grab sediment samples from the Straits of Melaka	204
5.10D	Concentrations of non-anthropogenic elements (ppm dry-weight) in the grab sediment samples from the Straits of Melaka	205
5.11A	Concentrations of anthropogenic elements (ppm dry-weight) in the grab sediment samples from the Strait of Melaka	206
5.11B	Concentrations of anthropogenic elements (ppm dry-weight) in the grab sediment samples from the Straits of Melaka	207
5.12A	Rare earth elements concentrations (ppm dry-weight) in the grab sediment samples from the Straits of Melaka	208
5.12B	Rare earth elements concentrations (ppm dry-weight) in the grab sediment samples from the Straits of Melaka	209
5.13	Comparison of elemental concentration ranges in the grab sediments of the Straits of Melaka with those in average shale and mean crustal material	221
5.14	Comparison of elemental concentration ranges and mean in the grab sediments of the Straits of Melaka with those of the Straits of Johor and the Penang Island	222
5.15	Comparison of elemental concentration ranges in the grab sediments Samples of the Straits of Melaka with guideline of sediment quality of Canadian, Netherlands, and USA-NYS	223
5.16A	Enrichment factors of determined elements in the grab sediment samples from the Straits of Melaka	216