



Enhancements and Health-Related Studies of Neutron Activation Analysis Technique

**A Thesis Submitted
By**

Mohamed Ali Moawad Soliman
Atomic Energy Authority

To

**Department of Chemistry,
Faculty of Science,
University of Ain Shams**

**In
Partial Fulfillment of the Requirements for a
PhD Degree in Chemistry**

Cairo, 2012

Enhancements and Health-Related Studies of Neutron Activation Analysis Technique

A Thesis Submitted

By

Mohamed Ali Moawad Soliman

Atomic Energy Authority

To

Department of Chemistry, Faculty of Science,
University of Ain Shams

In

Partial Fulfillment of the Requirements for a
PhD Degree in Chemistry

Supervised by

Prof. Dr. Ebtissam A. Saad

*Department of Chemistry,
Faculty of Science,
University of Ain Shams*

Prof. Dr. Samir K. Youssef

*Department of Radiation
Protection & Civil Defense,
Nuclear Research Centre,
Atomic Energy Authority*

Prof. Dr. Moustafa A. Sohsah

*Department of Radiation
Protection & Civil Defense,
Nuclear Research Centre,
Atomic Energy Authority*

Dr. Nader M. Abdelhalim

Mohamed
*Egypt Second Research Reactor,
Atomic Energy Authority*

Cairo, 2012

Enhancements and Health-Related Studies of Neutron Activation Analysis Technique

Thesis Submitted

By

Mohamed Ali Moawad Soliman
Atomic Energy Authority

Thesis Advisors:

Signature

- 1- Prof. Dr. Ebtissam Ahmed Saad**
Department of Chemistry,
Faculty of Science,
University of Ain Shams
- 2- Prof. Dr. Samir K. Youssef**
Department of Radiation Protection & Civil Defense,
Nuclear Research Centre,
Atomic Energy Authority
- 3- Prof. Dr. Moustafa A. Sohsah**
Department of Radiation Protection & Civil Defense,
Nuclear Research Center,
Atomic Energy Authority
- 4- Dr. Nader M. Abdelhalim Mohamed**
Egypt Second Research Reactor,
Atomic Energy Authority

Head of the Department of Chemistry

Prof. Dr./ M. S. Antonios

ACKNOWLEDGMENTS

All praise to Almighty Allah, We repose our trust in him, and look forward to him for assistance, which his generosity and blessings were the stimulus for success in my life.

*I would like to express my deep gratitude to **Prof. Dr. Ebtissam A. Saad**, Chemistry Department, Faculty of Science, Ain Shams University; for her sponsorship of this work, and constructive discussions.*

*The author would like to express his deep thanks to **Prof. Dr. Samir K. Youssef**, protection & Civil Defense Department, Atomic Energy Authority; for his sincere advice and valuable discussions.*

*Also, I want to express my sincere appreciation to **Prof. Dr. Moustafa A. Sohsah**, Radiation protection & Civil Defense Department, Atomic Energy Authority; for his continuous supervision and valuable discussions.*

*I am greatly indebted to **Dr. Nader Mohamed**, Egypt Second Research Reactor (ETR-2), Atomic Energy Authority for planning of the experimental work, effective supervision, valuable discussions, sincere advices and continuous encouragement during all phases of carrying this work.*

*Deep appreciations to **Dr. Mohamed Gaheen**, **Dr. Ashraf Moustafa Abdelmoneam** and **Dr. Ahmed Mohamed Osman**, Atomic Energy Authority; for helping during the practical parts of this thesis.*

M. Soliman

Cairo, 2012

Abstract

The work presented in this thesis covers two major points. One algorithm concerns with establishment of an accurate standardization method with multi-elemental capabilities and low workload suitable for NAA standardization at ETRR-2. The second one deals with constructing and developing an effective non-destructive technique for analysis of liquid samples based on NAA using (very) short-lived radionuclides.

To achieve the first goal, attention has been directed toward implementation of the k_0 -method for calculation of the elements concentrations in the samples. The k_0 -method of NAA-standardization has a considerable success as a method for accurate multi-elemental analysis with comparable low workload. The k_0 -method is based on the fact that the unknown sample is irradiated with only one standard element as comparator. To access the implementation of this method at ETRR-2, careful and complete characterization of the neutron flux parameters in the irradiation positions as well as the efficiency calibration of the γ -ray spectrometer must be carried out. The required neutron flux parameters are: the ratio of the thermal to epithermal neutron fluxes (f) and the deviation factor (α) of the epithermal neutron flux from the ideal $1/E$ law. The work presented in Chapter 4 shows the efficiency calibration curve of the γ -ray spectrometer system which was obtained using standard radioactive point sources. Moreover, the f and α parameters were determined in some selected irradiation sites using sets of Zr-Au as neutron flux monitors. Due to different locations relative to the reactor core, the available neutron fluxes in the selected irradiation positions differ substantially, so that

different irradiation demands can be satisfied. The reference materials coal NIST 1632c and IAEA-Soil 7 were analyzed for data validation and good agreement between the experimental values and the certified values was obtained. The obtained results have revealed that the k_0 -NAA procedure established at the ETRR-2 can be regarded as a reliable standardization method of NAA and as available analytical method for elemental analysis of samples especially those for which are difficult to find a proper reference material. The analysis of reference materials indicates that under our experimental conditions, results may have maximum biases of less than 5% from the true values for elements analyzed using the so-called $1/v$ nuclei.

To solve the problems of liquid samples, *Flowing Sample Neutron Activation Analysis (FSNAA)* set-up was constructed in this work. The developed set-up involves a continuously flowing of the liquid sample between the irradiation site and the detector in a polyethylene tube line by the aid of mechanical pump. Due to unavailability of irradiation facility in ETRR-2 suitable for accommodation of the developed set-up, a ^{252}Cf neutron source was used to carry out the irradiation process. This arrangement aims to achieve several objects. Firstly, the complicated pretreatment (preconcentration) steps of liquid samples can be omitted via analysis of large volume of the sample. Secondly, saving time and irradiation containers since the preparing of replicates is not required. Finally, the effect of dead time can be minimized, since flowing sample continuously feeds the detector with fresh radioactive material, keeping the radioactivity level constant during the whole period of measurement.

Modeling calculations using MCNP, version 5 were performed to optimize the γ -ray counting configurations and derive the required correction factors. An MCNP simulation was used to define the best thickness of paraffin fixed between the source and helical irradiation hose to get the highest intensity of thermal neutrons.

The repeatability of FSNA was investigated. Less than 3% standard deviation between the results of several measurements was achieved. The detection limits, accuracy and ability to remove spectral interference of the new system were tested by analysis of synthetic single and multi-elements standards solutions. The obtained detection limits compare favorably with those obtained by conventional INAA methods and other analytical method. Besides, the developed method seems to have many advantages when compared with conventional INAA methods. These include:

- Ability to analyze liquid samples without preconcentration steps
- Low detection limits
- Simplicity and no need for blank correction
- Ability to analyze inhomogeneous solutions (like colloidal or suspended solutions) with pretreatment processes, if total elemental content is required

In addition, the developed FSNA procedure was tested for determination of trace and ultra-trace elements of nutritional and toxicological significance in water sample collected from the Mediterranean Sea in some areas of Alexandria, Egypt. Therefore, it is necessary to determine its elemental content in order to

evaluate its effect on food chains and hence on the health of human being. Due to low intensity of the neutron source, only Na and Cl were determined in the examined sample. It was expected that more elements could be measured if high neutron flux source (like nuclear reactor) is used.

The obtained results indicate that the FSNA is a simple procedure which is promising analytical method for analysis of liquid samples with low detection limits. It can be used for monitoring the elements levels in environmental samples (water or compressed air), industrial wastewater and other liquid samples. It can also be utilized for analysis of urine and other animals' effluents for health-related studies.

Contents

<i>Title</i>	<i>Page</i>
Acknowledgements	i
Abstract	ii
Table of Contents	vi
List of Symbols	xi
List of Abbreviations	xiv
List of Tables	xv
List of Figures	xvii
 Chapter 1. General Introduction	 1
1.1 Motivation	1
1.2 Scope of the dissertation work	3
1.3 Literature Review	5
1.3.1 NAA standardization	5
1.3.2 CNAA	9
1.3.3 Elemental analysis of liquid samples using NAA	15
1.3.4 Conclusion	17
 Chapter 2. Theory of NAA	 19
2.1 Basic Idea of Neutron Activation Analysis	19
2.2 Classification of Neutron Activation Analysis	22
2.2.1 Cyclic Neutron Activation Analysis (CNAA)	23

2.2.1.1 Limitations of CNAA	25
2.2.1.1.1 Limitations on the type of samples	25
2.2.1.1.2 Limitations on the number of cycles	25
2.2.1.1.3 Limitations on the accuracy	26
2.3 Origin and Optimization of the Technique	27
2.4 Activation with Neutron	31
2.4.1 Neutron sources	31
2.4.1.1 Nuclear reactors	31
2.4.1.2 Neutron generators	33
2.4.1.3 Radioisotopic Neutron sources	34
2.4.1.4 Fission neutron sources	34
2.4.2 Neutron capture process	35
2.4.2.1 Reaction rate	35
2.5 Radioactivity measurement	40
2.5.1 Interaction of γ -rays with matter	41
2.5.2 Detection of γ -rays in neutron activation analysis	44
2.5.2.1 Detector resolution	44
2.5.2.2 Detector efficiency	45
2.5.3 Counting of activated sample	47
2.6 Interpretation of gamma-ray spectrum	49
2.6.1 Absolute method	50
2.6.2 Relative method	50
2.6.3 Single comparator method	52
2.6.4 The k_0 method	53
2.7 Detection Limits in INAA	54
2.8 Accuracy in INAA	57
2.8.1 Accuracy of qualitative analysis	58

2.8.2 Accuracy of quantitative analysis	59
Chapter 3. Experimental	62
3.1 Facilities and Apparatus	62
3.1.1 INAA facility at ETRR-2	62
3.1.1.1 Neutron irradiation sites at ETRR-2	62
3.1.1.2 Gamma-rays spectrometer	64
3.1.2 FSNAAs set-up	64
3.1.2.1 Irradiation cell	65
3.1.2.2 Detection system	66
3.1.2.3 Mechanical pump	66
3.1.2.4 Reservoirs	66
3.1.2.5 Pipeline	67
3.2 Materials and Reagents	68
3.2.1 Radionuclides standard sources	68
3.2.2 Neutron flux monitor	69
3.2.3 Standard solutions	70
3.2.3.1 Dysprosium standard	70
3.2.3.2 Silver standard	70
3.2.3.3 Indium standard	70
3.2.3.4 Vanadium standard	71
3.2.3.5 Manganese standard	71
3.2.4 Miscellaneous	72
3.3 Methods	72
3.3.1 Method applied for characterization of irradiation facility	72
3.3.2 General procedure for FSNAAs of liquid samples	73

3.3.3 Monte Carlo simulations	75
3.3.3.1 Gamma ray detection model	75
3.3.3.2 Neutron irradiation model	76
3.4 Data Analysis and Presentation	77
3.4.1 Estimation of neutron flux parameters	77
3.4.2 Concentration level	79
3.4.3 Method sensitivity	79
3.4.4 Detection limits	79
3.4.5 Repeatability of the system	80
3.4.6 Accuracy evaluation	80
 Chapter 4. Implementation of k_0- Standardization Method	 81
4.1 Calibration of Gamma-ray Spectrometer	81
4.1.1 Energy calibration	81
4.1.2 Energy resolution calibration	82
4.1.3 Efficiency calibration	83
4.2 Determination of the flux parameters	83
4.3 Analysis of Reference Materials	87
 Chapter 5. FSNA System Set-Up and Analysis Results of Liquid Samples	 90
5.1 Characterization of the FSNA System	90
5.1.1 Characterization of the detection system	91
5.1.1.1 Selection of counting geometry	91

Table of Contents

5.1.1.1.1 Selection of the pipeline diameter	91
5.1.1.1.2 Selection of the torus diameter	93
5.1.1.2 Efficiency calibration for point source	93
5.1.1.3 Derivation of the efficiency transfer function	94
5.1.2 Characterization of the transport system	95
5.1.2.1 Measuring the total volume	95
5.1.2.2 Determination of pump flow-rate	97
5.1.2.3 Effect of water head in the sample tank on pump flow-rate	98
5.1.3 Characterization of the neutron source	99
5.2 Testing the System Repeatability	101
5.3 Testing the Stability of Dead Time During Counting	102
5.4 Analysis of Single Element Standards	103
5.4.1 Effect of number of cycles	103
5.4.2 Effect of flow-rate	107
5.5 Analysis of Multi-Element Standard Solution	113
5.6 Analysis of Sea Water Sample	119
 Chapter 6. General Conclusions and Recommendations	 125
 References	 130
 Arabic summary	

List of Symbols

k'	Calibration constant
ϕ_{ep}	Epithermal neutron flux of energies between 0.55 e V and 0.5 MeV
ϕ_f	Fast neutron flux for energies more than 0.5 MeV
σ_r	Method repeatability
ϕ_{th}	Thermal neutron flux for energies up to 0.55 eV
ζ	Zeta score
$\phi(E)$	Neutron flux (neutron.cm ⁻² .s ⁻¹) of neutron with energy E
A	Source strength
A_p	Full-energy peak count rate
b	Barn, unit of cross-section. 1 $b = 10^{-24}$ cm ²
C	Counting factor
D	Decay factor
D_L	Detection limit
E	Neutron energy
f	Thermal neutron to epithermal neutron fluxes ratio
I_0	Infinite dilution resonance integral
k	k -factor
k_0	k_0 -factor
M	Atomic weight
N	Number of radioactive nuclei