



JOINT INSTITUTE FOR NUCLEAR RESEARCH
Frank Laboratory of Neutron Physics

FINAL REPORT ON THE START PROGRAMME

*Neutron activation and related analytical
techniques in environmental studies*

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Abstract

Water pollution by heavy metals has become a primary global concern. Heavy metals such as Fe, Mn, Cr, Zn, and Al in water have negative effects on the environment and human health, including allergies, hyperpigmentation, skin lesions, skin cancer, neurological effects, hypertension, cardiovascular disease, and pulmonary disease. Neutron activation analysis (NAA) was proved to be a powerful analytical method for determining the inorganic elemental composition in quantitative and qualitative terms and was used in environmental research and the solution of ecological problems by using different species such as plants, spirulina, and algae. The analysis was conducted at JINR, Dubna, Russia to calculate the concentrations of elements in samples using Genie2000 software that was developed by Canberra, which was used for determining the activity of isotopes, then the "CalcConc" software that was developed by (Dmitriev and Pavlov, 2013), and it was used to calculate the concentrations of elements.

1. INTRODUCTION

The concentrations of elements in various materials can be determined by using Neutron Activation Analysis (NAA). NAA ionizes the treated material by using neutrons., which causes it to emit gamma rays. It makes it possible to identify and measure every element in the sample, even trace ones. it is used in chemistry, as well as in forensic science, environmental monitoring, medicine, archaeology, and even geology (Frontasyeva, 2011). Due to its sensitivity, neutron activation analysis is frequently used to search for minor elements in very low concentrations. The technique is essential in semiconductor processes because it is especially helpful for the analysis of trace elements, as in high-purity materials. Additionally, it can find trace elements in minerals, biological matter, water, and archeological objects by using the "fingerprint" of the individual element composition in their raw materials that can offer helpful information about the provenance of objects (Frontasyeva, 2011; Witkowska et al., 2005)

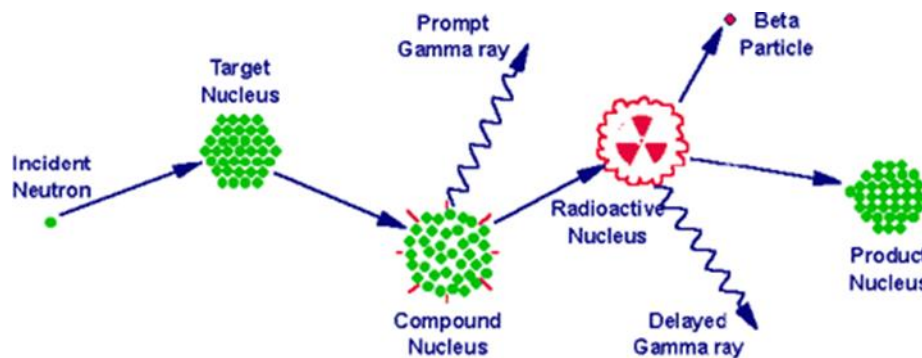


Fig. 1: Gamma rays are emitted after neutrons are captured by a target nucleus.

1.1. NAA IS A POWERFUL ANALYTICAL TECHNIQUE

Nowadays, sample analysis methods include atomic absorption spectrometry (AAS), X-ray fluorescence analysis (XFA), inductively coupled plasma-atomic emission spectrometry (ICP-AES), inductively coupled plasma-mass spectrometry (ICMP-MS), synchrotron radiation, neutron activation analysis (NAA), and other nuclear physics methods. In Fig. 2, the detection thresholds for various analytical techniques are displayed. NAA can identify up to 55 elements, as shown in fig. 3, with minimum detection limits varying from 10^{-7} to 10^{-15} g/g depending on the elements and matrix materials. Numerous neutrons can be gathered by some nuclei, which can then maintain their relative stability for weeks, months, or even years without transmutation or disintegration. The detection limits are extremely varied because different nuclei have different cross-sections,

half-lives, and intensity levels of gamma rays that are released. In trace element analyses, NAA is frequently used to identify rare earth elements (REE) because they have extraordinarily high thermal neutron cross-sections (Frontasyeva, 2011).

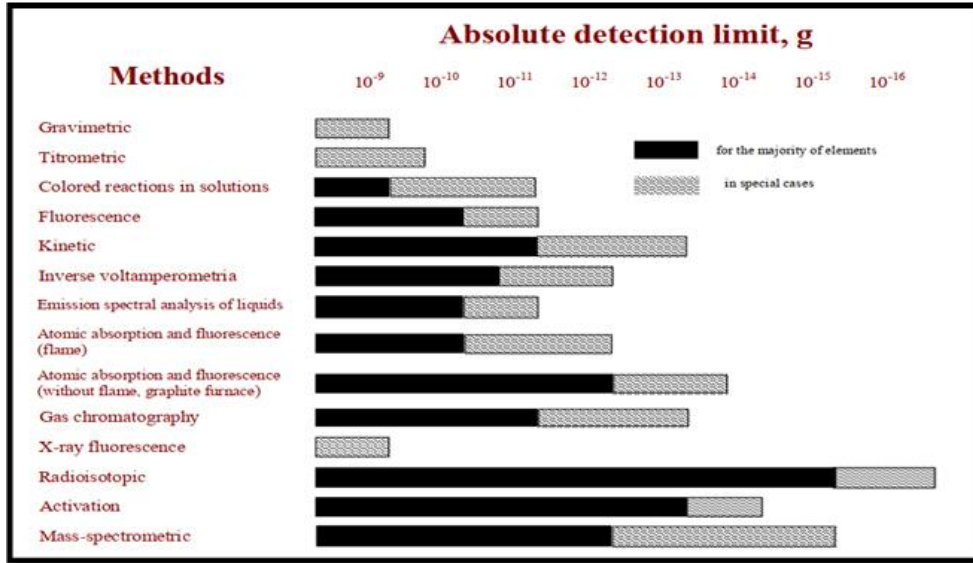


Fig. 1: A number of analytical techniques and absolute detection limit in grams.

H																			He
Li	Be											B	C	N	O	F			Ne
Na	Mg											Al	Si	P	S	Cl			Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br			Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I			Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At			Rn
Fr	Ra	Ac**											Rf	Db	Sg	Bh			Hs
		*	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
		**	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw			

Figure 3. Elements can be obtained by NAA

1.2. FUNDAMENTALS OF NAA

NAA is a method for determining elements that rely on nuclear processes to convert stable nuclei to radioactive nuclei. The nuclear reactions are triggered by bombarding the material to be analyzed with neutrons. The reaction products to be measured are either the radiation, produced almost instantly upon neutron capture, or the induced radioactivity, released as the new nuclei decay. All stable elements have features that allow them to produce radioactive isotopes at various reaction rates. several factors could be used to distinguish the radionuclides such as (i) decay constant, and (ii) the kind and energy of the released radiation. This technique has the benefit of not destroying the material, so it has been used to examine historical artifacts and works of art. and consider one of the most effective methods for multi-element analysis. that has been explored and used to study major, minor, and trace elements at the Joint Institute for Nuclear Research's Frank Laboratory of Neutron Physics. Examples of situations where NAA techniques can produce accurate results include the following:

- Determining the composition and concentration of elements in archaeological artifacts, especially ceramics, cultural heritage, and pottery, and research characteristics.
- Analyzing the concentrations of rare-earth, uranium, thorium, and other elements in geological samples to meet the demands of clients, particularly mineral resource geologists.
- The examination of the trace element composition of rock samples.
- Measuring the amount of toxic and contaminated heavy elements in various samples, including sediment, soil, and plants, using accepted reference material.

1.3. TYPES OF NAA:

NAA is divided into two types:

1- Nondestructive NAA means that the radioactive sample is not destroyed. However, there will be changes at the nucleus level. some nondestructive NAA examples (Bode et al., 2009; Greenberg et al., 2011):

- a. Instrumental Neutron Activation Analysis Activation INAA
- b. Epithermal Neutron Activation Analysis Activation ENAA
- c. Fast Neutron Activation Analysis Activation FNAA
- d. Cyclic Neutron Activation Analysis Activation CNAA
- e. In Vivo - Neutron Activation Analysis Activation In-vivo NAA.

2- Destructive NAA: Following irradiation, the radioactive sample undergoes chemical processing or decomposition. Only the following type is included in this kind:

- Radiochemical or destructive neutron activation analysis RNAA or DNAA

1.4. Types of Neutron Energy

- Thermal (0.025 eV – 0.5 eV)
- Epithermal (0.5 eV – 10 keV)
- Fast (10 keV – 25 MeV)

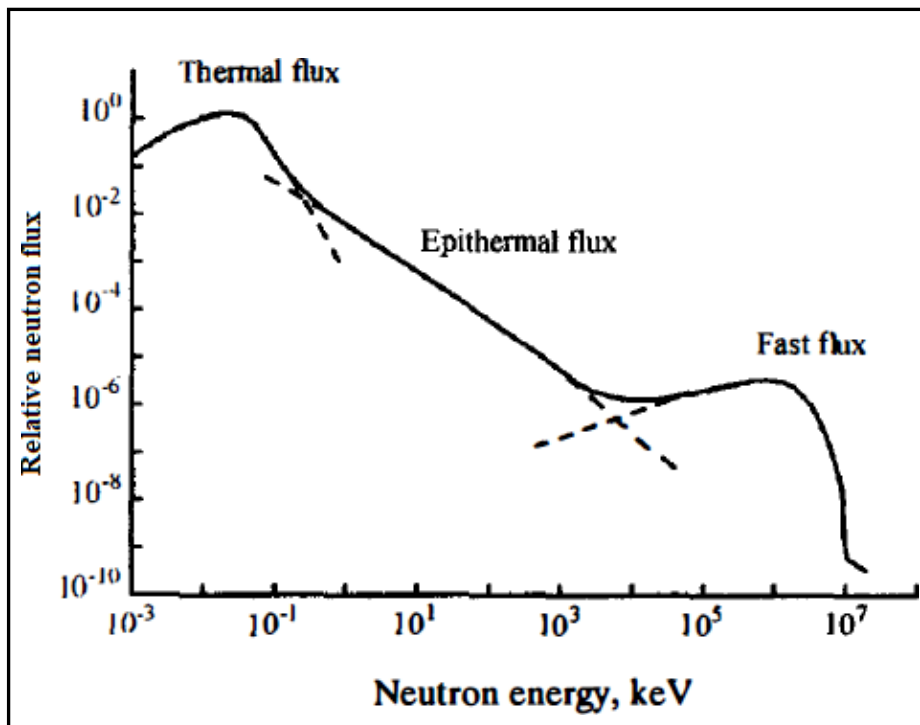


Fig 4: Flux spectrum of neutrons in a nuclear reactor as shown in a schematic

1.4.1. Thermal neutron activation analysis (TNAA)

NAA is sometimes referred to as thermal NAA (TNAA) to emphasize the role of thermal neutrons in the activation process. Using (n, γ) reactions, more than 70 natural elements can produce radionuclides. The TNAA has significant advantages, including high activation cross sections and no interfering reactions. The main disadvantage is that highly absorbing samples disturb the thermal neutron flux (Csikai et al., 2002; Witkowska et al., 2005)

1.4.2. Epithermal neutron activation analysis (ENAA)

The main purpose of non-thermal neutrons is to improve the detection limits and accuracy of elements like U, Ta, Co, Sb, Ti, Ag, Br, In, and Au. When a nuclide with a high ratio of resonance activation integral (I₀) to thermal neutron cross-section (σ₀): I₀/σ₀. Utilizing thermal neutron filters made of cadmium or boron on the neutron channel lowers the activity of nuclides when the ratio of resonance activation integral to the thermal neutron cross section is low. This method is therefore appropriate for geological samples with a low I₀/σ₀ ratio and a high concentration of interfering nuclides, such as ²⁴Na, ³⁸Cl, ⁴²K, ⁴⁶Sc, ⁵¹Cr, and ⁵⁹Fe (Capote Rodríguez et al., 1997; Landsberger et al., 1994; Witkowska et al., 2005)

1.4.3. Fast neutron activation analysis (FNAA)

It utilizes fast neutrons produced by a nuclear research reactor or neutron generator as well as an isotopic neutron source and is also referred to as 14 MeV neutron activation analysis. The use of fast neutrons from a neutron generator for field measurements, like the detection of metal contamination in soil, is one advantage of the FNAA. The study of oxygen concentration in a variety of matrices, such as metals, geologic materials, coal, liquid fuels, ceramic materials, petroleum derivatives and fractions, and chemical reaction products, is the most significant application of FNAA. Furthermore, measurements of nitrogen in biological materials and their determination in fertilizers, explosives, and polymers are all pertinent applications. Additionally, FNAA may assess a few additional factors including Fe, Mn, Mg, Zn, Cu, P, Sn, Si, Ag, Al, and Au (James, 1997)

1.5. STANDARDIZATION:

The primary result of the NAA procedure is a gamma-ray spectrum, and the standardization can be established by calculating the proportionality factor F (g-1), which connects the net peak areas in the gamma-ray spectrum to the concentrations of the elements present in the sample under the specified irradiation conditions:

$$F=A/w$$

1.5.1. Absolute standardization:

in terms of the literature and precise measurement of the values of The physical parameter determining the proportionality factor, (E), Φ(E), and ε

$$m = \frac{A_{nc} \cdot W}{0,6023 \cdot \theta \cdot \Phi(E) \sigma(E) s \cdot \epsilon_p \cdot S.D.C}$$

1.5.2. Relative Standardization

The unknown sample is exposed to radiation alongside a calibration sample that contains known concentrations of the desired element(s). The calibration sample is handled similarly to the sample (e.g., sample-to-detector distance, sample size, and if possible, composition). Standards must contain all of the components, and m_s and A_{nc} are primarily responsible for errors.

$$m = \frac{A_{nc} e^{-\lambda t_{e,s}} m_s}{A_{nc,s} e^{-\lambda t_e}}$$

1.6. ADVANTAGES AND LIMITATIONS OF NAA

1.6.1. Advantage (Frontasyeva, 2011) :

1. Sensitivity: NAA has very high sensitivity, up to 10-10 g in some cases, for a variety of elements.
2. Effects of the matrix: Since nuclear processes are involved, it is not necessary for the bulk compositions of samples and standards to match exactly, regardless of the matrix's chemical or physical properties.
3. Contamination: Since a reagent blank is not required, there is a significantly reduced or eliminated risk of reagent or equipment contamination.
4. multi-element technique: This technique has many applications and is non-destructive.
5. Isotopic ratios: In some cases, activation analysis can be used to calculate isotopic ratios.
6. Non-destructive technique: A non-destructive technique can be used to activate materials in any state of matter, including solid, liquid, and gaseous states. No need to convert a solid substance into a solution when not activated.

1.6.2. Limitations (Frontasyeva, 2011) :

7. Not every element has radioactive nuclides that are suitable; either formation cross-sections are low, or half-lives are either very long or very short, resulting in poor sensitivity.
8. INAA procedures for environmental samples may require decay periods of up to one month to determine some long-lived nuclides. As a result, the procedure will cause some results to be delayed.
9. Not all laboratories have access to nuclear reactors.

1.7. APPLICATION OF NAA

In Environment, Geology, archaeology, Cosmos, Anthropology, Food products, Medicinal plants, Bio-nanotechnology, and Biomonitoring i.e., vegetation. So, I used an example of using the plant as an adsorbent of heavy metals from water to show how to use the NAA in environmental studies.

2. EXPERIMENTAL WORK

2.1. Experimental Work

The plant and soil are collected from Egypt and put in water with heavy metals as contamination "Fe, Mn, Cr, Zn, and Al" and acidified with concentrate nitric acid to prevent the adsorption of heavy metals on the walls of the container (Badawy et al., 2019; Badawy et al., 2020; Badawy et al., 2022b).

2.2. Sample preparation

The samples are collected, and the water is to measure the concentration of heavy metals every day by ICP-MS, soil and the plants are separated into roots and shoots, dried at 105 °C for 2 hours in a dry oven to constant weight, and the soil which was ground for 5 minutes to become a fine powder, soil samples around 100 mg were transferred to polyethylene bags for irradiation. The shoots and roots of the plant are made of small pieces and weigh about 100mg then transferred to a polyethylene bag, then samples are packaged in polystyrene transport containers for determination of elements with short-lived and long-lived as shown in fig 5, (Badawy et al., 2019; Badawy et al., 2020; Badawy et al., 2022b; Zhang, 2007).



Fig 5: Steps of sample preparation in the laboratory

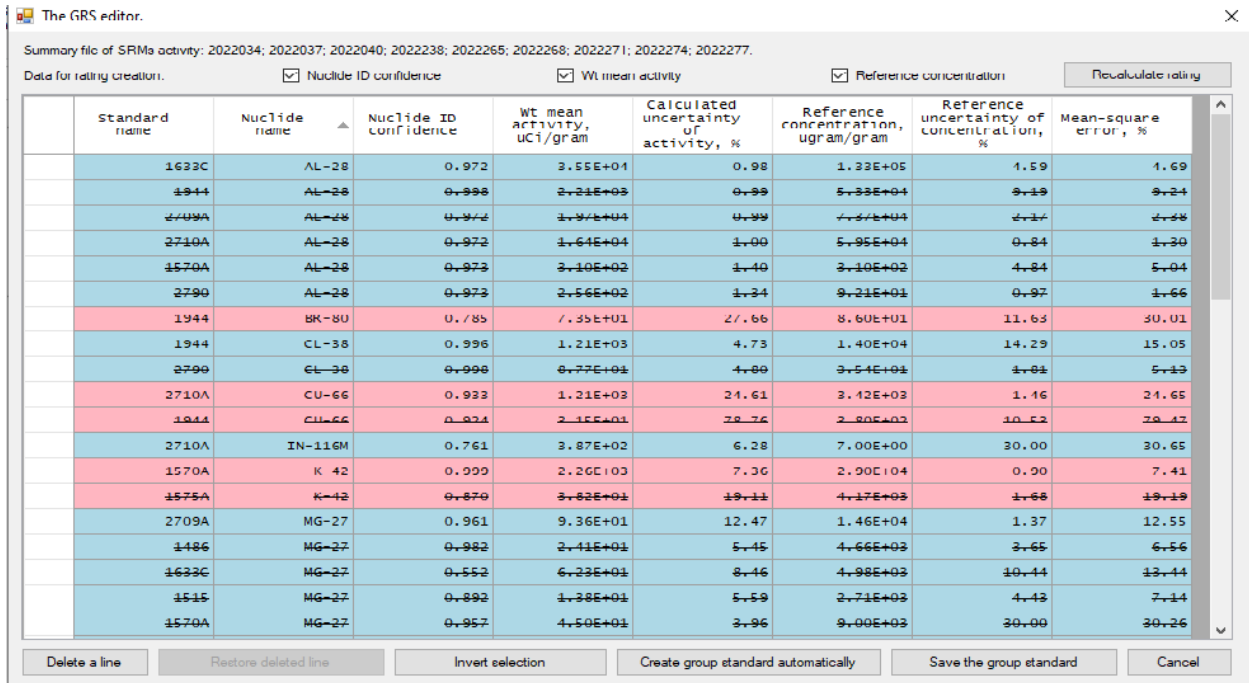


Fig 7: CalcConc software

3. Results and discussion

The activity of the irradiated samples was measured with a Canberra GC-2018 detector, and the resulting gamma radiation was processed with Genie 2000 software as follows:

For short-lived isotopes:

The sample's and the standard samples' gamma-ray charts as in Figures (8-9) respectively.

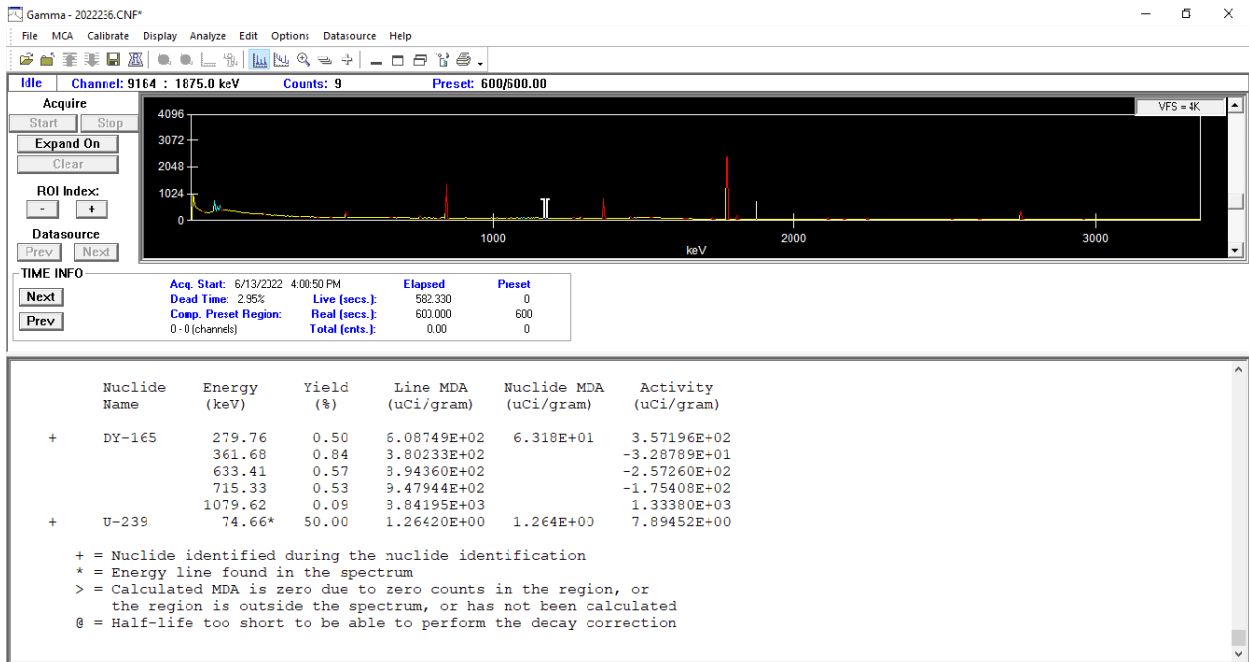


Fig 8: SLI gamma ray chart for sample

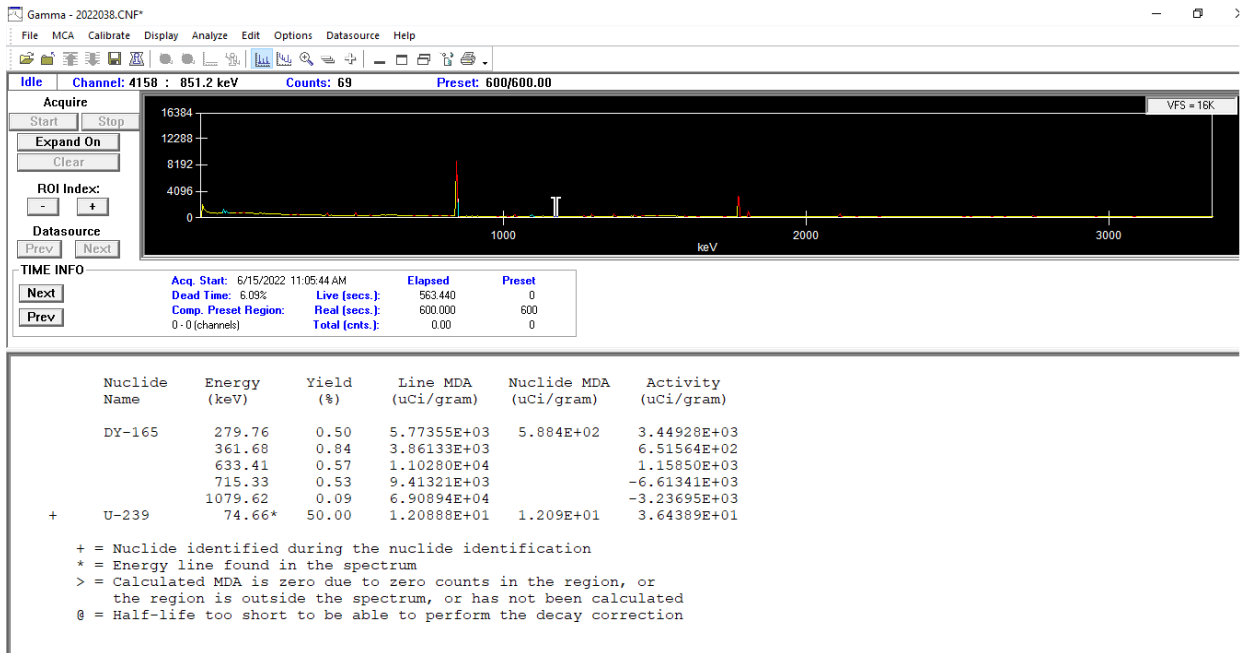


Fig 9: SLI gamma ray chart for a standard sample

For Long-lived isotopes:

The sample's and the standard samples' gamma-ray charts as in Figure (14)

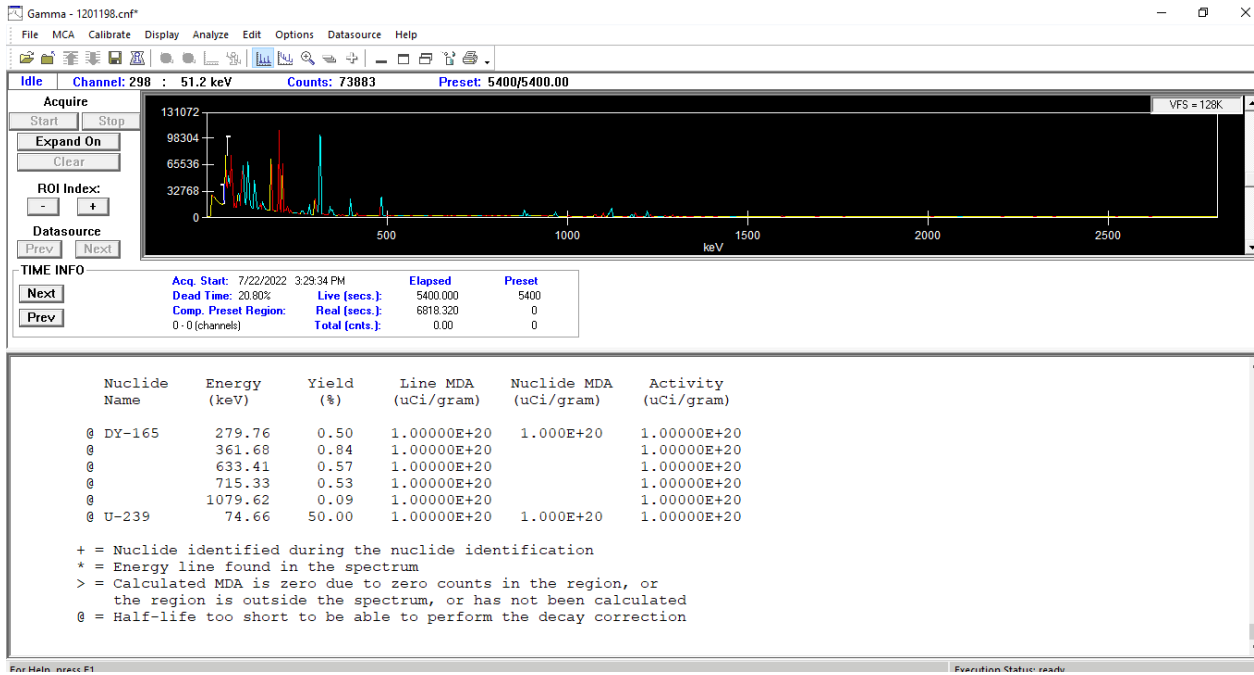


Fig 10: LLI gamma ray chart for sample

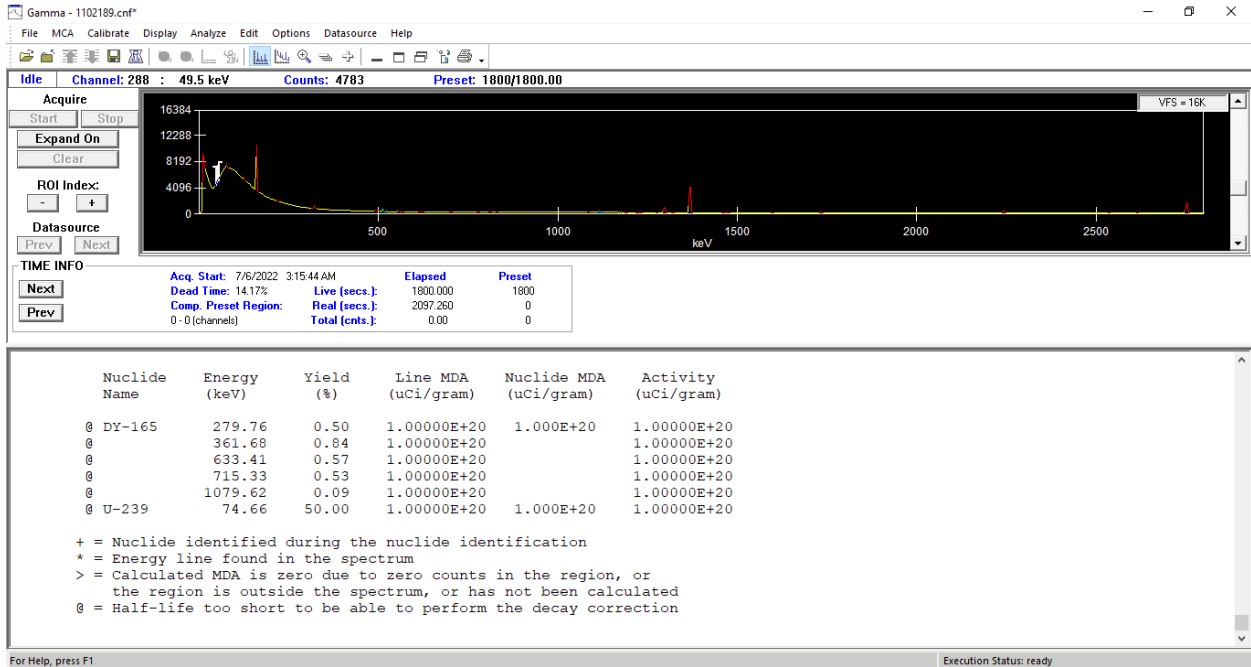


Fig 11: LLI gamma ray chart for a standard sample

The CalcConc software was used to create group standards for short-lived and long-lived isotopes after determining the activities of the elements in samples, as in figures (12-13).

The screenshot shows 'The GRS editor' software. It displays a table of standard names and nuclide names. The table has the following columns:

Standard name	Nuclide name	Nuclide ID confidence	WT mean activity, uCi/gram	Calculated uncertainty of activity, %	Reference concentration, ugram/gram	Reference uncertainty of concentration, %	Mean-square error, %
1632C	AL-28	0.972	3.55E+04	0.98	1.32E+05	1.59	1.69
1944	AL-28	0.998	3.21E+03	0.99	5.33E+04	9.19	9.24
2710A	AL-28	0.972	1.64E+04	1.00	5.95E+04	0.84	1.30
1570A	AL-28	0.973	3.10E+02	1.40	3.10E+02	4.84	5.04
2790	AL-28	0.973	2.56E+02	1.34	9.21E+01	0.97	1.66
1944	BK-80	0.785	7.35E+01	27.66	8.60E+01	11.63	30.01
1944	CL-36	0.996	1.21E+03	4.73	1.40E+04	14.29	15.05
2790	CL-36	0.996	9.77E+01	4.00	3.54E+01	1.01	5.13
2710A	CU-66	0.933	1.21E+02	24.61	3.12E+02	1.16	24.65
1944	CU-66	0.934	2.15E+01	28.76	2.80E+02	10.62	28.47
2710A	IN-116M	0.761	3.87E+02	6.28	7.00E+00	30.00	30.65
1570A	K-42	0.999	2.26E+03	7.36	2.90E+04	0.90	7.41
1575A	K-42	0.879	3.82E+01	19.11	4.17E+03	1.68	19.19
2709A	MG-27	0.961	9.36E+01	12.47	1.46E+04	1.37	12.55
1486	MG-27	0.982	2.41E+01	5.15	4.66E+02	2.65	6.56
1632C	MG-27	0.553	6.23E+01	8.46	4.98E+02	10.44	13.44
1515	MG-27	0.892	1.38E+01	5.59	2.71E+02	4.43	7.14
1570A	MG-27	0.957	4.50E+01	3.96	9.00E+02	30.00	30.26

Fig 12: Short-lived isotopes

The GRS editor. X

Summary file of SRMs activity: 2022035; 2022038; 2022041; 2022239; 2022266; 2022269; 2022272; 2022275; 2022278.

Data for rating creation: Nuclide ID confidence Wt mean activity Reference concentration

	Standard name	Nuclide name	Nuclide ID confidence	Wt mean activity, uCi/gram	Calculated uncertainty of activity, %	Reference concentration, ugram/gram	Reference uncertainty of concentration, %	Mean-square error, %
	1633C	AL-28	0.900	3.57E+04	1.07	1.33E+05	4.59	4.71
	2709A	AL-28	0.900	1.98E+04	1.08	7.37E+04	2.17	2.43
	1944	AL-28	0.981	2.22E+02	1.10	5.33E+04	9.19	9.26
	2710A	AL-28	0.900	1.62E+04	1.11	5.95E+04	0.84	1.39
	1570A	AL-28	0.900	2.62E+02	2.93	3.10E+02	4.84	5.66
	1515	AL-28	0.899	2.80E+02	2.33	2.85E+02	2.04	3.10
	2790	AL-28	0.900	2.64E+02	2.10	9.21E+01	0.97	2.33
	1575A	AL-28	0.898	3.68E+01	2.09	5.80E+02	5.17	5.58
	2709A	BA-139	0.995	3.72E+01	25.74	9.79E+02	2.86	25.89
	1944	BR-80	0.771	8.11E+01	18.48	8.60E+01	11.63	21.84
	1486	CA-49	0.885	4.72E+02	2.81	2.66E+05	0.90	2.95
	2709A	CA-49	0.886	2.68E+01	7.74	1.91E+04	4.71	9.06
	1570A	CA-49	0.875	2.75E+01	4.13	1.53E+04	4.33	5.98
	1515	CA-49	0.873	2.62E+01	3.84	1.53E+04	0.66	3.90
	1633C	CA-49	0.872	2.33E+01	9.95	1.37E+04	2.93	10.38
	1575A	CA-49	0.870	7.05E-01	5.74	2.50E+03	4.00	6.99
	1515	CL-38	0.999	1.25E+02	4.53	5.82E+02	2.58	5.21
	1944	CL-38	0.996	1.20E+03	4.43	1.40E+04	14.29	14.96
	2790	CL-38	0.999	9.04E+01	4.54	3.54E+01	1.81	4.89

Buttons: Delete a line, Restore deleted line, Invert selection, Create group standard automatically, Save the group standard, Cancel

Fig 13: Long-lived isotopes

Once the elemental concentrations of the elements in the samples were calculated using the mass fraction of the short- and long-lived samples, an excel sheet for all elemental analyses of each sample was created, as shown in figure 14.

sample	SLI-1	SLI-2	LLI-1	LLI-2	Na ²⁴ mg/kg		Na ²⁴ MDC, mg/kg	
					mg/kg	%	mg/kg	%
A-20	2022259.CON	2022260.CON			5860	23	501	21
A14	2022241.CON	2022242.CON			8380	23	579	21
A21	2022262.CON	2022263.CON			6590	23	466	21
a-01	2022199.CON	2022200.CON			3090	23	82.6	22
a-02	2022202.CON	2022203.CON			3460	23	82.7	22
a-03	2022205.CON	2022206.CON			3910	23	55.6	22
a-04	2022208.CON	2022209.CON			4870	23	91.8	21
a-05	2022211.CON	2022212.CON			4160	23	83.3	22
a-06	2022214.CON	2022215.CON			2940	23	67.8	22
a-07	2022217.CON	2022218.CON			3310	23	69.8	22
a-08	2022220.CON	2022221.CON			4060	23	72.8	22
a-09	2022223.CON	2022224.CON			1330	23	189	22
a-10	2022226.CON	2022227.CON			522	27	336	22
a-11	2022229.CON	2022230.CON			1030	23	146	22
a-12	2022232.CON	2022233.CON			1300	23	164	22
a-13	2022235.CON	2022236.CON			5040	23	530	21
a-15	2022244.CON	2022245.CON			6500	23	464	21
a-16	2022247.CON	2022248.CON			4940	23	453	21
a-17	2022250.CON	2022251.CON			5850	23	402	21

Fig 14: Excel sheet of concentration of elements for all samples

4. Conclusion

In the course of my practice, I have gained a lot of experience with one of the most significant and powerful analytical techniques, neutron activation analysis in the Neutron Activation Analysis Group at the IREN facility FLNP. I learned the theory behind it and passed the theoretical part of NAA. I also participated in sample preparation and packing for the determination of short and long-lived isotopes. I was also involved in an experiment on the removal of inorganic pollutants from the aquatic systems using different plant parts and species such as roots and leaves. During my training, I learned how to process the spectra we collected from induced activity by NAA using gamma ray spectrometer. After that, I learned how to process the radioactivity reports obtained and how to determine the concentrations of each element in the sample studied. Later I obtained the concentrations and started to process them statistically for further work.

In this short time, I have had quite a great experience, which in turn will help me in my work in Egypt, as I am studying for an MSc degree and will be working in the Egyptian Museum. This will greatly help me in the restoration of various archeological artifacts and cultural objects. Also, it would be a great advantage if I could use the knowledge I have acquired in solving ecological problems such as water pollution in Egypt.

5. Acknowledgment

I would like to express my sincere gratitude to my colleagues and supporting me throughout my study. First, I wish to express my sincere gratitude to my supervisor, Dr. Wael Badawy, for his enthusiasm, patience, insightful comments, helpful information, practical advice, and unceasing ideas that have helped me tremendously at all times. His immense knowledge, profound experience, and professional expertise in Neutron activation Analysis have enabled me to gain more knowledge and experience. I could not have imagined having a better supervisor in my study. I would also like to express a deep sense of gratitude to the Head of the group of neutron activation analysis Dr. Andrey Dmitriev for his support as he permitted me to use all the required equipment and the necessary material in the laboratory. Finally, I wish to acknowledge the Joint Institute for Nuclear Research for participating in the summer session of Student Advanced Research Training (START) and all the colleagues of the University centre JINR.

6. Reference

- Badawy, W., Sarhan, Y., Dului, O., Frontasyeva, M., El-Samman, H., Hussein, A.A. and Arafa, W., Year, Heavy and Trace Elements Distribution in Plants and Soils of Urban and Rural Areas of Egypt: A Comparison. Conference of the Arabian Journal of Geosciences, 191-193.
- Badawy, W., Elsenbawy, A., Dmitriev, A., El Samman, H., Shcheglov, A., El-Gamal, A., Kamel, N.H. and Mekewi, M., 2022a, Characterization of major and trace elements in coastal sediments along the egyptian mediterranean sea. *Marine Pollution Bulletin*, 177: 113526.
- Badawy, W.M., Dului, O.G., Frontasyeva, M.V., El-Samman, H. and Mamikhin, S.V., 2020, Dataset of elemental compositions and pollution indices of soil and sediments: Nile River and delta-Egypt. *Data in brief*, 28: 105009.
- Badawy, W.M., Sarhan, Y., Dului, O.G., Kim, J., Yushin, N., Samman, H.E., Hussein, A.A., Frontasyeva, M. and Shcheglov, A., 2022b, Monitoring of air pollutants using plants and co-located soil—Egypt: Characteristics, pollution, and toxicity impact. *Environmental Science and Pollution Research*, 29: 21049-21066.
- Bode, P., Greenberg, R. and Fernandes, E.D.N., 2009, Neutron Activation Analysis: A primary (Ratio) Method of Determine SI-Traceable Values of Element Content in Comple Samples. *Chimia*, 63: 1-3.
- Capote Rodríguez, G., Rivero, A., Bermúdez, J., Guevara, S., Arribére, M., Insfrán, J. and Zayas, G., 1997, Determination of selenium in nickel and cobalt concentrates applying epithermal neutron activation analysis. *Journal of Radioanalytical and Nuclear Chemistry*, 223: 217-220.
- Csikai, J., Király, B., Sanami, T. and Michikawa, T., 2002, Studies on thermal neutron perturbation factor needed for bulk sample activation analysis. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 488: 634-641.
- Dmitriev, A.Y. and Pavlov, S.S., 2013, Automation of the quantitative determination of elemental content in samples using neutron activation analysis on the IBR-2 reactor at the frank laboratory for neutron physics, joint institute for nuclear research. *Physics of Particles and Nuclei Letters*, 10: 33-36.
- Frontasyeva, M., 2011, Neutron activation analysis in the life sciences. *Physics of particles and nuclei*, 42: 332-378.
- Greenberg, R.R., Bode, P. and Fernandes, E.A.D.N., 2011, Neutron activation analysis: a primary method of measurement. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 66: 193-241.

- James, W., 1997, Fast neutron activation analysis at Texas A&M University. *Journal of Radioanalytical and Nuclear Chemistry*, 219: 187-190.
- Landsberger, S., Peshev, S. and Becker, D., 1994, Determination of silicon in biological and botanical reference materials by epithermal INAA and Compton suppression. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 353: 601-605.
- Witkowska, E., Szczepaniak, K. and Biziuk, M., 2005, Some applications of neutron activation analysis. *Journal of Radioanalytical and Nuclear Chemistry*, 265: 141-150.
- Zhang, C., 2007, *Fundamentals of environmental sampling and analysis*. John Wiley & Sons