JOINT INSTITUTE FOR NUCLEAR RESEARCH
Frank Laboratory of Neutron Physics

FINAL REPORT
ON STAGE 1 OF THE INTERNATIONAL STUDENT PRACTICE

"Nuclear and related analytical techniques in archaeological and ecological studies"

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Participation period:
01-24 March

Dubna, 2022

Abstract

Knowing the elemental composition of archaeological artifacts can help researchers learn more about the age of cultural artifacts, as well as their behaviors, origins, and sources of clay raw materials. Neutron activation analysis is a potent analytical technique for determining the elemental abundances of a material in both quantitative and qualitative terms. The elemental content of artifacts, particularly ceramics and cultural heritage, aids in the extraction of further information about the provenance of the discovered ceramics. Depending on the evidence gathered and available in the archaeological sites, the provenance of the ancient pottery can be determined in a variety of methods. On the other hand, NAA in environmental research and the solution of ecological problems. Many organizations and committees have researched and confirmed the physical, chemical, and biological features of sediments, as well as the processes that contribute to their role as a monitoring tool. Heavy metals and other harmful compounds in the environment, including air, water, sediment, and soil. As a result, the geochemical data we gathered aided us in characterizing these samples in terms of pollution and identifying pollution sources. These data will be used as a baseline value in the future. Finally, statistical data analysis, contamination measurement, and exposure assessment are carried out.

1. INTRODUCTION

Neutron Activation Analysis (NAA) is used to determine the concentrations of elements in a wide range of materials. NAA uses neutrons to ionize the treated material, causing it to release gamma rays. It enables the exact identification and quantification of all elements in the sample, including trace elements. NAA is used in chemistry, it has uses in geology, archeology, medicine, environmental monitoring, and even forensic science [1].

Because neutron activation analysis is sensitive, it's often employed to look for minor elements in extremely low concentrations. The method is particularly useful for trace element analysis, such as in high-purity materials, and is thus crucial in semiconductor processes. It's also capable of detecting trace elements in water, biological matter, and minerals. In archaeology, NAA can provide useful information about the provenance of items based on the "fingerprint" of individual element composition in their raw materials. It is frequently utilized as a key reference for other types of analysis [1, 2]. The scheme of neutron capturing is illustrated in Fig. 1.

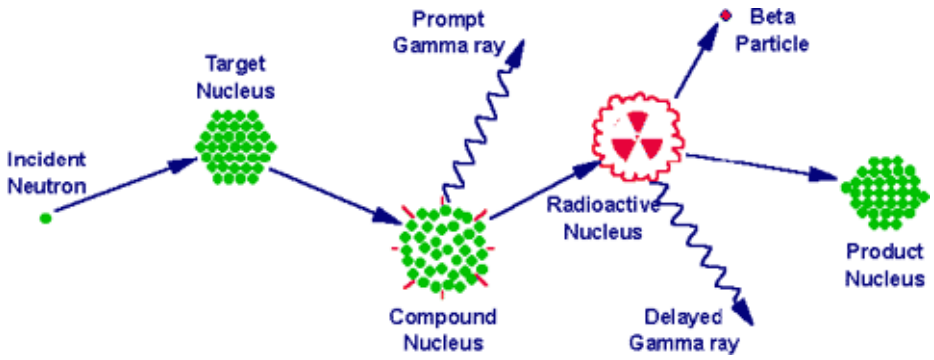


Fig. 1: The capture of neutrons by a target nucleus is followed by the emission of gamma rays.

1.1. HISTORY OF NAA

In 1934, Frederic and Irene Joliot-Curie succeeded in bombarding Aluminum with alpha particles to produce the phosphorus isotope P-30. After that the discovery of neutron, Enrico Fermi could produce artificial radionuclides more efficiently than alpha particles, and this was the start of the Neutron Activation Analysis, which George Charles de Hevesy introduced in 1936 by performing rare earth element analysis using neutrons from a Ra–Be source [3].

In 1965, high-resolution Ge (LI) semiconductor detectors and improved multichannel (2048, 4096) pulse analyzers were introduced as the next stage in the development of the method.

Multi-element INAA of varied samples with low quantities of elements to be determined became achievable. In addition, mathematical and statistical approaches for processing spectrometric data and interpreting analytical results played an important role in the creation of INAA. So Hungarian radiochemist George Charles de Hevesy won the Nobel Prize in Chemistry in 1943. Neutron Activation Analysis was first discovered in 1936.

1.2. NAA IS POWERFUL ANALYTICAL TECHNIQUE

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 techniques are now used to analyze samples. The detection limits for several analytical procedures are shown in Fig. 2.

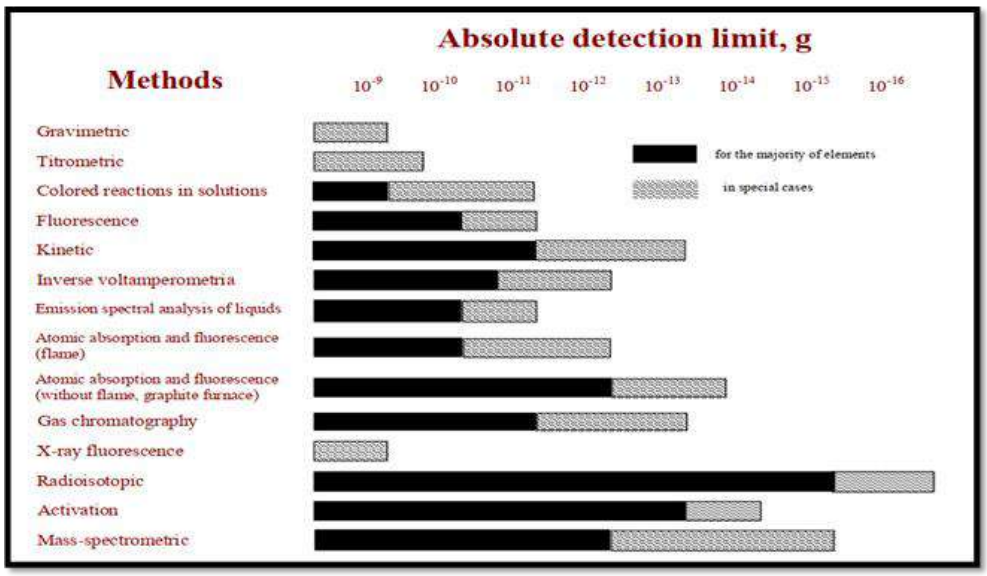


Fig. 2: Several analytical methods, the absolute detection limit in grams.

Depending on the experimental approach, NAA can detect up to 55 elements as shown in fig 3, with minimum detection limits ranging from 10^{-7} to 10^{-15}g/g, depending on the elements and matrix materials. Some nuclei can collect a large number of neutrons and stay relatively stable for months or even years without transmutation or disintegration. Because various nuclei have varying cross sections and half-lives, as well as different intensities of emitted gamma-rays, the detection limits are extremely diverse. Because rare earth elements (REE) have extremely high thermal neutron cross sections, NAA is frequently used to determine REEs in trace element analyses[1].

Because the process relies on neutron activation, it necessitates the use of a neutron source. The elements in the sample are bombarded with neutrons, resulting in the formation of radioactive isotopes. Each element's radioactive emissions and radioactive decay routes are well-

known. It is feasible to analyze the spectra of the radioactive sample's emissions and determine the concentrations of the elements within it using this knowledge. This technique has the advantage of not destroying the material, and it has thus been used to analyze works of art and historical objects. (NAA) is one of the most powerful approaches for multi-element analysis in real time. The Frank Laboratory of Neutron Physics at the Joint Institute for Nuclear Research has explored and implemented this approach to study major, minor, and trace elements. The following are examples of where NAA techniques can provide accurate results:

- Determination of elements content and concentration in archaeological objects as artifacts, particularly ceramics, cultural heritage and pottery and studying characteristics.
- Determination of rare-earth, uranium, thorium, and other element concentrations in geological samples in accordance with the needs of clients, notably geologists looking for mineral resources.
- The analysis of trace element content in rock samples.
- Evaluation of the ratio of toxicity and contamination with heavy elements using standard reference material, toxic elements in different matrices such as sediment and soil.

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 obtained by NAA

1.3. FUNDAMENTALS OF NAA

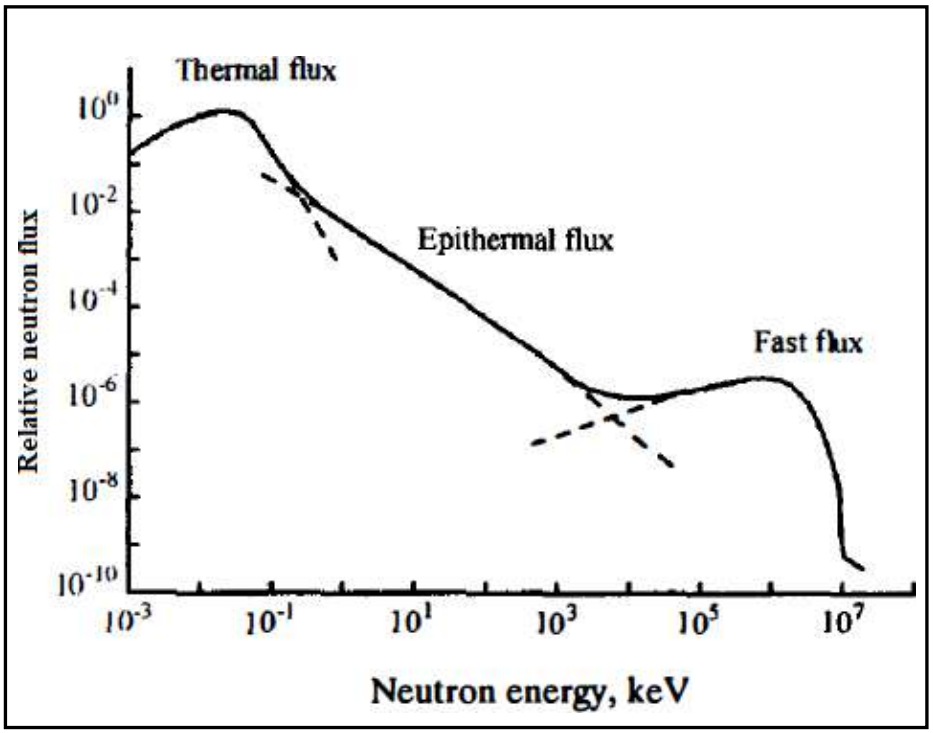
The initial stage of an NAA technique is neutron activation. Its goal is to turn some stable nuclei into radioactive nuclei that produces

radiation that can be employed in experiments. Understanding the reactions that may occur during activation in determining the relationship between the radioactive nucleus observed, its

target nucleus, and the associated element. For quantitative analysis and a priori predictions of the feasibility of an analysis, insight into reaction rates is critical. During irradiation, each atomic nucleus can capture a neutron. A nuclear reaction occurs, in which the nuclear mass frequently changes; energy in the form of photons and/or particles is expelled immediately after the capture ('immediately'). It's possible that the freshly generated nucleus will be unstable. When something is unstable, it begins to decay to a stable state by emitting radiation via one or more of the following processes: -decay, +decay, electron capture, -decay, or internal transition decay.

1.4. Types of Neutron Energy

- Thermal (0.025 eV – 0.5 eV) [2, 4]
- Epithermal (0.5 eV – 10 keV) [2, 5, 6]



- Fast (10 keV – 25 MeV) [7]

Fig 4: Schematic representation of the neutron flux spectrum in a nuclear reactor.

1.5. TYPES OF NAA:

NAA are divided into Two types:

1- Nondestructive NAA, i.e., the radioactive sample produced is not destroyed. There will, however, be alterations at the nucleus level. The types of nondestructive NAA are as follows [3, 8]:

   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: After irradiation, the radioactive sample is decomposed or chemically processed in destructive NAA. This kind including only the following type:

- Radiochemical or destructive neutron activation analysis RNAA or DNA.

1.6. STANDARDIZATION:

The gamma ray spectrum is the main output of the NAA process, and the standardization can be determined by determining the proportionality factor F (g^{-1}), which relates the net peak areas in the gamma ray spectrum to the amounts of the elements present in the sample under the given irradiation conditions:

$$F = \frac{A}{w}$$

1.6.1. Absolute standardization:

Here, the values of the physical parameter determining the proportionality

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

factor, σ(E), Φ(E) and ε are taken from theliterature and accurate measurement.

1.6.2. Relative Standardization:

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

Here, the unknown sample is irradiated together with a calibration sample containing a known amount of the element(s) of interest. The calibration sample is treated under the same conditions as the sample (e.g., sample-to-detector distance, sample size, and if possible, composition). It requires standards to have all the elements, and the error mainly depends on m_s and A_{nc}.

1.7. ADVANTAGES AND LIMITATIONS OF NAA

Neutron activation analysis, like most analytical techniques, has advantages and limits when compared to other approaches. The main benefits and drawbacks arestated below:

1.7.1. Advantage [1, 9]:

1. Sensitivity: NAA has a very high sensitivity for several elements, up to 10^{-10} g in some cases.
2. Effects of the matrix: Because nuclear processes are involved, the chemical or physical properties of the matrix are irrelevant, the bulk compositions of samples and standards do not have to be identical.
3. Contamination: there is no need for a reagent blank, and the risk of contamination from apparatus or reagents is considerably reduced or avoided.
4. multi-element technique: This method is non-destructive and multi-element for numerous applications.
5. Isotopic ratios: activation analysis can be used to determine isotopic ratios in some circumstances.
6. Non-destructive technique: Materials can be activated in any state of matter, including solid, liquid, and gaseous states. Before activation, there is no requirement to transform solid material into a solution.

1.7.2. Limitations [1, 9]:

1. Not all elements have radioactive nuclides that are acceptable; either formation cross-sections are low, or half-lives are either long or very short, leading in poor sensitivity.
2. Decay periods of up to one month may be required in INAA procedures for environmental samples in order to determine some long-lived nuclides. As a result, some findings will be delayed by the procedure.
3. Nuclear reactors are not available in all laboratories.

1.8. Application of NAA

Basic life science branches are divided into:

1. Environment
2. Geology
3. Cosmos
4. Anthropology
5. Food products
6. Medicinal plants
7. Bio nanotechnology
8. Biomonitoring i.e., vegetation

We are concerning to Application of NAA in:

1- Environmental studies
2- Archaeological studies

2. Experimental work.

The main procedures of the INNA are carried out according to the scheme in fig 5.

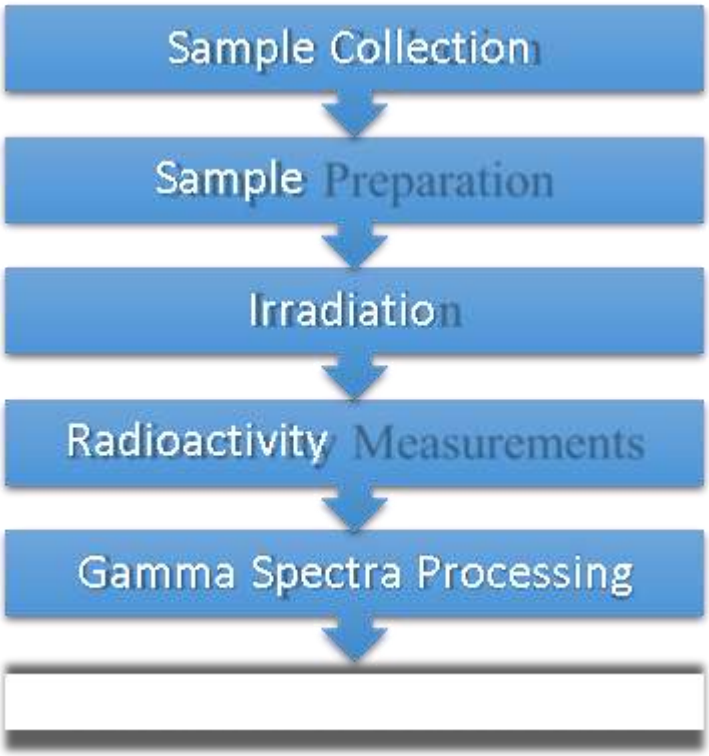


Fig. 5 “steps of experimental work

2.1. Sample collection in environmental science studies

The majority of the samples are of plant type (such as Moss), soil, and sedimentation. To avoid absorbing pollutants from the air, the harvested plant should be wrapped and kept out of the air. To avoid contaminating the samples with metal, soil or sedimentation samples should not be obtained with metal tools as shown in figure 6 [10].

Fig 6

2.2. Sample preparation

After drying for one hour in an electric oven, the samples were crushed to a fine powder. A total of 5–8 minutes of grinding time was chosen, with a rotation speed of 600 rpm. The powder was then carefully put into labeled glass vials for short-term storage. Each sample weighed in at around 0.1 gram. As shown in Fig 7. [10].

Fig 7

2.3. Sample Packaging

There are two forms of packaging: rigid and flexible. Long-term irradiation samples are packed in metal cups as shown in Fig. 8, whereas short-term irradiation samples are heat-sealed in polyethylene foil bags. Certified reference materials (CRMs) samples are pelletized and packed in the same way as the samples to be irradiated and measured with them. It is later utilized in the comparative approach to calculate the concentrations. These samples are placed at the top, middle, and bottom of transport containers to ensure that all samples get consistent irradiation [10].

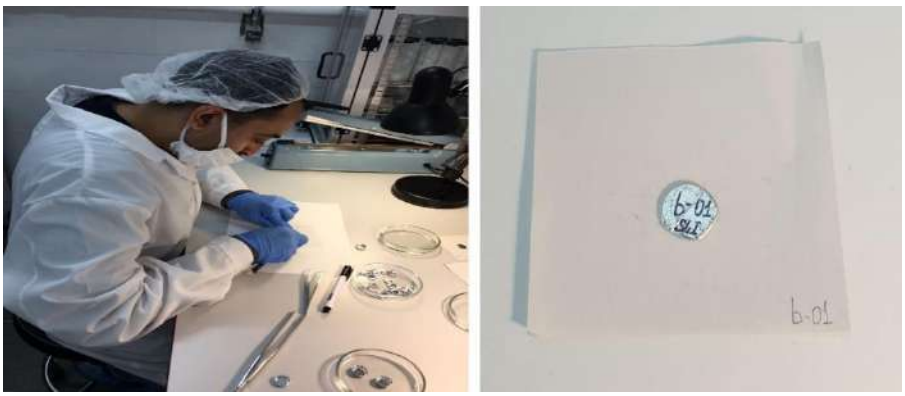


Fig. 8

2.4. Transport containers:

Samples are packaged in polystyrene transport containers for short-term irradiation and aluminum transport containers for long-term irradiation. Samples and standards were repacked from aluminum capsules into clean plastic containers five days after the irradiation ended. The first 30 min after repacking, the first measurements of the induced activity spectra were made. The second spectral measurements began 22 days after the irradiation ended. Within 90 min the spectra were measured. The data was collected using an automatic technique developed and effectively used at FLNP JINR for measuring the spectra of induced activity. The spectra were taken with a Canberra GC4018 HPGe detector with a resolution of 2.1 keV for the ^{60}Co gamma line with an energy of 1332.5 keV and a resolution of 2.1 keV for the ^{60}Co gamma line with an energy of 1332.5 keV. IBR-2 is a pulsed fast reactor powered by PuO_2. With a power of 1850 MW in pulse, its unique technical approach creates one of the world's most intense neutron fluxes at the moderator surface: 10^{16} n/cm^2 s^{-1} (Fig.9). Its reactivity is controlled by the movement of two mechanical pieces in opposite directions: the main moveable reflector and the auxiliary movable reflector. The reactor condition shifts from subcritical to supercritical when the two reflectors meet at the core20 [11].

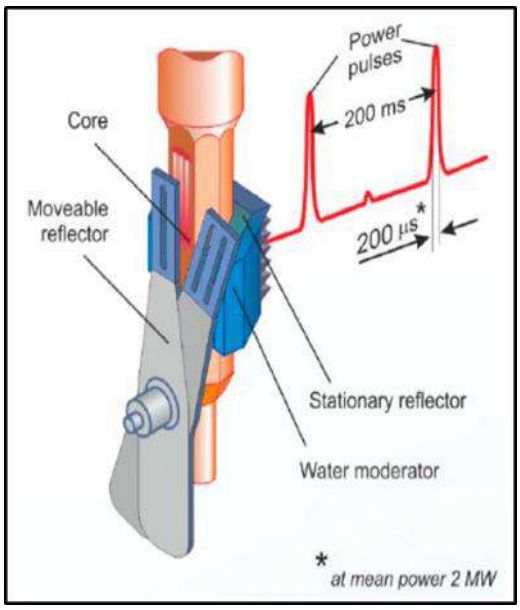


Figure 9. Core of the IBR-2 reactor with a movable reflector

2.5. Analytical Investigations at facility IREN and IBR-2

Life science:

- Studying the elemental composition of archaeological artefacts and cultural heritage
- Biomonitoring of atmospheric deposition of heavy metals and other elements
- Assessment of different ecosystems and their impact on human health
- Gold mining studies

2.6. Measurement sequences:

The system of detection consists of 2 HPGe detectors with spectrometric electronics, three sample changers and the original control software. Each sample changer is made up of a DriveSet (DriveSet.de) two-axis linear positioning module M 202A and a disk with 45 slots for sample containers.


Fig 10

2.7. Analysis spectra from NAA

The Canberra Genie-2000 program was used to process the spectra. The activities of the isotopes detected in the examined materials are the ultimate result of the Genie-2000 program's work, as illustrated in Fig 11.

The mass fractions of the elements were calculated using a tool developed at FLNP JINR (Dmitriev 2013) for the concentration computations. When processing neutron flux monitors, two lines of Zr-95 were considered: 724.2 keV (intensity 44.2%) and 756.7 keV (intensity 54%), as shown in Fig

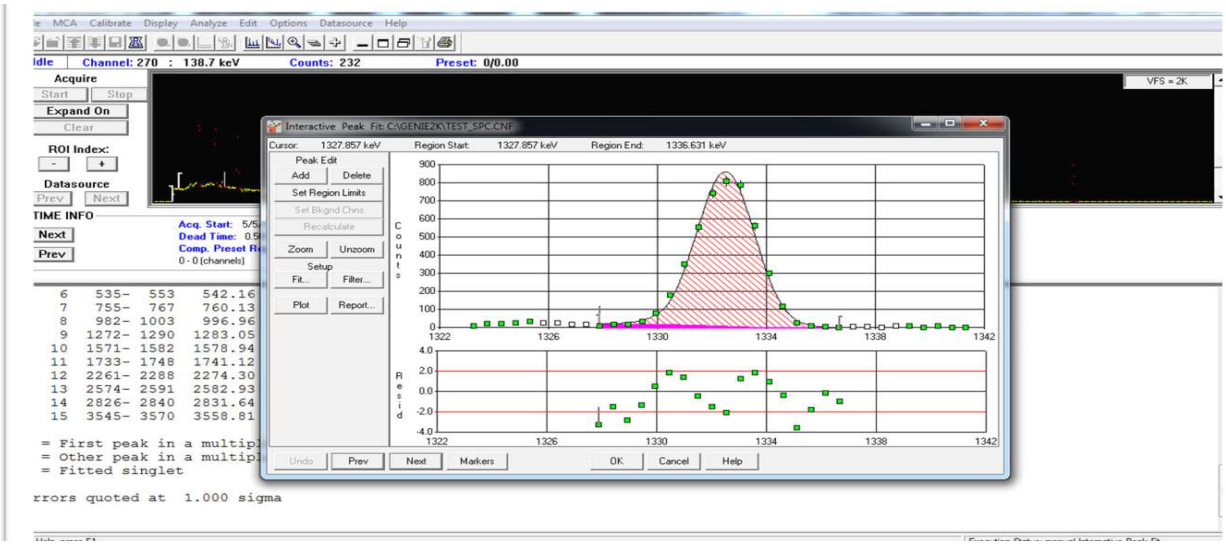


Fig 11 Program Genie-2000 during the analysis of long-lived sample

To acquire the fractional mass of elements as indicated in Fig. 1, the results must be processed using the program CalcCONC.

2. Results and discussion

We performed our work on samples have been irradiated previously by Dr. Wael badawy, because the reactor isn't working now. The activity of the irradiated samples was measuered using HPGe detector, then the obtained gamma radiation have been processed using Genie 2000 softwares as follow:

For the Intermedite -lived isotopes

The gamma ray charts for the intermediate sample and the standard samples are shown in figure (12-13) respectively.

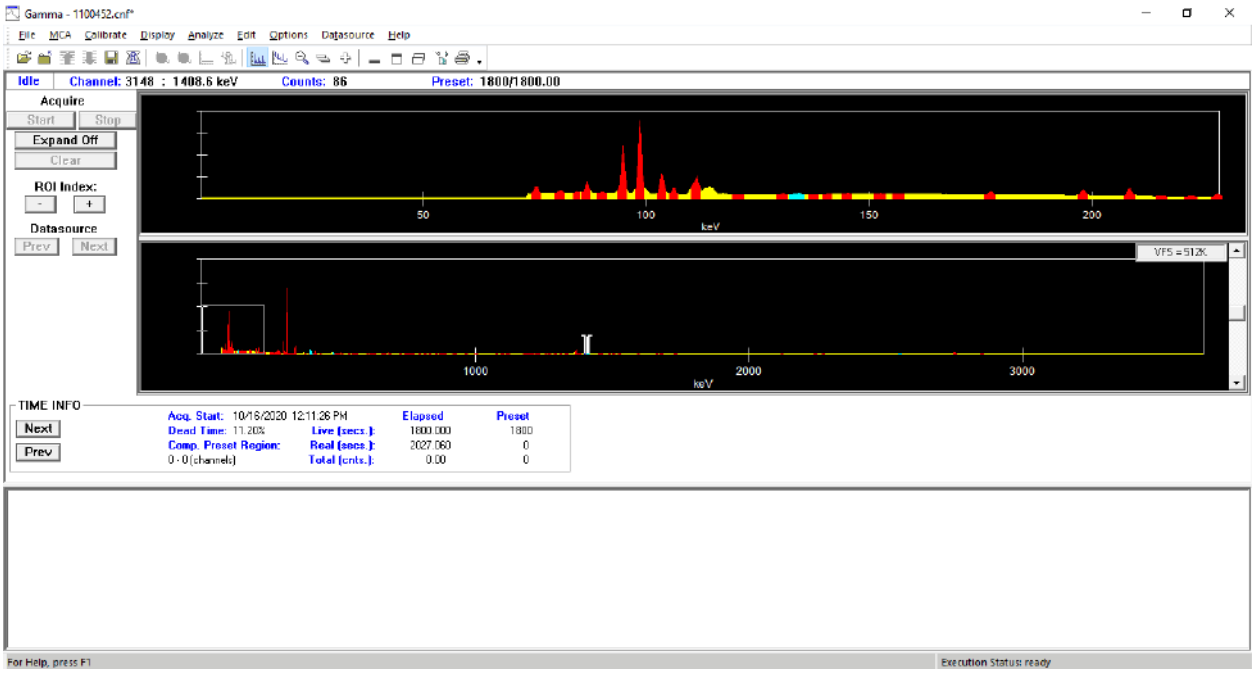


Fig 12 Sample intermediate live isotopes

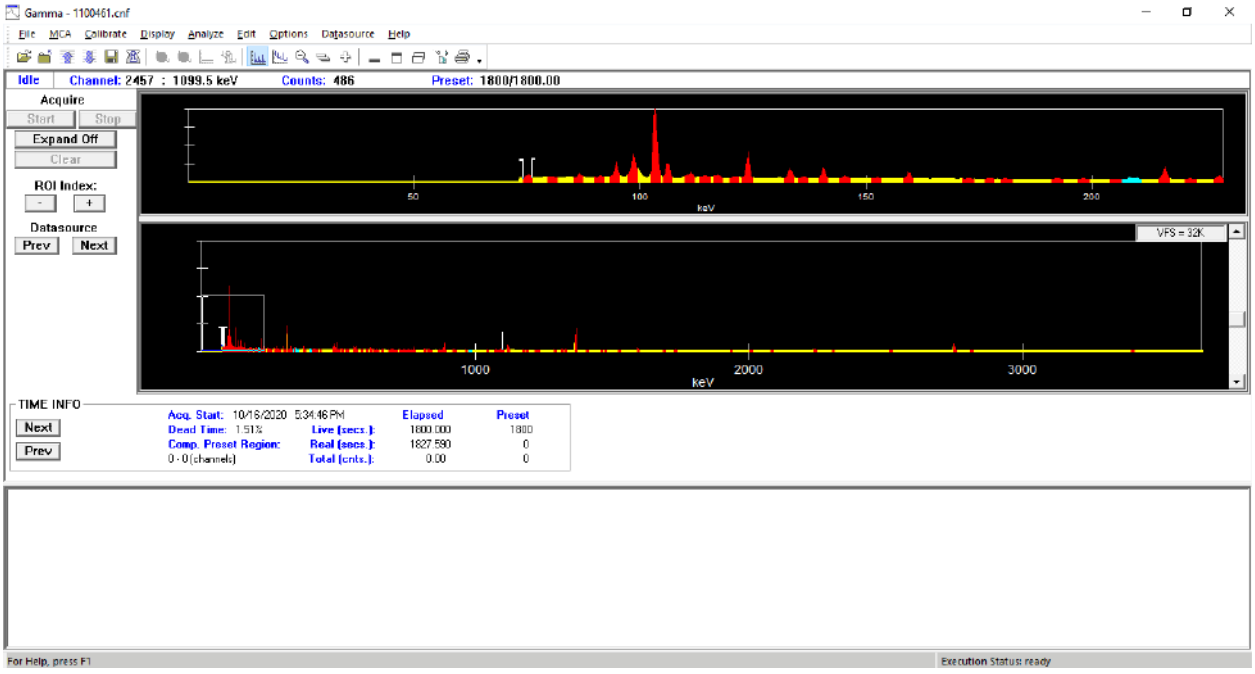


Fig 13 Standard intermediate live isotopes

For Long lived isotopes:

The gamma ray charts for the sample and the standard samples are shown in figure (14)

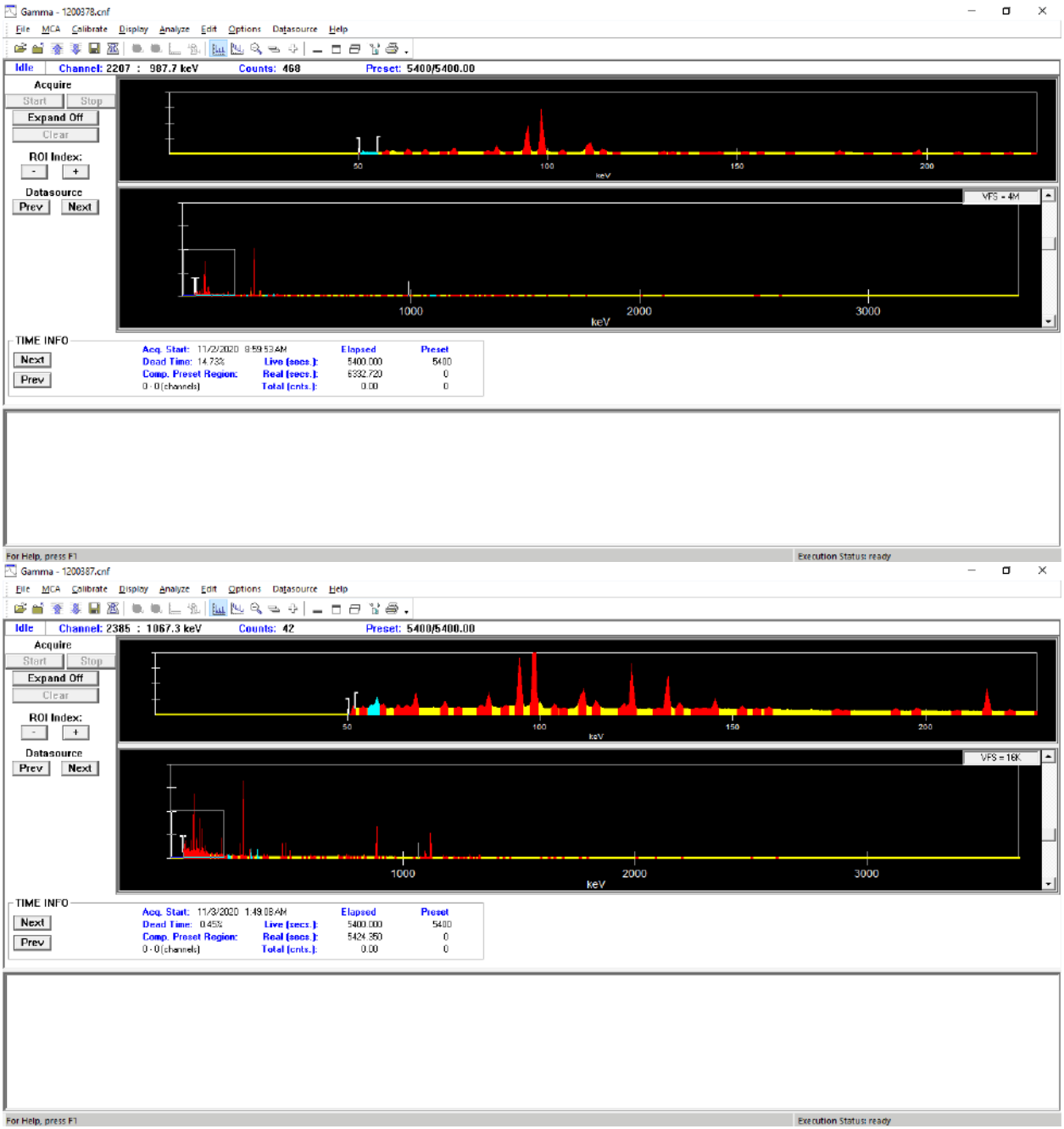


Fig. 14

After obtaining the activities of the elements in our samples, the Calconc software was used to make group standard for the intermediate-lived and long-lived isotopes as shown in figures (15-16).

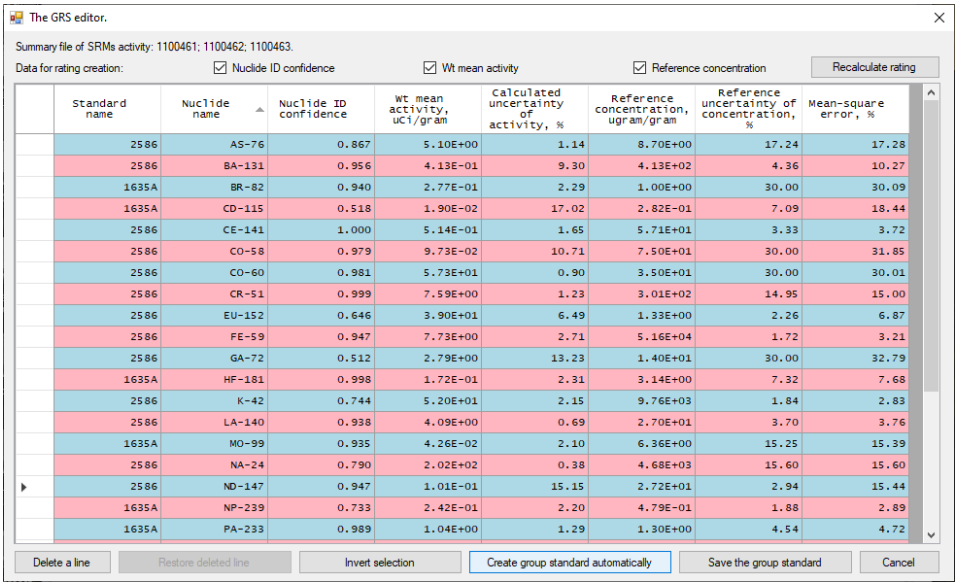


Fig 15

Fig 16

After that, calculate the mass fraction of the intermediate-lived and long-lived samples which provide the elemental concentrations of the elements in the samples as shown in fig (17,18).

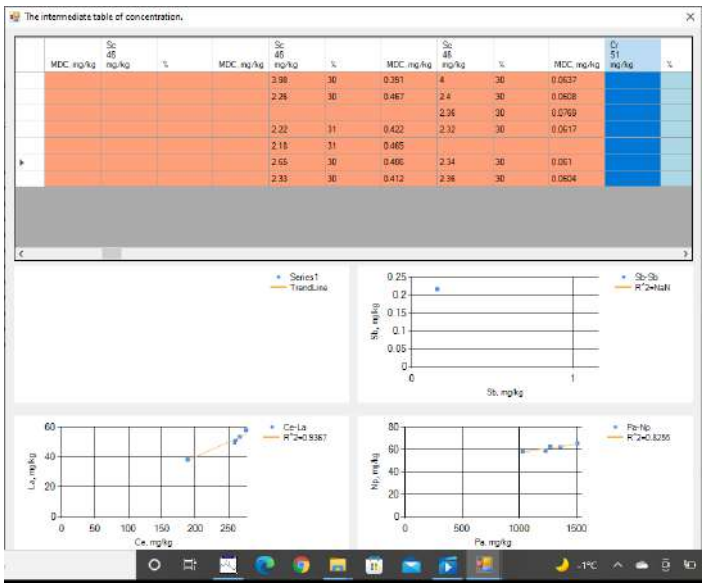


Fig 17

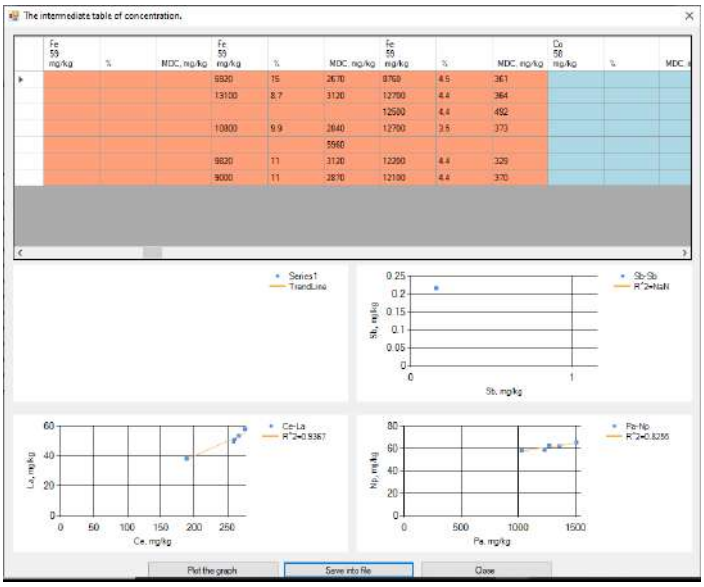


Fig 18

After calculating the mass fraction for each element in the samples, an excel sheet for all elemental analysis of each sample has been obtained, as shown in figure 19

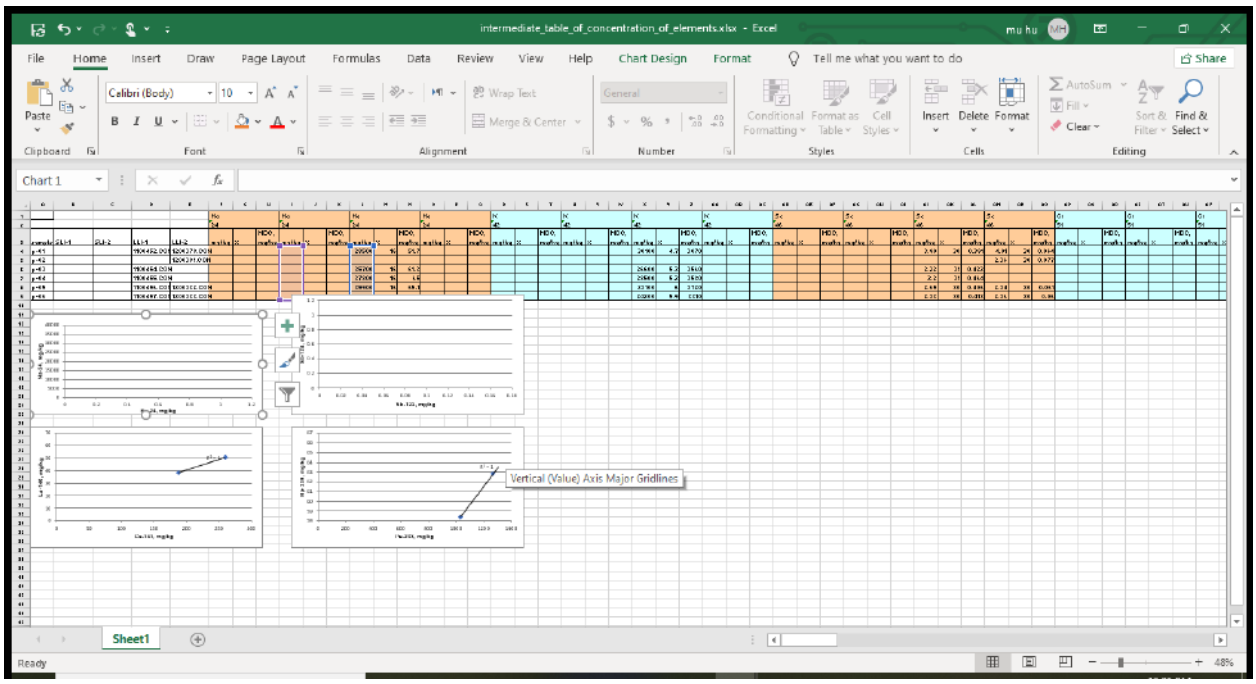


Fig 19

3. Conclusion

The application of neutron activation analysis archeology and ecology has demonstrated the technique's ability to solve practical problems that cannot always be solved by other analytical techniques. The elemental makeup of artifacts, particularly ceramics and cultural heritage, aids in the extraction of further information about the provenance of the discovered ceramics. Depending on the evidence gathered and available in the archaeological sites, the provenance of the ancient pottery can be determined in a variety of methods. The NAA has been done at the IBR-2 reactor in Frank Laboratory of Neutron Physics (JINR, Dubna, Russia) to evaluate the concentration of elements in the samples. The emitted gamma radiation has been processed using Genie2000 and CalcConc software to determine the activity of elements, as well as the concentrations of elements.

4. Acknowledgement

I cannot begin to express my deepest appreciation to my supervisor Dr. Wael Badawy for support me, encourage me and dedication to guide me to do many researches to know new applications that help me in my current work. In addition, I would like too thank all the team in the group of neutron activation analysis GNAA at IREN facility headed by Dr. Andrey Dmitriev. I am grateful to Dr. Walaa Seif and Dr. Medhat Ibrahim to follow up my practice in my project, gave me valuable advices. I would like to extend my sincere thanks to the Egyptian academy of scientific research and technology (ASRT) that gave me the opportunity to participate in Stage 1 of the International Student Practice in JINR. I would like to extend my sincere thanks to JINR

for preparing good program to get more information during our practice. Many thanks for Ms. Julia, Elena, and lyndish for the excellent organization.

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