JOINT INSTITUTE FOR NUCLEAR RESEARCH
Frank Laboratory of Neutron Physics

FINAL REPORT
ON STAGE 1 OF THE INTERNATIONAL STUDENT PRACTICE

“Neutron activation in environmental Studies”

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Abstract

Air pollution has become a major issue in recent decades, with serious toxicological consequences for human health and the environment. Therefore development of instrumental neutron activation analysis (INAA) and its applications in the environmental studies is very important. In present report, NAA was used in environmental studies by demonstrating an example of using the moss plant as a biomonitoring system for atmospheric trace element pollution in the Republic of Moldova. The analysis has been done at the installation REGATA of the IBR-2 reactor (Frank Laboratory of Neutron Physics, JINR, Dubna, Russia) to evaluate the concentration of air pollutants in the samples. The Genie2000 software was used for processing the collected gamma spectra to determine the activity of elements, as well as the "CalcConc" software was utilized to calculate the concentrations of elements. Factor analysis (FA) was performed using statistica software to identify chemical element correlations and reduce the number of variables for the collected data.

1.1. Introduction

Recent studies in ecology, biology, biotechnology, medicine, environmental monitoring and even in the forensic science have spontaneously merged into a unified research field known as the life sciences. The necessity to summarize scientific knowledge from multiple biosphere research areas and devising a unifying strategy to assessing the role of chemical elements in biological processes has arisen as a result of the accumulation of scientific information in various biosphere research areas [1]. Air pollution has become a major issue in recent decades, with serious toxicological consequences for human health and the environment. Both natural and artificial sources emit a variety of substances into the air [2]. Volcanic eruptions, geothermal sources, forest fires, emissions from land and water, sea salt in coastal areas, biological waste, and radiological decomposition are all examples of natural sources of air pollution. Natural air pollution has not been considered a big problem because it is a part of natural environmental equilibrium. However, the major challenge for the world today is to overcome anthropogenic pollution sources [3]. Population growth leads to higher pollution levels, which in turn leads to higher energy and consumer goods demands. Anthropogenic sources are traditionally classified into two main categories: fixed and mobile [3]. Industrial activity, mining, transportation, and agricultural systems are the most significant anthropogenic contributors to air pollution [2, 4, 5]. Air pollution can cause respiratory infections and inflammations, cardiovascular dysfunctions, and cancer, resulting in millions of deaths each year in some cases [2, 6, 7]. Many countries have implemented emission reduction policies to decrease the air pollution levels and solve their problems. Despite these efforts, environmental pollution is increasing in some areas, necessitating continuous monitoring of toxic element concentrations and investigating their effects on ecosystems [8].

Rühling and Tyler introduced the moss biomonitoring technique in the 1960s, and it is now frequently used to check air quality [8, 9]. This approach is based on the determination of toxic element deposition from the atmosphere to terrestrial systems through the use of a time-integrated methodology. The moss plant is characterized by the absence of roots and a significant reduction in the cuticle that allows for the adsorption and trapping of nutrients and pollutants throughout the entire surface by functional groups on the cell wall [8, 10]. As a result, mosses are able to respond to changes in hazardous element loadings much more quickly than tracheophytes [8, 11]. Furthermore, the technique does not require the installation of a large number of deposition

collectors, so it is easier and less expensive than traditional analysis. As a result, higher sampling density can be achieved. After that, the data can be analyzed using analysis methods that link the results of moss surveys to data from deposition monitoring [12]. In 2015/2016, mosses were sampled at about 5000 locations across 36 countries in Europe and Asia, and the concentrations of Al, As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Sb, V, and Zn in naturally growing mosses were reported [13].

There are many analytical techniques that can detect trace amounts of elements. One of such technique is the neutron activation analysis (NAA). It is a current important nuclear-physics technique, to solving significant issues in the studies of the chemical composition of objects in the biosphere with the aim of understanding the role of various elements in the functioning of living organisms and ecosystems under anthropogenic effects on nature, which frequently result in irreversible changes in the environment and human health [1]. NAA is a very sensitive technique that can be used for analysis of trace elements, that are present in very low concentrations. It can also be used to detect trace element in water, biological material, minerals, as well as air pollutants. It is usually used as an important reference for other analysis methods [14]. NAA is a method for determining elements that relies 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, which is produced almost instantly upon neutron capture, or the induced radioactivity, which is released as the new nuclei decay [15]. 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 – (the probability for the nuclear decay in unit time), (ii) the kind and energy of the released radiation. Of the several types of the emitted radiation, gamma-radiation has the best characteristics for the selective and detection of radionuclides simultaneously and thus of elements.

The activation process will produce a mixture of radioactivities that can be evaluated for individual contributions using one of two methods: (i) The resulting radioactive sample is chemically decomposed, and the elements are chemically separated: Destructive or Radiochemical Neutron Activation Analysis (RNAA), (ii) The elements are determined via non-destructive or instrumental neutron activation analysis, which takes advantage of differences in decay rates by measurements at different decay intervals using equipment with a high energy resolution (INAA)[15, 16]. INAA procedures include (i) activation via irradiation with neutrons, (ii)

detection of gamma-ray radiation after one or more decay times, and (iii) analysis of the resulting gamma-ray spectra in terms of radionuclides, related elements, and their mass fractions, see figure 1.

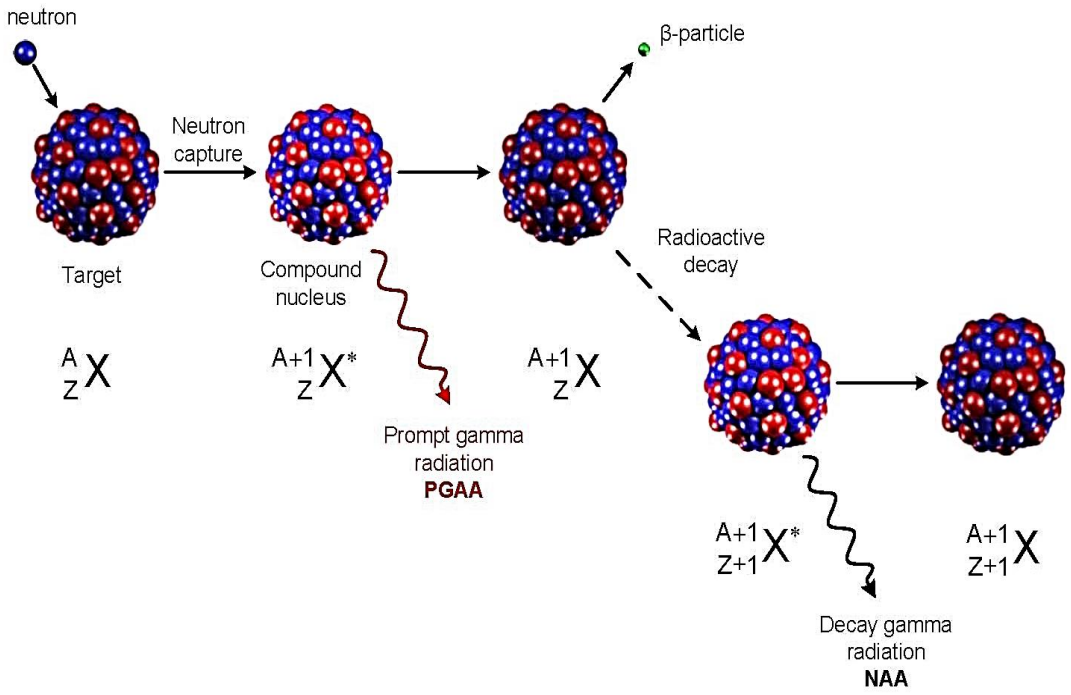

Figure 1. Schematic overview of the basic principle of NAA

1.2. Thermal, epithermal and fast neutron activation analysis

1.2.1. Thermal neutron activation analysis (TNAA)

NAA is frequently referred to as thermal NAA (TNAA) to indicate the importance of thermal neutrons in the activation process. More than 70 natural elements can produce radionuclides by using (n, γ) reactions. The TNAA has key advantages: high activation cross sections and no interfering reactions. The main disadvantage is the perturbation of thermal neutron flux by highly absorbing samples[14, 17].

1.2.2. Epithermal neutron activation analysis (ENAA)

Non-thermal neutrons are mostly employed to improve the detection limits and precision of elements including U, Tl, In, Au, Ta, Ag, Br, Co, I, and Sb. ENAA is typically used when elemental content could be determined using a nuclide with a high ratio of resonance activation integral (I_0)

to thermal neutron cross section (σ_0): I_0/σ_0. The activity of nuclides is lowered by utilizing thermal neutron filters made of cadmium or boron on the neutron channel when the ratio of resonance activation integral to thermal neutron cross section is low [14, 18, 19]. As a result, this method is appropriate for geological samples with a high number of interfering nuclides (e.g., ^{24}Na, ^{38}Cl, ^{42}K, ^{46}Sc, ^{51}Cr, ^{59}Fe) and a low I_0/σ_0 ratio, as well as for determining Br and I in biological materials [14, 20, 21].

1.2.3. Fast neutron activation analysis (FNAA)

It's also known as 14 MeV neutron activation analysis, and it uses fast neutrons produced by nuclear research reactor or neutron generator, as well as isotopic neutron source. The use of fast neutrons from a neutron generator allows for field measurements, such as metal contamination detection in soil, which is one of the FNAA's advantages [22]. The study of oxygen concentration in a wide range of matrices, including metals, geologic materials, coal, liquid fuels, ceramic materials, petroleum derivatives and fractions, and chemical reaction products, is the most important application of FNAA [23, 24]. Furthermore, nitrogen determination in fertilizers, explosives, and polymers, as well as nitrogen measurement in biological materials, including nitrogen as a protein content [14], are all relevant uses. In addition, some other elements could be evaluated by FNAA, such as Ag, Al, Au, Si, P, F, Cu, Mg, Mn, Fe, Zn, As, and Sn [25, 26].

1.3. NAA features the following advantages [1, 27]

- High sensitivity to a wide range of elements, particularly heavy metals with $Z > 10$.
- Good selectivity due to specific nuclear-physics characteristics of elements.
- The ability to determine a huge number of elements at the same time.
- Independence of the results on the form of chemical compounds.
- A nondestructive nature, which eliminates the possibility of reagent contamination or partial dissolution of samples.
- The preparation of samples for analysis is a simple procedure.
- In determining concentrations of the order of ppm (10^{-6} g), there is a good accuracy of about ±10 –15%.
- A possibility of eliminating systematic errors.
- A possibility of minimizing the effect of matrix elements of samples.

- Ease of preparation of standards for comparison.

1.4. The disadvantages of NAA [1, 27]

- The necessity of using nuclear reactors
- The issues associated with nuclear waste storage and disposal.
- Not all elements could be detectable.
- It takes long time for measurements.
- Samples irradiated in NAA will remain radioactive for a period of time

1.5. Aim of the Work

In this report, I have demonstrated how to utilize the NAA in environmental studies by demonstrating an example of using the moss plant as a biomonitoring system for atmospheric trace element pollution in Moldova. As well as, the report includes an introduction to neutron activation analysis, instructions on how to prepare samples for NAA analysis, and ultimately, processing the obtained gamma spectra with the GENIE 2000 software and data processing with the Statistica software.

2. Experimental work

2.1. Collecting samples

Moss samples were collected across the Moldova country at 41 locations. The samples were collected in accordance with the monitoring manual of International Cooperative Program on Effects of Air Pollution on Natural Vegetation and Crops. According to the guidelines, each country should collect at least 1.5 moss samples/1000 km^2. if this is not possible, at least two moss sample sites per each grid (50 km × 50 km) should be sampled. In this study, moss samples were gathered in a grid with a spacing of about (30 km × 30 km). Samples were taken at least 300 meters away from villages and industries, and at least 100 meters away from smaller roads. The sampling criteria were as follows: at each sampling point, around 0.5 kg of fresh moss was collected, consisting of five to ten subsamples of the same moss species.

2.2. Sample preparation for NAA

The collected samples were cleaned of foreign material, dried at 105 °C to constant weight, pelletized, and packed in polyethylene foil bags and in aluminum cups for the determination of elements with short-lived and long-lived isotopes, respectively

Figure 1 shows the first step in sample preparation process (a) collected moss sample, (b) drying samples in a drying oven, and (c) weighing samples to a constant weight.

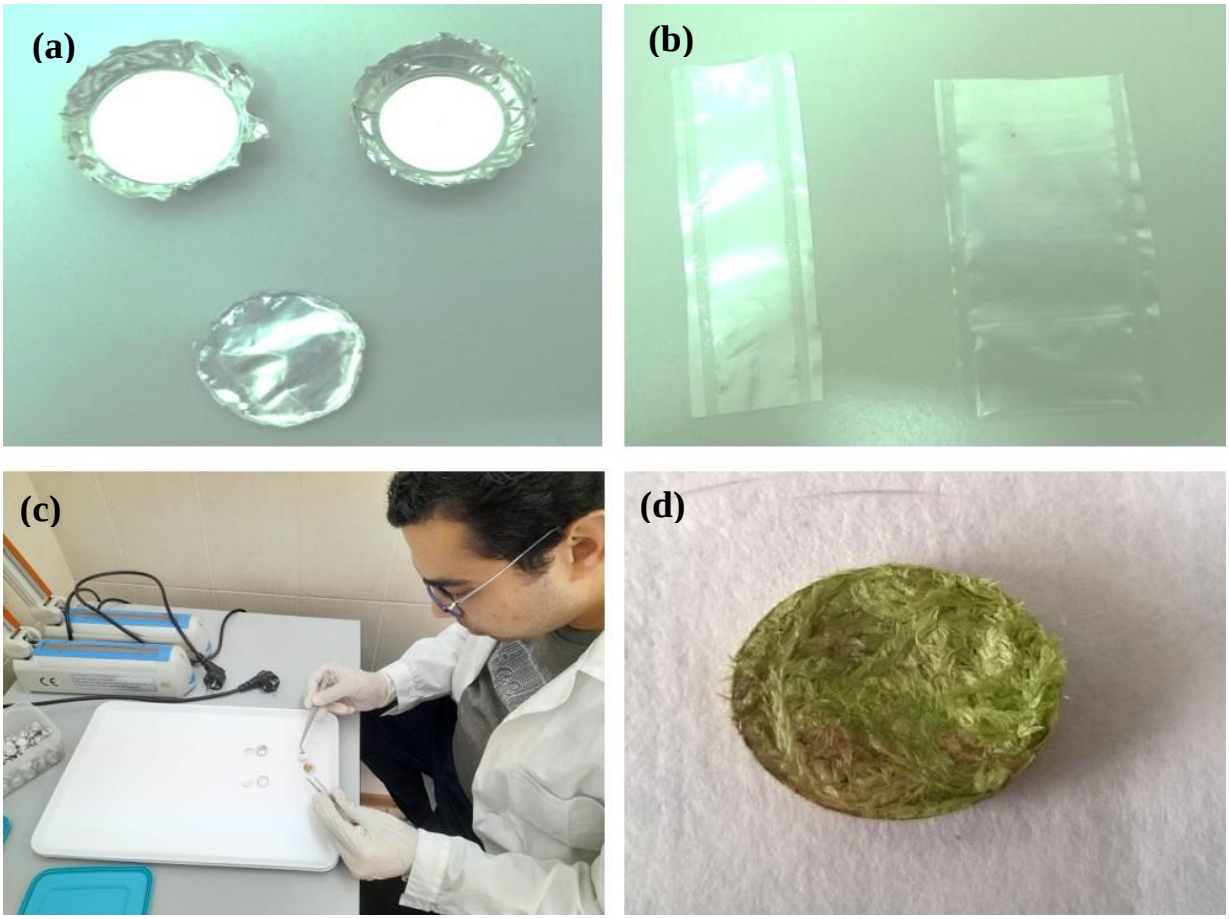

Figure 2 shows the second step in the sample preparation process: "Sample Packing". (a) aluminum cups and (b) polyethylene foil bags for long -lived and short -lived isotopes, respectively. (c) and (d) preparing disks and pellets for long -lived and short -lived isotopes, respectively.

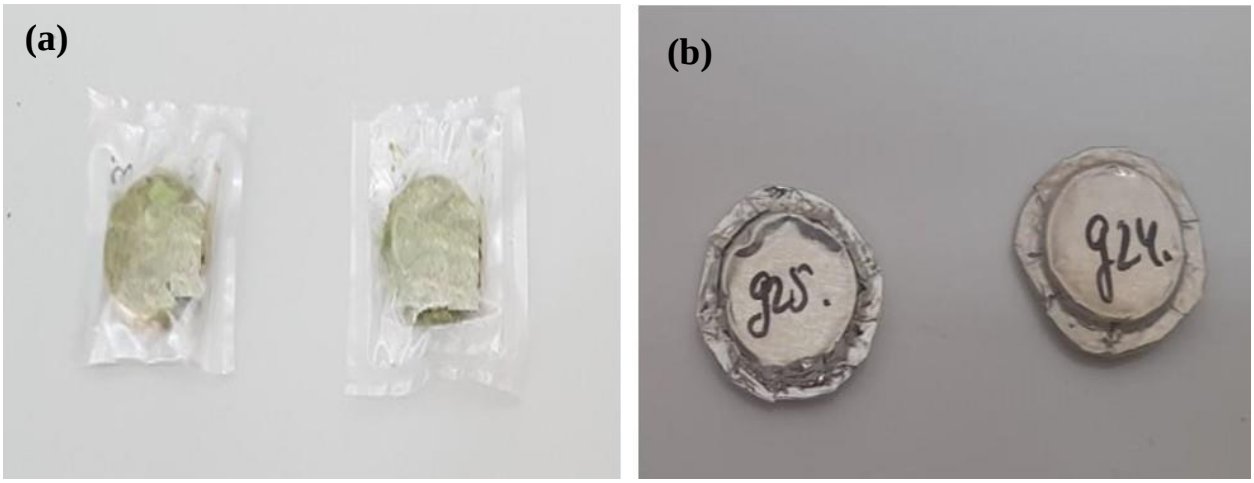

Figure 3 shows the third step in the sample preparation process: Moss samples were wrapped in (a) polyethylene bags and (b) aluminum cubs for short- and long-lived irradiations respectively.

2.3. Data analysis

The NAA was used at the IBR-2 reactor (JINR, Dubna, Russia, see figure 4) to evaluate the concentration of Al, V, Cr, Fe, Ni, Zn, As, Rb, Hg, and Sb in the samples, in mg/kg (ppm) dry weight.

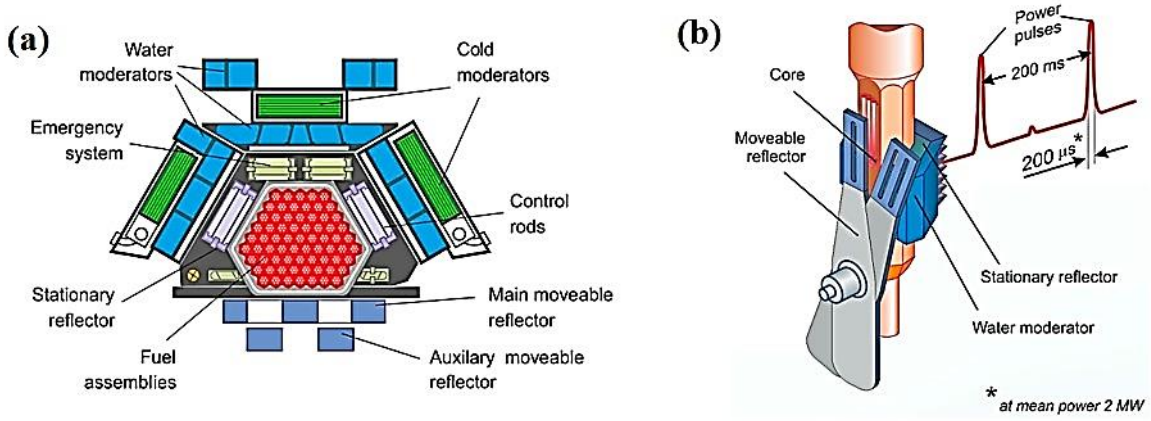

Figure 4. (a) Main part of the IBR-2 reactor, (b) Core of the IBR-2 reactor with a movable reflector[28].

Short-lived irradiation was used to determine the concentration of Al and V in the sample, which was irradiated for 3 minutes with a thermal neutron flux of 1.6×10^{12} n/cm^2/s and then measured directly after 15 minutes.

Long-lived irradiation was used to determine the concentration of Cr, Fe, Ni, Zn, As, Rb, Hg, and Sb in the sample, which was irradiated for 4 days with a neutron flux of 3.3×10^{11} n/cm^2/s, after irradiation and cooling, the samples were re-packaged and measured twice using HP-Ge detectors after 4 and 20 days of decay, respectively.

Note

The concentrations of Cd, Cu, and Pb elements in the collected samples were measured using an Atomic Absorption Spectrometer (iCE 3400 AAS).

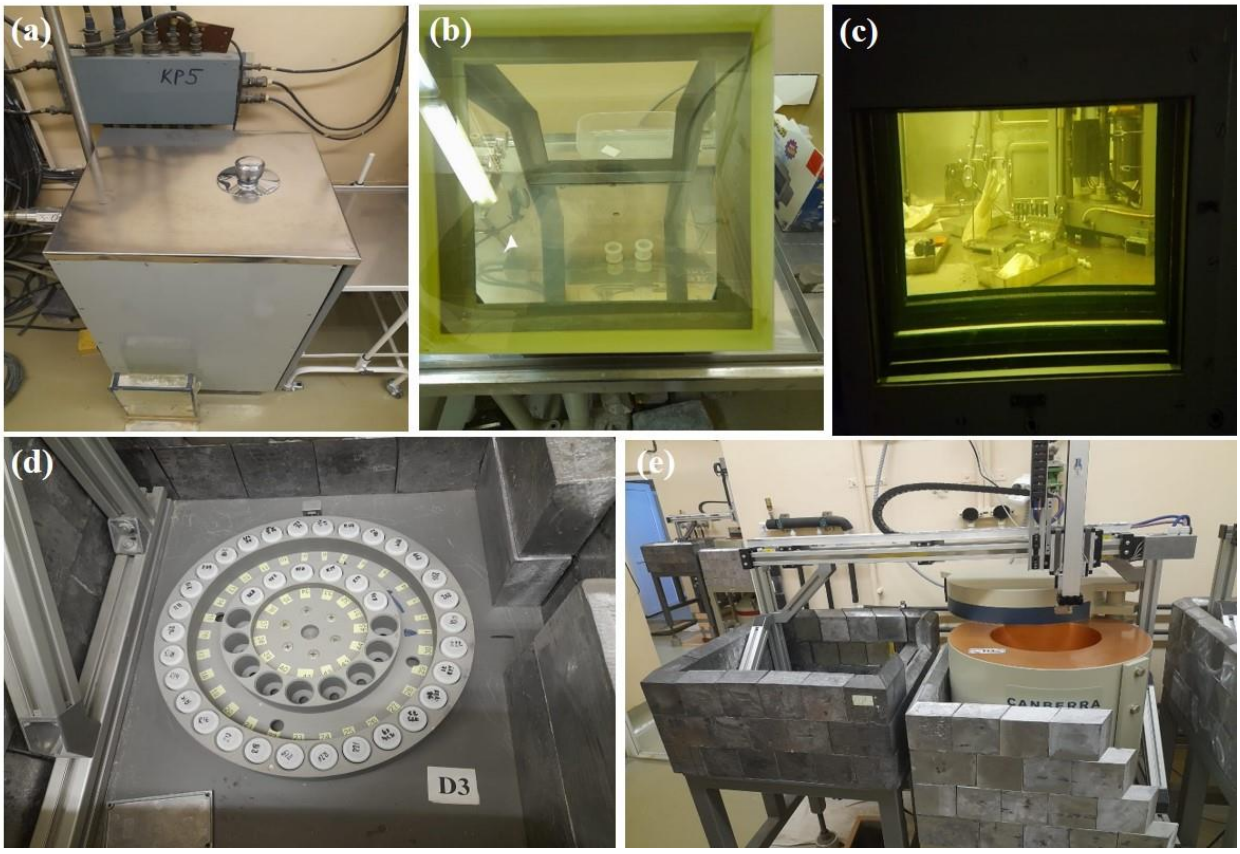

Figure 5. Post Irradiation processes (a) sample inlet, (b) shielded glass box for re-packaging the long-lived irradiation samples, (c) Remote handling of samples in hot cell environment, (d-e) HP-Ge detector for detection the emitted gamma radiation.

The Genie2000 software was used for processing the collected spectra to determine the activity of elements, as well as the "CalcConc" software was utilized to calculate the concentrations of elements, see figure 6.

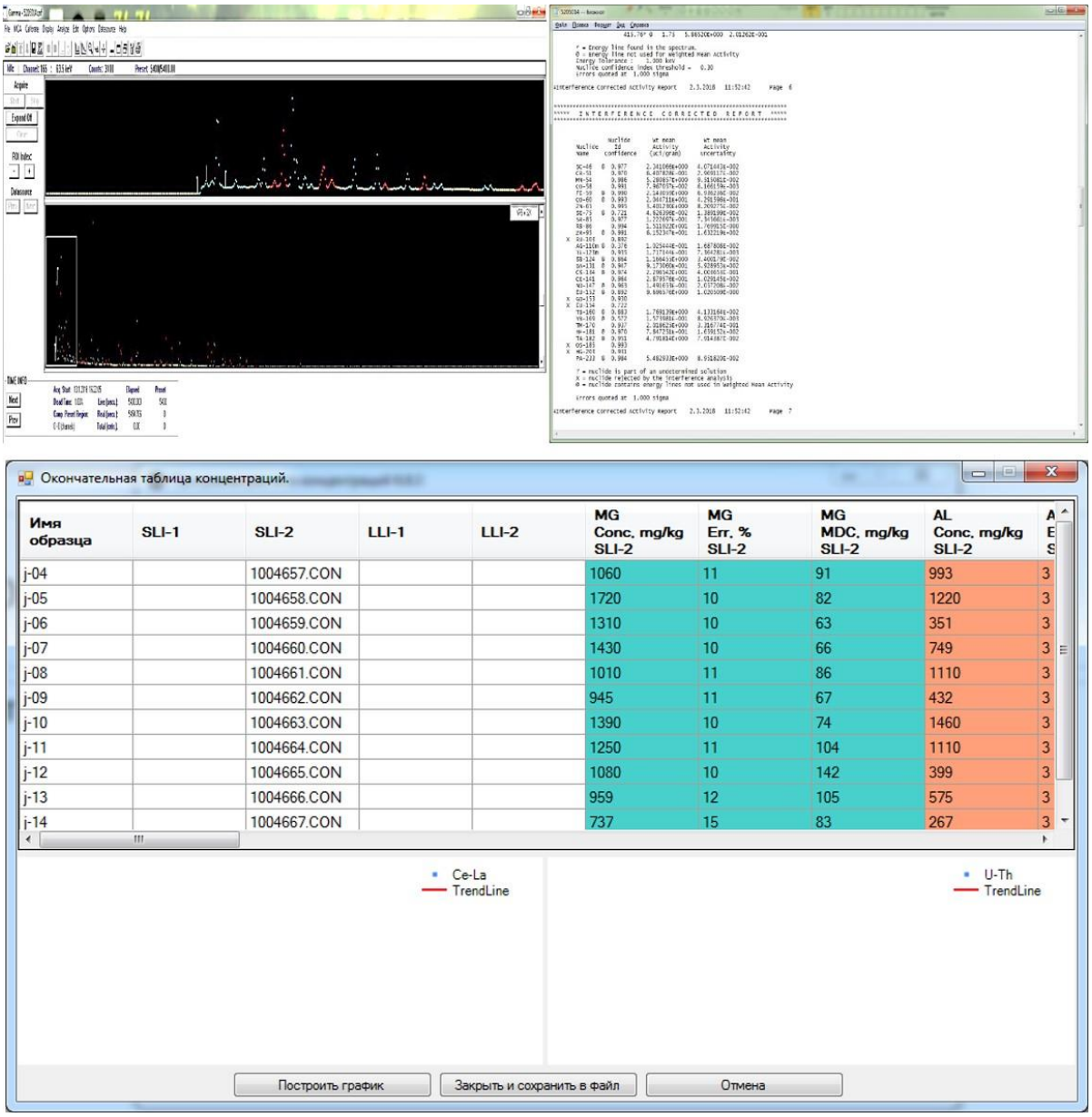

Figure 6. (a) Genie2000 software was used for processing the collected gamma radiation, (b) the activity of elements obtained from Genie2000 software, (c) CalcConc" software which utilized to calculate the concentrations of elements.

3. Result and discussion

3.1. Statistical Analysis

Factor analysis (FA) was used to identify chemical element correlations and reduce the number of variables for the collected data. FA is a multivariate statistical method used in environmental research to simplify large data sets with the aim of identifying pollution sources and their relative elemental composition, as well as determining each source's contribution to the total pollution level.

To estimate the degree of air pollution, several indicators were calculated. The contamination factor (CF) is defined as the ratio of an element's content to its background value in a sample.

$$\mathrm{CF} = \frac{C_m}{C_b}$$

where C_m is the content of a selected element and C_b is the background concentration for the same element. the background concentrations of heavy metals were defined as those obtained by measuring the amounts of various elements in places that were thought to be undisturbed by human activities. The matrix of the dominant rotated factors obtained using FA is shown in Table 1.

Table 1. Factor Loadings (Varimax normalized)
Extraction: Principal components

(Marked loadings are >.600000)

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Multiple R-Square
Na_2	0.93	0.18	0.14	-0.02	0.98
Mg_2	0.53	0.68	0.26	0.17	0.95
Al_2	0.60	0.54	0.41	0.27	1.00
Cl_2	-0.18	0.18	0.82	-0.07	0.82
K_2	0.08	0.03	0.86	-0.15	0.85
Ca_2	0.02	-0.81	-0.06	0.38	0.76
Sc_2	0.97	0.14	0.12	-0.07	1.00
Ti_2	0.62	0.55	0.36	0.25	0.98
V_2	0.58	0.56	0.42	0.20	1.00
Cr_2	-0.91	-0.21	-0.09	0.11	0.94
Fe_2	-0.97	-0.14	-0.08	0.06	0.99
Co_2	-0.95	-0.12	-0.01	0.10	0.98
Ni_2	-0.86	0.02	-0.14	0.28	0.89
Zn_2	0.05	-0.13	-0.25	0.84	0.87
As_2	-0.87	-0.27	0.00	0.22	0.95
Br_2	0.46	-0.09	0.67	-0.22	0.91
Rb_2	0.89	-0.17	0.23	-0.02	0.94
Sr_2	0.24	0.81	-0.13	-0.19	0.87
Sb_2	-0.62	-0.14	0.00	0.61	0.92
Cs_2	-0.94	-0.24	-0.01	0.13	0.99
Th_2	0.96	0.11	0.15	-0.05	0.99
U_2	0.91	0.22	0.10	-0.25	0.98
Cd_2	-0.14	0.55	-0.19	0.61	0.85
Pb_2	0.38	0.12	0.15	-0.72	0.85
Cu_2	-0.45	0.10	-0.66	0.32	0.82
Expl.Var	11.80	3.43	3.12	2.77	21.12
Prp.Totl	0.47	0.14	0.12	0.11	0.84

Three factors were identified, which included 22 % of the variability of the treated dataset. The first factor (F1) was dominated by Na, Sc, Ti, Co, Ni, As, Cu, Rb, and Sb, explaining 11.8 % of the total variance. These elements can originate from natural sources, as well as industrial and agricultural activities. Mineral particles released into the atmosphere as a result of weathering of rocks and soils have a significant impact on the amount of these elements in mosses. However, it has been found that these elements have higher concentrations in urban regions, which could be

owing to road dust particles being re-suspended by tire, brake, and clutch wear, road surface wear, and other vehicle and road component degradation. Sb and Cu may originate from both natural and anthropogenic sources. This could be related to the agricultural activity in Moldova, since these elements are components of different pesticides. The second factor (F2) contained high loadings for the elements Mg, Ca, and sr, accounting for 3.43% of the total variance. These elements can originate from natural sources but in the mining industries. The third factor (F3) contained high loadings for the elements Cl, K, and Be, and Cu accounting for 3.12% of the total variance. These elements can originate from agricultural activity in Moldova, since these elements are components of different fertilizers. The fourth factor (F4) contained high loadings for the elements Zn, Sn, Cd, and Pb accounting for 2.77 % of the total variance. These elements can originate from fuel combustion, transport and agricultural sources.

4. conclusion

The application of neutron activation analysis in the biological sciences and environmental analysis has demonstrated the technique's ability to solve practical problems that cannot always be solved by other analytical techniques. Air pollution is one of the world's major issues today. It can be reduced or avoided with continuous air quality monitoring. Air quality monitoring approaches that have been used in the past have been shown to be ineffective and costly. The moss biomonitoring approach could be used as a low-cost and effective technique for estimating contaminants in the air. The NAA has been done at the IBR-2 reactor in Frank Laboratory of Neutron Physics (JINR, Dubna, Russia) to evaluate the concentration of air pollutants in the samples. The emitted gamma radiation has been processed using Genie2000 and CalcConc softwares to determine the activity of elements, as well as the concentrations of elements. Factor analysis (FA) was calculated using Statistica software to identify chemical element correlations and reduce the number of variables for the collected data.

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