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FINAL REPORT ON THE START PROGRAMME

Report on the elemental analysis of hydrothermal sediments extracted from Los Azufres, Mexico, using the NAA technique at JINR, Dubna, Russia.

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Abstract

This study employed Instrumental Neutron Activation Analysis (INAA) to determine the elemental composition of hydrothermal sediments collected from the Los Azufres volcanic complex in Michoacán, Mexico. The samples were analyzed at the Joint Institute for Nuclear Research (JINR) in Dubna, Russia, using high-purity germanium detectors to identify and quantify trace and rare elements. Key elements identified include uranium (U), tungsten (W), europium (Eu), terbium (Tb), lutetium (Lu), and antimony (Sb), with concentrations consistent with those observed in other geothermal regions.

The study highlights the effectiveness of INAA as a non-destructive method for analyzing environmental and geological samples. The findings underscore the potential of Los Azufres as a source of rare elements, suggesting their role as indicators of geothermal activity. Additionally, the results have implications for environmental monitoring, resource exploration, and assessing potential health impacts in the region. This analysis contributes to understanding geological processes and the redistribution of elements from the Earth's core to the surface in hydrothermal systems and fumaroles.

Content.

1.- Introduction.

Activation Analysis is a method for determining the elemental composition of samples based upon the use of induced radioactivity in the nuclei using particles (proton, neutron, or photons) to activate the nuclei, causing them to emit radiation (for example, Gamma Rays), which can be measured to identify and/or quantify the elements in the sample.

In Neutron Activation Analysis (NAA), the nuclear reaction is induced via bombardment of the sample using neutrons, this causes neutron capture in the nuclei which cause the creation of a radioactive isotope.

Each radionuclide is characterized for its decay constant and the type of radiation emitted.

We could separate to approaches for NAA:

(i) Destructive or Radiochemichal Neutron Activation Analysis.
(ii) Instrumental Neutron Activation Analysis (INAA)

For this study, we employed the INAA method, and therefore, we will focus on this approach.

1.1.- Instrumental Neutron Activation Analysis

Instrumental Neutron Activation Analysis (INAA) is a highly sensitive and non-destructive analytical technique used to determine the elemental composition of samples. The method leverages the principles of nuclear physics, particularly neutron-induced reactions. In INAA, the sample is irradiated with a flux of thermal neutrons ($\phi \approx 10^{13}$ to 10^{14} cm^{-2} s^{-1}) inside a nuclear reactor. This process transforms stable isotopes into radioactive isotopes through neutron capture:

$$ {}^{A}_{Z}X + \mathrm{n} \rightarrow {}^{A+1}_{Z}X' \rightarrow {}^{A+1}_{Z}X + \gamma $$

Here, ${}^{A}_{Z}X$ represents the stable isotope, n is the neutron, and ${}^{A+1}_{Z}X$ is the radioactive isotope that decays by emitting gamma radiation (γ) characteristic of its elemental origin.

After irradiation, the samples are allowed to decay to optimize detection. This ensures short-lived isotopes decay sufficiently, reducing interference from overlapping gamma emissions. The decay period depends on the half-life of the isotopes of interest, which ranges from seconds to days or even weeks and more.

The emitted gamma rays are detected and analyzed using high-purity germanium detectors, providing both qualitative (element identification via energy of gamma rays) and quantitative (element concentration via gamma-ray intensity) information. The sensitivity of the method can detect elements at trace levels, often in the range of μg/g or better.

1.2.- Detection Method

The detection system focuses on analyzing gamma-ray emissions to provide both qualitative and quantitative data. Gamma rays have discrete energy levels unique to each isotope. The detector identifies these peaks with high precision to pinpoint the elemental identity. The number of gamma rays detected for a given energy peak is proportional to the concentration of the corresponding element. High-sensitivity systems reduce noise and improve trace element detection.

To determine the content of elements in samples quantitatively, the relative NAA method was used. According to this method, the sample and the standard sample are irradiated simultaneously or in the same conditions. The elemental mass fractions in the standard are known and certified. It is possible to calculate activities of isotopes in the sample and in the standard as a result of neutron-induced gamma activity spectra collection and processing. The final result of NAA – mass fractions of elements in the sample – is calculated by proportionally comparing gamma-activities of the same isotopes for the sample and the standard and content of elements in the standard.

1.3.- Detectors for INAA

Lithium-drifted germanium detectors, commonly abbreviated as Ge(Li), are key component in INAA for detecting gamma radiation. These detectors leverage the semiconductor properties of germanium, which is modified through a lithium-drifting process to enhance its performance at detecting high-energy gamma rays with precision.

The detectors operate on the principle of a P-I-N junction, where "I" represents an intrinsic region devoid of charge carriers. This intrinsic region is sensitive to ionizing radiation, particularly gamma photons, which interact with the detector to produce electron-hole pairs. These charge carriers are collected under a reverse bias, generating an electrical signal proportional to the energy of the incoming radiation.

The lithium-drifting process is used to create a sufficiently large intrinsic region. Lithium ions are diffused into the germanium crystal, compensating for acceptor impurities like gallium atoms, thereby neutralizing charge carriers and forming the intrinsic region. This process typically involves high temperatures (~400°C) to alloy lithium into the germanium lattice and reverse-biasing the detector to facilitate ion drift and bonding.

Ge(Li) detectors must be cooled to cryogenic temperatures (77 K) using liquid nitrogen. This minimizes thermal noise and prevents lithium migration, which can degrade the detector. The cooling also stabilizes the reverse leakage current, enhancing resolution and detection efficiency. These detectors are particularly favored for their high atomic number, making them highly efficient in detecting high-energy gamma photons compared to silicon detectors.

1.4.- Advantages of INAA

This method is Non-Destructive compared to ICP. Results depend on nuclear reactions, making it unaffected by the sample's chemical composition. No dissolution or decomposition required, avoiding contamination or loss of volatile elements.

1.5.- Applications

INAA is routinely applied in fields such as environmental monitoring, certification of reference materials, geological and archaeological studies, and biomedical research. For example, it is used for certifying Standard Reference Materials (SRMs) by providing homogeneity assessments and detecting heavy metals in environmental specimens.

For this work specifically, this method was used to obtain the elemental composition of samples obtained in a volcanic region in Mexico called Los Azufres, Michoacan.

1.6.- Los Azufres

Los Azufres is a volcanic region located in the state of Michoacán. This area features various steam vents, hot springs with high temperatures and acidic pH, as well as different minerals and heavy elements originating from the Earth's core. This region is situated at an altitude of approximately 3000 meters and experiences mild temperatures almost year-round.

The area where the samples were collected is called Maritaro, which contains hot springs with high-temperature sediments, various fumaroles, and crystals formed from different sediments scattered throughout the region. Samples were collected from three different parts of this area. The first samples were taken from a small spring with multiple levels, where sample 1S was collected. This sample contains a combination of water and sediment.

Figure 1. Hot Springs of Maritaro.

A little further ahead from these springs is a small area with sulfur crystals, where sample 1AZ was collected. From the largest fumarole, sample 3A was taken, and sample 3A-B was collected from another fumarole next to it. From the same area, sample 3S was also taken.

Figure 2. Big Fumarole in Maritaro

2.- Materials and Methods.

2.1.- Sample Preparation.

The selected samples for this work were the following: 1Az, 1S, 3A, 3A-B and 3S. A portion of the colloidal part of the 3A-B sample was decanted using a pipette, obtaining 93.5 ml. This 3A-B sample, as well as the 3A sample, has smooth sediment along with liquid taken from the same area; this sample presents an orange or yellowish color, just like sample 3A.

Five Petri dishes were weighed for each of the solid samples. Some of the sediment from the 3A-B sample was added to one of the Petri dishes, same for the 3A.

Two Falcon tubes were used to remove 7 ml of supernatant in each tube, totaling 14 ml removed. The remaining supernatant liquid, 79.5 ml, was returned to the original sample. Twenty milliliters of distilled water were added to the sediment of the 3A-B sample. For sample 3A, the same procedure as the previous sample was followed, with part of the supernatant decanted into a graduated cylinder and the remaining liquid filled with a Pasteur pipette, obtaining a total of 100 ml. Fourteen milliliters were added to two Falcon tubes, divided into 7 ml each.

The 3A-B sample was deposited in a Petri dish, and 20 ml of distilled water were added. The 14 ml tubes from sample 3A and sample 3A-B were subjected to an ultrasonic bath for 31 minutes. After coming out of the ultrasonic bath, the tubes were centrifuged at 2000 rpm for 10 minutes.

We used four glass containers to store each of the samples, wrapped them in aluminum foil, and then in bubble wrap before finally placing them in a sealable bag.

The sediment samples 3A and 3A-B were placed in an oven at 80°C for 1 day. The 1S sample and the 3S sample were deposited in Petri dishes and placed in the oven with 3A and 3A-B for 1 day.

The 1Az sample was cleaned with a scalpel and then put in the oven with the 3A, 3A-B, 1S and 3S samples at 40º C, the 1Az sample remained in the oven for 4 days.

The samples were taken out of the oven one by one and weighed immediately after removal, while still in their Petri dish.

Then, we used a porcelain mortar to ground the samples, and afterward, we used a sieve of 105 μ to obtain smaller particles. We did this with all of the sediment samples except with the sulfur crystal’s, sample 1Az.

When we finished with the sieving, we weighted each sieved sample and the empty Petri dishes, for finally put all the samples in the oven for a final 4 days at 40º C.

We weighed each container in which the sediment samples would be transported to JINR, to weigh the samples one last time after the 4-day drying process, as well as the empty Petri dishes. After that, we proceeded to store the samples in these containers. Each one was placed in a sealable bag, wrapped in aluminum.

For the irradiation of the samples, approximately one hundred milligrams of each sample is added to small polyethylene bags. Three bags are filled for short-lived isotopes (SLI) and three for long and medium-lived isotopes (LLI and MLI) for each sample, we used an analytical balance to weigh each of these bags. Standard reference materials were packed in the same way.

In the next table we could see the new names used for each one of the bags for the irradiation and also the weight of each bag:

Sample	Original Sample name	SLI (weight in g)	LLI (weight in g)
g-01	3A/1	0.10085	0.10015
g-02	3A/2	0.10138	0.10005
g-03	3A/3	0.10124	0.10055
g-04	3A-B/1	0.1012	0.10034
g-05	3A-B/2	0.1011	0.10051
g-06	3A-B/3	0.10117	0.10012
g-07	1AZ/1	0.10117	0.10073
g-08	1AZ/2	0.10136	0.10047
g-09	1AZ/3	0.10154	0.10061
g-10	1S/1	0.10102	0.10039
g-11	1S/2	0.10127	0.10004
g-12	1S/3	0.10037	0.10075
g-13	3S/1	0.10084	0.10034
g-14	3S/2	0.10143	0.1009
g-15	3S/3	0.10166	0.10039

Table 1.
These names are the same for SLI and for LLI.

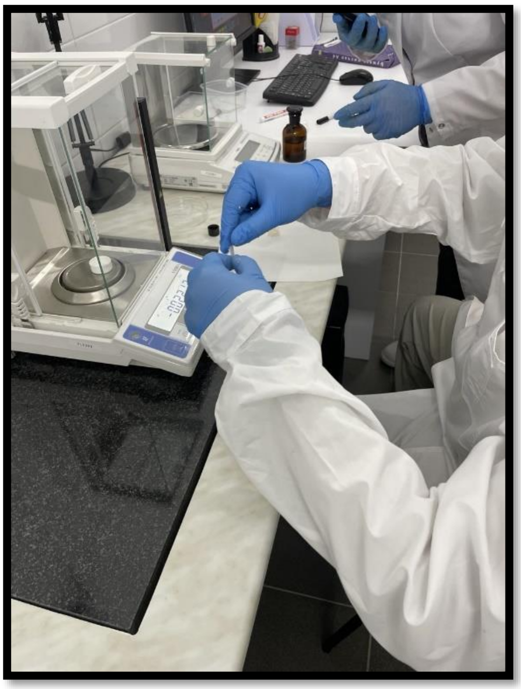

Figure 3. The weighing of the samples

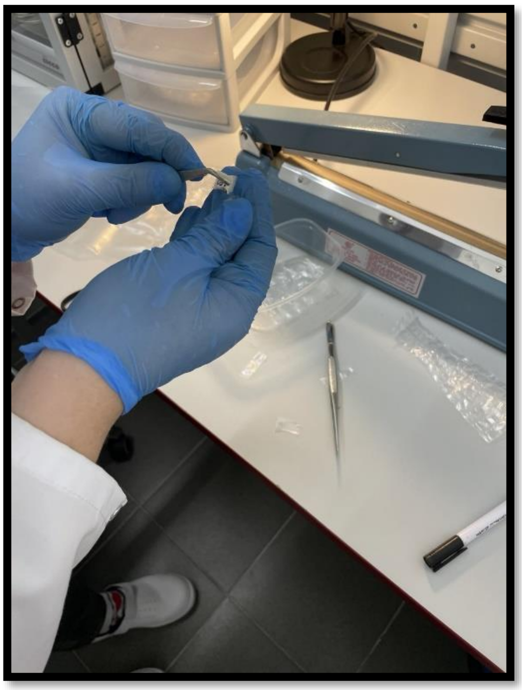

Figure 4. The sealing of the bags

After these, the bags are sealed and stored for the irradiation. These samples were prepared to go to Kazakhstan for the irradiation at the Institute of Nuclear Physics (Almaty, Kazakhstan).

2.2.- Sample Irradiation

The sample irradiation was performed on the Institute of Nuclear Physics of Kazakhstan, with the reactor WWR-K. To determine the elemental composition by SLI samples were irradiated for about 60 s in a "dry" channel. Pneumatic transport system was used to deliver samples to irradiation zone and back. The approximate flux density of thermal neutrons in the "dry" channel is 4×1012 n/(cm2 s), resonance ones − 4×1010 n/(cm2 s). The SLI spectra were measured by the Canberra GC-2018 detector (relative efficiency 20%, resolution 1.8keV at 1332keV). To obtain MLI and LLI samples were manually loaded into one of the "wet" channels for 1.5 h. In the "wet" channel the fluxes of thermal and resonance neutrons are approximately 6× 1013 and 3× 1012 n/(cm2 s) respectively. The MLI spectra were collected six days after the end of irradiation, and the LLI – about three weeks after irradiation, using the automatic spectra measurement system developed in FLNP JINR [7, 8]. The system includes the ORTEC GEM40P4-83 detector (relative efficiency 40%, resolution 1.85keV at 1332keV).

2.3.- Data Processing

The Gamma-Ray Spectra Analysis was performed using the Software Genie-2000 of Canberra, with this software we could work with the Spectra generated after irradiation and then identifying the energy peaks of each element. The calculation of the concentration of elements was performed using the Concentration software. [9, 10]. NIST standard reference materials (SRM) were used for mass fraction calculation and quality control. The SRM utilized for this work were the following:

1. 1632e; Trace Elements in Coal (Bituminous).
2. 1944; New York/New Jersey Waterway Sediment.
3. 2556; Used Auto Catalyst (Pellets).
4. 2586; Trace Elements in Soil Containing Lead From Paint (Nominal Mass Fraction of 500 mg/kg Lead).
5. 2684c; Bituminous Coal (Nominal Mass Fraction 3 % Sulfur).
6. 2706; New Jersey Soil, Organics and Trace Elements.
7. 2709a; San Joaquin Soil.
8. 2780a; Hard Rock Mine Waste.
9. 2782; Industrial Sludge.

In the following table we have the weight utilized of SRM:

SRM	SLI (weight in g)	LLI (weight in g)
1632e-27	0.10056	0
1944-31	0.10129	0.10031
1944-32	0.10092	0.10032
1944-33	0.10144	0.1004
1944-34	0	0.10033
2556-14	0	0.10096

2556-15	0	0.10035
2556-16	0	0.10081
2556-17	0	0.10017
2586-56	0	0.10007
2684c-11	0.10111	0
2684c-12	0.10045	0
2684c-13	0.10153	0
2706-33	0.10129	0.10026
2709a-42	0.10125	0
2780a-07	0	0.10018
2782-32	0	0.10031
2782-33	0	0.10077
2782-34	0	0.10037

Table 2.

3.- Results

Using this method we found 40 different elements in these samples, ranging from common elements to rare earth elements.

The following table shows the mass concentrations of some elements identified.

	Sb	Eu	Tb	Yb	Lu	W	U
sample	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
g-01	3±0.282	1.11±0.072	0.31±056	0.897±0.03	0.212±0.015	1.83±0.152	1.52±0.213
g-02	3.67±0.327	1.27±0.077		0.994±0.033	0.216±0.015	1.98±0.160	1.6±0.224
g-03	3.39±0.305	1.1±0.070		0.908±0.03	0.214±0.015	1.63±0.143	1.52±0.213
g-04	4.31±0.362	1.13±0.070		0.955±0.032	0.258±0.018		1.56±0.218
g-05	3.3±0.290	1.14±0.068		0.969±0.031	0.237±0.017		1.47±0.206
g-06	3.25±0.289	1.47±0.081		1.09±0.035	0.234±0.016	1.95±0.158	1.71±0.239
g-07		0.962±0.066	0.35±0.067	0.977±0.031	0.246±0.017		1.35±0.189
g-08		1.07±0.071	0.262±0.066	0.982±0.031	0.245±0.017		1.47±0.206
g-09		0.995±0.067		0.926±0.03	0.219±0.016		1.39±0.195
g-10	12.7±0.965	1.93±0.097	0.728±0.	1.83±0.055	0.438±0.03	3.93±0.248	1.79±0.251
g-11	12±0.912	1.87±0.097		1.84±0.055	0.42±0.029	3.97±0.250	1.55±0.217
g-12	13.2±1.003	1.99±0.101	1.02±0.	1.86±0.056	0.433±0.029	4.54±0.272	1.72±0.241
g-13	3.08±0.280	1.22±0.073		0.87±0.03	0.217±0.015		1.64±0.23
g-14	2.96±0.266	1.12±0.068		0.89±0.029	0.194±0.014		1.47±0.206
g-15	3.13±0.282	1.13±0.069		0.938±0.031	0.222±0.016		1.55±0.217

Table 3.

As we could see, the levels of U, W, Eu, Tb, Sb and Lu are around the levels of other thermal regions, this could be indicative of the rare earth elements that goes from the

Earth´s Core to the surface in these fumaroles, hot springs and in the soil of this little region [11, 12, 13].

4.- Conclusions

As we could see on the Table 2, the Rare Earth Elements are very interesting to be found in these samples. This could be an interesting area of studies to see if these elements are the ones causing health problems of the people of this region, and also could be useful to detect new mines or other types of forms to exploit these resources. The use of INAA provides enormous opportunities for different studies in Mexico, as we could see with this work, this method is very useful to detect toxic elements in populated areas.

Mexico's rich history and cultural heritage could benefit from INAA by enabling precise characterization of artifacts such as pottery, obsidian tools, and metals. This method allows researchers to trace the origins of raw materials and trade routes. Future collaborations with nuclear facilities could prioritize creating a comprehensive database of elemental fingerprints of archaeological samples.

5.-Acknowledgments

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