Instrumental Neutron Activation Analysis (INAA) of Rock Samples from Blue Nile Gorge, East Gojjam, Ethiopia

Asres Yihunie Hibstie, A.K.Chaubey, Awoke Taddesse Hailu and Dilbetigle Assefa Mamo

Abstract: Neutron activation analysis (NAA) is an analytical technique based on the measurement of radio-nuclides formed directly or indirectly by neutron irradiation of the material of interest. The main objective of this study is to assess elemental availability and concentration in rock samples of the Blue Nile Gorge area between Gohatsion and Dejen towns. The hydrocarbon potential of the Paleozoic sediments is much debated in this Grand Canyon.The authors maintain that the hydrocarbons were frequently remobilized and redistributed into younger sediments. Paleozoic rocks could have produced significant amount of hydrocarbons in areas characterized by strong Mesozoic sedimentary subsidence. The recent developments in activation analysis techniques now offer the prospect of rapid, reliable analyses for many elements in concentrations as small as parts per million or parts per billion. The neutrons obtained from isotopic neutron source of (α, n) type were used in this paper.

Key words: Blue Nile Gorge, Grand Canyon, Paleozoic/ Mesozoic sediments, hydrocarbons

Introduction*:* Ethiopia is in the tropical zone lying between the Equator and the Tropic of Cancer. It is located in the horn of Africa and a largely (Sileet, 2001) mountainous country, which is the origin and water tower or source of much of the rivers flow reaching the Blue Nile River (Seleshi, et al, 2008) contributing greater Nile flow (Melesse, et al, 2004) . The economy of Ethiopia is primarily based on Agricultural production. The main food staffs are "teff" (Eragrostis teff), small grain cereal crops, wheat, barley, sorghum, millet, yams, potatoes, and beans. The mineral potential of Ethiopia lies mainly with the development of gold, potash, thermal energies and industrial materials. The Mesozoic sediments are important for their associated industrial and building materials including limestone, sand, sandstone, gypsum and clay

The Blue Nile Gorge (Africa's Grand Canyon) is one of the nicest canyons in Africa. From all over the highlands of Ethiopia including Choke Mountain range (Teferi et al, 2010), huge rivers pour into the Blue Nile Gorge.

This majestic and enormous gorge is the most captivating gorge in Africa. It has a magnificent captivating physical feature, natural beauty, a unique eco-system and it is a tremendous obstacle for travelling and communication from the northern half to the southern half of the country. The river (Teferi et al, 2010;Seleshi,et al,2008) got the 'blue' part of its name because of its muddy color due to the huge amount of fertile soil it erodes (Yihunie et al, 2011) from the Ethiopian highlands. Why they called it blue rather than the more logical color of brown, dark brown or even black is open to conjecture. It is this spectacular flood of the Blue Nile that sets it apart from many great river systems of the world.

The Abay river section is exposed along a road cut at the Addis Ababa to Debre Markos highway, between kilometer marks 198 and 215. This road connects Addis Ababa to the northern part of the country which passes through the gorge of Blue Nile where there is a high susceptibility landslide. Rock falls on the other hand exist largely as discernible block topples and wedge failures all along mountains, valley walls and road cuts (Lulseged**, 2003).** The main objective of this study is to assess elemental availability and concentration in rock samples of the (Wolela, 2008) Blue Nile Gorge area between Gohatsion and Dejen towns. Due to population growth and shortage of land resources (Seleshi, et al,2008), farmers tend to use sloppy terrains, for settlements, cropland and infrastructure construction along this gorge (Vitale, 2005) using poor land management practices since agricultural investments are difficult to make in these ecosystem due to natural barriers.

Gohatsion and Dejen are two small towns located just outside the gorge in the South and in the North sides of the gorge respectively. The study area can be reached easily using the asphalt road that goes from Addis Ababa to the northern part of the country. The road passes through the gorge crossing the two small towns in the north and south edge of the valley. Sometimes landslide destructs retaining walls and breaks the road hindering and interrupting traffic movements. The Blue Nile River and its tributaries cut deep into the rocks (Lulseged, 2003) forming spectacular valley with vertical cliffs and deep gorges

in which landslide problem is common in the area mainly during the rainy season. The Blue Nile passes through deep valley and gorge as a raging torrent during and after the wet seasons conveying large sediment loads (Sileet, 2001).

Instrumental Neutron Activation Analysis (INAA):

The radioisotopes production can be performed through different nuclear reactions, which could take place in isotopic neutron source. This method of obtaining radioisotopes through a mechanism of irradiation with neutron consists of bombarding some elements with different neutrons energy.

When an isotope of a stable element is irradiated by the nuclear particles produced in an isotopic neutron source, some of the atoms of the isotope interact with the bombarding particles and are converted into a radioactive isotope of the same element. Depending on the nature of the bombarding particle, the atom can be converted into different radioisotopes of the same element or into isotopes of different elements.

As these radioactive nuclides decay, they emit gamma rays whose energies are characteristic for each nuclide. Neutron Activation Analysis (Michael, 2003) is one of the most sensitive and powerful technique for performing non-destructive (Vega-Carrillo et al, 2006), rapid, quantitative, simultaneous multi-elemental analysis**.** A gamma-ray spectroscopy system (Robu, 2009) consists of a detector (and high voltage power supply for the detector), pre-amplifier, spectroscopy amplifier, analog-to-digital converter, multi-channel analyzer, and an output device. A high-resolution gamma-ray spectrometer is used to detect those delayed gamma-ray(s) in the presence of artificially induced radioactivity in the sample for both qualitative and quantitative analysis. In order to minimize thermal noise the detector is kept at cryogenic temperatures (liquid nitrogen, temperature = 77K). The signal is shaped by the spectroscopy amplifier and then converted from an analog to a digital signal by the analog-to-digital converter.

Experimental work:

Instrumentation: The irradiation block used has one isotopic source of Am-Be having 2 Ci. This source is introduced in a closed-end tube which is placed inside a paraffin block. The function of the pure paraffin block is to slow down the neutrons through a multiple collisions with the hydrogen atoms. The gamma spectra of the obtained radioisotopes were acquired using a Hype Pure Germanium (HPGe) detector, coupled to a multichannel analyzer. The radionuclide activity **(**Daraba et al, 2005) is calculated as:

$$\Lambda = \frac{A}{1800 \cdot \varepsilon \cdot p} \qquad \text{---------- (1)}$$

Where Λ- represents the activity in μci, A-the area of the peak, Ɛ-the efficiency, p-the probability of transition at this particular energy as a result from the disintegration scheme,1800-represents the acquisition time.

Sample Collection and Preparation:

A total of 3 rock samples have been collected randomly from different sites in Blue Nile Gorge. The samples were stored in pre-cleaned polyethylene capped bottles and handled with extreme care until the moisture is completely removed from the samples' surface.

The dried rock samples were crushed into small pieces and grinded using mortar with pestle to fine and homogenized powder. It was after the polyethylene bags were treated in this way that they were used to package the samples for irradiation and cooling. The powdered samples were mixed and packed in plastic containers, weighed, wrapped in polyethylene films for irradiation and bombarded to a minimum period of one month to allow daughter products to come into radioactive equilibrium with their parents. Samples and standards were bundled and sandwiched together and irradiated at a thermal flux (Dias, 2007). Because of the low detection limits for many elements, sample collection and preparation is critical. Great care (Yihunie et al, 2011) must be taken into account not to introduce contaminants.

Irradiation and counting:

The isotopic neutron source is used in this paper. These neutrons beams provided by this source, were obtained from nuclear reaction initiated by the radio isotopic constituents. The irradiation of powdered rock samples was performed by the ^{241}Am-Be isotopic neutron source (Karadag et al, 2007; Karadag et al, 2003; Yűcel, 2005) immersed in paraffin moderator shielded with lead bricks. The samples were exposed to the neutrons in a fixed position in the irradiation hole of very large volume compared to the sample volume. Therefore, the effect of thermal flux depression at the irradiation site has been neglected (Karadag et al, 2007). The geometrical configuration of the neutron source and the irradiation holes of this neutron irradiation unit and the thermal neutron flux at the sample irradiation position of Am-Be neutron irradiator have been previously described in detail elsewhere (Yihunie et al, 2011).

Apparatus and Equipment:

Experimental setup: The basic instrumentation for performing neutron activation analysis consists of a nuclear source (Jack,1999) for irradiation the samples and standards, nuclear detector for detecting the gamma-emissions, and multichannel analyzer system that range from simple data acquisition systems to complex computerized data acquisition system and processing systems.

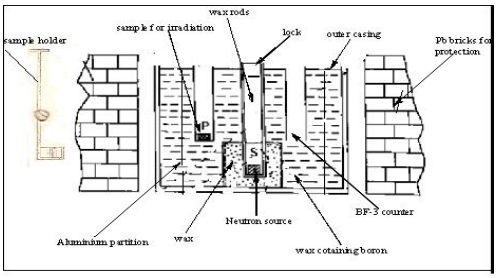

Fig.4. Am-Be neutron source used for activation purpose

The detector used (Karadag et al, 2007) in this measurement was high-purity germanium, manufactured by Canberra Inc. It is shielded in a number of layers starting with stainless steel (5mm thick) and lead (30mm thick) to reduce the background radioactivity on all sides. The spectrometer was calibrated for efficiency (Yihunie et al, 2011) and energy using multi-nuclide standard sources of Eu^{152} and Cs^{137}.

Calibration:

For calibrations, the standard source is placed above the detector in a well defined geometry, and the measurement is started. HPGe gamma spectroscopy detection systems are generally operated on an energy range of 0 to 2000 kev utilizing 4096 to 8192 channels of data acquisition storage. The dependency of the efficiency on the radiation energy was determined at 0.0 mm sample-detector distance (Yihunie et al, 20011). The detector efficiency decreases continuously with energy. The dependency of the efficiency on the volume of the sample was determined by a bottle (1000 ml). It can be noticed that the detector efficiency decreases with the volume of the sample in the energy-range of interest.

To minimize the effect of the scattered radiation from the shield, the detector is located in the center of the chamber. Then the sample was placed over the detector for at least 10 hr. The spectra were either evaluated with a computer software program, or manually with the use of a spreadsheet.

Data Collection:

In the laboratory, the final results are presented as concentrations, in weight percent, ppm, or some other convenient units. Among its many uses, INAA has been widely used to obtain analyses of the (El-Tahar, 2006) Rare Earth Elements (REE) including phonolites, granites, syenites and nepheline syenites. Nuclear data for the determination of the radioactivity for the thermal neutron cross-section are given in table of isotopes.

NAA data can then be critically reviewed and represented the absolute energy of each gamma-ray peak and the absolute efficiency associated with the determination of each peak area in any number of detection variation diagrams. Data on the gamma spectrum, accumulated in the multi-channel memory, can be sent to a cathode ray tube, a video terminal, a printer or a plotter. In this way, the peaks referring to the various spectrum energies are displayed in (Fig.5 and 6) below.

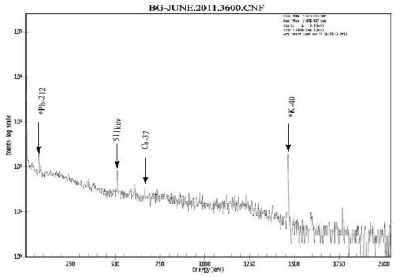

Fig.5. Analysis of gamma spectra for Room Background

The photopeaks in the spectrum indicate the presence of particular radioelement, and the amount of radioactivity they contain may be used to measure the amount of the radioelement present. Each spectrum was collected in the live-time.

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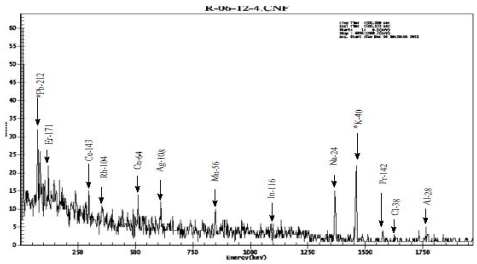

Fig.6. Analysis of Gamma spectra for rock samples

from Blue Nile Gorge obtained by irradiation with isotopic neutron source

A quantitative analysis may then be performed by identifying the peak energy value as well as a qualitative analysis, by determining the peak area proportional to the radioisotope activity (absolute measure)

Table.1. Analysis of Radionuclide of the Rock Sample from Blue Nile Gorge

The radionuclide	Natural Abundance (%)	The half-life	Cross-section in(barn)	Concentration values in (ppm)	Gamma energy (kev)	Gamma abundance in (%)
Er-171	14.88	7.52h	5.7 ± 0.2	2.347 ± 0.069	124	9
W-187	28.4	23.9h	37.0 ± 1.5	3.623 ± 0.09	134	9
Yb-177	12.73	1.9h	2.40 ± 2	4.363 ± 0.093	150	20
Ce-143	11.07	33h	0.950. ± 05	118.72 ± 0.49	293	42
Ru-105	18.6	4.44h	0.320. ± 02	60.059 ± 0.35	469	17
Ag-108	51.83	2.41m	37.271. ± 2	0.4447 ± 0.03	619/434	9/17
Mg-27	11.01	9.46m	0.0350 ± .02	86.369 ± 0.42	844	72
Mn-56	100	2.56h	13.30. ± 2	6.4458 ± 0.11	847	99
Rh-104	100	lm	10 ± 1	0.23099 ± 0.021	357	13
In-116	95.7	54m	81.3 ± 8	0.01896 ± 0.006	1097	56
Na-24	100	15.03h	0.13 ± 0.03	2.7048 ± 0.07	1369	100
Pr-142	100	19.2h	7.6 ± 0.3	3.1138 ± 0.08	1576	4
Cl-38	24.23	37.18m	0.376 ± 0.011	14.289 ± 0.17	1642	32
Al-28	100	2.246m	0.232 ± 0.003	135.502 ± 0.52	1779	100
Cu-64	69.1	12.7h	4.5 ± 0.02	93.6735 ± 0.43	511	37

Table.2. Concentration of radionuclide

Isotope	Iγ(%)	Major(%)	Minor(%)	Trace(%)
Cu-63	69.1	9.37		
Al-27	100	13.55		
Cl-37	24.23	1.43		
Ce-142	11.07	11.87		
Mg-26	11.01	8.63		
Ru-104	18.6	6.02		
W-186	28.4		0.364	

Er-170	14.88		0.234	
Yb-176	12.73		0.636	
Mn-55	100		0.645	
Na-23	100		0.271	
Pr-141	100		0.311	
Rh-103	100		0.023	
Ag-107	51.83		0.0445	
In-115	95.7			0.0006

From the table above major elements include (Cu, Al, Cl, Xe, Ce, Mg, Kr, and Ru), minor elements include (W, Er, Yb, Mn, Na, Pr ,Rh, and Ag) and trace elements include (In).

Some Experimental identification and half-life determination:

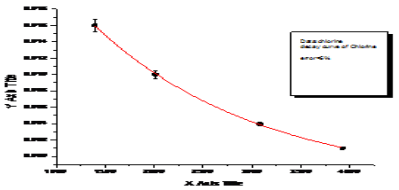

Fig.7.the exponential decay of activity of Cl in Linear plot

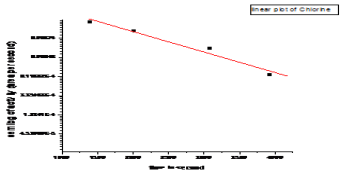

Fig.8. the exponential decay activity of Cl in semilog plot

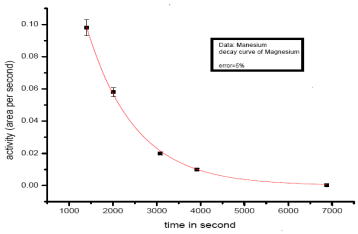

Fig.9. the exponential decay of activity of Mg in linear plot

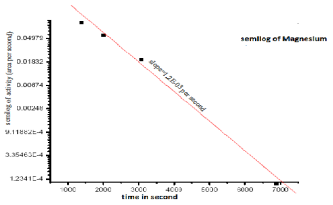

Fig.10. the exponential decay of activity of Mg in semilog plot

Sources of errors: The procedures and methods described herein are best applied with high-resolution gamma-ray detectors but care must be exercised to avoid unnecessary errors, and the ultimate accuracy will not be as good. The most important fact in applying gamma-ray spectroscopy is that the raw count rate for a given gamma-ray is not usually proportional to the amount of the nuclides emitting the gamma-ray. Accurate gamma-ray assays demand accurate corrections for both the electronic losses and the losses caused by sample self-attenuation.

Significant counting errors associated with high count rates are unlikely to occur because the dead time losses were kept well below 10%.

Results and Discussions:

A non-destructive neutron activation analysis (Kogo et al, 2009) technique was applied with success to determine the concentration of these elements in such complex samples (Soliman, 2006). Some gamma-ray lines appeared in the spectra, due to background emitted from the shielding materials. These have been subtracted from each spectrum by using an empty container and measured at the conditions of samples measurement.

By using the isotopic neutron source, some radioisotopes with great importance in Environmental Science: Cu, Al, Cl, Pr, Na, In, Rh, Mn, Mg, Ag, Ru, Ce, Yb, W, Er including the background elements have been appeared in the measured spectra. The elements (^{63}Cu, ^{27}Al, ^{37}Cl, ^{142}Ce, ^{26}Mg, and ^{105}Ru) are found as major elements, the elements (^{186}W, ^{170}Er, ^{176}Yb, ^{55}Mn, ^{23}Na, ^{141}Pr,^{103}Rh and ^{105}Ag) are found as minor elements and the element (^{115}In) is found as trace element. The INAA technique has lead to a successful determination of fifteen elements in the rock samples around the research area. Heavy metals such as: (Al, Cr, Er, Mn, Cu, Mg, Ag, Pr) produced using NAA technique have different applications. Some of these heavy metals have been known to be (Zukowska , 2008) toxic and dangerous to human health especially when they are found in ground water and growing crops. Some values of their concentration were as high as (2.347 ± 0.069 ppm for Er-171, 3.623 ± 0.09 ppm for W-187, 4.363 ± 0.093 ppm for Yb-177, 118.72 ± 0.49 ppm for Ce-143, 60.059 ± 0.35 ppm for Ru-105, 0.447 ± 0.03 ppm for Ag-108, 86.369 ± 0.42 ppm for Mg-27, 6.4458 ± 0.11 ppm for Mn-56, 0.23099 ± 0.021 ppm for Rh-104, 0.01896 ± 0.006 ppm for In-116, 2.7048 ± 0.07 ppm for Na-24, 3.1138 ± 0.008 ppm for Pr-142, 14.289 ± 0.17 ppm for Cl-38, 135.502 ± 0.52 ppm for Al-28 and 93.6735 ± 0.43 ppm for Cu-64) and the elements (Ce, Pr, Er, and Yb) are rare earth elements (El-Tahar, 2006) found inside the rock sample. . The heavy metals that most commonly cause problems include (Al, Cr, Cu, and Mn). All heavy metal poisoning and chemical toxicity lead to the accumulation of toxins in our tissues and organs causing nutritional deficiencies, hormonal imbalances and the breakdown of the immune system, the central nervous system, and the organs of the body.

As with the other elements, aluminum is observed and accumulated in the body, and has been linked to serious illnesses including osteoporosis, extreme nervousness, anemia, headache, decreased liver and kidney functions, forgetfulness, speech disturbances and memory loss (Morcola, 2003).

A special computer program called Genie-2000 is used for identifying the elemental constituents of each sample under investigation. Data were manipulated (Dias, 2007) using a variety of methods including spreadsheet. Due to its (Trkov, 2007) selectivity and sensitivity, NAA occupies an important place among the various analytical methods. Sensitivities and accuracy of NAA depend on the concentration of the element and radionuclide parameters (i.e, parent isotope abundance, neutron cross-section, half-life, and gamma-ray abundance).

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