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k_0-INAA METHOD AT THE PNEUMATIC STATION OF THE IEA-R1 NUCLEAR RESEARCH REACTOR. APPLICATION TO GEOLOGICAL SAMPLES.

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ABSTRACT

There is a significant number of analytically important elements, when geological samples are concerned, whose activation products are short-lived (seconds to minutes) or medium-lived radioisotopes (minutes to hours). As part of the process of implementation of the k_0-INAA standardization method at the Neutron Activation Laboratory (LAN–IPEN), São Paulo, Brazil, this study presents the results obtained for the analysis of short and medium-lived nuclides in geological samples by k_0-INAA using the program k_0-IAEA, provided by The International Atomic Energy Agency (IAEA). The elements Al, Dy, Eu, Na, K, Mn, Mg, Sr, V and Ti were determined with respect to gold (^{197}Au) using the pneumatic station facility of the IEA-R1 5 MW swimming-pool nuclear research reactor, São Paulo. Characterization of the pneumatic station was carried out by using the "bare triple-monitor" method with ^{197}Au-^{96}Zr-^{94}Zr. The Certified Reference Material IRMM-530R Al-0,1% Au alloy, high purity zirconium, Ni and Lu comparators were irradiated. The efficiency curves of the gamma-ray spectrometer used were determined by measuring calibrated radioactive sources at the usually utilized counting geometries. The method was validated by analyzing the reference materials basalt BE-N (IWG-GIT), basalt JB-1 (GSJ), andesite AGV-1 (USGS), granite GS-N (IWG-GIT), SOIL-7 (IAEA) and sediment Buffalo River Sediment (NIST–BRS-8704), which represent different geological matrices. The concentration results obtained agreed with certified, reference and recommended values, showing relative errors less than 10% for most elements.

1. INTRODUCTION

The neutron activation analysis laboratory at IPEN (LAN-IPEN) has been analyzing geological samples for decades, using the comparative method of analysis by neutron activation with the IEA-R1 nuclear research reactor of IPEN [1]. In this method, samples and standards are irradiated simultaneously with neutrons under the same conditions. Elemental concentrations are calculated by comparison of the activities of the gamma-rays from the sample and standard. This procedure requires the preparation of element standards, which is very laborious and time consuming. Furthermore, some elements present in the sample can not be analyzed due to the absence of a corresponding element standard. The k_0-NAA method, developed by the Institute of Nuclear Sciences, Gent, Belgium [2], has been increasingly used, as it requires only a single comparator such as ^{197}Au for multielement determination instead of multielement standards required in the relative method. Some attempts to introduce the k_0-NAA at LAN-IPEN have been made [3] but, in fact, the INAA comparative method is actually used at LAN-IPEN. In spite of the fact that this standardization method is still considered one the most accurate methods of INAA, neutron activation laboratories in Brazil and in other countries all over the world has been using the k_0-NAA method, due to the improvement of the analysis procedure and time and still quite accurate results [4-9].

Many INAA laboratories developed k_0 software using different approaches. The k_0-IAEA program was developed to be distributed free of charge by the IAEA, in order to assist users of the k_0-approach in NAA to harmonize their results, and to encourage NAA laboratories to adopt the k_0-standardization method. The mathematical approach used and how k_0 data catalogue together with additional information on coincidence and sum peaks are incorporated in the program are described by Rossbach et al [10].

There is a significant number of analytically important elements when geological samples are concerned, such as Al, Dy, Eu, K, Mg, Mn, Sr, Na, Ti and V, whose activation products are short-lived (seconds to minutes) or medium-lived radioisotopes (minutes to hours). The IEA-R1 reactor has a pneumatic station facility adequate for short time irradiations, providing accurate irradiation and decay times. Samples are sent to irradiation pneumatically and, after irradiation, are sent back automatically to the station. Samples can then be measured in gamma-ray spectrometers located in counting rooms next to the pneumatic station to allow rapid measurement of the induced activity.

As part of the process of implementation of the k_0-INAA standardization method at the Neutron Activation Laboratory (LAN–IPEN), São Paulo, Brazil, the objective of the present study was to assess the applicability of the k_0-INAA method with the k_0-IAEA software, in the pneumatic station of the IEA-R1 nuclear reactor, to analyse the elements Al, Dy, Na, K, Mn, Mg, Sr, V and Ti in geological matrices. For this purpose, the characterization of the neutron flux parameters in the pneumatic station irradiation position was performed. The geological reference materials basalt BE-N (IWG-GIT), basalt JB-1 (USJ), granite GS-N (IWG-GIT), SOIL-7 (IAEA) and sediment Buffalo River Sediment (NIST–BRS-8704) were analyzed for data validation.

2. EXPERIMENTAL

2.1. Irradiation Facility

The IEA-R1 is a nuclear research reactor (5 MW) immersed in a pool containing 273 m^3 of demineralized water. The pool has about 9 m deep by 3 m wide and 11 m length. The reactor core is located 6.9 m from the surface of the pool, and has the form of a parallelepiped composed by 20 standard fuel elements, 4 control fuel elements, about 25 reflectors, 7 positions to irradiate samples and caps embedded vertically in an aluminum matrix board. This board is supported by a trellis attached to a mobile platform which allows their movement along the pool.

A fast pneumatic rabbit system station specifically designed for INAA of short-lived and medium-lived nuclides was installed and utilized to perform, with a transfer time of approximately 12 s, short irradiations up to 30 min, in polyethylene rabbits. In this station, samples (up to 1 g) are enclosed into polyethylene capsules (rabbit) and fed into the loading/reception station. The loading/reception station is connected to a terminal station (irradiation head) by means of a tube and air supply line. The sending and receiving station these capsules are placed in a laboratory located outside of the reactor building. The irradiation head is installed near the reactor core. The neutron flux is expected to be mixed of thermal, epithermal and fast neutrons.

2.2. Measurement facility

The measurements of the induced gamma-ray activity were carried out using a GX20190 hyperpure Ge detector. The multichannel analyzer was a 8192 channel Canberra S-100 plug-in-card in a PC computer. The resolution (FWHM) of the system was 1.90 keV for the 1332 keV gamma-ray of ^{60}Co. For calibration (energy and efficiency) of the HPGe detector, standard radioactive point sources were used: ^{137}Cs and ^{152}Eu, provided by the Nuclear Metrology Laboratory, IPEN-CNEN/SP. Figure 1 shows the full-energy peak efficiency curve for the coaxial HPGe detector fitted using the k_0-IAEA software.

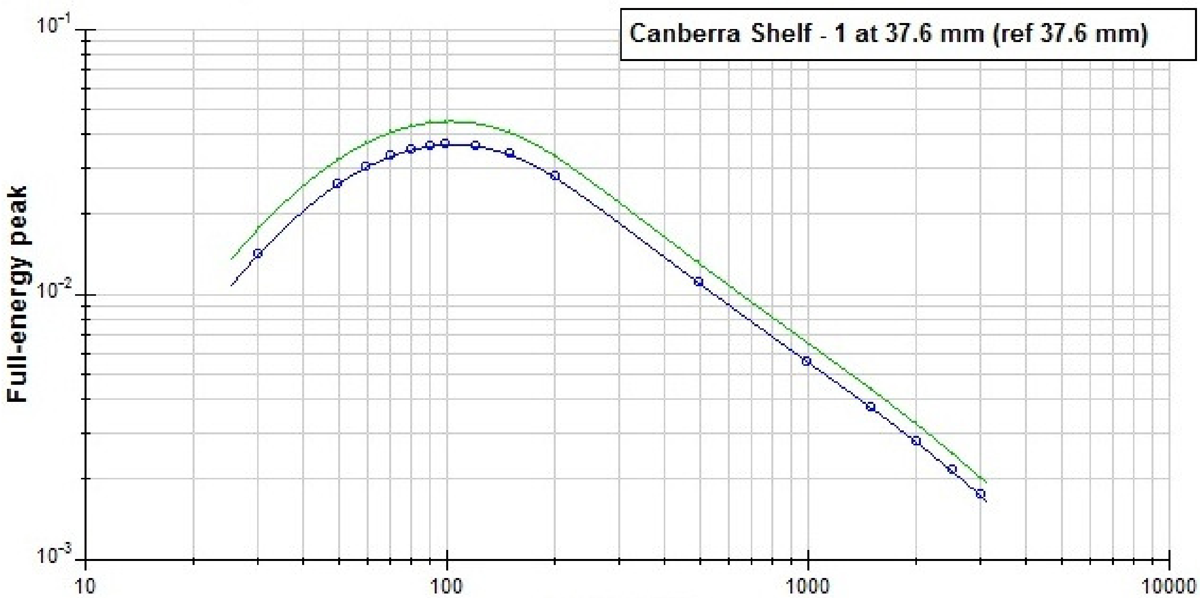

Figure 1. Peak efficiency curve for the coaxial HPGe detector fitted using the k_0-IAEA software.

2.3. Flux Parameters

The parameters f and α for the short irradiation facility of the IEA-R1 nuclear reactor were determined by irradiating a set consisting of approximately 20 mg of a 0.127 mm thick Zr foil (purity 99.5%) together with 3 mg of Al-0.1% Au wire (Certified Reference Material IRMM-530R) for 2 min. A nickel monitor (25 mg of a Ni wire 0.762 mm thick, 99.95% purity) was irradiated to calculate the epicadmium-to-fission neutron flux ratio. The neutron temperature was evaluated by irradiation of approximately 1.5 mg Lu foil (purity 99.963%). The flux parameters determined for the pneumatic station of IEA-R1 are in Table 1.

Table 1. Flux parameters for irradiation in the Pneumatic Station of IEA-R1

Parameters	Values
Thermal neutron flux, Φ_{th} (m^{-2} s^{-1})	$(8.6 \pm 0.2) \cdot 10^{16}$
Neutron temperature, T_n, (K)	310.00 ± 0.01
Thermal to epithermal flux ratio, f	44 ± 6
Deviation of the epithermal neutron flux distribution from the ideal 1/E law, α	-0.08 ± 0.02

2.4. Analysis of reference materials

The reference materials (50-100 mg) and 4-5 mg of a gold flux monitor (Al-0.1%Au) were irradiated for 10 seconds and the induced gamma-activities were measured using the calibrated gamma-spectrometers. The radioisotopes used, their gamma-ray energies and half-lives, and the decay times for counting are shown in Table 2.

Table 2. Radioisotopes, gamma-ray energies and half-lives, and decay times for counting for each element analyzed

Element	Radionuclides	Energy (keV)	Half-life	Decay time (minutes)
Al	Al-28	1778.97	2.2414 min	5
Dy	Dy-165	94.7; 361.68	2.334 h	60 - 90
Eu	$Eu-152^m$	121.78; 344.28	9.3116 h	60 - 90
K	K-42	1524.7	12.360 h	60 - 90
Mg	Mg-27	843.74; 1014.42	9.458 min	5
Mn	Mn-56	846.77; 1810.77	2.5785 h	60 - 90
Na	Na-24	1368.63	14.9590 h	60 - 90
Sr	$Sr-87^m$	3885.32	2.81 h	60 - 90
Ti	Ti-51	320.08	5.76 min	5
V	V-52	1434.07	3.743 min	5

3. RESULTS AND DISCUSSION

The results obtained for the reference materials basalt BE-N (IWG-GIT), basalt JB-1 (GSJ), andesite AGV-1 (NIST), granite GS-N (IWG-GIT), SOIL-7 (IAEA) and Buffalo River Sediment (NIST–BRS-8704) (mean and standard deviation of six replicate analysis), as well as certified and recommended values, are shown in Tables 3 to 8 , respectively. The analysis of the reference materials provided measurement bias < 10% and coefficients of variation < 15%.

The results were analysed by using the z-score criterion [11], where z is given by:

$$z_i = (C_i - C_{ref.i}) / (\sigma^2_i + \sigma^2_{ref.i})^{1/2} \quad (1)$$

C_i = obtained concentration for the element i in the reference material
$C_{ref.i}$ = certified value of the element i in the reference material
σ_i = uncertainty in the concentration obtained for the element i in the reference material
$\sigma_{ref.i}$ = uncertainty of the certified value of the element i in the reference material

Table 3. Results obtained for the reference material basalt JB-1(GSJ)

Element	Certified values	Obtained values	z
Al (%)	7.69 ±0.2	7.67 ±0.08	-0.09
Dy (mg kg^{-1})	4.1 ±0.38	4.3 ±0.3	0.41
Eu (mg kg^{-1})	1.5 ±0.15	1.45 ±0.04	-0.32
K (%)	1.179 ±0.07	1.19 ±0.03	0.14
Mg (%)	4.661 ±0.16	4.76 ±0.09	0.54
Mn (%)	0.124 ±0.011	0.115 ±0.001	-0.81
Na (%)	2.07 ±0.12	1.99 ±0.02	-0.66
V (mg kg^{-1})	211 ±20	210 ±3	-0.05

Table 4. Results obtained for the reference material basalt BE-N (IWG-GIT)

Element	Certified values	Obtained values	z-score
Al (%)	5.33 ± 0.04	5.59 ± 0.10	2.45
Dy (µg g^{-1})	6.4 ± 0.20	6.5 ± 0.5	0.22
Eu (µg g^{-1})	3.6 ± 0.18	3.62 ± 0.08	0.1
K (%)	1.15 ± 0.02	1.21 ± 0.03	1.53
Mg (%)	7.93 ± 0.05	7.59 ± 0.13	-2.49
Mn (µg g^{-1})	1550 ± 30	1470 ± 20	-2.23
Sr (µg g^{-1})	1370 ± 30	1340 ± 50	-0.5
Na (%)	2.36 ± 0.03	2.28 ± 0.02	-2.21
Ti (%)	1.56 ± 0.02	1.54 ± 0.03	-0.61
V (µg g^{-1})	235 ± 10	230 ± 3	-0.47

Table 5. Results obtained for the reference material granite GS-N (IWG-GIT)

Element	Certified values	Obtained values	z-score
Al (%)	7.76 ± 0.05	7.83 ± 0.14	0.45
Dy (µg g^{-1})	3.1 ± 0.3	3.23 ± 0.17	0.36
Eu (µg g^{-1})	1.7 ± 0.1	1.48 ± 0.06	-2.66
K (%)	3.84 ± 0.05	3.84 ± 0.13	0.02
Mg (%)	1.78 ± 0.05	1.93 ± 0.07	1.73
Mn (µg g^{-1})	430 ± 30	386 ± 10	-1.4
Na (%)	2.8 ± 0.04	2.63 ± 0.05	-2.66
Ti (%)	0.41 ± 0.03	0.37 ± 0.01	-1.21
V (µg g^{-1})	65 ± 8	65 ± 2	0

Table 6. Results obtained for the reference material AGV-1 (USGS)

Element	Certified values	Obtained values	z-score
Al (%)	9.1 ± 0,3	9.19 ± 0,15	0.32
Dy (µg g^{-1})	3.6 ± 0.4	3.73 ± 0.12	0.3
Eu (µg g^{-1})	1.6 ± 0.1	1.65 ± 0.08	0.44
K (%)	2.42 ± 0.27	2.48 ± 0.08	0.2
Mg (%)	0.9 ± 0.1	0.93 ± 0.06	0.04
Mn (µg g^{-1})	710 ± 50	681 ± 15	-0.56
Na (%)	3.16 ± 0.12	3.13 ± 0.05	-0.25
Ti (%)	0.63 ± 0.05	0.59 ± 0.06	-0.46
V (µg g^{-1})	120 ± 11	120 ± 3	-0.04

Table 7. Results obtained for the reference material Buffalo River Sediment (NIST–BRS-8704)

Element	Certified values	Obtained values	z-score
Al (%)	6.1 ± 0.2	6.1 ± 0.1	0.06
Eu (mg kg^{-1})	1.31 ± 0.04	1.28 ± 0.04	-0.58
K (%)	2 ± 0.04	2.11 ± 0.07	1.36
Mg (%)	1.2 ± 0.02	1.21 ± 0.05	0.25
Mn (mg kg^{-1})	544 ± 21	562 ± 16	0.68
Na (%)	0.55 ± 0.02	0.60 ± 0.01	2.48
Ti (%)	0.45 ± 0.02	0.45 ± 0.04	0.08
V (mg kg^{-1})	95 ± 4	99 ± 3	1

Table 8. Results obtained for the reference material SOIL-7 (IAEA)

Element	Certified values	Obtained values	z-score
Al (mg kg^{-1})	47000 ± 2000	48000 ± 1000	0.54
Dy (mg kg^{-1})	3.9 ± 0.5	3.8 ± 0.5	-0.16
Eu (mg kg^{-1})	1.0 ± 0.1	0.98 ± 0.04	-0.23
K (mg kg^{-1})	12100 ± 400	12200 ± 400	0.19
Mg (mg kg^{-1})	11300 ± 200	12700 ± 500	2.43
Mn (mg kg^{-1})	631 ± 12	636 ± 13	0.29
Na (mg kg^{-1})	2400 ± 50	2290 ± 50	-1.48
Ti (mg kg^{-1})	3000 ± 300	3000 ± 200	0.06
V (mg kg^{-1})	66 ± 4	67 ± 2	0.20

Figures 2 to 7 show the standardized difference or z-score for each reference material analysed. The z-score were all within $|z|<3$, showing that the results are in a confidence level of 99% of the certified value. It is important to notice that the results obtained were randomly above and below the certified values, showing that there is not a systematic error.

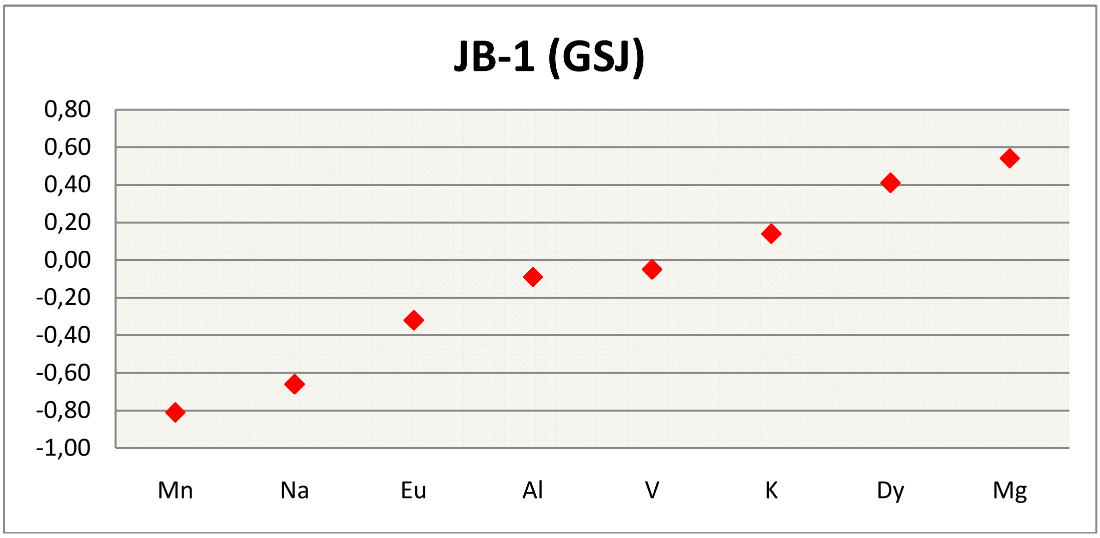

Figure 2. Control chart (z-score values) for elements in JB-1(GSJ)

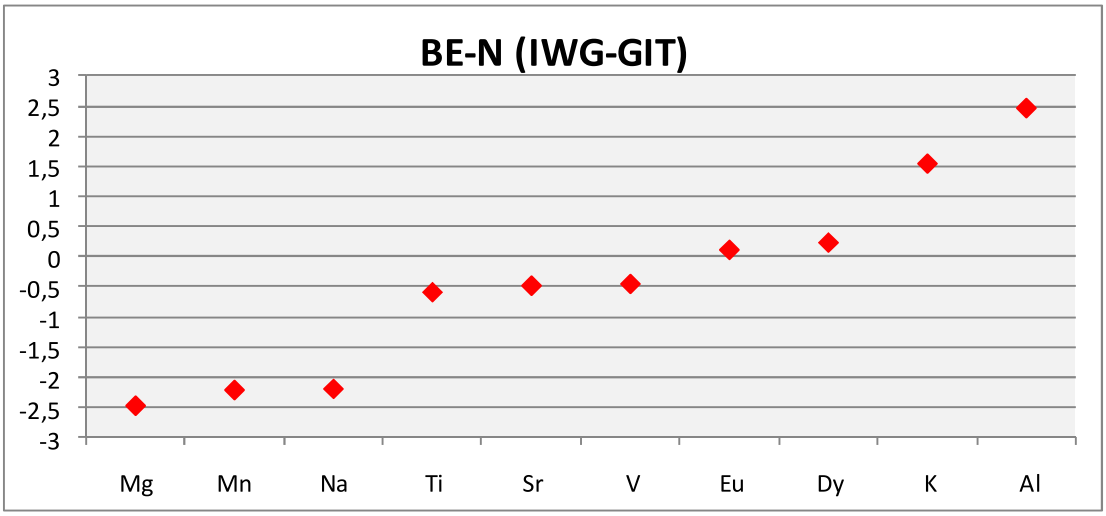

Figure 3. Control chart (z-score values) for elements in BE-N (IWG-GIT)

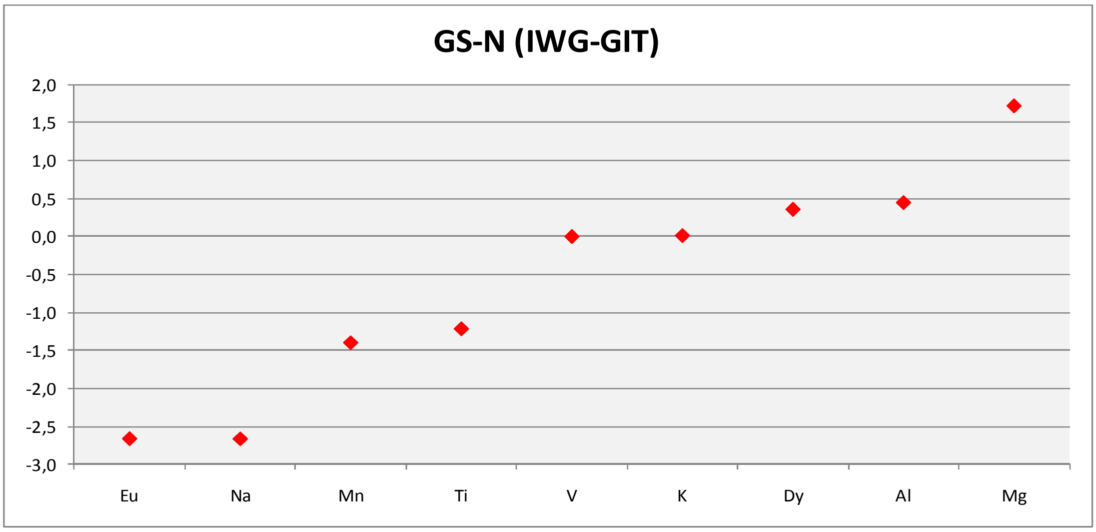

Figure 4. Control chart (z-score values) for elements in GS-N (IWG-GIT)

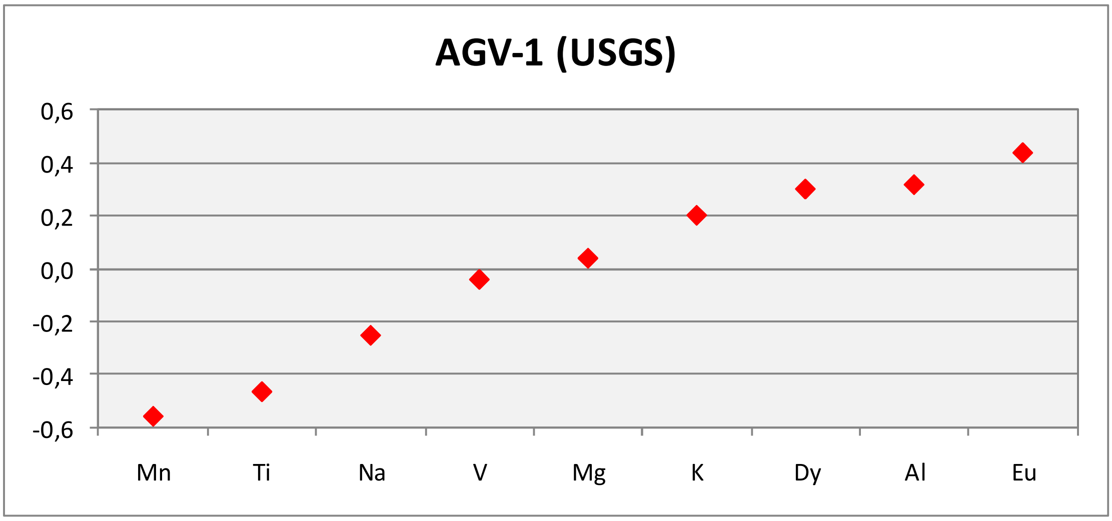

Figure 5. Control chart (z-score values) for elements in AGV-1 (USGS)

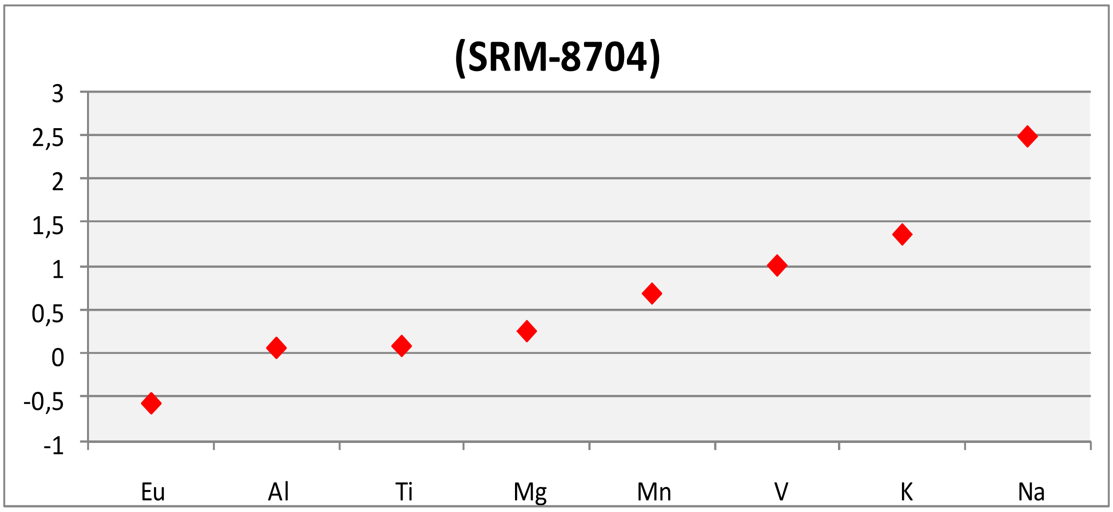

Figure 6. Control chart (z-score values) for elements in SRM 8704

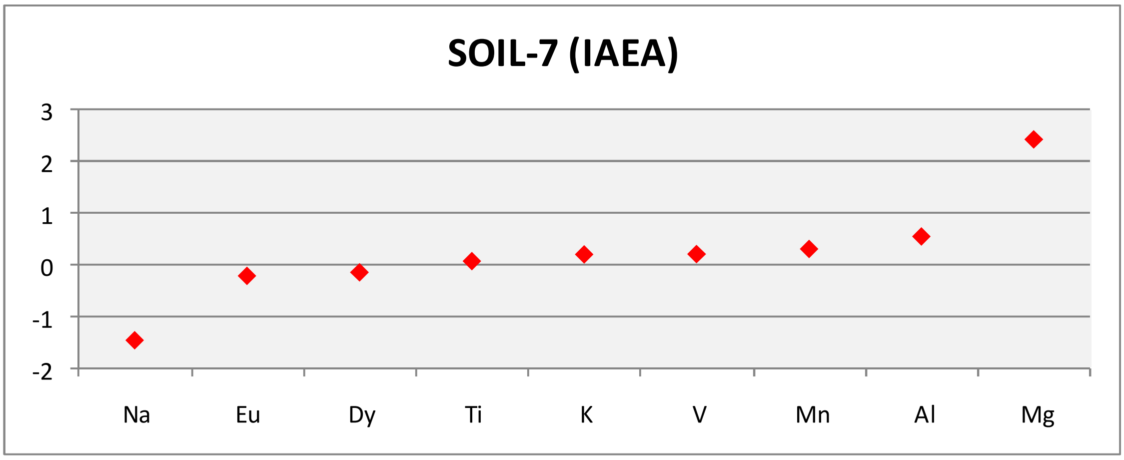

Figure 7. Control chart (z-score values) for elements in SOIL-7 (IAEA)

4. CONCLUSIONS

The k_0-NAA method with the k_0-IAEA software provided results for several elements in the geological reference materials analyzed.

The obtained results showed that the k_0-INAA procedure with the k_0-IAEA software at the pneumatic station of the IEA-R1 nuclear research reactor can be considered a reliable standardization method of INAA for the analysis of Al, Dy, Eu, K, Mg, Mn, Sr, Na, Ti and V in geological samples. This study will continue characterizing the flux parameters of irradiation positions for long irradiation purpose at IEA-R1 reactor, in order to determine long-lived isotopes.

The results indicate that the implementation of the k_0-NAA at the Neutron Activation Laboratory LAN-IPEN should increase the analytical potential of the laboratory, maintaining the quality of the analytical results.

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