

## DETERMINATION OF IRON AND NICKEL IN GEOLOGICAL SAMPLES BY ACTIVATION ANALYSIS WITH REACTOR FAST NEUTRONS

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*Rec. 10/3/2009*

*Accept. 27/10/2009*

Threshold reactions induced by reactor fast neutrons are well recognized. The geological samples consisting of five mafic (gabbro) and four ultramafic (serpentine) rocks were collected from El-Sid gold district, Central Eastern Desert, Egypt. The concentration of Fe and Ni were determined in these samples by activation analysis with fast neutrons, using the threshold reactions  $^{54}\text{Fe}(n,p)^{54}\text{Mn}$  and  $^{58}\text{Ni}(n,p)^{58}\text{Co}$  respectively. The fast neutron flux was determined using the  $^{92}\text{Mo}(n,2n)^{92m}\text{Nb}$  reaction. The determined concentrations of Fe and Ni were checked by determining them in the GSJ JB-1 reference material using the same (n,p) reactions. Good agreements were obtained between the measured and recommended values. The concentrations of Fe were also determined by (n, $\gamma$ ) reactions in the samples using the  $k_0$  - NAA method. There are good agreements between the determined concentrations from (n,p) and (n, $\gamma$ ) reactions.

**Keywords:** *threshold reactions, neutron activation analysis, fast neutron flux, elemental concentration.*

### INTRODUCTION

Threshold reactions of the types (n,p), (n,n'), (n, $\alpha$ ) and (n,2n) induced by the fast component of the reactors neutron spectrum [1] as well as the (n, $\gamma$ ) capture reactions produced by thermal and epithermal neutrons [2] are well recognized. Activation analysis with reactor fast neutrons (fast neutron activation analysis, FNAA), using threshold reactions is not widely used, because of the low-flux density of fast neutrons in reactors, the small cross sections of many threshold reactions and the relatively high-threshold energy of neutrons. Consequently, very low activities are produced, which may further

obscured by those from the  $(n, \gamma)$  reaction products. However, threshold reaction can be used to determine the content of some elements in samples on the conditions; the density of the fast neutrons is high enough to compensate the smallness of the cross section, and the elemental contents in the sample under investigation are relatively high (for example in range of mg/g) [1,2].

Threshold reactions provide useful alternative reactions for the determination of certain elements by NAA if the  $(n, \gamma)$  reaction products are formed with unfavourable radioactive properties. As an example, determining Ni using the  $^{58}\text{Ni}(n, p)^{58}\text{Co}$  reaction ( $t_{1/2}$  of  $^{58}\text{Co}$  is 70.82 days) is favoured instead of using neutron capture reactions ( $^{64}\text{Ni}(n, \gamma)^{65}\text{Ni}$ ), which need pneumatic irradiation rabbit system due to the short half life time of  $^{65}\text{Ni}$  [1,2].

Fe and Ni were determined in blue-green algae using the reactions  $^{54}\text{Fe}(n, p)^{54}\text{Mn}$  and  $^{58}\text{Ni}(n, p)^{58}\text{Co}$  [3]. The iron isotopic abundances were determined in iron materials using threshold reactions [4]. Fast determination of Fe by instrumental neutron activation analysis through the formation of  $^{56}\text{Mn}$  from both  $^{55}\text{Mn}(n, \gamma)^{56}\text{Mn}$  and  $^{56}\text{Fe}(n, p)^{56}\text{Mn}$  using both reactor neutrons and epithermal neutron irradiation was described and evaluated [5].  $^{58}\text{Co}$  production from natural nickel in nuclear reactor was described with particular consideration of interfering nuclear reaction [6].

The reaction  $^{47}\text{Ti}(n, p)^{47}\text{Sc}$  was used as a tool for neutron activation analysis of titanium in geological samples [7]. The  $^{29}\text{Si}(n, p)^{29}\text{Al}$  reaction was used for determining silicon in both iron reference standard materials and steel alloys [8,9]. Thallium was determined in environmental samples using fast reactor neutrons [10] using the reaction  $^{203}\text{Tl}(n, 2n)^{202}\text{Tl}$ .

Fast neutron reactions may also be selected for the analysis, in cases where the  $(n, \gamma)$  reaction product is also produced by an interfering reaction. For instance, the determination of aluminum in the presence of silicon, it may be better to use the  $^{27}\text{Al}(n, p)^{27}\text{Mg}$  or  $^{27}\text{Al}(n, \alpha)^{24}\text{Na}$  rather than  $^{27}\text{Al}(n, \gamma)^{28}\text{Al}$ , which may be seriously interfered with by the  $^{28}\text{Si}(n, p)^{28}\text{Al}$  reaction [ 8,11,12] depending on the relative concentrations of aluminum and silicon in the sample.

Neutron activation analysis (NAA) using  $k_0$ -standardization technique ( $k_0$  – NAA) has been developed in the 1970s [2,13,14] for multi-element analysis.  $k_0$  – NAA involves the simultaneous irradiation of a sample and a neutron flux monitor, such as gold, and the use of a composite nuclear constant called  $k_0$ -factor. The  $k_0$ -factor is independent of irradiation and measuring conditions. The  $k_0$ -NAA uses input parameters. These are thermal to epithermal neutron flux ratio ( $f$ ), the epithermal neutron flux shape factor ( $\alpha$ ), the absolute efficiency of the detector ( $\varepsilon$ ),  $k_0$  factor, and  $Q_0$  (resonance integral to thermal neutron cross section). The values of  $f$  and  $\alpha$  are determined for each irradiation site while  $k_0$  factor and  $Q_0$  can be either taken from literature or measured.

Therefore the aim of the present work is:

- (i) determination of the concentrations of Fe and Ni in nine geological samples (five mafic (gabbro) and four ultramafic (serpentinite) rocks) and the Jb-1 reference material, issued by the Geological Survey of Japan (GSJ), using neutron threshold reactions.
- (ii) To credit the results, Fe content in the samples is determined by  $k_0$  – NAA .

### THEORETICAL TREATMENT

The concentration of any element  $\rho_A$  is determined in a sample of weight ( $W$ ) by neutron threshold reaction (FNAA), using the equation [11, 13,15]:

$$\rho_A = \left( \frac{N_p}{t_m W S D C} \right)_A \times \left( \frac{M}{N_a \theta I \sigma} \right)_A \times \frac{1}{\phi_f} \times \frac{1}{\varepsilon_A} , \quad (1)$$

where  $N_p$  is the net number of counts in the full-energy peak,  $t_m$  is the measuring time,  $\varepsilon$  is absolute detector efficiency,  $S = 1 - \exp(-\lambda t_{irr})$ ,  $\lambda$  is the decay constant,  $t_{irr}$  is the irradiation time,  $D = \exp(-\lambda t_D)$ ,  $t_D$  is the decay time,  $C = [1 - \exp(-\lambda t_m)] / \lambda t_m$ ,  $M$  is the atomic weight,  $N_a$  is Avogadro's number,  $\theta$  is the isotopic abundance,  $I$  is gamma-ray intensity;  $\sigma$  and  $\phi_f$  are average cross section and fast flux over the fission neutron spectrum of  $U^{235}$  respectively. Eq.(1) is used not only for determining the elemental concentration but also, for determining the fast neutron flux and cross section.

While, the elemental concentrations ( $\rho_a$ ) of an analyte “a” in a sample is determined by  $k_0$  – NAA using the following equation [2,13,14]:

$$\rho_a = \frac{\left( \frac{N_p}{t_m \text{ WSDC}} \right)_a}{\left( \frac{N_p}{t_m \text{ WSDC}} \right)_{\text{Au}}} \times \frac{1}{k_{0,\text{Au}}(a)} \times \frac{f + Q_{0,\text{Au}}(\alpha)}{f + Q_{0,a}(\alpha)} \times \frac{\varepsilon_{\text{Au}}}{\varepsilon_a}, \quad (2)$$

where ‘‘Au’’ refers to the co-irradiated gold monitor,  $W$  is the weight of the sample,  $w$  is the weight of the gold monitor,  $f$  is the thermal to epithermal neutron flux ratio,  $Q_0 = I_0/\sigma_0$  is the resonance integral ( $I_0$ ) to 2200  $\text{ms}^{-1}$  neutron cross-section ( $\sigma_0$ ) ratio,  $\alpha$  is the measure for the epithermal neutron flux distribution, approximated by  $1/E^{1+\alpha}$  dependence with  $\alpha$  considered to be independent of neutron energy.

## EXPERIMENTAL DETAILS

Nine geological samples consisting of five mafic (gabbro) and four ultramafic (serpentine) rocks, which represent some gold-bearing rocks, were collected from the Eastern Desert of Egypt (further details on the preparation of these samples, maps of the location and their  $k_0 - \text{NAA}$  are found in reference [16]). These samples and the GSJ-Jb1 reference material, altogether with the standard samples consisting of Au, Mo, Sn and Zr were co-irradiated in the inner irradiation site #2 near the core periphery of the Second Egyptian Research Reactor (ETRR-2) for 2.5 hours.

**Table 1.** Nuclear data for some threshold reactions

Reaction	Target			Reaction product		
	Threshold Energy (MeV) [19]	Isotopic abundance (%) [17]	Cross section (mb) [19]	Gamma ray energy (keV) [18]	Emission probability (%) [19]	Half life [17]
$^{58}\text{Ni}(n, p)^{58}\text{Co}$	2.6	68.077±0.009	111±3	810.76	99.45±0.01	70.86±0.06 d
$^{54}\text{Fe}(n, p)^{54}\text{Mn}$	2.8	5.845±0.035	81.7±2.2	834.85	99.97±0.01	312.12±0.06d
$^{92}\text{Mo}(n, p)^{92\text{m}}\text{Nb}$	6	14.48±0.35	7.3±0.4	934.44	99.07±0.04	10.15±0.02 d
$^{95}\text{Mo}(n, p)^{95}\text{Nb}$	-	15.92±0.13	0.1348±0.0035	765.900	99.808±0.007	34.997±0.006 d

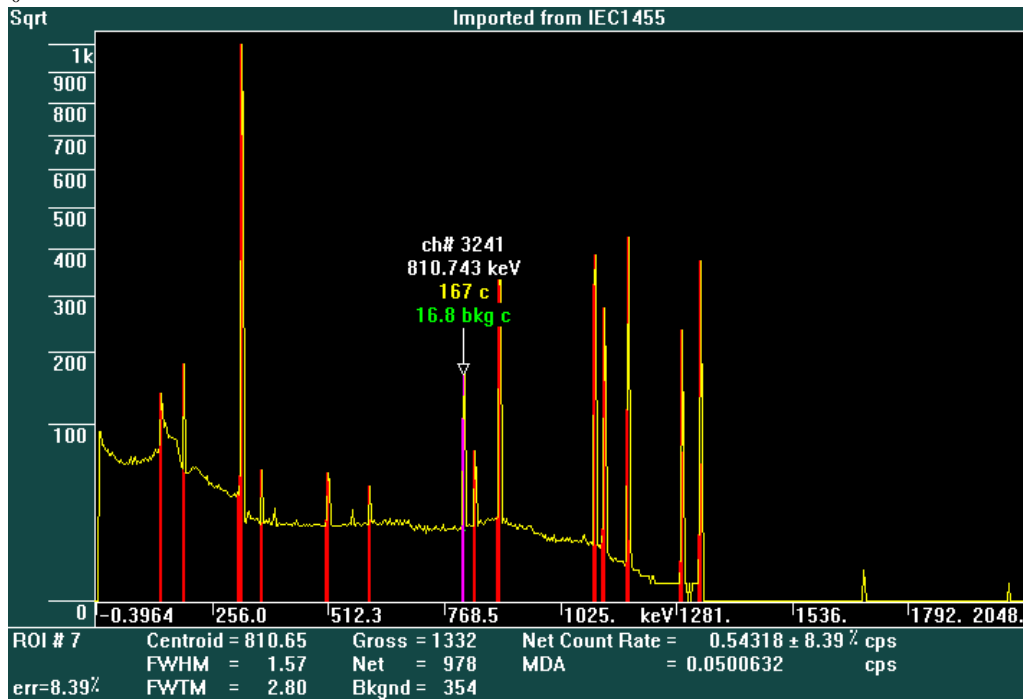
Before irradiation, the samples were wrapped with clean aluminum foils. After a proper cooling time (4 -7 days), the Al-foils were removed, and the samples were transferred to clean Polyethylene vials. The fast neutron flux  $\phi_f$  was determined using the threshold reaction  $^{92}\text{Mo} (n,2n) ^{92m}\text{Nb}$  (Table 1).

## RESULTS AND DISCUSSION

The fast neutron flux determined using the reaction  $^{92}\text{Mo} (n,2n) ^{92m}\text{Nb}$  was found to be  $\phi_f = 1.45 \times 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$ . While, at this irradiation position, the thermal and epithermal neutron fluxes are:  $\phi_{th} = 7.7 \times 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$  and  $\phi_{ep} = 3.85 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$  respectively. The neutron spectrum parameters  $\alpha$  and  $f$ , needed to perform  $k_0 - \text{NAA}$  were found [20] to be:  $\alpha = -0.01$  and  $f = 20$ . Guevara et al. [21] determined the fast neutron flux using threshold reactions having neutron threshold energies ranging from 2.6 MeV to 13.4 MeV. They found that the fast neutron flux does not depend on the neutron threshold energies. This can be checked in the #1 irradiation position characterized by the neutron spectrum parameters  $\alpha = -0.028$ ,  $f = 49$ ,  $\phi_{th} = 5.3 \times 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$  and  $\phi_{ep} = 1.08 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ . The fast neutron fluxes were determined using the reactions  $^{92}\text{Mo} (n,2n) ^{92m}\text{Nb}$ ,  $^{95}\text{Mo}(n,p)^{95}\text{Nb}$  and  $^{54}\text{Fe}(n,p)^{54}\text{Mn}$  and found to be  $\phi_f = 7.86 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ ,  $7.3 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$  and  $7.9 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$  respectively.

Eq.(1) was used to determine the concentration of Fe and Ni in the samples, using the threshold reactions  $^{54}\text{Fe}(n,p)^{54}\text{Mn}$  and  $^{58}\text{Ni}(n,p)^{58}\text{Co}$  respectively. Fig. (1) shows the gamma-ray spectrum for one of the investigated samples (Sd#1). The gamma-ray lines due to the decay of Co-58 and Mn-54 are also shown in Fig.(1). Moreover, the concentrations of Fe in these samples were also determined by neutron capture reaction using the  $k_0 - \text{NAA}$  method using Eq.(2). The concentration of Ni in the samples investigated were not determined by the neutron capture reaction  $^{64}\text{Ni}(n,\gamma)^{65}\text{Ni}$  due to the short half life time of  $^{65}\text{Ni}$  ( $t_{1/2} = 2.517 \text{ h}$ ). The deduced average values of four measurements together with their standard deviations are listed in Table (2). As one can see, there is a good agreement between the determined values by both methods of analysis. To credit our results, the concentration of Fe and Ni were determined in Jb-1 reference material using the same threshold reactions and the results are found to be  $67 \pm 4 \text{ mg/g}$  and  $133.4 \pm 13 \text{ }\mu\text{g/g}$ . These values agree very well with recommended concentrations of

66.6 mg/g and 133  $\mu$ g/g for Fe and Ni respectively. Moreover, the Fe content of the JB-1 reference material determined in this work, agrees with our previous result reported in ref. [20] ( $66.2 \pm 8.6$  mg/g) which was determined by neutron capture reaction using  $k_0$  – NAA.



**Figure 1.** The measured gamma-ray spectrum for the sample Sd #1.

The obtained agreement of the Fe content by both nuclear reactions  $^{54}\text{Fe}(n,p)^{54}\text{Mn}$  and  $^{58}\text{Fe}(n,\gamma)^{59}\text{Fe}$  proves that the interference of Co via threshold reaction  $^{59}\text{Co}(n,p)^{59}\text{Fe}$  in Fe determination via the neutron capture reaction  $^{58}\text{Fe}(n,\gamma)^{59}\text{Fe}$  is negligibly small. Since the interference depends on the Co/Fe ratios in these samples. These ratios are less than 0.1%. The concentrations of Co and other elements in these geological samples, using neutron capture reactions ( $k_0$  – NAA) are given in reference [16]. The contribution of Mn via reaction  $^{55}\text{Mn}(n,2n)^{54}\text{Mn}$  in Fe determination via

reaction  $^{54}\text{Fe}(n,p)^{54}\text{Mn}$  is expected to be very small, because of the high-neutron threshold energy (11.6 MeV) and the small neutron cross section (0.258 mb).

The determined concentrations of Fe and Ni are different from one sample to another. However, it reflects the capabilities and advantages of both FNAA and  $k_0$  – NAA methods to discriminate between different types of rock samples.

**Table 2.** Elemental concentrations of Fe and Ni by fast neutron activation analysis (FNAA) and  $k_0$  – NAA methods

Sample code	Fe (mg/g)		Ni (ppm)
	FNAA	$k_0$ – NAA	FNAA
Sd#1	40.3 ± 3.4	47.0 ± 1.7	45.7 ± 3.8
Sd#2	37.4 ± 1.7	37.7 ± 1.8	55.4 ± 2.3
Sd#3	59.0 ± 1.7	60.0 ± 1.0	70.0 ± 5.0
Sd#4	11.8 ± 0.5	11.0 ± 0.6	12.0 ± 0.5
Sd#5	54.0 ± 4.0	48.7 ± 1.7	137.0 ± 14
Sd#6	41.0 ± 2.6	40.0 ± 1.2	181.0 ± 8.0
Sd#7	64.2 ± 4.7	60.1 ± 3.0	208.0 ± 9.0
Sd#8	42.0 ± 2.0	36.0 ± 0.6	6.0 ± 0.08
Sd#9	50.5 ± 1.6	47.9 ± 1.2	2595 ± 21

## CONCLUSIONS

Fast neutron activation analysis, using the (n,p) reactions was used to determine the concentrations of Fe and Ni in nine geological samples (five mafic (gabbro) and four ultramafic (serpentinite) rocks). To check these results, the concentrations of Fe and Ni were determined in Jb-1 reference material, using the same threshold reactions and the results were found to be in good agreement with recommended concentrations. In addition, the concentration of Fe was determined in the samples, using the  $k_0$  – NAA. The Fe concentrations determined by both (n,p) and (n, $\gamma$ ) reactions were found also to be in good agreement.

The present work may attract the attention and trigger efforts to perform further studies in different fields using fast neutrons, especially in radioisotope production - the fast neutron flux of our second Egyptian Research Reactor (ETRR-2) is of the order  $\sim 10^{13}$  n/cm<sup>2</sup>.s.

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## تعيين تركيزات الحديد والنيكل في عينات جيولوجية باستخدام التحليل بالتنشيط التشعيعي بالنيوترونات السريعة للمفاعلات

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### خلاصة

في هذا البحث تم تعيين تركيز الحديد والنيكل , في تسع عينات جيولوجية عبارة عن خمس عينات من الصخور المافية و أربعة عينات من الصخور الفوق مافية من منجم السد بالصحراء الشرقية الوسطي بمصر وذلك بالتحليل التنشيطي بالنيوترونات السريعة لمفاعل الابحاث المصري الثاني (ETRR-2) باستخدام تفاعلي العتبة  $^{54}\text{Fe}(n,p)^{54}\text{Mn}$  و  $^{58}\text{Ni}(n,p)^{58}\text{Co}$  علي الترتيب. تم تعيين كثافة فيض النيوترونات السريعة باستخدام التفاعل  $^{92}\text{Mo}(n,2n)^{92\text{m}}\text{Nb}$  . و للتحقق من صحة تعيين تركيزات الحديد والنيكل بالعينات فقد تم تعيين تركيزهما في العينة العيارية GSJ JB-1 باستخدام نفس تفاعلات (n, p) حيث وجد تطابق مرض لقيم التركيزات المقاسة و المعتمده. تم كذلك تعيين تركيز الحديد بالعينات الجيولوجية باستخدام تفاعلات (n,  $\gamma$ ) بطريقة k<sub>0</sub>-NAA حيث وجد تطابق مرض للتركيزات المعينة باستخدام تفاعلات (n,  $\gamma$ ) و (n, p) .