ISSN : 0974-7419 Volume 14 Issue 3
Analytical CHEMISTRY
An Indian Journal
Full Paper
ACAIJ, 14(3) 2014 [100-105]

k_0- Neutron Activation Analysis in terms of the Høgdahl and Westcott conventions: A study using the k_0 –IAEA program

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ABSTRACT

This study shows the development of k_0 neutron activation analysis (k_0-INAA) method at the Egyptian Atomic Energy Authority MTR reactor. The study demonstrates the use of k_0-IAEA software. The Høgdahl and the modified Westcott conventions describing 1/v and non-1/v (n, γ) reaction nuclides were used to determine the neutron spectrum parameters. The accuracy of the method was evaluated by analyzing IAEA-Soil 7 and JB1 as reference materials. The results show an acceptable level of consistency.

INTRODUCTION

Neutron activation analysis (NAA) using k_0-standardization (k_0-NAA) is well-known method for elemental analysis. It is based on the HØgdal and the modified Westcott conventions[1,2], which describe reaction rate of neutrons with nuclides. HØgdal convention is more popular in literature. It deals with 1/v nuclides (the nuclides whose thermal neutron cross section vary with 1/v, v is the neutron velocity). However, this convention does not deal with non 1/v nuclides. The modified Westcott convention deals with both 1/v and non 1/v nuclides. Recently, the International Atomic Energy Agency (IAEA) has developed IAEA- k_0 software[3,4]. It is based on the physical principals of k_0-NAA using the HØgdal and the modified Westcott conventions. The software makes the analytical procedures easier and faster than the traditional manual procedures.

In this work k_0-NAA is extended to deal with non 1/v nuclides using the IAEA- k_0 software. The input parameters : the average neutron temperature, the modified spectral indexes, the neutron flux ratio and the epithermal neutron flux indexes needed in k_0-NAA are determined for three inner irradiation positions at the MTR reactor.

THEORETICAL BACKGROUND

According to HØgdal convention, the reaction rate of neutrons per target nucleus is given by[1,2]:

$$R = \sigma_{th}\phi_0 + I_0\phi_{ep}, \quad (1)$$

where σ_{th} is the thermal neutron cross-section, φ_0 is the thermal neutron flux defined by $\varphi_0 = n(v)v_0$, $n(v)$ is the neutron density at a neutron velocity v, v_0 is the neutron velocity at 2200 m/s which corresponds to the modal velocity of the Maxwell-Boltzmann distribution, φ_{ep} is the epithermal neutron flux, I_0 is the resonance integral defined by

$$I_0 = \int_{E_{cd}}^{\infty} \frac{\sigma(E)}{E}\, dE, \quad (2)$$

where E_{cd} is the cadmium cut-off energy (0.55 eV), E is the neutron energy and $\sigma(E)$ is the epithermal

neutron cross-section. In defining I_0 in Eq. (2), the validity of the 1/E- law is followed- the flux density of the epithermal neutrons per unit energy interval is inversely proportional to the neutron energy E. The first term of Eq. (1), in the absence of resonances, ($R = \sigma_{th} n(v) v_0$) describes the rate of slow neutron capture and indicates that σ ~1/v (1/v-law). σ ~1/v means that the capture rate of slow neutrons increases with the time slow neutrons stay or spend near or within the nucleus. It has become traditional to tabulate σ_{th} at σ_0 which corresponds to neutron velocity of v_0 =2200 m/s or neutron temperature $T_0 = 20\ ^0C$. Thus Eq. 1 can be rewritten as[1,2]:

$$R = \sigma_0 \phi_{th} + I_0 \phi_{ep} \quad (3)$$

Therefore, in HØgdal convention the cross sections are constants. They neither depend on the neutron spectrum nor the neutron temperature.

As most reactors do not operate at a temperature of exactly 20 ^{0}C, there must be A convention for converting the cross-section, σ_0, at the tabulated energy to the effective cross-section, σ, at the actual temperature of the reactor. This convention should deal with nuclides, which have resonances in the cross-section in the thermal neutron energy range, i.e non-1/v nuclides. Westcott[5] developed a method for converting σ_0 to σ by describing the neutron spectrum as a combination of a Maxwellian - Boltzmann velocity distribution function which is characterized by a temperature, T, and a component of epithermal energy neutrons, whose neutron flux distribution is proportional to the reciprocal of the neutron energy, i.e. dE/E. For a non-1/v nuclide, the reaction rate per target nucleus is given by:

$$R = \varphi_0 \sigma(T) = n v_0 \sigma_0 [g(T) + r\sqrt{T/T_0}\, s_0], \quad (4)$$

where $\sigma(T)$ is the effective cross section defined as[1,2,5]:

$$\sigma(T) = \sigma_0 [g(T) + r\sqrt{T/T_0}\, s_0], \quad (5)$$

where $g(T)$ is a parameter which represents the departure of the cross section from the 1/v-law in the thermal region (=1 if the nuclide obeys the 1/v law in this energy region) and which can be calculated from the expression

$$g(T) = (2/\sqrt{\pi E_0}\,\sigma_0) \int_0^\infty \sqrt{E}\, \sigma(E) \sqrt{E/E_T} \exp(-E/E_T)\, dE/E_T, \quad (6)$$

where $E_T = E_0 T / T_0$, E_0 =0.0253 eV and T_0 =293 ^{0}K, $r\sqrt{T/T_0}$ is the epithermal flux index which denotes the strength of the epithermal flux; it is zero for a pure thermal flux and s_0 is a parameter which represents the ratio of the reduced resonance integral and thermal cross section such that:

$$s_0 = (2/\sqrt{\pi}\,\sigma_0) \int_{\mu KT}^\infty \left(\sigma(E) - g(T)\sigma_0 \sqrt{E/E_0}\right) dE/E = (2/\sqrt{\pi})\,(I'_0/\sigma_0), \quad (7)$$

where k is the Boltzmann constant, μ varies with the type of the reactor's moderator and I'_0 is further defined as:

$$I'_0 = \int_{\mu KT}^{E_{cd}} \left(\sigma(E) - g(T)\sigma_0 \sqrt{E/E_0}\right) dE/E + \int_{E_{cd}}^\infty \left(\sigma(E) - g(T)\sigma_0 \sqrt{E/E_0}\right) dE/E = \Delta I' + I'_. \quad (8)$$

where $I'_.$ is the epicadmium resonance integral excluding the 1/v part and $\Delta I'$ the part, shielded by Cd-filter, which depends on the neutron temperature and is negligibly small for nuclides obeying the 1/v law in the thermal energy region. However, for those nuclides where resonance peaks lie near the cut-off energy, such as Cd-113, Eu-151, Lu-176, Ta-182, Ir-191, Pa-231, Pu-239 etc, the value of $\Delta I'$ becomes very large and can not be neglected. For 1/v thermal cross-section behavior, one has to a good approximation:

$$s_0 = (2/\sqrt{\pi})\, Q_0 - 0.484, \quad (9)$$

where $Q_0 = \dfrac{I_0}{\sigma_0}$.

The concentration of analye a, ρ_a is determined by k_0-NAA in terms of Westcott and HØgdal conventions using the following equations[2]:

$$\rho_a = \frac{\left(N_P / t_m WSDC\right)_a}{\left(N_P / t_m wSDC\right)_{Au}} \times \frac{1}{k_{0,Au}(a)} \times \frac{[g_{Au}(T) + r(\alpha)\sqrt{T/T_0}\, s_{0,Au}(\alpha)]}{[g_a(T) + r(\alpha)\sqrt{T/T_0}\, s_{0,a}(\alpha)]} \times \frac{\varepsilon_{Au}}{\varepsilon_a}, \quad (10)$$

and

$$\rho_a = \frac{\left(N_P / t_m WSDC\right)_a}{\left(N_P / t_m wSDC\right)_{Au}} \times \frac{1}{k_{0,Au}(a)} \times \frac{f + Q_{0,Au}(\alpha)}{f + Q_{0,a}(\alpha)} \times \frac{\varepsilon_{Au}}{\varepsilon_a}, \quad (11)$$

respectively, where "Au" refers to the co-irradiated gold monitor and N_p is the net number of counts in the

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full-energy peak, W is the weight of the sample, w is the weight of the gold monitor, t_m is the measuring time, $S = 1 - \exp(-\lambda t_{irr})$, λ is the decay constant, t_{irr} is the irradiation time, $D = \exp(-\lambda t_D)$, t_D is the decay time, $C = [1 - \exp(-\lambda t_m)]/\lambda t_m$, f is the thermal, φ_{th} to epithermal, φ_{ep} neutron flux ratio, $s_0(\alpha) = s_0 (\bar{E}_r)^{\alpha}$, $\bar{E}_r$ is the effective resonance energy, $Q_0(\alpha) = (I_0(\alpha)/\sigma_0)$ (resonance integral to 2200 ms^{-1} cross-section σ_0) ratio, α is the measure for the epithermal neutron flux distribution, ε_p is the full-energy peak detection efficiency and $k_{0,Au}(a)$ is a composite nuclear data constant factor[6,7]. g(T), $r(\alpha)\sqrt{T/T_0}$, α and f. are the input parameters in the k_0-NAA. They should be determined experimentally to perform k_0-NAA

Determination the neutron spectrum parameters

Determining f, α, $r(\alpha)\sqrt{T/T_0}$ and the average neutron temperature T are necessary to perform NAA using k_0 standardization based on HØgdal and Westcott's conventions. The parameters f and $r(\alpha)\sqrt{T/T_0}$ as a function of α are given by the so-called bare bi-isotopic monitor method as:

$$f(\alpha) = \frac{Q_i(\alpha) - Q_{ref}(\alpha)(A_{Sp,i}/k_{0,Au}(i)\,\varepsilon_{p,i})/(A_{Sp,ref}/k_{0,Au}(ref)\,\varepsilon_{p,ref})}{(A_{Sp,i}/k_{0,Au}(i)\,\varepsilon_{p,i})/(A_{Sp,ref}/k_{0,Au}(ref)\,\varepsilon_{p,ref}) - 1} \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}, \quad \textbf{(12)}$$

and

$$r(\alpha)\sqrt{T/T_0} = \frac{g_i(T) - g_{ref}(T)(A_{Sp,i}/k_{0,Au}(i)\,\varepsilon_{p,i})/(A_{Sp,ref}/k_{0,Au}(ref)\,\varepsilon_{p,ref})}{s_{0,ref}(\alpha)(A_{Sp,i}/k_{0,Au}(i)\,\varepsilon_{p,i})/(A_{Sp,ref}/k_{0,Au}(ref)\,\varepsilon_{p,ref}) - s_{0,i}(\alpha)}, \quad \textbf{(13)}$$

respectively, where $A_{sp} = \left(N_P / t_m WSDC\right)$, ref refers to a reference isotope, say Au-198, and i refers to any other isotopes such as Zr-95/Nb-95 or Zr-97/Nb-97m. Thus, the activated set Au-198, Zr-95/Nb-95, Zr-97/Nb-97 is used to construct three curves for $f(\alpha)$ vs. α. Every curve consists of a pair of the following isotopes: Au-198, Zr-95/Nb-95; Au-198, Zr-97/Nb-97; and Zr-97/Nb-97, Zr-95/Nb-95. the plots of $r(\alpha)\sqrt{T/T_0}$ Vs. α intersect in a unique point which gives simultaneously and .Thus, the same set of isotopes are used to determine f, α and $r(\alpha)\sqrt{T/T_0}$. The neutron temperature T is determined by co-irradiating a non 1/v monitor such as Lu-monitor, which has a strong deviation from the 1/v shape in the thermal region and 1/v monitor such as Au or Zr. The following equation is used to determine T:

$$\frac{\left[A_{Sp}/k_{0,Au}\,\varepsilon_p\right]_{Lu}}{\left[A_{Sp}/k_{0,Au}\,\varepsilon_p\right]_{1/v}} = \frac{g_{Lu}(T) + r(\alpha)\sqrt{T/T_0}\,s_{0,Lu}(\alpha)}{g_{1/v}(T) + r(\alpha)\sqrt{T/T_0}\,s_{0,1/v}(\alpha)}, \quad \textbf{(14)}$$

Since $g_{1/v}(T) = 1$, Eq. (14) yields $g_{Lu}(T)$ and from tables giving $g_{Lu}(T)$ versus T[8], T can be determined.

EXPERIMENTAL

IAEA Soil-7 and Jb1 reference materials altogether with Al–0.1% Au, Al–0.1% Lu and 99.8% Zr set[9]; were irradiated in positions A, B and C near the core of the MTR research reactor for 2,3 and 3 hours respectively. The Al–0.1% Lu was irradiated only in position A. The Jb1 reference material was irradiated in positions A and B. The set of the standards consisting of 99.98% Ni,99.9% Mo, 99.9% W, and 99.9% Fe were irradiated in position A. Irradiation of elelemnts such as Fe And Ni is used to determine fast neutron flux, ϕ_{fast} via thereshold reactions. The gamma ray detection system consists of p-type coaxial EG&G Ortec HPGe detector of 29.4 % relative efficiency and 1.66 keV FWHM at 1332.5 keV of ^{60}Co. A Canberra 10 cm thickness low background lead shield with low carbon steel casing is used in shielding the detector. A guine card of 16384 channels ADC is mounted on PC for data acquisition and analysis. The absolute efficiency curves of the HPGe detector were performed as follow: ^{226}Ra gamma ray point source was used to establish the relative efficiency curve at a distance of 15.5 cm away from the detector head. This efficiency curve was converted to absolute curves at 15.5 cm, 10.5 cm, 5.5 cm and 0 cm distances using the ^{137}Cs, ^{60}Co and ^{155}Eu gamma ray point sources of well known activities.

The IAEA - k_0 program was installed in accordance with the four step process recommended in the users' manual of the k_0 –IAEA package. In the permanent data base of the IAEA - k_0 program, certificates of

some radionuclides such as ^{137}Cs, ^{60}Co and ^{155}Eu and monitors such as Al–% Au, Al–0.1% Lu, 99.98% Ni, 99.8% Zr, 99.9% Mo, 99.9% W, and 99.9% Fe were created. The HPGe detector dimensions were created in the counting facilities. The neutron spectra parameters f, α, thermal neutron flux, fast neutron flux and neutron temperature were inserted in facilities of the software. In the series data base, the absolute efficiency values were inserted manually to the program at the distance 15.5 cm. Background and energy calibration spectra acquired by the HPGe detector were defined. Weights and irradiation times for the samples in each irradiation positions were inserted.

RESULTS AND DISCUSSION

The flux ratio (f), the modified spectral index ($r(\alpha)\sqrt{T/T_0}$) and α were calculated (Eqs 12&13) using the activated isotopes of ^{198}Au, $^{95}Zr/^{95}Nb$ and $^{97}Zr/^{97m}Nb$. The average neutron temperature[10] of the thermal neutrons in the irradiation position A was determined (equation 14) using the activated ^{177}Lu isotope (non 1/v monitor) and the ^{198}Au (1/v monitor). The average neutron temperature value was found 38 ± 2 ^{0}C (311 K). Results are listed in TABLE 1. Fast neutron flux were determined using the threshold reactions $^{54}Fe(n,p)^{54}Mn$ and $^{58}Ni(n,p)^{58}Co$ and result is listed in TABLE 1.

The first runs of the program were performed to determine the elemental contents for some activated standards such as Fe, Mo, Au, Ni and Zr which are counted separately and at different distances from the detector.The gamma ray spectra of the activated isotopes of these standards were interpreted successfully by the IAEA - k_0 program. The program uses the values of the absolute efficiency at the reference distance 15.5 cm (inserted manually) from the HPGe detector head to determine absolute efficiency curve at any distance during the sample's interpretation process. The process of absolute efficiency calculation at any distance with the knowledge of a reference efficiency curve is carried out based on solid angle calculations[3,4] at different geometries.

The gamma ray spectra of the JB-1 and IAEA-Soil-7 samples were interpreted by program. The numerical output of the elemental concentrations for IAEA-Soil-7 and JB-1 samples is listed in TABLES 2&3, respectively.

TABLE 1 : The neutron spectrum parameters f , α , $r(\alpha)\sqrt{T/T_0}$, T and ϕ_{fast} for the irradiation positions A, B and C.

Position	f	$r(\alpha)\sqrt{T/T_0}$	α	ϕ_{fast} (n cm^{-1} s^{-1}	T (^{0} C)
A	13.7	0.062	0.053	2.54 x 10 ^{13}	38 ± 2
B	15.1	0.057	0.059		-
C	17.1	0.0505	0.061		-

TABLE 2 : The concentrations determined for the IAEA Soil-7 in (mg/kg or μg/g)

Element	Concentration			Recommended value (95% confidence interval)
	Position A	Position B	Position C	
Na [a]	2.31	2.3	2.38	2.4 (2.3-2.5)
Ca [a]	166.6	175	151.8	163 (157-174)
Sc	9.00	8.9	8.661	8.3 (6.9-9)
Cr	62	60	65.27	60 (49-74)
Fe [a]	25.84	24.2	25.76	25.7(25.2-26.3)
Co	8.788	8.28	8.91	8.9 (8.4-10.1)
As	13.1	11.95	-	13.4 (12.5-14.2)
Rb	51.68	49.90	48.08	51(47-56)
Sb	1.32	1.6	1.79	1.7 (1.4-1.8)
Cs	5.2	5.9	5.05	5.4 (4.9-6.4)
Ba	145	160	162	159 (131-196)
La	29.41	27.5	29	28 (27-29)
Ce	64.28	65.6	58.95	61.0(50-63)
Nd	30.00	32	31.66	30 (22-34)
Sm	4.90	5.70	5.40	5.1 (4.8-5.5)
Eu	0.95	0.90	0.89	1.0 (0.9-1.3)
Tb	0.52	0.58	0.61	0.6 (0.5-0.9)
Yb	2.22	2.35	2.47	2.4 (1.9-2.6)
Lu	0.28	-	-	0.3 (0.1-0.4)
Hf	4.635	5.1	5.251	5.1(4.8-5.5)
Ta	0.792	0.75	0.70	0.8(0.6-1.0)
Th	7.94	8.1	8.82	8.2 (6.5-8.7)
U	2.13	2.39	2.55	2.6 (2.2-2.3)

[a] mg/g

Deviation of measured concentrations from recommended values for IAEA Soil-7 and Jb-1 samples are sgown in Figures 1 and 2, respectively. As one can see, most determined elements are within 10% of the recommended values. Larger deviations – beyond the limit of

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TABLE 3 : The concentrations determined for the Jb1

Element	Concentration		Recommended value
	A	B	
Na [a]	21	21.3	20.5
Ca [a]	51.8	56.1	
Sc	26.7	29.1	27.5 ± 1.95
Cr	490	486	425 ± 63 (469)[b]
Fe [a]	61.8	59.8	62.9
Co	34	38.3	38.2 ± 5.2
Ni	140	-	133
Zn	84	83.7	85.2 ± 9.9
W	19.6	16.5	17.1 ± 3.5 (20)[a]
Rb	42	42.1	41.3 ± 5.1
Ba	474	490	493 ± 46
La	38.4	36.5	*38.6 ± 4.3*
Nd	26.7	26.7	*26.8 ± 2.3*
Eu	1.56	1.35	1.49 ± 0.15
Tb	0.8	0.84	0.82 ± 0.19
Ce	66	68.2	67.8 ± 6.8
Yb	2.12	2.7	2.13 ± 0.26
Lu	0.29	-	0.31
Hf	3.33	3.43	3.31 ± 0.56
Ta	2.87	2.7	2.93 ± 0.79 (2.7)[b]
Th	8.5	9.2	9.3 ± 0.71
Sr	456.4	-	444 ± 29
Zr	135	141	141 ± 22
U	1.6	1.79	1.7 ± 0.28
Mo	26	28	27.4 ± 10.2 (34)[b]

[a] mg/g, [b] ref [13]

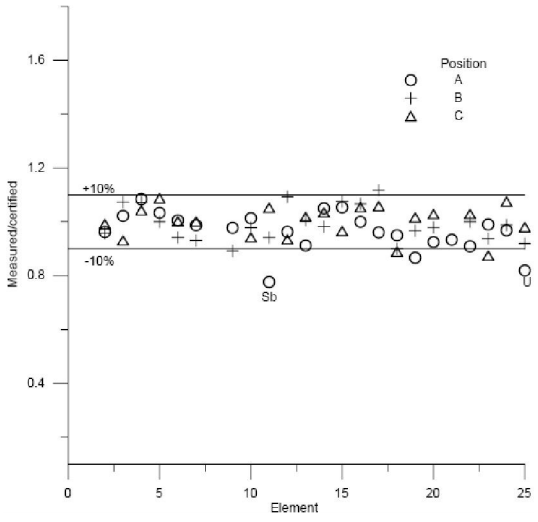

Figure 1 : Deviation of measured concentrations from recommended values for IAEA Soil-7 sample– the horizontal lines represent ±10% deviations.

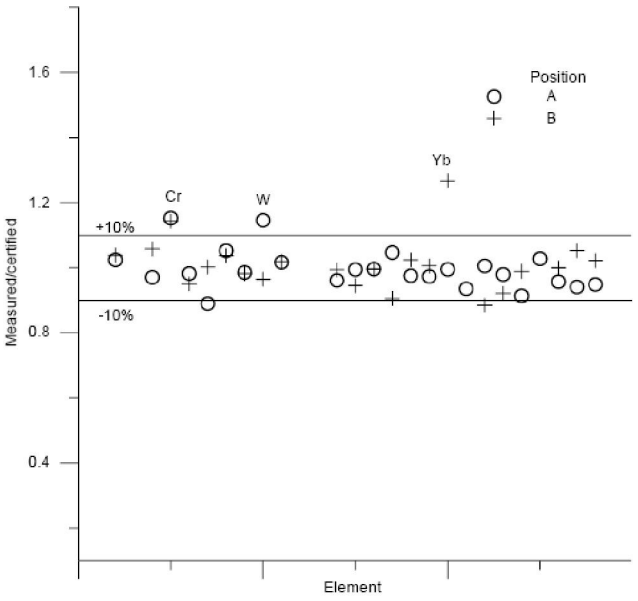

Figure 2 : Deviation of measured concentrations from recommended values for Jb-1 sample – the horizontal lines represent ±10% deviations.

10%- can be noticed (Figure 1) for Sb and U for the soil-7 sample. The average elemental content of both Sb and U determined for irradiation positions A, B and C are 2.35 μg/g and 1.57 μg/g, respectively are within 10% of the reported values. For the Jb-1 sample, the deviations (Figure 2) can be noticed for the determined element Cr, W and Yb. It was reported that concentration of Cr in Jb-1 sample show some scatter[13]. It can be attributed to its inhomogenous distribution in the sample. The average value of Cr (488 μg/g) is within 5% from the value determined in ref[13]. For W, in spite of there some scatter in its value in literature[13], the determined values in this work are within reported range. For Yb its average value(2.41) lies within reported uncertainty.

Strong non- 1/v nuclide such as Lu was determined in the investigated samples irradiated at position A using the k_0-IAEA program. This requires the knowledge of the average neutron temperature. So, concentrations of non-1/v nuclides cannot be determined at positions B and C. Moreover, more element are determined and computation time was shortened[11,12] (Jonah et al., 2009; Moon et al., 2009). This in contrast to the usual procedures of analysis the gamma ray spectra manually.

CONCLUSION

(1) The neutron spectrum parameters needed to carry

NAA using the k_0-IAEA program were determined.

(2) The k_0-IAEA program based on k_0- standardization method of NAA was used successfully to interpret spectra of some reference samples..

(3) The concentrations of elements determined in the reference samples are mainly within reported ranges.

(4) Analysis time was shorted and more elements including non-1/v nuclide were determined.

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