DETERMINATION OF k0-FACTORS FOR k0-INAA OF ENVIRONMENTAL SAMPLES

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The k_0-factors for 24 nuclides, used in reactor neutron activation analysis, were determined in the Fixed Irradiation System (SIFCA) and in the Pneumatic Irradiation System (SINCA) respectively, of the TRIGA MARK III reactor at the NNRI, Mexico, using a multielemental monitor. The k_0-factors determined by "bare monitor" and "Cd - subtraction" methods shows a good agreement with the calculated data and with the reported experimental k_0-factors, using high pure materials. With the aim of carrying out the analytic confirmation of the experimental k_0-factors, the concentrations of some elements presented in the CRM-SL-1 (for the "large-life" isotopes), and for ^{28}Al ^{52}V, ^{27}Mg, ^{56}Mn ^{24}Na in the CRM-SOIL-7, were determined in three replicas by k_0-standardization method. The results shows a good correlation with the reported concentrations in the mentioned environmental CRM

INTRODUCTION

In the k_0-standardization technique in reactor neutron activation analysis (INAA) the concentration of any element in the sample is determined by a conventional activation analysis formula containing a k_0-factor -a compound nuclear constant- defined as:

$$k_{0,c}(s) = \frac{M_c \theta_s \sigma_{0,s} \gamma_s}{M_s \theta_c \sigma_{0,c} \gamma_c} \qquad (1)$$

where $\underline{s}$ refers to the standard, $\underline{c}$ to the comparator and, M - atomic weight, θ - the isotopic abundance of the target nuclide, σ_0 - thermal neutron cross section at a $v_0 = 2200$ m.s^{-1} and γ - absolute γ -intensity.

Usually, to obtain a good accuracy, the k_0-factor experimental determination is performed using high pure materials [1], but unfortunately their do not always agree with the k_0's calculated from the tabulated values of the nuclear constants, and sometimes, the measured values disagree from one measurement facility to another [2-5]. It is the reason which the k_0-factor experimental determination is recommended for the reactor facilities where k_0-INAA is implemented [6].

In order to apply the k_0-standardization method in the INAA Laboratory of the NNRI of Mexico, it is necessary to determinate the k_0-factors for usually studied nuclides. In this case, we try their determination using the Certified Reference Materials (CRM) IAEA: SOIL-7 [7] and SL-1 [8], comparing the obtained results with the reported experimental data, to evaluate the possibility of multiple determination of k_0-factors for the INAA element of interest.

MATERIAL AND METHODS

Six replicas of IAEA-SOIL-7 standard were irradiated in the Fixed Irradiation System (SIFCA) of the TRIGA MARK III reactor at NNRI, Mexico ($\Phi = 3,4.10^{12}$ n.s^{-1}.cm^{-2}, $\alpha = -0.08$ and $f = 64$) [9]. Container with CRM samples (Figure 1) was irradiated during 25 hours to analyze the "large-life" nuclides.
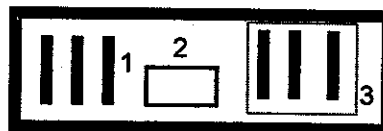

Figure 1.- Irradiation container for k_0-determination.
(1 - bare samples, 2 - paper box, 3 - Cd-covered samples)

Similarly, for the "short-life" nuclides, six containers with two replicas of CRM IAEA: SL-1 standard were irradiated in the Pneumatic Irradiation System (SINCA) ($\Phi = 1,32.10^{13}$ n.s^{-1}.cm^{-2}, $\alpha = -0.14$ and $f = 43$) [9]. The samples were irradiated during 1 or 2 minutes. After 7 days of cooling time (for the "large-life" nuclides) and few minutes (for the "short-life" nuclides), the irradiated samples were measured ($t_m = 30$ min.) in a well-know efficiency HPGe detector (ORTEC, 78 cm^3, 1.65 keV for 1332 keV γ-line of ^{60}Co, $\epsilon = 3,99.10^{-13}E^4 - 2,17.10^{-9}E^3 + 4,52.10^{-6}E^2 - 5,19.10^{-3}E + 9,78$ - determined for ^{152}Eu γ-lines). All spectra were processed with the program SA [10].

The k_0-factors were determined according to the "Bare monitor" method [11] as:

$$k_{0,c}(s) = \frac{A_{sp,s}}{A_{sp,c}} \cdot \frac{G_{th,c} \cdot f + G_{ep,c} \cdot Q_{0,c}(\alpha)}{G_{th,s} \cdot f + G_{ep,s} \cdot Q_{0,s}(\alpha)} \cdot \frac{\epsilon_{p,c}}{\epsilon_{p,s}} \qquad (2)$$

and to the *"Cd-subtraction"* method as (for de "large-life" nuclides):

$$k_{0,c}(s) = \frac{A_{sp,s} - \dfrac{(A_{sp,s})_{Cd}}{F_{Cd,s}}}{A'_{sp,c} - \dfrac{(A_{sp,c})_{Cd}}{F_{Cd,c}}} \cdot \frac{G_{th,c}}{G_{th,s}} \cdot \frac{\varepsilon_{p,c}}{\varepsilon_{p,s}} \qquad (3)$$

and, for de "short-life" nuclides, as:

$$k_{o,c}(s) = \frac{\left(\dfrac{A_{esp}}{\varepsilon_p}\right)_s - \left(\dfrac{A_{esp}}{\varepsilon_p . F_{Cd}}\right)_{s,Cd}}{\left(\dfrac{A_{esp}}{\varepsilon_p}\right)_c - \left(\dfrac{A_{esp}}{\varepsilon_p . F_{Cd}}\right)_{c,Cd}} \cdot \frac{G_{th,c}}{G_{th,s}} \qquad (4)$$

where:

$$A_{sp} = \frac{N_p/t_c}{S.D.C.w} \qquad \text{and}$$

$$Q_0(\alpha) = \frac{I_0(\alpha)}{\sigma_0}$$

with

- A_{sp} - specific count rate,
- N_p - area in the full-energy peak corrected for pulse losses.
- t_c - counting time (s),
- S - saturation factor,
- D - decay factor,
- C - counting factor,
- w - mass of the element in the CRM (in g.),
- G_{th} - correction factor for the thermal neutron self-shielding,
- G_{ep} - correction factor for the epithermal neutron self-shielding,
- f - thermal-to-epithermal neutron flux ratio,
- α - correction factor for the non-ideality of the epithermal neutron flux distribution ($1/E1+\alpha$),
- $I_0(\alpha)$ - resonance integral for ($1/E^{1+\alpha}$) epithermal neutron spectrum,
- ε_p - full-energy peak detection efficiency,
- F_{Cd} - correction factor for the Cd-transmission of epithermal neutrons.

Scandium and Sodium presents in CRM were chosen as the monitors for the "large" and "short" life nuclides respectively, attended to its good activation and to its resonance integral to thermal cross section is approximately equal to the expected of a 1/v cross section.

Calculated $k_{0,Sc/Na}$ - factors were also determined by expression (1), using nuclear data taken from the Ref. [1,5,12]. Its was performed (as both mentioned experimental methods) with program KCERO in an IBM/PC.

RESULTS AND DISCUSSION

Experimental and calculated $k_{0,Au}$- were estimated from $k_{0,Sc/Na}$ as:

$$k_{0,Au}(Element) = k_{0,Au}(Sc/Na) \times k_{0,Sc/Na}(Element)$$

using the experimental values $k_{0,Au}(Sc/Na)$ and calculated $k_{0,Au}(Sc/Na)$ reported by De Corte in Ref. [1].

Calculated factors and the comparison of estimated $k_{0,Au}$ -factors using CRM and high pure standards [1,5] for the "large-life" nuclides are presented in Table 1. In the same way, the k_0 factors for the "short-life" nuclides are shown in Table 2.

Systematical errors for both methods were in range 13-20% for "bare monitor" and 27-38% for "Cd-subtraction method (see Table 1). Here, the errors of the elemental concentration values reported for SOIL-7 are the major contributor. In the Cd-covered method, the poor statistic in the Cd-covered samples of the γ-activity for some elements is considerable too.

A correlation between the experimental results with the expected calculated values for $k_{0,Sc}$ (Table 3) shows the relative advantage for the bare monitor method respect to Cd-subtraction. Only for 604.7 keV line of [134]Cs, the Student Test [13] is not available (see Figure 2). It is possible, because usually for this line, a very strong interference of [124]Sb is present.

On the other hand, is relevant the good coincidence for all nuclides (except the mentioned [134]Cs line) between the obtained in this work $k_{0,Au}$-factors and the experimental factors reported in [1,5].

In Table 2, the systematic errors for the experimental methods, were between the 5-19% for the method of "Cd-Subtraction" and between 13-29% for the of "bare monitors" contributing considerably to these errors (as in the "large-life" nuclides case) the elemental concentrations values reported for the SOIL-7 and SL-1.

The results obtained after using the method of the "Cd- Subtraction" are better, since carrying out the irradiations with Cd-covered, the errors product of the imprecision of the nuclear data (I_0, σ_0, Q_0) and of the characteristic parameters of the flux of the reactor (α, f) are eliminated.

Had to be discarded for the analysis, the lines of 843,8 keV of the [27]Mg and 1811,2 keV of the [56]Mn,

for being interfered (in the case of the Cd-covered samples) with the "large-life" element ^{101}Mo, as well as the lines of 1644,13 keV and 2170,36 keV of the ^{38}Cl, since this element is present in both MRC, but its concentration is not reported.

The presence of high content of Aluminum in both MRC, limited the determination of more elements, due to the irradiation regimens (even 1 minute), the obtained activities were extremely elevated, for this reason, was necessary to increase the cooling time for the irradiated samples and it attempted again the observation of the characteristic γ lines of nuclides of very short-lives (between 2-5 minutes), for example, many rare earth elements, Potassium, etc.

With the aim of carrying out the analytic confirmation of the experimental k_0-factors, the concentrations of some elements presented in the CRM-SL-1 (for the "large-life" isotopes), and for ^{28}Al ^{52}V, ^{27}Mg, ^{56}Mn ^{24}Na in the CRM-SOIL-7, were determined in three replicas by k_0-standardization method. The results (see Table 4) shows a good correlation with the reported concentrations in the CRM.

The analysis of precision for $k_{0,Sc}$-ratios was tested by method introduced by Heydorn in [14], according to the European Community Bureau of Reference (BCR) as

Table 1.- Average k_0-factor values for "large-life" nuclides by "bare monitor" and "Cd-subtraction" methods, using a Certified Reference Material SOIL-7.

Nuclides	Energy (keV)	k_0 (bare)	k_0 (Cd)	$k_{0,Sc}$ (calculated)	$k_{0,Sc}$ [15]
^{177}Lu	112.9	$4,03.10^2$	$-^{x)}$	$4,15.10^2$	$4,16.10^2$
	208.4	$6,87.10^{-3}$		$6,93.10^{-3}$	$7,14.10^2$
^{181}Hf	133.0	$2,21.10^{-2}$	$2,04.10^{-2}$	$2,24.10^{-2}$	$2.37.10^{-2}$
	482.0	$4,58.10^{-2}$	$4,23.10^{-2}$	$4,75.10^{-2}$	$4,56.10^{-2}$
^{99}Mo	140.5	$5,88.10^{-4}$	$5,87.10^{-4}$	$6,09.10^{-4}$	$5,27.10^{-4}$
^{59}Fe	192.3	$4,23.10^{-6}$	$3,98.10^{-6}$	$4,27.10^{-6}$	$3,78.10^{-6}$
	1099.2	$7,47.10^{-5}$	$7,32.10^{-5}$	$7,72.10^{-5}$	$7,77.10^{-5}$
	1291.0	$6,51.10^{-5}$	$6,44.10^{-5}$	$5,91.10^{-5}$	$5,93.10^{-5}$
^{169}Yb	197.9	$1,99.10^{-2}$	$1,95.10^{-2}$	$2,04.10^{-2}$	$1,64.10^{-2}$
^{131}Ba	215.1	$3,21.10^{-5}$	$3,17.10^{-5}$	$3,62.10^{-5}$	$2,91.10^{-5}$
	496.3	$7,76.10^{-5}$	$7,60.10^{-5}$	$7,95.10^{-5}$	$6,84.10^{-5}$
^{232}Th	311.9	$2,22.10^{-2}$	$2,19.10^{-2}$	$2,23.10^{-2}$	$2,52.10^{-2}$
^{160}Tb	298.6	$8,14.10^{-2}$	$8,00.10^{-2}$	$8,40.10^{-2}$	$8,25.10^{-2}$
^{51}Cr	320.1	$2,68.10^{-3}$	$2,54.10^{-3}$	$2,72.10^{-3}$	$2,62.10^{-3}$
^{175}Yb	396.3	$1,62.10^{-2}$	$1,63.10^{-2}$	$1,65.10^{-2}$	$3,12.10^{-2}$
^{82}Br	554.3	$2,34.10^{-2}$	$2,04.10^{-2}$	$2,34.10^{-2}$	$2,38.10^{-2}$
	776.5	$2,76.10^{-2}$	$2,51.10^{-2}$	$2,77.10^{-2}$	$2,76.10^{-2}$
^{124}Sb	602.7	$2,89.10^{-2}$	$2,70.10^{-2}$	$2,96.10^{-2}$	$2,96.10^{-2}$
	1691.0	$1,56.10^{-2}$	$1,48.10^{-2}$	$1,51.10^{-2}$	$1,41.10^{-2}$
^{134}Cs	604.7	$3,87.10^{-1}$	$3,67.10^{-1}$	$4,29.10^{-1}$	$4,76.10^{-1}$
	795.8	$3,83.10^{-1}$	$3,64.10^{-1}$	$3,76.10^{-1}$	$4,15.10^{-1}$
^{140}La	815.8	$2,92.10^{-1}$	$2,79.10^{-2}$	$2,99.10^{-2}$	$3,32.10^{-2}$
	1596.5	$1,23.10^{-1}$	$1,11.10^{-1}$	$1,27.10^{-1}$	$1,34.10^{-1}$
^{86}Rb	1076.1	$7,04.10^{-4}$	$7,05.10^{-4}$	$7,40.10^{-4}$	$7,65.10^{-4}$
^{65}Zn	1115.5	$5,65.10^{-3}$	$4,94.10^{-3}$	$5,54.10^{-3}$	$5,72.10^{-3}$
^{60}Co	1173.1	$1,29$	$1,23$	1.31	1.32
	1332.0	$1,28$	$1,24$	1.31	1.32
^{47}Ca	1297.0	$9,74.10^{-7}$	$9,05.10^{-7}$	$1,01.10^{-6}$	$9,54.10^{-7}$

$^{x)}$ - γ-lines are not observed in the Cd-covered irradiated sample spectra.

Table2.- Average k_0-factor values obtained for "short-life" nuclides by "bare-monitor" and "Cd-subtraction" methods, using Certified Reference Materials SOIL-7 and SL-1.

Nuclides	Energy (keV)	k_0 (bare)	k_0 (Cd)	$k_{0,Sc}$ (calculated)	$k_{0,Sc}$ [15]
^{51}Ti	319,8	$3,380.10^{-4}$	$3,740.10^{-4}$	$3,87.10^{-4}$	$3,74.10^{-4}$
^{56}Mn	846,6	$3,790.10^{-1}$	$4,123.10^{-1}$	$5,14.10^{-1}$	$4,96.10^{-1}$
^{27}Mg	1014,4	$1,716.10^{-4}$	$9,347.10^{-5}$	$1,02.10^{-4}$	$9,80.10^{-5}$
^{52}V	1433,9	$1,905.10^{-1}$	$1,180.10^{-1}$	$2,07.10^{-1}$	$1,96.10^{-1}$
^{42}K	1524,7	$1,110.10^{-3}$	$1,110.10^{-3}$	$1,00.10^{-3}$	$9,46.10^{-4}$
^{28}Al	1778,9	$1,656.10^{-2}$	$1,636.10^{-2}$	$1,85.10^{-2}$	$1,75.10^{-2}$

Table 3.- Correlation between the experimental and calculated $k_{0,Sc}$-factors.

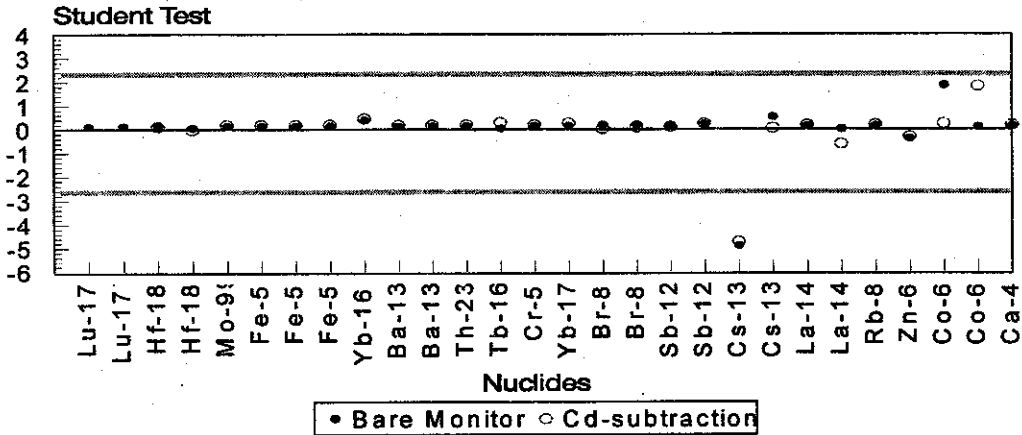| Method	Function	X-Y Correlation
Bare monitor	y = 1.01x - 0.0011	0.99962
Cd-subtraction	y = 0.97x - 0.0017	0.99954

Figure 2.- Student distribution (95% confidence level) for
determined $k_{0,Sc}$-factors (nuclides order from Table 1).

Table 4.- Determined concentrations in the SOIL-7 for the comparative and the k_0-methods, utilizing
the MRC SL-1 as comparator.

Element	Average concentration (μg/g)	Reported concentration (μg/g) [7,8]
Lu	0.52 ± 0.07	0.54*)
Hf	4.6 ± 0.9	4.16 ± 0.58
Mo	1.7 ± 0.2	1.3*)
Fe (%)	6.52 ± 0.13	6.74 ± 0.17
Yb	3.52 ± 0.56	3.42 ± 0.64
Ba	600 ± 66	639 ± 53
Th	12.3 ± 0.9	14 ± 1
Tb	1.7 ± 0.4	1.4*)
Cr	108 ± 12	109 ± 9
Br	— (+)	6.82 ± 1.73
Sb	1.36 ± 0.39	1.31 ± 0.12
Cs	6.97 ± 0.39	7.01 ± 0.88
La	51.1 ± 1.0	52.6 ± 3.1
Rb	105 ± 14	113 ± 11
Zn	239 ± 12	223 ± 10
Co	19.8 ± 1.2	19.8 ± 1.5
Ca (%)	— (+)	0.25*)
Al (%)	4.7 ± 0.4	4.62. ± 0.07
V	66.0 ± 7.0	68.7 ± 1.9
Mg (%)	1.13 ± 0.05	2.25
Mn	631.0 ± 18.9	540.2 ± 16.7
Na	2.4 ± 0.1	2.5 ± 0.1

*) - Non-certified element in MRC SL-1.
(+) - γ-lines no observed in the spectra.

$$T = \sum_i \frac{(k_{0,Sc} - K_{0,Sc})^2}{\sigma_i^2}$$

where σ_i is the expected standard deviation of each k_0-factor and K_0 the weighted mean value. Figure 3 shows the obtained Heydorn Test for $k_{0,Sc}(^{60}Co, 1173$ keV) as an example.

The comparison of the experimental $k_{0,Au}$-factors evaluated in this work with the experimental k_0-factors, obtained using a high pure standards[1,5] (see Table 1), shows the feasibility of CRM use (with very careful spectra analysis) for k_0-factor experimental determination.
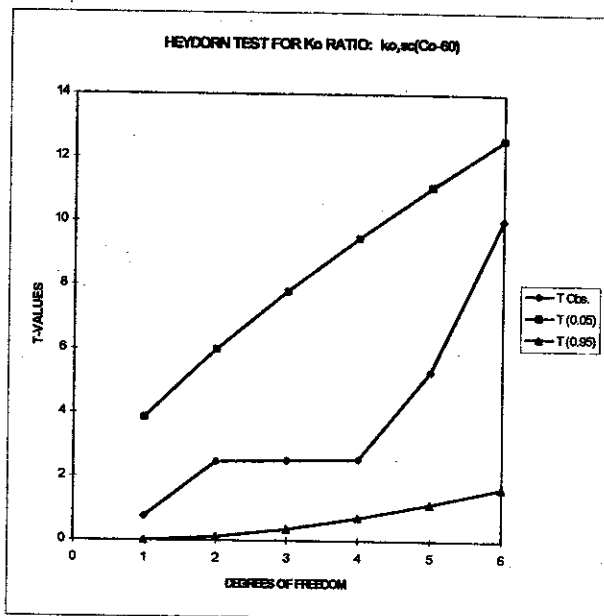
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Figure 3.- An example of the Heydorn Test application for $k_{0,Sc}$-factors

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