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APPLICATION OF THE k_0-INAA METHOD FOR ANALYSIS OF BIOLOGICAL SAMPLES AT THE PNEUMATIC STATION OF THE IEA-R1 NUCLEAR RESEARCH REACTOR

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ABSTRACT

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 biological samples by k_0-INAA using the program k_0-IAEA, provided by the International Atomic Energy Agency (IAEA). The elements Al, Ba, Br, Na, K, Mn, Mg, Sr and V were determined with respect to gold (^{197}Au) using the pneumatic station facility of the IEA-R1 4.5 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 and high purity zirconium comparators were used. 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 NIST SRM 1547 Peach Leaves, INCT-MPH-2 Mixed Polish Herbs and NIST SRM 1573a Tomato Leaves. The concentration results obtained agreed with certified, reference and recommended values, showing relative errors (bias, %) less than 30% for most elements. The Coefficients of Variation were below 20%, showing a good reproducibility of the results. The E_n-*number* showed that all results, except Na in NIST SRM 1547 and NIST SRM 1573a and Al in INCT-MPH-2, were within 95% confidence interval.

1. INTRODUCTION

The k_0-INAA method, developed by the Institute of Nuclear Sciences, Gent, Belgium [1], has been increasingly used in many neutron activation analysis laboratories, as it requires only a single comparator such as ^{197}Au for multielement determination instead of multielement standards required in the comparative method of neutron activation analysis [2-8]. 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 [9].

The IEA-R1 reactor has a pneumatic station facility adequate for short time irradiations. 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.

There is a significant number of analytically important elements when biological samples are concerned, such as Al, Br, K, Mg, Mn, Sr, Na and V, whose activation products are short-lived (seconds to minutes) or medium-lived radioisotopes (minutes to hours).

In continuation of the implementation of the k_0-INAA method at the Neutron Activation Analysis of IPEN (LAN-IPEN) [10 – 11], 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 analyze the elements Al, Br, Na, K, Mn, Mg, Sr and V in biological matrices, was evaluated. For this purpose, the characterization of the neutron flux parameters in the pneumatic station irradiation position was performed. The biological reference materials NIST SRM 1547 Peach Leaves, INCT-MPH-2 Mixed Polish Herbs and NIST SRM 1573a Tomato Leaves were analyzed for data validation.

2. EXPERIMENTAL

2.1. Irradiation Facility

A fast pneumatic rabbit system station specifically designed for INAA of short-lived and medium-lived nuclides was installed at the IEA-R1, a nuclear research reactor (5 MW) immersed in a pool containing 273 m^3 of demineralized water, at IPEN. This station is utilized to perform, with a transfer time of approximately 12 s, short irradiations up to 5 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 GX2020 hyperpure Ge detector, called Canberra 3. The resolution (FWHM) of the system was 2.07 keV for the 1332.5 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.

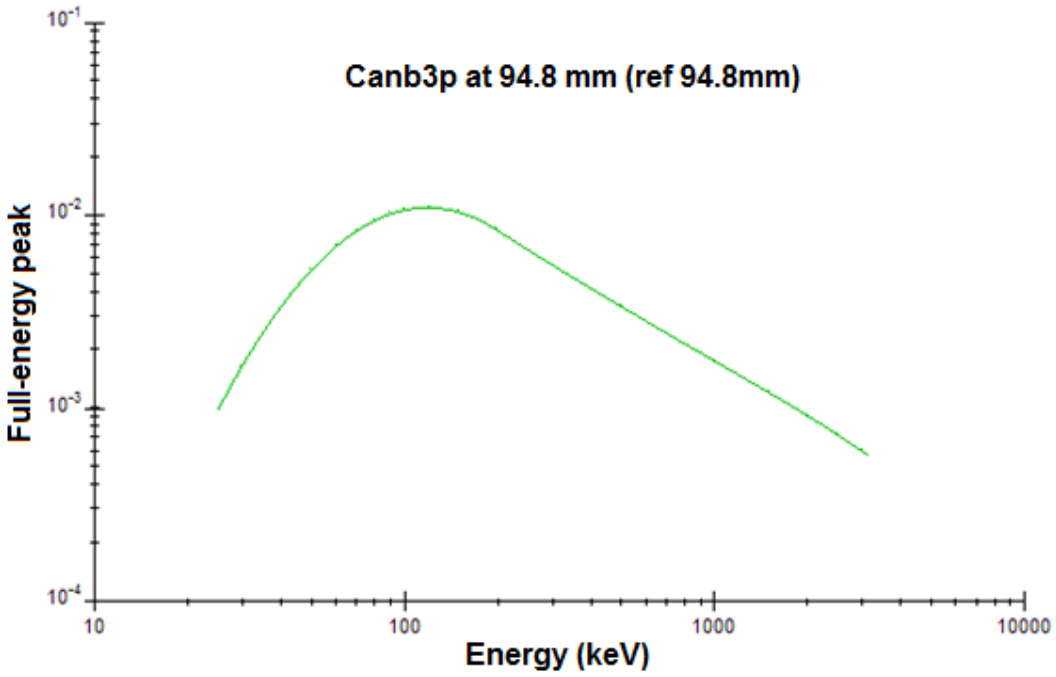

Figure 1. Peak efficiency curve for the coaxial HPGe detector fitted using the k_0-IAEA software.

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 40 mg of a 0.127 mm thick Zr foil (purity 99.5%) together with 8 mg of Al-0.1%Au wire with diameter of 1 mm (IRMM-530R) for 2 min. The flux parameters determined for the pneumatic station of IEA-R1 are given 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})	$(1.82 \pm 0.05)\times10^{16}$
Fast neutron flux, ϕ_{fast} (m^{-2} s^{-1})	$(3.66 \pm 0.37)\times10^{15}$
Neutron temperature, T_n, (K)	310 ± 5*
Thermal to epithermal flux ratio, f	35.6 ± 1.1
Deviation of the epithermal neutron flux distribution from the ideal 1/E law, α	0.0288 ± 0.0058

* - not determined in this experiment, taken as default value in the k_0-IAEA software.

2.4. Analysis of the Reference Materials

The reference materials (150 mg) sealed in polyethylene bags were irradiated for 60 seconds together with Al-0.1%Au standards (IRMM-530R) and the induced gamma-activities were measured using the calibrated gamma-spectrometer. Table 2 shows the decay time, counting time and distance between sample-detector of the samples.

Table 2 – Decay time, counting time and distance between sample-detector

	Decay time	**Counting time**	**Distance from HPGe detector**
Reference material	5 min	240 s	94.8 mm
Reference material	15 min	600 s	94.8 mm
Reference material	30 min	900 s	94.8 mm
Al-0.1%Au	2 h	7200 s	35.4 mm
Reference material	12 h	10800 s	35.4 mm

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Table 3 – Results obtained by k0-IAEA software for 6 replicates in mg/kg, if not stated otherwise

El.	NIST SRM 1547					INCT-MPH-2					NIST SRM 1573a				
	x_{cert}	x_{Lab} #	*Bias* (%)	CV (%)	E_n	x_{cert}	x_{Lab} #	*Bias* (%)	CV (%)	E_n	x_{cert}	x_{Lab} #	*Bias* (%)	CV (%)	E_n
Al	249±3	258±17	3.6	5.4	0.27	670±111	854±42	27.5	3.4	1.33	598±12	643±42	7.5	5.5	0.53
Ba	124±4	127±7	2.4	4.6	0.20	32.5±2.5	40.9±5.8	25.8	13.8	0.71	63[a]	**	**	**	**
Br	11[a]	11±1	0.0	3.7	*	7.71±0.61	8.31±0.61	7.8	6.4	0.44	1300[a]	1278±56	-1.7	2.7	*
Cl	360±19	368±31	2.2	7.6	0.12	0.284±0.020[b]	0.293±0.015[b]	3.2	3.7	0.25	6600[a]	7130±384	8.0	4.1	*
K(%)	2.43±0.03	2.45±0.12	0.8	3.2	0.09	1.91±0.12	1.96±0.11	2.6	4.7	0.19	2.70±0.05	2.78±0.15	3.0	4.0	0.27
Mg(%)	0.432±0.008	0.425±0.035	-1.6	7.4	0.10	0.292±0.018	0.290±0.017	-0.7	4.7	0.05	1.2[a]	1.14±0.08	-5.0	6.5	*
Mn	98±3	95±9	-3.1	8.9	0.16	191±12	197±11	3.1	4.3	0.24	246±8	251±11	2.0	2.7	0.21
Na	24±2	45±5	87.5	10.9	2.00	350[a]	441±33	26.0	6.7	*	136±4	179±16	31.6	8.1	1.35
Sr	53±4	59±10	11.3	16.6	0.29	37.6±2.7	**	**	**	**	85[a]	**	**	**	**
V	0.37±0.03	**	**	**	**	0.952±0.163	1.145±0.434	20.3	37.7	0.22	0.835±0.010	**	**	**	**

* – Not calculated
** – Not determined

– Laboratory combined standard uncertainty is calculated as follows: $U_{Lab\_Comb} = \sqrt{(St.dev.)^2 + u_{method}^2}$, where St.dev. is the standard deviation of independent measurements (n=6) and u_{method} is the estimated uncertainty of the method used (3.5% with a coverage factor k=1).
[a] – Information values
[b] – Percentage values

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3. RESULTS AND DISCUSSION

For a statistical accuracy evaluation, the E_n-numbers [12] was used. The E_n-number is defined by the following equation (1):

$$E_n = \frac{X_{Lab} - X_{Cert}}{\sqrt{U_{Lab}^2 + U_{Cert}^2}} \quad (1)$$

where U_{Lab} and U_{cert} are the expanded uncertainties (k=2) of the laboratory result and assigned value, respectively. The laboratory performance is satisfactory if $|E_n| \leq 1.0$ and unsatisfactory if $|E_n| > 1.0$. Expanded Laboratory uncertainty with a coverage factor k=2 is calculated as follows:

$$U_{Lab} = 2 \cdot U_{Lab\_Comb} = 2 \cdot \sqrt{(St.dev.)^2 + u_{method}^2} \quad (2)$$

where *St.dev.* is the standard deviation of independent measurements (n=6) and u_{method} is the estimated uncertainty of the k0-IAEA software (3.5% with a coverage factor k=1). In k_0-IAEA software, uncertainty is calculated by considering uncertainty sources such as literature values for $T_{1/2}$, $\bar{E}_r$, Q_0 and k_0, the irradiation, decay and measuring times, true-coincidence factor (COI), Au composition in Al-0.1%Au alloy, masses of sample and standard, neutron flux parameters (f, α, fast flux and neutron temperature) and detection efficiency.

Table 3 presents the analytical results of six replicates obtained by k0-IAEA software. Experimental values and assigned values were statistically compared (Bias (%) and E_n-numbers). For most of the elements, *Bias* (%) were in the range of 0 – 30% (except for Na in NIST SRM 1547 and NIST SRM 1573a) in relation to certified values. It is important to note that the results obtained were randomly above and below the assigned values, showing that there is no systematic error.

Coefficient of variation (CV) showed a deviation between replicates below 20% except for V in INCT-MPH-2 (37.7%, see Table 3). However, these values are still acceptable according to the criteria described by Wood [13].

The *E_n-number* showed that all the results, except Na in NIST SRM 1547 and NIST SRM 1573a and Al in INCT-MPH-2, are within 95 % confidence level (see Table 3). Higher data for Na in NIST SRM 1547 we observed also in our previous studies [14-15], as well as in literature [16]. This indicates instability of Na in this SRM. The higher data of *E_n-number* for Na in NIST SRM 1573a ($|E_n|$=1.35) can be associated with relatively small uncertainty of certified reference material (136±4 mg/kg, 2.94% for the 95% confidence interval). The higher data of *E_n-number* for Al in INCT-MPH-2 ($|E_n|$=1.33) can be associated with some problems with an accuracy of irradiation times at the pneumatic station of the IEA-R1 reactor for short radionuclides (^{28}Al, $T_{1/2}$ = 2.241 min, E_γ =1778.9 keV).

3. CONCLUSIONS

The k_0-INAA method with the k_0-IAEA software provided results for several elements in the biological 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, Ba, Br, Cl, K, Mg, Mn, Na, Sr and V in biological samples.

In the case of Na, higher values than expected were obtained. This indicates possible instability of Na in particular SRM. In case of Al some more investigation for more accurate irradiation time for short radionuclides is necessary. The results obtained showed the potentiality of the k_0-INAA method with the k_0-IAEA software for biological sample analysis, which may improve the potential of LAN-IPEN for the analysis of this kind of matrix.

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