2017 International Nuclear Atlantic Conference - INAC 2017
Belo Horizonte, MG, Brazil, October 22-27, 2017
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR – ABEN

Agência Brasileira do ISBN
ISBN 978-85-99141-07-6
9 788599 141076

k_0-NEUTRON ACTIVATION ANALYSIS BASED METHOD AT CDTN: HISTORY, DEVELOPMENT AND MAIN ACHIEVEMENTS

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ABSTRACT

Neutron Activation Analysis (NAA) is an analytical technique to assay the elemental chemical composition in samples of several matrices. It has been applied by the Laboratory for Neutron Activation Analysis, located at Centro de Desenvolvimento da Tecnologia Nuclear (Nuclear Technology Development Centre) /Comissão Nacional de Energia Nuclear (Brazilian Commission for Nuclear Energy), CDTN/CNEN, since the starting up of the TRIGA MARK I IPR-R1 reactor, in 1960. Among the methods of this technique, the k_0-standardization method, which was established at CDTN in 1995, is the most efficient and in 2003 it was re-established and optimized. This paper is about the history and the main achievements since then.

1. INTRODUCTION

1.1. History

The Laboratory for Neutron Activation, Centro de Desenvolvimento da Tecnologia Nuclear (Nuclear Technology Development Centre) sponsored by Comissão Nacional de Energia Nuclear (Brazilian Commission for Nuclear Energy), CDTN/CNEN, is located in Belo Horizonte, Minas Gerais. This Laboratory has developed its activities since the starting up of the TRIGA MARK I IPR-R1 research reactor in 1960 [1].

Until 1994, only Delayed Fission Neutrons [2] and Relative Neutron Activation Analysis, including Instrumental and Radiochemical methods [3], were applied. In 1995, due to the growing need to determine several elements in a unique sample meeting the clients' analytical needs and researches and following the general analytical tendency, the k_0 Instrumental Neutron Activation Analysis, k_0-INAA [4], was established at CDTN [5,6]. At this time, it was verified that the TRIGA MARK I IPR-RI reactor presented the suitable characteristics for applying the method, mainly due to stable and homogenous neutron fluxes.

The k_0-Instrumental Neutron Activation Method [4,5,6] uses neutron flux monitors instead of standards. The nuclear data which are unknown are replaced by compound nuclear constants

characterising the nuclides, k_0 factors. It is required good knowledge of spectral parameters of the neutron flux in irradiation channels of the reactor.

The establishment of the method had the collaboration of Dr. Eduardo H. Montoya Rossi (IPEN-Peru), ARCAL/IAEA Project. This method was called in house k_0-monostandard because instead of using flux monitors, a Na comparator was used. The average thermal and epithermal fluxes were determined for the rotating carousel facility (CF) of the TRIGA reactor as well as an average α (the parameter which measures the epithermal flux deviation from the ideal (1/E) distribution) and an average f (the thermal to epithermal flux ratio) were also determined [5]. Any variations in neutron flux distribution in different channels were not taken into account due to the symmetry of the core configuration and the rotary rack, until the reactor core configuration was changed in 2001 to enable a future increase of the reactor power from 100 to 250 kW. It was decided to rotate the CF only when inserting samples in the irradiation channels. This decision and the need to update the reactor flux distribution in typical irradiation channels and consequently the values of f and α, led the re-establishing of the k_0-method.

In 2003, due to the collaboration of Dr. Radojko Jaćimović (Expert Mission IAEA, International Atomic Energy Agency) BRA/0/018-01, Project Human Resource Development and Nuclear Technology Support), the k_0-method was completely re-established and improved. More suitable programs for spectral evaluation and for element concentration were acquired and the improvement of the k_0-standardization method was introduced successfully [6,7,8]. The method has been applied since then in diversified matrixes as soil, sediment, ore, biomaterial – human tissues and fluids (hair, nails), animal tissues (muscle, liver), plant (vegetable, pasture, fruit, etc.) - air filters, solid waste, industrial residue, petroleum, stainless steel, several precipitates, archaeological ceramic, and others.

1.2. Development

Thenceforward, several improvements were made and these changes were very important to make the application of the method more reliable.

- reduction of the absorbers (Plexiglas support where the samples are placed for gamma measurements);
- acquisition of new point-sources for calibration with small uncertainties;
- determination of spectral parameters f and α as well thermal neutron fluxes in defined irradiation channels with more suitable monitors;
- it was order the production of more suitable polyethylene vials;
- optimization of irradiation time;
- improvement of spacers keeping constant sample-detector distances;
- acquisition of better software for deconvolution of gamma spectra and other for elemental concentration. Forward, the both were updated, acquiring new versions of the software;
- consultancies were requested to experts.

2. MAIN ACHIEVEMENTS

The establishment of the methodology to analyze large sample was one relevant achievement. The methodology is about analyzing more than 1g sample with cylindrical geometry, applying the k_0-method [9,10,11], without changing the local facilities. It was necessary to

determine the volumetric efficiency, neutron self-shielding and neutron fluxes gradients during neutron irradiation and gamma ray attenuation within the sample during counting. The results pointed out that these parameters were negligible or, at least, they were within the uncertainty range, once the elemental concentration results are in good agreement with the certificate results.

After all the improvements, the k_0-method established reached a very good performance. This paper shows, as an example, the results of a proficiency test, the Intercomparison Program of Results organized by the International Atomic Energy Agency (IAEA), in several kinds of plants and soil samples provided by WEPAL (Wageningen Evaluating Programs for Analytical Laboratories). This program took place in 2015, rounds 2015-1 [12,13] and 2015-2 [14,15].

The analytical performance of k_0-INAA at LAN-CDTN was evaluated expressing the results through z-score, statistical test applied by WEPAL. The test z-score is calculated by comparing the difference between a participant's result and the assigned value for the PT sample with a standard deviation for proficiency assessment. The following equations were used in the calculations:

z-score:

$$z = \frac{Value_{Experimental} - Value_{Assigned}}{St.Dev._{Assigned}} \quad (1)$$

where $Value_{Experimental}$ is the reported value by the laboratory; $Value_{Assigned}$ is the mean of all values reported by laboratories participants calculated by WEPAL; $St.Dev._{Assigned}$ is the standard deviation of proficiency assessment calculated for the WEPAL's results.

To compare the results – experimental and assigned values - a criterion was applied, meaning that the evaluation of the performance of the method was satisfactory if $|z| \leq 2$, questionable, if $2 < |z| < 3$ and unsatisfactory, if $|z| \geq 3$. The interpretation is based on the properties of the normal distribution of data. In a normal distribution, approximately 95% of values are expected to lie within ±2 standard deviations of the mean value.

The test E_n-number [16] was applied by LAN-CDTN to evaluate the results of reference materials. E_n-number was calculated to measure the agreement between the experimental result and the assigned value, taking into account the expanded uncertainty (k=2) of the both values. To compare the results the criterion $|E_n| \leq 1$ was applied, meaning that the evaluation of the performance of the method was satisfactory and if $|E_n| > 1$, the performance was unsatisfactory.

E_n-number:

$$E_n = \frac{Value_{Experimental} - Value_{Assigned}}{\sqrt{U^2_{LabExpand} + U^2_{Assigned}}} \quad (6)$$

where $U_{LabExpand}$ and $U_{Assigned}$ are the expanded uncertainties (k=2) of the experimental result and the assigned result, WEPASL's result, respectively, and

$$U_{LabExpand} = 2 \cdot U_{Experimental} \quad (7)$$

$$U_{Assigned} = 2 \cdot St.Dev._{Assigned} \quad (8)$$

3. EXPERIMENTAL

The samples - four geological samples and four plant samples - were provided in the round for analysis sent by WEPAL, named ISE 2015-1 and IPE 2015-1, respectively, as well as ISE 20152 and IPE 2015-2. The samples had their humidity determined.

The k_0-standardisation method [6] routinely is applied irradiating the samples pile in the irradiation vial and intercalated by neutron flux monitor Al-Au (0.1%) IRMM-530RA foil cut into 6 mm diameter and 0.1 mm thick, around 7mg. The alloy Al-(0.1%)Au is a certified reference material IRMM-530R, from Institute for Reference Materials and Measurements, Belgium.

The sample geometry was a vial 4.3 mm inner height and 9.6 mm inner diameter for geological samples and another vial 7 mm inner height and 9.6 mm inner diameter for biological samples. As internal standard, certified reference materials were analysed together: GBW0805, Tea, and BCR-320R, Channel Sediment. The samples, certified reference materials and monitors were inserted in another polyethylene vial, stacked in "sandwich" form.

The irradiation, usually for 8 hours, was carried out in an irradiation channel in which the values for f and α are determined in this specific channel in the carousel of the TRIGA MARK I IPR-R1 research reactor, 100kW.

After suitable decay time, the gamma-spectroscopy was performed on HPGe detectors with 25% and 50% relative efficiencies (CANBERRA), connected to electronics and Genie 2K software, CANBERRA, for spectra acquisition.

For the spectra analysis - peak area evaluation - the HyperLab program [17,] was used. For the calculation of elemental concentrations, a software package called Kayzero for Windows [18] was applied. This program takes in account burn-up effects, spectral interferences, correction for reaction interferences, etc. All these corrections make the procedure much more accurate.

4. RESULTS AND DISCUSSION

4.1. Results for reference certified materials and the intercomparison program results

The internal quality control materials used were GBW0805, Tea, and BCR-320R, Channel Sediment, analysed in duplicate. Tables 1 and 2 show the experimental results and certified

and non-certified values for GBW 0805 and for BCR-320R. For both reference materials, E_n-number is also displayed. Observing E_n-number, all results are acceptable. It means that the experimental results of reference materials are inside the expanded uncertainties.

Table 1. Results for GBW 0805, Tea

Elements	GBW 0805, Tea (mg kg^{-1})		
	Experimental Values (mg kg^{-1})	Certified Values (mg kg^{-1})	E_n-number k=2
As	0.20 ± 0.01	0.191 ± 0.025	+0.33
Ba	14.0 ± 0.7	15.7 ± 2.4	–0.61
Br	2.06 ± 0.05	2*	-
Ca	3088 ± 184	2840 ± 227	+0.57
Ce	0.76 ± 0.03	0.686 ± 0.096	+0.69
Co	0.22 ± 0.01	0.2*	-
Cr	0.98 ± 0.03	0.8*	-
Cs	0.147 ± 0.004	0.13*	-
Fe	390 ± 10	373 ± 63	+0.26
K	21010 ± 537	19700 ± 1379	+0.75
La	0.44 ± 0.01	0.458 ± 0.023	–0.56
Na	157 ± 4	142 ± 14	+0.94
Rb	39 ± 1	36.9 ± 1.5	+0.70
Sb	0.041 ± 0.001	0.037 ± 0.003	+0.98
Sc	0.121 ± 0.003	0.1*	-

*, Non-certified values

Table 2: Results for BCR-320R (Channel Sediment)

Elements	BCR-320R (Channel Sediment)		
	Experimental Values (mg kg^{-1})	Certified Values (mg kg^{-1})	E_n-number k=2
As	23± 1	21.7 ± 2.0	+0.27
Co	10 ± 1	9.7 ± 0.6	+0.25
Cr	62 ± 4	59 ± 4	+0.31
Fe	26083 ± 1780	25700 ± 1300	+0.10
Sc	5.4 ± 0.4	5.2 ± 0.4	+0.26
Se	0.8 ± 0.1	0.96 ± 0.18	–0.76
Th	5.3 ± 0.5	5.3 ± 0.4	–0.05
U	1.4 ± 0.1	1.56 ± 0.20	–0.34

Table 3 shows a summary of the results for ISE – soil and sediment - and IPE – plant - samples in rounds, 2015-1 and 2015-2, related to z-score applied in the Proficiency Test. The results that were <2 were accepted.

Table 3. Summary of the results for Proficiency Test

Results Accepted basing on z-score	
ISE 2015-1	ISE 2015-2
93.3%	95.3%
IPE 2015-1	IPE 2015-2
91.5%	92%

Several Projects have been developed since 2000's determining chemical elements by k_0-method in diversified fields of science as medicine, geology, environment, health and nutrition, chemistry, biology, etc. Since then, several papers were published applying the k_0 method on studies about foodstuff [11,19]; studies about chemical contaminants in medicines [20, 21, 22, 23]; workplace and occupational health [24, 25, 26, 27, 28]; determination of several elements in environmental samples [29,30]; supporting Monte Carlo simulation studies [31].

5. CONCLUSIONS

Over the years, the Laboratory for Neutron Activation Analysis, CDTN, has invested to improve the k_0-method. The results of the investment can be measured by the number of papers published after 2003, dissertations and Ph.D theses concluded, coordination of projects, when the method was re-established and improved. The very good performance in intercomparison results point out that the method is working properly.

ACKNOWLEDGMENTS

We would like to thank Fausto Maretti Júnior, Luiz Claudio and Dante Zamgirolami, Supervisors of the TRIGA MARK I IPR-R1 reactor and Paulo Fernando Oliveira and Luiz Otávio Ivanenko Sette Câmara, Reactor Operators, for providing assistance and operating the reactor during the analysis. The authors also thank to IAEA, CNPq and FAPEMIG for the financial support.

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