Ko-NAA IMPLEMENTATION AND APPLICATION AT NEUTRON ACTIVATION ANALYSIS LABORATORY, IPEN, SÃO PAULO, BRAZIL

A.M.G.Figueiredo[1]*, M.B.Vasconcellos[1], D. Piccot[2], C.A. Nogueira[1], D.I.T.Fávaro[1], M. Saiki[1]

[1]Laboratório de Análise por Ativação, IPEN-CNEN/SP, C.P. 11049, Pinheiros, 05422-970, São Paulo, SP, Brasil.
* e-mail: grafigue@curiango.ipen.br
[2]Laboratory Pierre Süe, CEA-CNRS, Saclay, 91191 Gif-sur-Yvette, France.

ABSTRACT

This paper presents the implementation and application of k_o standardization method at the Neutron Activation Analysis Laboratory (LAN) at IPEN, São Paulo, Brazil. This method is an important alternative to comparative neutron activation analysis, which has been used for several years at IPEN. This quasi-absolute standardization method has been adopted by various laboratories employing neutron activation analysis, and presents a great advantage with relation to the comparative method, since it does not require the preparation of accurate individual standards for each analysed element, which is very laborious and time-consuming. The ko method allows the determination of almost all the elements whose gamma-ray peaks are present in the gamma spectrum. The efficiency curves of the gamma-ray spectrometers used at LAN were determined by measuring calibrated radioactive sources at the usually utilised counting geometries. The parameters *alfa* and *f* were determined by irradiating the Certified Nuclear Reference Material IRMM-530R Al-0.1% Au alloy and high purity zirconium comparators at the IEA-R1 nuclear reactor of IPEN. The K_0-LABSUE software, developed and used at the Pierre Sue Activation Laboratory, Saclay, France, was employed. Geological and biological certified reference materials were analysed and the results obtained were in good agreement with recommended values.

INTRODUCTION

The neutron activation analysis laboratory, at IPEN, has been analysing different kinds of matrixes such as geological, biological and archaeological, for more than thirty years, employing the comparative neutron activation analysis, at the IEA-R1 nuclear reactor. In this method, samples and standards are irradiated with neutrons under the same conditions, and the concentration of the element to be determined is calculated by comparing the gamma-ray activities obtained in the sample and in the standard. In multi-elemental analysis, this procedure requires accurate individual standards for each analysed element, which is very laborious and time-consuming. On the other hand, some elements present in the sample can not be analysed due to the lack of a corresponding standard.

To overcome this disadvantage, the k_0 standardization method was developed at the Nuclear Sciences Institute, Gent, Belgium[1]. This method consists on determining the irradiation conditions, such as thermal to epithermal neutron flux ratio and neutron energy pattern, by the irradiation of flux monitors. The concentration of the elements are calculated in relation to one element, usually gold, using k_0 and Q_0 literature values, eliminating the necessity of a standard.

The k_0-NAA method was adopted in numerous neutron activation laboratories world-wide[2-4], including Brazil[5,6], and significant developments were achieved in the determination of the physical constants involved[7], as well as in the improvement of computer softwares to perform the calculation necessary to the analysis[8]. The Pierre Sue Laboratory has been using extensively the k_0-NAA method, and has developed the computer software K0-LABSUE[9], successfully employed in the analysis of different kinds of samples.

In this paper, the results obtained with the implementation of the k_0-NAA method with the K0-LABSUE software in the Activation Laboratory at IPEN are presented. Obtaining an accurate gamma-ray detection efficiency curve is essential in the k_0 standardization method. For the implementation of the k_0 standardization method, the hyperpure germanium detectors used in the laboratory were calibrated for photopeak efficiency. The thermal to epi-thermal flux ratio f and the shape factor α of the epi-thermal flux distribution were determined for irradiation facility of the IEA-R1 nuclear reactor of IPEN. To obtain these factors, the "bare triple-monitor" method with ^{197}Au-^{96}Zr-^{94}Zr was used. To validate the method, the reference materials SOIL-7 (IAEA), granite GS-N(IWG-GIT), Buffalo River Sediment (NIST SRM 2704), Apple Leaves (NIST – SRM 1515) and Bovine Liver (NIST-SRM1577b) were analysed, once they represent the matrixes usually analysed in the laboratory.

EXPERIMENTAL

Determination of gamma-ray detection efficiency curves

The detector studied was an hyperpure germanium detector from Canberra, model GMX20190. The multichannel analyzer was a 8192 channel CANBERRA S-100 plug-in-card in a PC computer.

The gamma-ray detection efficiency curve for a sample-detector distance of 10 cm was obtained by measuring punctual gamma-ray sources with known activities of ^{241}Am, ^{109}Cd, ^{139}Ce, ^{57}Co, ^{60}Co, ^{137}Cs, ^{152}Eu, ^{54}Mn, ^{65}Zn. These sources allowed to determine the gamma-ray detection efficiency curve in the range from 59.5 keV to 1408 keV. In order to extend full-energy peak detection efficiencies curves up to 2754 keV, a source of ^{24}Na was measured and the ratio between the photopeaks of 1368.6 keV and 2754 keV was used to determine detection efficiency at 2754 keV.

K_0 factors

The parameters f and α for the irradiation facility 24A of the IEA-R1 nuclear reactor of IPEN, were determined by irradiating together about 5mg of the Certified Nuclear Reference Material IRMM-530R Al-0.1% Au alloy and 40 mg of high purity zirconium comparators for 30 min. An iron monitor was also irradiated to calculate the epicadmium-to-fission neutrons flux ratio using the nuclides ^{54}Mn and ^{59}Fe. This ratio is used to quantify the elements using the nuclides which are produced by threshold reactions (Ni by ^{58}Co, for example). In spite of not being the true k_0-method, this calculation was added into the K0-LABSUE software.

Analysis of the Reference Materials

The preparation of the samples, irradiation and counting conditions were the same usually employed at the laboratory in comparative INAA. One hundred mg of the reference materials SOIL-7 (IAEA), GS-N (IWG-GIT), Buffalo River Sediment (NIST SRM 2704), Apple Leaves (NIST-SRM1515) and Bovine Liver (NIST-SRM1577b), were accurately weighed in

polyethylene bags and were irradiated together with an iron monitor for 8 h at the 24A irradiation facility of the IEA R1 reactor. Two series of countings were performed: the first one five days after irradiation and the second one 15 days after irradiation. The counting times varied from 1 to 2.5 hours.

RESULTS AND DISCUSSION

The results obtained for the reference materials SOIL-7 and GS-N, as well as certified and recommended values, are exhibited in Table 1. The errors associated to the results are one standard deviation considering counting statistics. The errors in certified values are 95% confidence limits. It can be seen that the data obtained agreed with certified values, showing relative errors less than 5% for most elements, excepting Cr and U in SOIL-7 (relative errors of 15%), and Cr, Ce and U in GS-N (relative errors of 16%, 13% and 11%, respectively).

Table 2 presents the data obtained for Buffalo River Sediment, Apple Leaves and Bovine Liver, the certified and recommended values, and the standardized difference or z-value, calculated in relation to the certified value, as reported by Bode[10]. The z-value of a result is given by:

$$z_i = (C_i - C_{ref,i}) / (\sigma^2_i + (\sigma^2_{ref,i})^{1/2}$$

where:

C_i = obtained concentration of the element i in the reference material

$C_{ref,i}$ = concentration of the certified or consensus value for the element i

σ_i = uncertainty of the obtained concentration of element i in the reference material

$\sigma_{ref,i}$ = uncertainty of the certified consensus value for the element i

If $|z| < 3$, the obtained value should be in the 99% confidence level of the recommended value.

Observing Table 2, it can be seen that the results obtained for Buffalo River Sediment were in good agreement with certified values, showing precision better than 15% and relative errors less than 10%. The z-values were in the range $3 \leq |z| \leq 3$, demonstrating the accuracy of the results.

The results for the biological materials Apple Leaves and Bovine Liver were in agreement with certified values. The z-values were within $2 \leq z \leq 2$, except for Na in Apple Leaves, that presented concentration 56% greater than reference value. Precision was better than 20%, except for Fe in Apple Leaves, which showed a standard deviation of 39%. The calculated ratios between the concentration obtained and the recommended values (non-certified) for Buffalo River Sediment and Apple Leaves (Figures 1 and 2) also demonstrate a very good concordance and no systematic trend.

The control charts (z-values) for the analysed elements in relation to certified values for the reference materials SOIL-7 and GS-N are shown in Figures 3 and 4. It can be seen that the results obtained presented z values within the interval $2 \leq z \leq 2$, which shows the quality of the results. The data are well distributed in relation to certified values, not demonstrating a systematic trend.

CONCLUSIONS

The k_0-NAA method with the computer software K_0-LABSUE[9] provided results for about 25 elements in the geological reference materials, 17 elements in Apple Leaves, and 8 elements

in Bovine Liver, with good accuracy, indicating excellent possibilities of using this parametric method at the Neutron Activation Analysis Laboratory, IPEN.

The run-time of analysis is shorter than the comparative neutron activation analysis, since there is no need of preparation of standards, which is very time-consuming. The analysis of gamma-ray spectra and the calculation of concentration is all done by the K_0-LABSUE software, and the time spent to calculate, for instance, the concentration of 25 elements in 10 samples is of about 5 minutes.

As a conclusion, the results obtained indicate that the implementation of the k_0-NAA method at the Neutron Activation Laboratory will increase the potential of analysis of the laboratory, maintaining the quality of results.

Table 1. Results (mg kg^{-1}) obtained for the reference materials SOIL-7 (IAEA) and GS-N (IWG-GIT)

Element	SOIL-7		GS-N	
	Obtained	Cert./Recom.[a]	Obtained	Certified [b]
As	13.6±0.5	13.4 ±0.84	---	1.6 ± 0.3
Ba	133 ± 16	159 ± 28	1390 ± 130	1400 ± 44
Br	7.5± 0.3	7 ± 3	---	---
Ca (%)	16.8 ±0.7	16.3± 0.6	---	---
Co	8.8 ±0.4	8.9 ± 0.9	68 ± 2	65 ± 4
Cr	69± 3	60 ± 13	64 ± 5	55 ± 4
Cs	5.7 ±0.4	5.4 ± 0.7	5.4 ± 0.9	5.4 ± 0.26
Fe (%)	2.65±0.05	2.57 ±0.06	2.68 ± 0.09	2.62 ± 0.03
Hf	4.8 ±0.2	5.1 ± 0.4	6.4 ± 0.2	6.2 ± 0.33
K (%)	1.31 ±0.05	1.21 ±0.07	4.04 ± 0.25	3.84 ± 0.05
Na	2430 ± 12	2400±100	28700±357	27967 ± 37
Rb	53 ± 9	51 ± 4.5	197 ± 29	185 ± 5
Sb	1.62 ±0.07	1.7 ± 0.2	0.72 ± 0.10	0.7 ± 0.17
Sc	8.50±0.08	8.3 ± 0.1	7.21 ± 0.09	7.3 ± 0.4
Ta	0.78±0.02	0.8 ± 0.2	2.2 ± 0.3	2.6 ± 0.2
Th	8.3 ±0.3	8.2 ± 1.1	43 ± 1	41 ± 3.5
U	2.2 ± 0.3	2.6 ± 0.5	8.3 ± 0.9	7.5 ± 0.8
Zn	101 ± 9	104 ± 6	64 ± 13	48 ± 3.3
La	27.4 ± 0.2	28 ± 1	72.5 ± 0.4	75 ± 2.7
Ce	63 ± 1	61 ± 7	152 ± 3	135 ± 7
Nd	25 ± 3	30 ± 6	51 ± 4	49 ± 1.5
Sm	4.60±0.03	5.1 ± 0.4	7.47 ± 0.02	7.5 ± 0.22
Eu	0.96 ±0.08	1 ± 0.2	1.6 ± 0.1	1.7 ± 0.06
Tb	0.66 ±0.08	0.6 ± 0.2	0.8 ± 0.1	0.6 ± 0.04
Yb	2.3 ± 0.1	2.4 ± 0.4	1.5 ± 0.2	1.4 ± 0.15
Lu	0.36 ±0.02	0.3 ± 0.15	0.22 ± 0.02	0.22 ± 0.03

(---) not determined
[a] IAEA AQCS Reference Materials Catalogue 2000-2001, IAEA, Vienna, May 2000, p. 36.
[b] Govindaraju, *Geostand. Newsl.* v.19, Special Issue, 1-32, 1995.

Table 2. Results (mg kg⁻¹) obtained for the reference materials Buffalo River Sediment (NIST 2704), Apple Leaves (NIST SRM1515) and Bovine Liver (NIST SRM1577b), certified values and z-values.

Element	Buffalo River Sediment			Apple Leaves			Bovine Liver		
	Obtained	Certified[a]	z-value[10]	Obtained	Certified[b]	z-value[10]	Obtained	Certified[c]	z-value[10]
As	21.4±0.4	23.4±0.8	-2.24	---	0.038±0.007	---	---	(0.05)	---
Ba	444±56	414±12	0.52	41±7	49±2	-1.09	---	---	---
Br	---	(7)	---	1.47±0.08	(1.8)	---	8.9±0.3	(9.7)	---
Ca (%)	2.78±0.44	2.60±0.03	0.41	1.36±0.09	1.526±0.015	-1.82	---	116±4	---
Co	14.1±0.6	14.0±0.6	0.12	---	(0.09)	---	0.30±0.02	(0.25)	---
Cr	143±3	135±5	1.37	---	(0.3)	---	---	---	---
Cs	5.6±0.5	(6)	---	---	---	---	---	---	---
Fe (%)	4.19±0.05	4.11±0.10	0.71	67±26	83±5	-0.60	197±15	184±15	0.61
Hf	8.8±0.2	(8.0)	---	---	---	---	---	---	---
K (%)	2.08±0.11	2.00±0.04	0.74	1.54±0.03	1.61±0.02	-1.94	0.96±0.06	0.994±0.002	-0.57
Mo	---	---	---	---	0.094±0.013	5.83	3.9±1.1	3.5±0.3	0.35
Na	5960±100	5470±140	2.85	38±2	24.4±1.2	5.83	2310±14	2420±60	-1.78
Rb	106±12	(100)	---	10±2	10.2±1.5	-0.08	13.9±0.6	13.7±1.1	0.16
Sb	3.9±0.1	3.79±0.15	0.61	0.030±0.03	(0.013)	---	---	(0.003)	---
Sc	11.70±0.07	(12)	---	---	(0.03)	---	---	---	---
Th	9.1±0.6	(9.2)	---	---	(0.03)	---	---	---	---
U	2.7±0.2	3.13±0.13	-1.80	---	(0.006)	---	---	---	---
Zn	471±20	438±12	1.41	14±3	12.5±0.3	0.50	122±12	127±16	-0.25
La	29.7±0.2	(29)	---	19.1±0.1	(20)	---	---	---	---
Ce	74±1	(72)	---	4.5±0.2	(3)	---	---	---	---
Nd	29±2	---	---	17±1	(17)	---	---	---	---
Sm	5.8±0.2	(6.7)	---	2.53±0.01	(3)	---	---	---	---
Eu	1.17±0.16	(1.3)	---	0.21±0.02	(0.2)	---	---	---	---
Tb	0.84±0.15	---	---	0.33±0.03	(0.4)	---	---	---	---
Yb	3.2±0.1	(2.8)	---	0.19±0.01	(0.3)	---	---	---	---
Lu	0.49±0.02	(0.6)	---	0.018±0.002	---	---	---	---	---

(---) not determined
Values in brackets are recommended values
[a] NIST Certificate of Analysis Standard Reference Material 2704 Buffalo River Sediment, Jul.1990.
[b] NIST Certificate of Analysis Standard Reference Material 1515 Apple Leaves, Jan. 1993.
[b] NIST Certificate of Analysis Standard Reference Material 1577b Bovine Liver, Aug. 1991
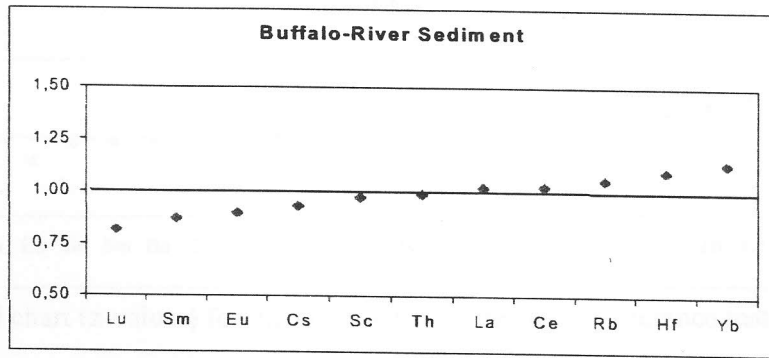
Figure 1. Ratios between obtained values and recommended (non-certified) values for Buffalo River Sediment
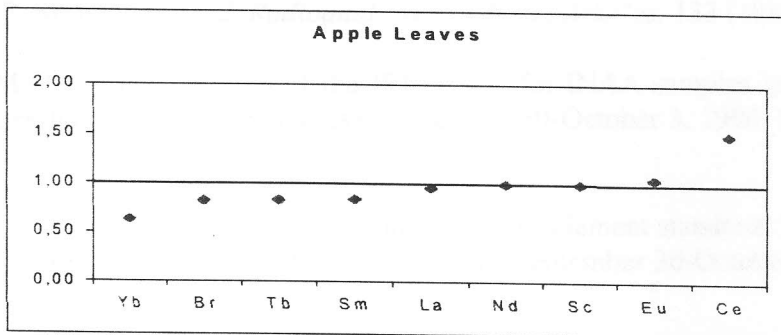

Figure 2. Ratios between obtained values and recommended (non-certified) values for Apple Leaves
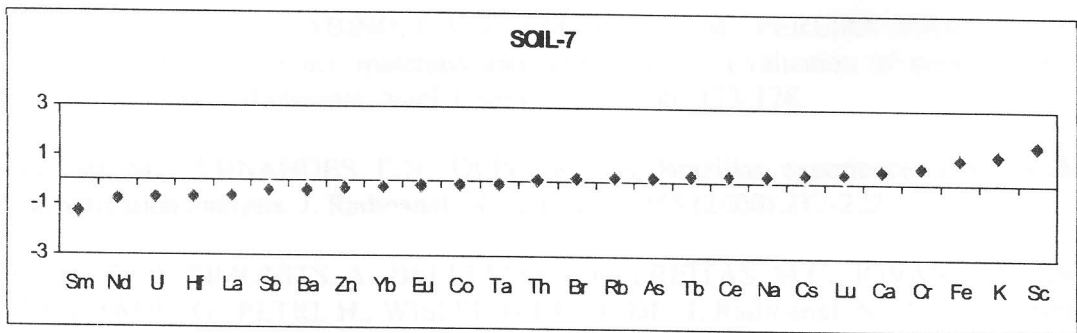

Figure 3. Control chart (z-values) for the analysed elements in the reference material SOIL-7
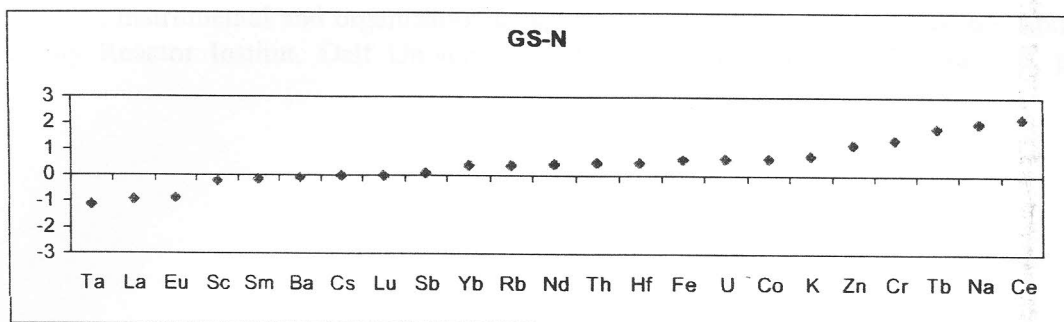
Figure 4.Control chart (z-values) for the analysed elements in the reference material GS-N

REFERENCES

1. DE CORTE, F.,SIMONITS, A *J. Radioanal. Nucl. Chem., Articles,* 133 (1989) 43-130.

2. BLAAUW, M. The Ko-calibration of the IRI system for INAA samples in the kg range. *2nd Int. Ko users workshop* (Ljubljana, Slovenia), September 30-October 3, 1996, Book of Abstracts, Sec. 1, p.3.

3. DE CORTE, F. et al., Towards European synthetic multi-element standards for QC/QA of Ko-NAA, *2nd Int. Ko users workshop* (Ljubljana, Slovenia), September 30-October 3, 1996, Book of Abstracts, Sec. 1, p. 5.

4. BRUSHWOOD, J., BEELEY, P.A., NEILSEN K., BENNETT, L.G.I. Analysis of two standard reference materials using the Shape Independent Model for k_0 based INAA. J. Radioanal. Nucl. Chem., 245 (2000) 205-207.

5. MENEZES, M.A.B.C., SABINO, C.V.S., AMARAL, A.M., PEREIRA MAIA, E.C. k_0-NAA applied to certificate reference materials and hair samples: Evaluation of exposure level in a galvanising industry J. Radioanal. Nucl. Chem., 245 (2000) 173-178.

6. BACCHI, M., FERNANDES, E.N., OLIVEIRA, H. Brazilian experience on k_0 standardized neutron activation analysis. J. Radioanal. Nucl. Chem., 245 (2000) 217-222.

7. DE CORTE, F.,SIMONITS, A., BELLEMANS, F., FREITAS, M.C., JOVANIC, S., SMODIS, B., ERDTMANN, G., PETRI, H., WISPELAERE, A. DE. J. Radioanal. Nucl. Chem., 169 (1993) 125.

8. KAYZERO/SOLCOI User's Manual, Version 4, DSM Research, December 1996.

9. D. PICCOT, D. DESCHAMPS, R. DELMAS, G. REVEL. Ko-Labsue: A quasi non-dependent data format package for K$_0$-quantification, *9th Int. Conference on Modern Trends in Activation Analysis* (Seoul, Korea), September 24-30, 1995, Proceedings, Sec. III, paper No. 147.

10. P.BODE, Instrumental and organizational aspects of a neutron activation analysis laboratory, Interfaculty Reactor Institut, Delf University of Technology, Delft, The Netherlands, p. 147, 1996.