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Comparison of two methodologies for spectra analysis in coincidence neutron activation analysis

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ABSTRACT

The Research Reactor Center (CERPq) of IPEN-CNEN/SP has been developing a facility for Coincidence Neutron Activation Analysis (CNAA), a variation of the Neutron Activation Analysis technique in which gamma-gamma coincidence is used to reduce spectral interferences and improve detection limits of some elements. As the acquisition results in 2D-coincidence spectra, the spectrum analysis has to be dealt with accordingly. There are two distinct ways to perform these analyses, either directly, by fitting bidimensional peaks in the coincidence matrix, or by gating the spectra in one detector around each peak of interest and fitting the resulting 1D-spectrum in the usual way. In this work, the concentrations of As, Co, Cs, Sb and Se were determined in geological and biological reference materials by CNAA using two different methodologies of analysis, using the BIDIM software, which provides 2D-peak-fitting; and a combination of the AnalisaCAEN suite, which gates the 2D-spectra, with Canberra's Genie2000, which fits the resulting unidimensional spectra. The outcomes allow for a discussion of the advantages and shortcomings of each method, both in terms of usability and of the reliability of the results.

Keywords: **Coincidence neutron activation analysis, data reduction, analytical methods, nuclear instrumentation.**

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1. INTRODUCTION

Coincidence Neutron Activation Analysis (CNAA) is a variation of Neutron Activation Analysis (NAA) in which two coincident gamma rays are required in order to identify the presence of the interest elements on the sample [1]. Studies related to CNAA have started in the 1960's [2, 3, 4], and since then it is possible find some papers on the literature describing the principle of this technique [2, 5-7].

Some authors point out that CNAA measurements can lead to improvements on detection limits for some elements [2, 4, 5, 7] due to the reduction of spectral structures arising from Compton scattering and bremsstrahlung effect when compared with the NAA, since just coincident gamma rays are recorded; this characteristic also gives CNAA the possibility of diminishing spectral interference problems.

Although CNAA has the aforementioned features, some authors suggest that this technique is not widely used due to low memories of computers in the beginning of its development and due to restricted number of radioisotope that can be determined by CNAA [8] as studied by Cooper in 1971 [5]. In the recent years, in virtue of the development and improvements of the computer systems and digital electronic associated in coincidence measurements, CNAA has been applied more frequently. Another characteristic of CNAA is the possibility of using different techniques for data reduction and treatment, allowing the analyst to choose or develop suitable analytical tools. The NIST has developed the qpx-gamma software [9] to be applied on data acquisition and treatment of coincidence measurements using the PIXIE 4 digitizer [10], for instance.

The present work determined the concentration of As, Co, Cs, Sc, Sb and Se in geological and biological Certified Reference Materials (CRMs) by CNAA, using data treatment methodologies for 2D spectra (by means of the BIDIM software) [11] and by energy gating the 2D matrix and fitting 1D spectra in the Genie 2000 software [12]. The comparison between these two treatments allows pointing out the advantages of each approach.

1.1 Neutron activation analysis and coincidence neutron activation analysis

The basic principle of comparative NAA is the simultaneous irradiation of a sample and a standard with well-known mass of the elements of interest inside the same device of irradiation. The identification of the element is carried out by specific gamma transitions, which are a kind of signature of the radionuclide. The quantification of the element is performed using equation 1.

$$C = \frac{R_{Sa} \cdot m_s \cdot e^{\lambda(t_{sa}-t_S)}}{R_S \cdot m_{Sa}^t} \tag{1}$$

where:

R_{Sa} and R_S are counting rates of sample and standard; m_S is mass of the element of interest in the standard; m_{Sa}^t is the total mass of the sample; λ is the decay constant of the radioisotope of interest and t_{sa} and t_s are the decay times of sample and standard; respectively.

CNAA is based on the principle of the coincident photons detection, the concentration is determined using two coincident gamma transitions from a cascade decay. This approach can lead to a better level of discrimination when compared with NAA, since CNAA presents more strict criteria for validation of an event. In other words, the concentration is determined using just gamma transitions that arrive in both detectors in a short time interval; this criteria restrict the number of registered events and has the capacity of reducing spectrum continuum caused by bremsstrahlung and Compton effect, besides eliminating spectral interferences.

The concentration of an interest element present on the sample is determined using the equation (2).

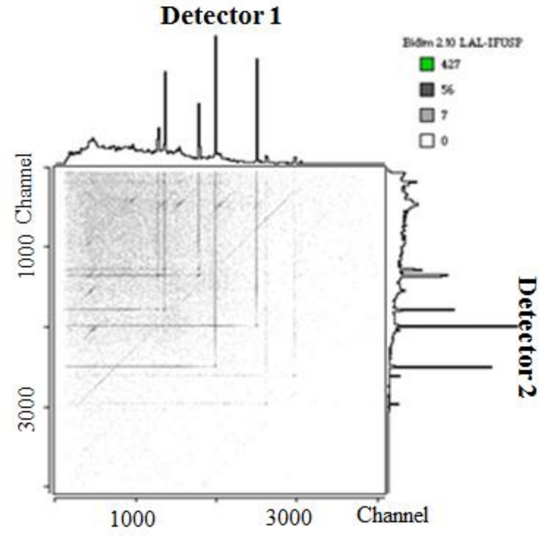
$$C^{ab} = \frac{R_{Sa}^{ab} \cdot m_s \cdot e^{\lambda(t_{Sa}-t_s)}}{R_s \cdot m_{Sa}^t} \tag{2}$$

where the ab index is related to the coincident gamma transition ab.

1.2 Two–dimensional approach analysis

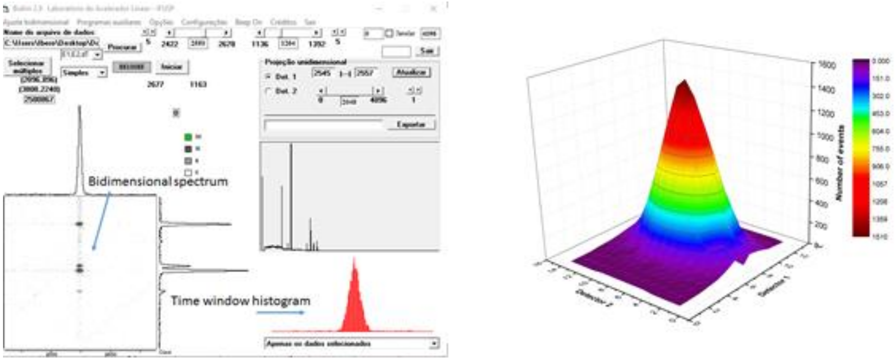
In coincidence measurements, only events that arrive in both detectors in a short interval of time (called by *time window*) are accepted. As result from this condition, for each gamma ray registered by one detector (generically called detector 1) a coincident gamma transition will be registered by detector 2, generating a two-dimensional spectrum as shown in Figure 1.

Figure 1: *Two-dimensional spectrum obtained by CNAA.*



CNAA can be carried out using suitable softwares for two-dimensional peak analysis - in the case of this study the BIDIM software was used, which fits a two-dimensional Gaussian function with several peak shape corrections [11]. For this kind of analysis, the region of interest must be selected manually and the software will perform the fit using the least squares method. Figure 2 shows the region of interest for the fit and the two-dimensional peak adjusted by BIDIM, respectively.

Figure 2: *Bidimensional fit of coincidence spectrum, (left) selection of the area of interest, (right) 2D peak fitted..*



In this methodology it is necessary to perform the fit peak by peak - in other words, for each coincident gamma transition the analyst must select the region of the interest and perform the fit.

1.3 One-dimensional analysis

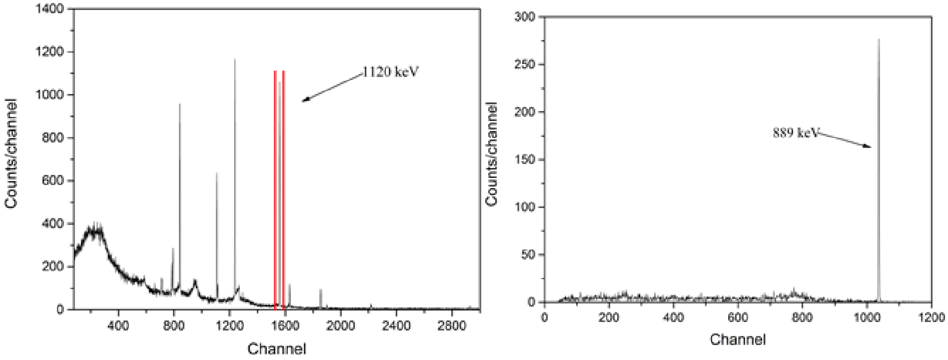
This analysis is performed by energy-gating the 2D spectrum (in case of this study using AnalisaCaen software [13]), then fitting the resulting 1D-spectra with a suitable software, in this case the Genie 2000 software [12] was used.

The data reduction for this approach was carried out using AnalisaCaen software, which provides one spectrum of all events registered for each detector in a time window of 1 microsecond (called open window spectrum); a matrix of coincident events in the format [channel1, channel 2, number of registered events] and a time-difference spectrum of the registered events.

By means of the time-difference spectrum, the random events are subtracted from the total events, and then a matrix containing only true events is generated, together with new one-dimensional spectra with only the real events for each detector [13-15].

The next step for this kind of approach is select the region of the energy of interested in a full coincident spectrum of the one detector, and then gate the selected region on the matrix of real events (see Figure 3, on the left). As a result, a spectrum of the events in coincidence with the selected region in the other detector is obtained. To illustrate, Figure 3 (right side) shows the spectrum obtained by gating around the energy of 1120 keV in one detector, resulting in an almost clean 889 keV transition on the other detector (this coincidence is from the decay of ^{46}Sc).

Figure 3: *Unidimensional fitting of a coincdence spectrum, (left) Open window of detector 1 showoing the region of 1120 keV (from decay of ^{46}Sc) selected for gatting, (right) gated spectrum obtained for detector 2.*



2. MATERIALS AND METHODS

2.1 Preparation and irradiation of the synthetic standards and reference materials

Synthetic standards of the elements were prepared pipetting 50 µL onto Whatman No 40 filter paper using solutions provided by SpexCertiprep USA, which were diluted in purified water. Subsequently, the filter papers were dried at room temperature for 24 h inside a desiccator and then heat-sealed into demineralized polyethylene bags. The masses of the elements are presented on Table 1.

Table 1: Mass of the elements present at the synthetic standards.

Element	**Mass (ηg)**
As	150.2
Co	150.35
Cs	600.1
Sb	600.9
Sc	100
Se	8007.05

In the present study the reference materials selected were: NIST SRM-2709 (San Joaquin Soil), for the As, Sb, Sc and Se determination; BE-N (Basalt-CNRC), for Co and Cs determination; and

DORM4 (Fish Protein-NRCC) for Se determination. For each of these CRMs, approximately 120 mg were weighted and sealed into the same type of polyethylene bag used for the standards. The concentration results were calculated using the dry masses of the reference materials, determined according to their certificates.

All synthetic standards and reference materials were irradiated together inside the same irradiation vial at the IEA-R1 nuclear research reactor of IPEN-CNEN/SP under a neutron flux of 10^{12} $cm^{-2}s^{-1}$ for 8 hours. For As determination data were acquired with 5 days of decay whereas for the other elements the decay time was 20 days.

2.2 Activity measurements

The measurement of activities was carried out using a CAEN v1724 digitizer and two HPGe detectors placed in face-to-face geometry within a distance of 1 cm, with the output of the pre-amplifier of each detector coupled directly to the input of the digitizer – the acquisition was controlled using the software MC2 Analyzer [16]. The basic characteristics of the detectors used on the measurements are presented on Table 2 – it is worth mentioning that the energy resolution (FWHM) presented is the de facto resolution, obtained experimentally; for the PopTop detector this is much larger than the expected nominal resolution due to the age of the detector, as well as some persistent vacuum issues.

Table 2: Basic characteristics of the detectors used in the present measurements.

Name	Efficiency (%)	Volume (cm^3)	FWHM (1332 keV)*
PopTop	35	106	4.2
Cacá	13	39	2.2

* These are the *de facto* resolutions, quite worse than the nominal ones.

Table 3 presents the energies used for the concentration calculation for the elements of interest.

Table 3: Energies used for gate and energies used on the calculation of concentration.

Radioisotope	Half life	Energy gate (keV)	Energy used on calculation (keV)	Probability (%)
^{76}As	26.3 h	657	559	2.4
^{60}Co	5.2 y	1173	1332	99.99
^{134}Cs	2.0 y	604	795	83.34
^{124}Sb	60.2 d	722	602	10.63
^{46}Sc	83.8 d	889	1120	99.97
^{75}Se	119 d	136	264	34.34

3. RESULTS AND DISCUSSION

Three different reference materials were analyzed using CNAA and data treatment was carried out by two different methodologies: 1) Two-dimensional spectrum analysis (using BIDIM software; 2) 1D spectrum analysis (using AnalisaCaen and Genie2000 software). The concentration results obtained by the aforementioned methodologies and the certified values are presented on Table 4.

Table 4: Concentration of As, Co, Cs, Sb, Sc and Se in SRM2709, BE-N and DORM4 reference materials using two-dimensional and one-dimensional approach.

Element	Reference Material	Concentration (mg/kg)		
		Two-dimensional (RSD)	One-dimensional (RSD)	Certificate (RSD)
As	SRM2709	18.4 ± 4.7 (0.25)	17.3 ± 3.8 (0.22)	17.7 ±0.8 (0.04)
Co	BE-N	50.4 ± 8.5 (0.16)	51.7 ± 6.5 (0.12)	60 ± 2 (0.03)
	SRM2709	11.3 ± 1.1 (0.17)	11.7 ± 1.5 (0.13)	13,4 ± 0.7 (0.05)
Cs	BE-N	0.84 ± 0.25 (0.29)	1.08 ± 0.25 (0.23)	0.8 ± 0.1 (0.12)
	SRM2709	5.7 ± 0.9 (0.16)	6.02 ±0.70 (0.13)	5.0 ± 0.1 (0.02)
Sb	SRM2709	7.6 ± 0.1 (0.01)	7.4 ± 0.6 (0.08)	7.9 ± 0.6 (0.07)
Sc	BE-N	23.5 ± 1.2 (0.05)	23.2 ± 0.9 (0.04)	22.0 ± 1.5 (0.07)
	SRM2709	12.0 ± 0.6 (0.05)	11.8 ± 0.4 (0.04)	11.1 ± 0.1 (0.09)
Se	DORM4	3.83 ± 0.09 (0.02)	3.76 ± 0.15 (0.04)	3.45 ± 0.40 (0.11)
	SRM2709	1.52 ± 0.09 (0.06)	1.72 ± 0.11 (0.06)	1.57 ± 0.08 (0.05)

RSD=Relative Standard Deviation

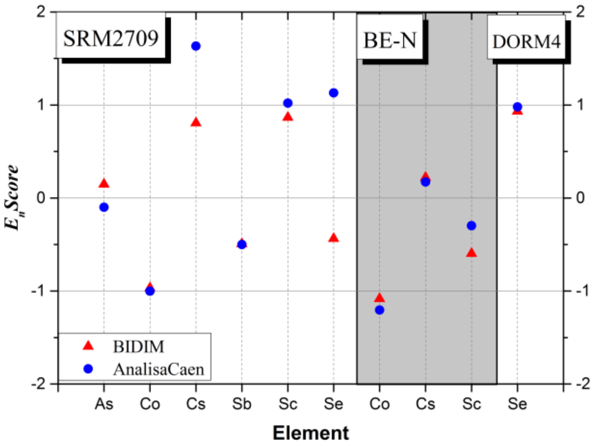
Table 4 shows that the results obtained by two-dimensional and one-dimensional analyses are in agreement, indicating that both methods provide consistent results.

It can be noted that the Relative Standard Deviation (RSD) values obtained are larger than the the tipycal values obtained in NAA mesaurements, due to the fact that CNAA registers less events than common NAA, which implies in higher RSD values. The acquisition time for synthetic standards and reference materials was about 36,000 and 86,400 s, respectively, but even with these long counting times it was not possible to decrease the RSDs for either methodology.

In order to evaluate the accuracy of the obtained results, the E_n*score* [17] for each result was calculated.

The results obtained accurate resultsfrom both analyses, as seen in Figure 4. The most part of E_n*score* values are between -1 and 1, which are considered satisfactory [17]. The E_n*score* for Se in SRM2709 is 1.13 (one-dimensional methodology) and for Cs it is 1.6 (one-dimensional approach); even being little higher than the values proposed by Konieska [17], these results can be considered satisfactory for a confident level of 95%. The same occurs with Co in BE-N for both methodologies. It is worth to mention that Se determination is difficult due to the spectrum region where the peaks lie, and several authors have been studying Se determination [2,18]. It should be noted, also, that both methodologies gave satisfatory results for Sb, which has spectral interferences from Cs.

Figure 4: *$E_n$score for As, Co, Cs, Sb, Sc and Se in SRM2709, BE-N and DORM4 reference materials.*



4. CONCLUSION

In this study the concentrations of As, Co, Cs, Sb, Sc and Se were determined in different reference materials using two different ways to treat data from CNAA. The E_n*score* results point out that both methodologies provide accurate results, and the results obtained by both methodologies are equivalent as well, indicating that both one dimensional and two-dimensional methodologies can be used in data analysis for CNAA.

Either method shows advantages and shortcomings; for example, the two-dimensional approach requires more time for the analysis as there are several parameters to be manually adjusted (see [11]), however this methodology provides parameters about the quality of the peak fit, such as chi-square and residues.

The one-dimensional methodology, as well as the two-dimensional methodology, provided reliable results, and the operation of the AnalisaCaen and Genie2000 software is faster than the analysis using BIDIM; on the other hand, in the former the analyst does not have easy access to all parameters used on the area calculation - this way more complex cases should be analyzed manually.

Results showed that both methodologies can be applied in data reduction and analysis of CNAA experiments. However, the analysis using BIDIM has the advantages to be free of costs, since this software is free, whereas Genie 2000, used to fit one-dimensional peaks in this study, is a commercial software, which implies in costs for analysis, however this kind of analysis can also be done using free software developed for this purpose.

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