

Study of the gamma spectrum of ^{16}N with a BGO detector, for the purpose of calibration and of determining the fluorine grade of mineral samples

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Abstract The study of ^{16}N 's gamma spectrum has two main uses: calibrating gamma detectors in a high energy range, and determining the fluorine grade of mineral samples of fluorite. This article examines and compares the gamma ray spectrum of ^{16}N as recorded by a $\text{Bi}_4\text{GeO}_{12}$ detector, as well as the resolution of this detector at high energy levels, and the signal–background relationship of an experimental laboratory cyclic activation unit. ^{16}N is the product of the reaction $9\text{-F-}^{19}(\text{n},\alpha)7\text{-N-}^{16}$, which takes place during the neutron activation of mineral samples of fluorspar, and its production depends, among other factors, upon the grade of fluorite. The technique used in this study is cyclic-type neutron activation for recording delayed gamma rays, carried out with an americium–beryllium neutron source with an activity of 1 Ci. Lastly, a correlation is established between the area below the peak amount of ^{16}N emitted by the sample, and the sample's fluorite grade.

Keywords Spectrum · Fluorspar · Fluorite · Gamma rays · Cyclic activation

Introduction

The energy of the gamma rays emitted by a sample, recorded as a series of peaks on a radiation detector's

energy spectrum, can be used to identify a radioactive element and quantify its grade within the sample. Radiation detectors, which classify incident gamma-ray energy into different channels, must be calibrated in order to convert this channel scale into an energy scale (keV). Cs and Co sources are commonly used to calibrate detectors up to an energy level on the order of 1,500 keV, which corresponds to Co. Therefore, the study of ^{16}N 's gamma ray spectrum can be applied to the calibration of detectors at high energy levels, as ^{16}N has a principal gamma emission of 6,128.63 keV at an intensity of 67 %, and 7,115.15 keV at an intensity of 4.9 %.

The study of ^{16}N 's gamma spectrum can also be applied to determining the fluorine grade of geological samples. In the specific case of fluorspar samples, the fluorine grade can be determined through an analysis of acid-grade calcium fluoride [1], though this sort of analysis takes approximately one full day to carry out. In order to overcome this inconvenience, we propose using neutron activation techniques that make it possible to analyze such samples in a matter of minutes. Neutron activation techniques are well-known [2–4], and many analytical methods for studying fluorine through neutron activation have been reported [5–12]. These methods involve bombardment by isotopic neutrons, reactor neutrons, or accelerator neutrons, and counting the radioactive products. Along these lines, the present study is part of a larger research project about the feasibility of using neutron activation and an isotopic americium–beryllium neutron source to determine the fluorine grade of fluorspar samples from mineral concentration plants. Both of the above applications were detailed in Rey-Ronco et al. [13–15].

^{16}N is an artificial radioactive element with a very short half-life ($T_{1/2} = 7.13$ s) that can be produced in the nuclear reaction $9\text{-F-}^{19}(\text{n},\alpha)7\text{-N-}^{16}$, and which has a high

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cross-section at the energy level of the neutrons emitted by an americium–beryllium source. Fluorite (CaF_2) is a substance that is both naturally abundant and easy to handle, and is found, with different levels of concentration, in fluor spar. As such, the reaction mentioned above can be caused by subjecting mining samples of fluor spar to neutron bombardment [13]. In previous papers neutron activation was used to analyze 200 g samples of fluor spar from a fluorite concentration plant, with CaF_2 grades of between 4 and 97 %. The samples were activated using a 1 Ci americium–beryllium source for 120 s, after which the gamma spectrum emitted was recorded over a subsequent counting time of 25 s. A multichannel Canberra and a $2'' \times 2''$ diameter NaI detector were used, along with a manual system for transferring the sample from the neutron irradiation position to the gamma ray counting position.

The result of these experiments was essentially that very little ^{16}N was produced, due to the low activation of the sample [16–18]. We concluded that it would be interesting to use a BGO detector, which in principle is better-suited to ^{16}N 's high level of gamma energy. Another conclusion was that the sample's level of activation would have to be increased, as in these studies it was necessary to add up a large number of gamma-ray spectra in order to clearly detect ^{16}N 's characteristic peaks. In this case it was found that the area of the peak around 6,218 keV on the “sum” spectrum, corresponding to ^{16}N , was proportional to the CaF_2 grade in the sample. Given the sample's short decay time, the spectrum must be recorded immediately after activation, and within a limited window of time. Because the ability to control this window throughout the trials was crucial to the interpretation of the results, and since the activation had to be repeated a number of times, we explored the idea of automating the transfer of the sample during cyclic activation [19, 20].

As a consequence, the team decided to modify the equipment and parameters for the initial experiment. The reason behind this was the need to carry out the cyclic neutron activation process with precision and accuracy, by transferring the samples automatically over the shortest possible distance. To this end, the transfer and stop times were controlled, along with the stop and acceleration positions, and the beginning and end of the spectrum recordings in each counting phase. Likewise, the $2'' \times 2''$ NaI detector was substituted with a $2'' \times 2''$ BGO detector.

The parameters that were modified were, on the one hand, the irradiation and counting times, which were made equal for each cycle, and, on the other, the number of cycles. The present article discusses the results achieved with these new parameters and equipment.

Procedure

Equipment

The equipment for the experiments is partially based on that described in previous papers, and basically consists of an americium–beryllium neutron source with 1 Ci of activity (5) placed in a borated paraffin enclosure (7 and 9), and a hollow guide (10) along which the sample is transferred (8) (Fig. 1). The new prototype has been adapted for cyclic activation, i.e. the following parts have been added, as indicated in the Fig. 1: a linear sample-transfer motor (11) and a base support structure to absorb the exertions of the system (1). Additionally, a $2'' \times 2''$ BGO detector (3) and an Osprey multichannel are now used in place of the old $2'' \times 2''$ NaI detector and Canberra multichannel. Osprey is an all-in-one HVPS, preamplifier, and digital MCA, which is compatible with all standard 14-pin scintillation detectors, optional temperature-stabilized NaI probes, USB 2.0 connection for PC plug-and-play, PHA, MCS, SCA, MSS, List, and Time-stamped List modes and fully supported by Genie™ 2000 software and programming libraries.

The motor is managed using a control program created with c-language, which controls the position, velocity, acceleration and first jolt of the sample as the motor transfers it, for a programmed number of cycles, between the activation position, where the neutron source is located (5), and the position where gamma rays are counted in front of the detector (3). This transfer takes place very quickly and with a high level of precision, as the base support structure absorbs the vibrations and jolts caused by the acceleration of the sample. Speeds of 2 m/s and accelerations of 6.15 m/s^2 are reached. Likewise, the program controls the gamma ray detector's recording software. In this way, the spectrum is only read during the time that the sample is placed in front of the detector. Lastly, when the programmed number of cycles has been reached, the program can record the final spectrum accumulated over the course of the n counting cycles.

Characteristics of the series of experiments

The set of experiments detailed in this paper addresses the conclusions reached in previous studies [13–20]: the mass of the sample should be increased as much as possible, a higher-resolution detector should be used for high-energy gamma rays, equal activation and counting times (11 s) should be assigned, the transfer time should be kept as low as possible, and the number of cycles should be high. With all this in mind, the characteristics are as follows:

- Sample mass of 350 g
- Type and size of the $2'' \times 2''$ BGO detector
- Osprey multichannel

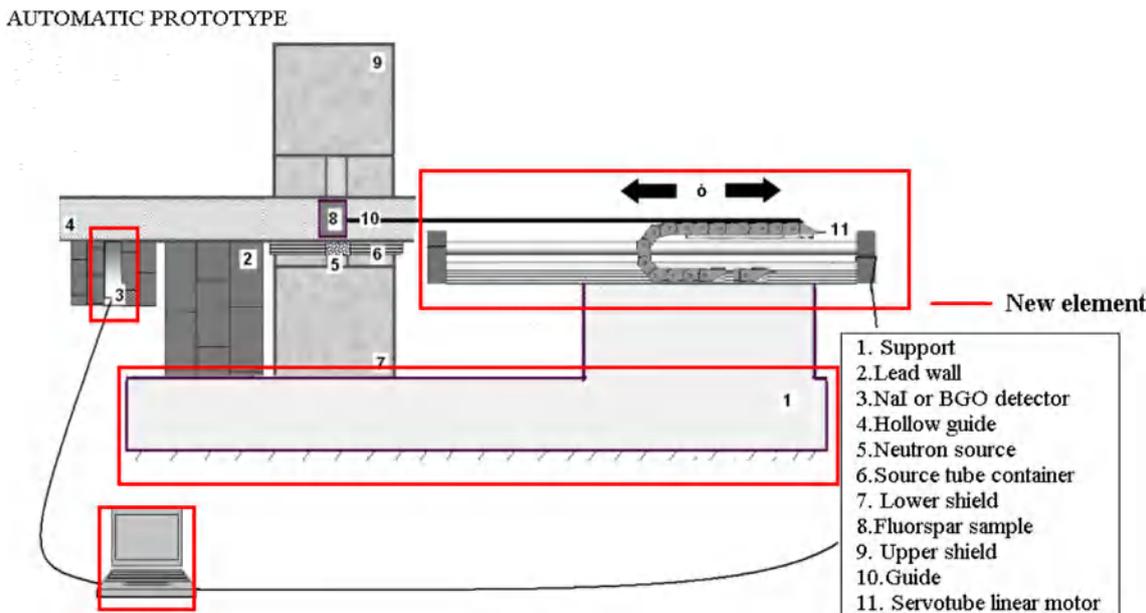


Fig. 1 Automatic prototype [19, 20]

- t_a → Activation time → 11.213 s
- t_1 → Counting time → 11.213 s
- n → Number of cycles → 144
- t_d → Transfer time → 0.325 s

Eight samples of fluorspar were prepared, with CaF_2 grades of between 2.28 and 97.60 %. These results were obtained using conventional chemical analyses (ASTM E1506-08). Each sample is referred to as indicated in Table 1. As part of the neutron activation process, one analysis was carried out without a sample in order to obtain a reading of the background. This reading was then called G_0 .

Lastly, each sample was activated cyclically for a maximum of 144 cycles.

Because of this, the spectra are referred to with the following nomenclature: SG_aN_b , where a is the fluorite grade in the fluorspar sample, and b is the number of cycles.

Table 1 Total number of experiments

Sample name	CaF2 grade of each sample [%] (conventional chemical procedure)
Sample analyzed	
G_{98}	97.60
G_{90}	90.98
G_{76}	76.50
G_{60}	59.92
G_{42}	42.05
G_{27}	27.05
G_{11}	11.39
G_2	2.28
G_0	Analysis is without sample (Background)

Analysis of the results

Calibration of the gamma spectrum and ^{16}N peaks

Figure 2a shows the gamma ray spectrum emitted by two sources, a Cs and a Co calibration source, of the sort that are conventionally used to calibrate gamma spectra at energy levels of around 1,000 keV, and recorded with a BGO detector and an Osprey multichannel. Figure 2b shows spectra recorded at high channel numbers, emitted by different samples of fluorspar activated cyclically over 144 activation and counting cycles. The samples had four different CaF_2 grades. One can clearly see the peaks in the spectrum, which increase alongside the sample's CaF_2 grade. It has been shown that ^{16}N is the only radioactive product that emits in this high channel-number range, and that as such, all the peaks that appear are caused by the presence of ^{16}N . This means that the peaks in the spectrum must correspond to gamma energy emitted by ^{16}N , which is 6,218.63 keV with a relative intensity of 67 %, and 7,115.15 keV with a relative intensity of 4.9 %. These gamma rays produce escape peaks with energy levels that are 511 keV less than the energy level of the photopeak. The escape peaks show up most intensely at the 6,128 keV photopeak, which is the most intense (Fig. 2c).

These peaks can be used to calibrate the original spectrum (in channels) into an energy spectrum, by adjusting the cubic polynomial:

$$f(x) = p_1 \cdot x^3 + p_2 \cdot x^2 + p_3 \cdot x + p_4$$

where $f(x)$ is the energy in keV and x is the channel

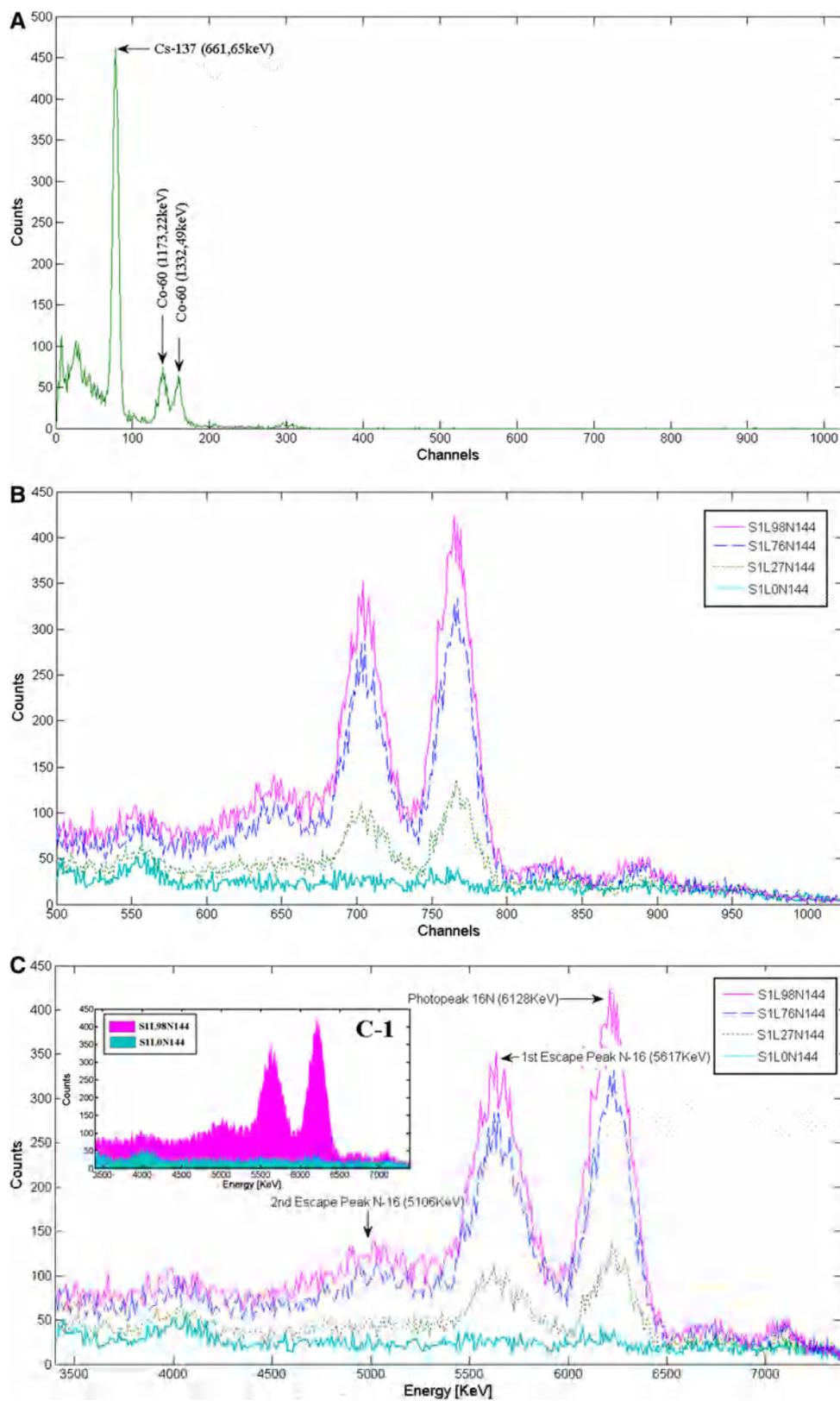
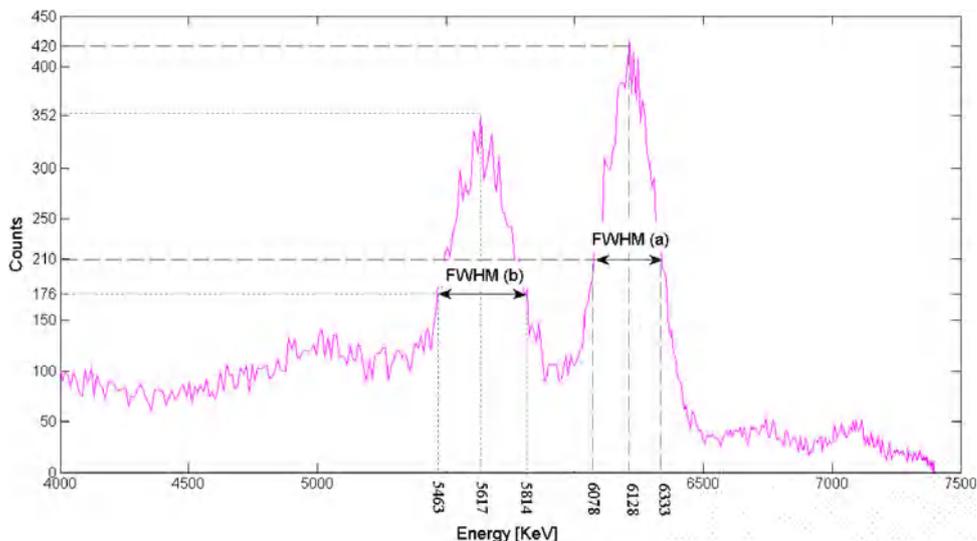


Fig. 2 **a** Gamma ray spectrum emitted by a ^{137}Cs and a ^{60}Co calibration source. **b** The whole set of spectra from series 1 (S1G98N144, S1G74N144, S1G27N144 and S1G0N144). **c** Spectrum obtained with a BGO detector for a sample with 98 % CaF_2 and N144

Fig. 3 BGO resolution



Coefficients (with 95 % confidence bounds):

- $p_1 = -1.846e - 005 (-3.086e - 005, -6.055e - 006)$
- $p_2 = 0.03066 (0.0101, 0.05122)$
- $p_3 = -5.698 (-16.01, 4.618)$
- $p_4 = 892.7 (-523.3, 2309)$

Goodness of fit:

SSE: 3.476e + 004
 R^2 : 0.9992
 Adjusted R^2 : 0.9984
 RMSE: 107.6

Meaning that the channel corresponding to the photopeak at 6,128 keV is 755.

Resolution of the BGO detector

In previous studies, we had used a 2'' × 2'' NaI detector, for which we had calculated a resolution of 0.1328. For the present experiments, the resolution of the 2'' × 2'' BGO detector was determined based on the spectrum of experiment S1G98N144, which is shown in Fig. 3, where the energy levels calculated after the calibration of the spectrum are shown on the x-axis.

The data concerning the centroid and the FWHM, used for calculating the detector’s resolution and taken from the spectrum, have been gathered in Table 2.

Table 2 BGO resolution

	Centroid (energy)	FWHM (energy)	Resolution ratio (FWHM/centroid)
S1G98N144			
Photopeak	6128	255	0.04
First escape peak	5617	351	0.06

Given the high gamma energy range involved, it can be concluded that this resolution is perfectly adequate, and that it constitutes an improvement over the resolution ratio of the NaI detector.

Signal–background relationship

In order to assess the quality of an activation experiment, it is important to record what is called the background spectrum, which is recorded without a sample in order to determine the general conditions in the area where the samples will be activated. It is an indicator of the influence that the various elements in the environment of the experiment, including the direct radiation from the neutron source, have on the rest of the spectra.

In order to study this relationship, we used, as a comparative parameter, the peak area of ¹⁶N’s spectrum (in the interval between channels 640 and 762) corresponding to the gamma ray spectra of the irradiated samples, and the same interval in the background gamma spectrum of each series of experiments. (Fig. 2, c-1).

Table 3 shows the sum of the counts calculated for ¹⁶N’s channel intervals, for both S1G98N144, as well as the background measurement experiments for the same number of cycles. The last column shows the relationship B/C, which is the result of dividing the sum total of the background counts recorded in the interval of interest in series S1, by the sum total of the counts recorded for a sample with a 98 % CaF₂ grade in series S1 over the same interval. This relationship is expressed as a percent. The higher the value of the B/C relationship, the greater the influence of the background on a fluorite sample’s spectrum, and, consequently, the lower the “quality” of the experiment.

This percentage is the minimum obtained after reaching the maximum possible thickness of the lead enclosure between the source and the detector.

Table 3 Calculating the B/C coefficient

Type of detector	Channel interval considered	Sum of counts in the interval				B/C (%)
		B		C		
BGO (2'' × 2'')	640–762	S1G0N144	2972	S1G98N144	21976	13.5

Fig. 4 Correlation between mineral grade and peak area for N144

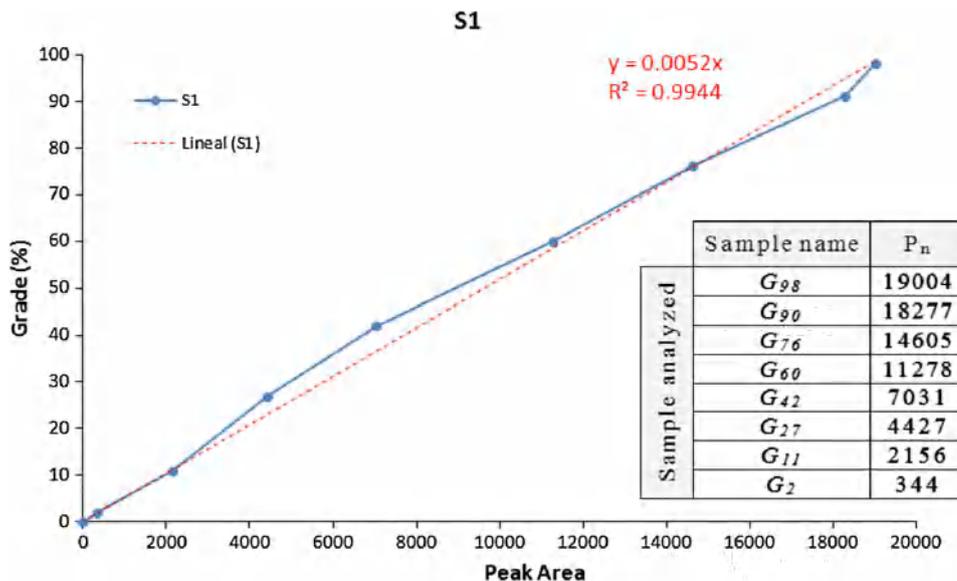
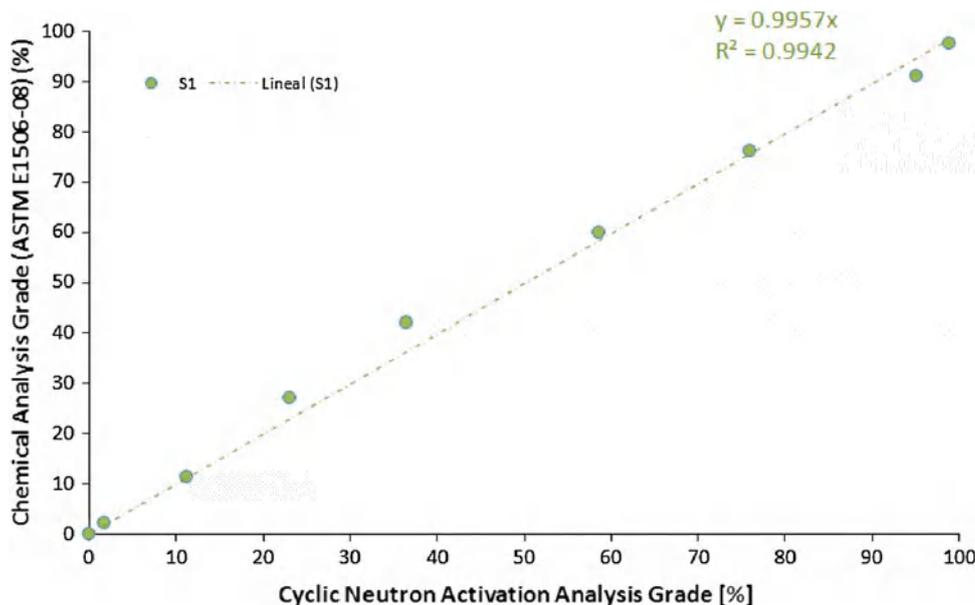


Fig. 5 Chemical analysis versus cyclic neutron activation analysis for N144



Relationship between the sample’s fluorine grade and its spectrum

Correlations were made between, on the one hand, the fluorite grade of the sample (directly proportional to its

fluorine grade), which was found in the chemical analyses (ASTM E1506-08), and, on the other, the peak area of the gamma spectrum produced beneath the 6,128 keV photopeak, and the first escape peak caused by ¹⁶N. The net peak area (P_n) is calculated by subtracting, from the area below

the curve obtained in the activation of the samples, the background spectrum corresponding to the same interval. For example, in (Fig. 2, c-1), the net peak area is the peak area of SIL98N144 minus the peak area of SILON144. These values are the same ones represented on the graph in (Fig. 4), which shows the results of the linear regression between the net peak area and the fluorite grade of the samples. This high correlation coefficient of more than 0.99 was obtained in all the series of experiments.

Lastly, the graph in Fig. 5 compares the fluorite grade as obtained both through neutron activation, and through chemical analysis.

It can be observed that the line defined by calibration is $y = 0.9957 \cdot x$ with a high correlation coefficient, a considerable improvement over the correlation coefficient of previous results on the order of 0.94 [19].

Conclusions

A system was designed and built to carry out cyclic neutron activation, consisting of: a 1 Ci americium–beryllium neutron source, a $2'' \times 2''$ BGO scintillation detector, an Osprey multichannel, a Servotube linear motor for automatically transferring samples, a support structure for the whole system, and an enclosure to contain the neutrons.

The gamma spectra emitted by Cs and Co calibration samples for energy levels of around 1,000 keV, and by ^{16}N for energy levels of around 6,000–7,000 keV, were also obtained using this system. ^{16}N was produced artificially by subjecting a mining sample of CaF_2 to neutron bombardment, and through the reaction $9\text{-F-}19(n,\alpha)7\text{-N-}16$. The presence of ^{16}N in the sample was confirmed through its gamma spectrum, whose height increases alongside the sample's CaF_2 grade. These channel values made it possible to calibrate the detection equipment and obtain the energy spectrum.

^{16}N 's escape peaks have been found at 511 keV below the respective photopeak. The spectrum of ^{16}N is quite visible, and its peak has a high resolution ratio of 0.04. The experiment's signal–background relationship was found to be 13.5 %.

The net peak area was then correlated with the fluorine grade of the sample, with a correlation coefficient of 0.9944.

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