

## Ni-59 DETERMINATION BY MEASUREMENT OF ANNIHILATION ENERGY

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### ABSTRACT

Radioactive waste is subject to regulations regarding its inventory, transportation and final deposition. Such standards require the knowledge of the tailing contents in a way that is possible to accommodate them in a repository capable of containing their radiation completely. In this study a methodology was established for determining the concentration of  $^{59}\text{Ni}$  using the annihilation energy (0.511 MeV) between a positron from its  $\beta^+$  emission, and an electron that is widely present in matter. To ensure the reliability of the methodology, the area of the annihilation peak was compared to  $^{59}\text{Ni}$   $K\alpha$  and  $K\beta$  x-ray peaks. To make this method viable the separations of Ni from the other components of the sample was necessary. This was done by using dimethylglyoxime (DMG) for Ni precipitation. Of all the Ni radioisotopes only  $^{59}\text{Ni}$  have a half-life longer than a few days, so that  $^{59}\text{Ni}$  can be determined without radioisotopical interferences. After precipitation with DMG, the substrate was vacuum filtered on filter paper, using an apparatus to preserve the geometry of the precipitate in different samples. The  $^{59}\text{Ni}$  precipitate was then counted in an extended range gamma spectrometer and the 511 keV peak compared to the Ni x-rays in order to verify the reliability of the method.

### 1. INTRODUCTION

In 1930 Dirac demonstrated mathematically the annihilation interaction between an electron and a “positron” [1], but as the positron hadn’t yet been discovered this left a gap in the work, acknowledged by the author, as the proton mass was much larger than the electron mass. In 1932, cosmic ray photographs taken with a Wilson camera indicated the existence of the positron, with the same rest mass of the electron [2].

Nowadays the electron (and positron) mass is known with very good precision [3], and the electron-positron annihilation is a very well established phenomenon, where the particle-antiparticle pair annihilate, usually at very low kinetic energies, releasing a pair of 511 keV gamma rays [4].

$^{59}\text{Ni}$  is a long-lived radionuclide ( $T_{1/2} \approx 76000$  years) frequently found in nuclear waste that decays to  $^{59}\text{Co}$  mostly by electron capture, but also very rarely (0.000037% of the time) by the emission of a positron, either way with no subsequent gamma-ray emission. When the

nucleus decays by electron capture, there is a subsequent x-ray emission, mostly either the cobalt  $K\alpha$  (6.92 keV, I = 30.8%) or  $K\beta$  (7.65 keV, I = 3.70%) lines [5]; the problem, however, is that these very low energy x-ray lines are rather difficult to determine by direct detection as they are very easily stopped by any material located between the source and the detector.

The proposal of this work is to assess the possibility of determining  $^{59}\text{Ni}$  in radioactive waste samples using the 511 keV annihilation peak instead of the cobalt x-rays, greatly simplifying the quantification process for this radionuclide.

## 2. MATERIALS AND METHODS

$^{59}\text{Ni}$  is the only  $\beta^+$  emitting isotope of nickel with a half-life (76000 years) longer than a few days [6]; therefore, the simple separation of nickel from the sample should be sufficient to guarantee that there will be no interference.

### 2.1. Sample preparation

The samples came from Angra 1 power plant, and were from the resins used to filtrate the water from the reactor, as those resins retained a lot of radionuclides they became radioactive waste. From all the samples received, this paper will only cover 4 of them.

Approximately 300mg were taken from each resin and dissolved with  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$ , diluted to 100 mL and then an aliquot of 10 mL was used to measure the  $^{59}\text{Ni}$ .

### 2.2. Separation of Nickel

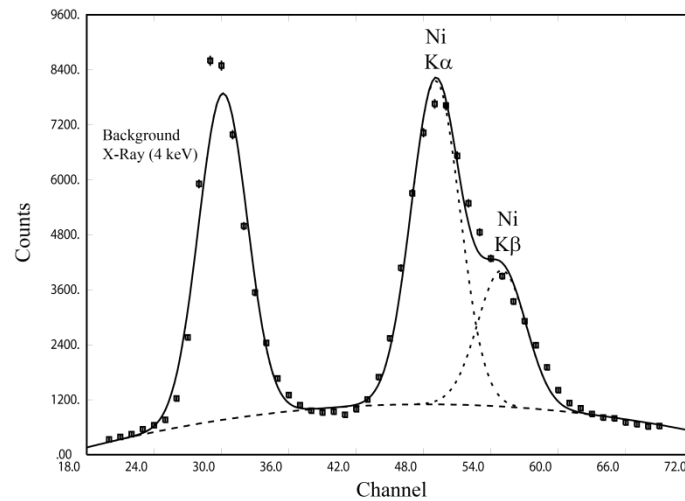
The 10 mL aliquots of samples solution were heated to 70-80°C and 10mL of DMG were added (dimethylglyoxime) 1% (m/v) to selectively precipitate Ni; then, under agitation, a 0.1M  $\text{NH}_4\text{OH}$  solution was added drop by drop until the solution acquired a red color. Finally, an extra amount of 1 mL of DMG was added to warrant the full precipitation of nickel [7-9].

A glass fiber filter was dried by 24h at 50°C and then used to filter the nickel precipitate – this procedure was performed under vacuum to assure proper homogeneity and fixation. This filter was then dried again and covered in Parafilm® for gamma-counting. A total of 4 samples were produced.

### 2.3. Gamma Counting

The samples were analyzed in a 40% Canberra XtRa Extended Range Coaxial HPGe which has an operating range from 3 keV to >10 MeV [10]. In order to minimize the absorption of the Co low-energy x-rays, only an additional foil of Parafilm® was used between the sample and the detector, and the sample was placed upside down, with the precipitate looking down. The samples were counted for 10-15 hours each, and the results of a recent background measurement were subtracted from the sample results (this was especially important for the annihilation peak, as the cobalt x-rays were absent from the background).

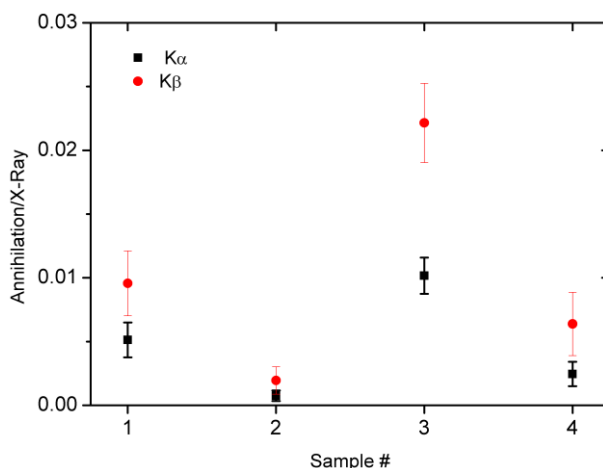
Originally the idea was to analyze the spectra using Canberra's Genie-2000 software, which has been proven to give reliable results in most cases [11], but the complexity of the low-energy spectra in this region (see Fig. 1) led Genie-2000 to be unable to separate the  $K_\alpha$  and  $K_\beta$  peaks in some samples, so for consistency the spectra had to be analyzed manually by fitting the peaks with a Gaussian with an exponential tail, coupled to step function and a parabolic background (taken from [12]) – again, for consistency, the 511 keV peaks were analyzed the same way.



**Figure 1: Fit of the low-energy spectrum of the  $^{59}\text{Ni}$  samples; the lower energy peak is from the background (probably from inside the detector), and it is quite clear that the separation between the  $K_\alpha$  and  $K_\beta$  cobalt x-ray peaks is quite difficult to accomplish.**

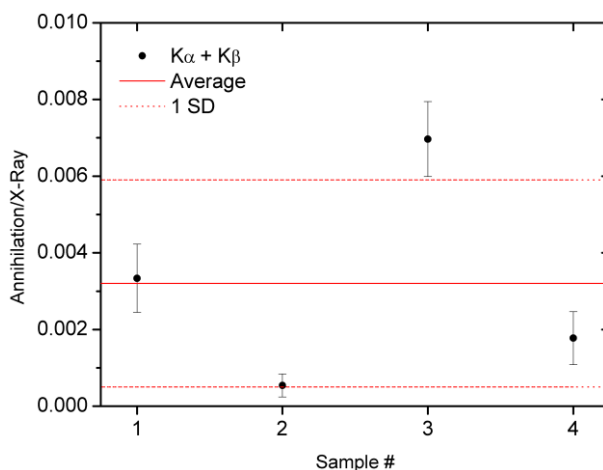
### 3. RESULTS AND DISCUSSION

The ratio between the area of the 511 keV peak and the areas of each of the cobalt x-ray lines is shown in Fig. 2, where it is possible to observe some oscillation among samples, indicating a possible underestimation of the uncertainties; the size of the annihilation peak in sample #2 is well below the other samples, while in sample #3 the x-ray peaks seem to be smaller – samples 1 and 4 are very similar. Moreover, for sample #3 the difference between  $K_\alpha$  and  $K_\beta$  lines is much larger than in the other samples, indicating possible issues in the fit of the low-energy part of the spectrum.



**Figure 2: Ratio of the area of the 511 keV annihilation peak to the areas of each of the relevant cobalt x-rays lines.**

In order to improve the statistics in the analysis and circumvent the difficulty in properly fitting the overlapping peaks in the x-ray spectra (see Fig. 1), the areas of both x-ray lines were summed and the ratio between the area of the annihilation peak and this “summed x-ray” area were determined – this is shown in Fig. 3, where the lines represent the unweighted average and the 1 standard deviation interval. Once again these results indicate that uncertainties may be somewhat underestimated, possibly due to the difficulty in fitting the x-ray spectra and also to some inconsistencies in the geometry of the samples, which can be rather important for very low energies as is the case with the x-ray lines.



**Figure 3: Ratio of the area of the 511 keV annihilation peak to the sum of areas of each of the cobalt  $K_{\alpha}$  and  $K_{\beta}$  x-rays lines.**

These results show that there seems to be a relation between the annihilation peak and the cobalt x-ray lines emitted in the electron capture decay of  $^{59}\text{Ni}$ , with the 511keV peak almost three orders of magnitude lower than the sum of the x-rays; however, for a more precise determination of this ratio, the geometry of the samples will have to be much more similar, as self-attenuation in the 6keV energy region is very large. However, given the difficulties in the

precise measurement and fit of the low-energy x-ray lines, and the fact that the measurement of the 511 keV line can be performed in the regular geometry used in the laboratory, the use of the annihilation peak can prove very handy in daily measurements. It must be stressed, however, that the issue with sample #2, where the annihilation peak was much lower than on the other samples, must be thoroughly investigated before this procedure is considered adequate. More measurements should be performed in order both to check if sample #2 was an isolated case and to properly assess the standard deviation of the ratios.

#### 4. CONCLUSIONS

The analysis of four  $^{59}\text{Ni}$  samples showed that the precise fitting of the low-energy x-ray spectra is tricky, requiring a manual procedure to warrant consistency – this procedure is rather time-consuming and requires a trained analyst to be properly executed. Moreover, it became clear that even this careful fit is unable to precisely divide the area of the complex  $\text{K}_\alpha + \text{K}_\beta$  doublet peak, so that the sum of both peaks seem to be a better measurement; on the other hand, the fit of the 511 keV peak is rather straightforward.

The comparison of area of the annihilation peak and the summed area of the x-ray lines showed that for 2 out of the 4 samples analyzed the results were very consistent. However, for sample #2 the results were much lower – the reasons for that are under investigation, and more measurements shall be required to check if this was just an isolated issue; also, for sample #3 the x-ray lines were somewhat lower than in the other samples, indicating a possible problem with the sample geometry. All these issues have to be analyzed and solved before this method is considered ready for use, but the advantages may prove this method to be useful.

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