

## STRONTIUM-90 ( $^{90}\text{Sr}$ ) DETERMINATION USING LIQUID SCINTILLATION COUNTING

Cheberle, L.T.V.<sup>1,2</sup>, Rosa, M.M.L.<sup>1,3</sup>, Ferreira, M. T.<sup>1</sup> e  
Taddei, M.H.T.<sup>1</sup>

<sup>1</sup> Comissão Nacional de Energia Nuclear / Laboratório de Poços de Caldas (CNEN / LAPOC)

<sup>2</sup> Centro Universitário Octávio Bastos (UNIFEOB)

<sup>3</sup> Comissão Nacional de Energia Nuclear / Instituto de Pesquisas Energéticas e Nucleares (CNEN / IPEN)

### ABSTRACT

This procedure describes a method for separation and measurement of strontium  $^{90}\text{Sr}$  in water, soils, and biological samples. Water samples may be concentrated using evaporation or calcium phosphate coprecipitation. Soils and biological materials must be dissolved using wet digestion. Tracers and carriers must be added before the attack. Radioactive strontium is separated employing a specific resin before determination by liquid scintillation counting using the double energetic window method. The resin is used to concentrate strontium from samples. Stable strontium is used to monitor method yields and correct results to improve precision and accuracy. The presence of elemental strontium in the sample may bias the gravimetric yield determination. If it is suspected that natural strontium is present in the sample, its concentration should be determined by a suitable means (ICP), and the yield calculation properly modified. Sr-Spec resin with an 8M  $\text{HNO}_3$  load solution is used to effectively remove  $^{140}\text{Ba}$  and  $^{40}\text{K}$  isotopes, as well as other interferences from the matrix. Tetravalent plutonium, neptunium, cerium and ruthenium, however, are not removed using nitric acid. The radiochemical procedure was tested using PROCORAD intercomparison exercises and PNI samples.

**Keywords:** Strontium-90, Liquid Scintillation Counting, environmental and biological samples.

### 1. INTRODUCTION

$^{90}\text{Sr}$  is a radioactive isotope of high importance due to its radiotoxicity and relatively long half life ( $T_{1/2} = 28.82$  years) [1]. Strontium can migrate to the environment from nuclear reactors, therefore its control is necessary in environmental samples and food, even those that will be forwarded for export [2].

Industrial, agricultural, mining and energy activities can generate problems of environmental pollution, and the pollutants of radioactive origin are among these, resulting from tests or nuclear accidents, or even from a controlled discharge of waste into the environment [3].

From the point of view of environmental contamination,  $^{90}\text{Sr}$  stands out due to its chemical similarity to calcium, and tends to accompany it biologically, depositing in the bones. Therefore, the monitoring of this radionuclide is of great radioenvironmental importance [1].

The methodology validation ensures the reliability of such methods during the routine use; it can be seen as a process that provides documentary evidence that the method performs according to what is provided for [4].

Some methods using ion exchange resins have been attempted for rapid determination of radioactive strontium in food and environmental samples [5]. In this work, the radioactive strontium was separated using a specific resin prior to the determination by Liquid Scintillation Counting. This methodology was validated by analyzing water samples from the National Intercomparison Program (PNI) organized by the Institute of Radiation Protection and Dosimetry (IRD), and urine samples of the intercomparison test organized by PROCORAD (*Association pour la Promotion du Contrôle de Qualité des Analyses de Biologie Médicale en Radiotoxicologie*).

## 2. MATERIALS AND METHODS

### 2.1. Preparation of water samples

1 mL of SrCO<sub>3</sub> carrier was added in an aliquot of 50 mL in each sample of the Intercomparison National Program (PNI) organized by the Institute of Radiation Protection and Dosimetry (IRD), then it was evaporated and retaken in HNO<sub>3</sub> 8 mol.L<sup>-1</sup>.

### 2.2. Preparation of urine samples

An aliquot of 400 mL of urine sample was used and 1 mL of SrCO<sub>3</sub> carrier was added to each sample. It was then heated on an electric plate until boiling, 30 mL of H<sub>2</sub>O<sub>2</sub> were added and kept under heating in order to obtain a clear sample.

1 mL of phosphoric acid 1 mol.L<sup>-1</sup> and 2 mL of Ca(NO<sub>3</sub>)<sub>2</sub> 1.25 mol.L<sup>-1</sup> were added. Time was given for cooling down until about 70-80 °C and, under stirring, the sample was precipitated with concentrated NH<sub>4</sub>OH until pH reaches 8.5.

The sample was allowed to decant until the following day. The supernatant was then siphoned and the precipitate was diluted in HNO<sub>3</sub> 8 mol.L<sup>-1</sup>.

### 2.3. Radiochemical separation of <sup>90</sup>Sr

For each sample, a column was placed in the support containing Sr-Spec resin (Eichrom Technologies) [6] conditioned with HNO<sub>3</sub> 8 mol.L<sup>-1</sup>, and the samples were percolated in the resin, and subsequently washed with 20 mL of the same acid; this effluent was discarded. <sup>90</sup>Sr was then eluted with 40 mL of HNO<sub>3</sub> 0.05 mol.L<sup>-1</sup> (Fig.1).

0.3g of oxalic acid was added to the eluted fraction. The obtained solution was then heated. Strontium was hot precipitated with concentrated NH<sub>4</sub>OH. The pH of the solution was raised to 9.5-10.

The sample was allowed to rest for approximately 1 hour. The precipitate was filtered through a “blue belt” paper. Finally, the precipitate dried for 1 hour in an oven previously heated at 100°C.

$^{90}\text{Sr}$  recovery factor was determined by gravimetry from the recovery of the Strontium stable carrier.

The filter containing the precipitate was transferred to a scintillation vial, and 1 mL of  $\text{HNO}_3$  1 mol.L<sup>-1</sup> was added to the vial, along with 15 mL of the Ultima Gold AB Packard cocktail (Fig. 1).

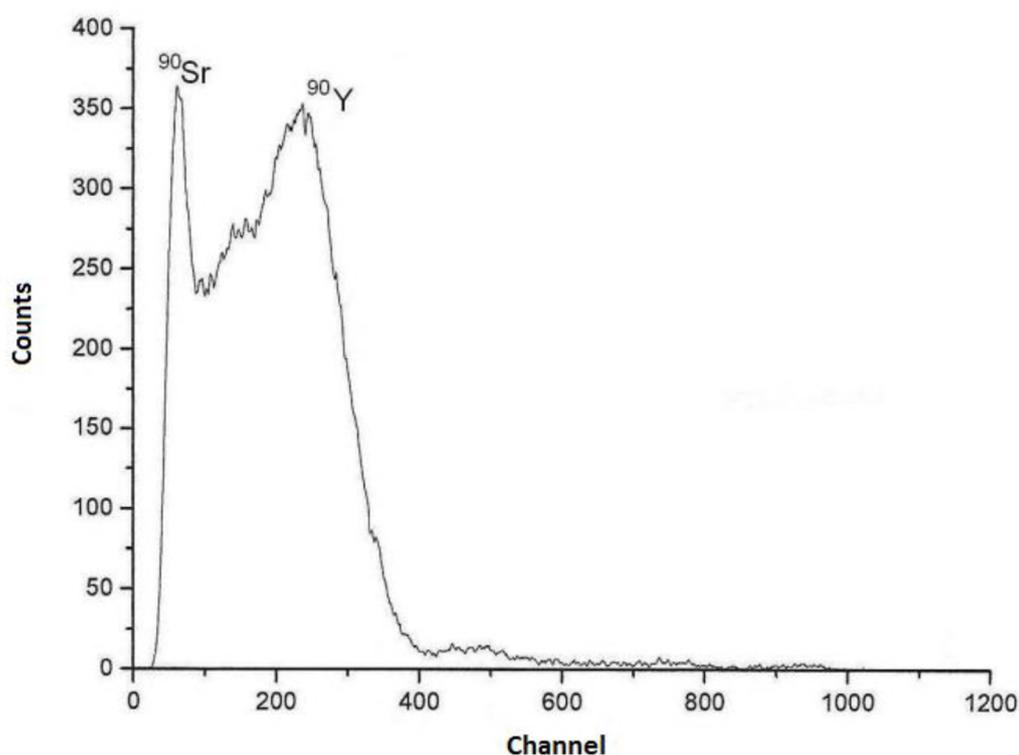


**Figure 1: Adding the Ultima Gold AB Packard cocktail to the scintillation vial**

#### **2.4. Quantification of $^{90}\text{Sr}$**

The determination of  $^{90}\text{Sr}$  concentration was performed using the double energetic window method for 4 hours by Liquid Scintillation Counting (LSC).

In the beta particles spectrum resulting from  $^{90}\text{Sr}$  measured by the LSC, there were two regions which overlapped. The first region, designated by window A and located at the beginning of the spectrum (channels from 25 to 250), included the entire spectrum of  $^{90}\text{Sr}$  and also the low energy range of the  $^{90}\text{Y}$  spectrum, while the second region, designated by window B and located beyond the spectrum (channels 250 to 10000) included the high energy range of the  $^{90}\text{Y}$  spectrum (Fig. 2). In order to determine the activity concentration of  $^{90}\text{Sr}$ , it was necessary to subtract the concentration of  $^{90}\text{Y}$  in the region A by using the amount of  $^{90}\text{Y}$  recorded in the region B and the measurement of ratio between the amounts of  $^{90}\text{Y}$  recorded in region A and region B [7].



**Figure 2: Beta particles spectrum resulting from  $^{90}\text{Sr}+^{90}\text{Y}$  measured by the LSC**

### 3. RESULTS AND DISCUSSION

The methodology used is an adaptation of existing methods, which use Sr-Spec resin, with solution of  $\text{HNO}_3$  8M, used to effectively remove the isotopes of  $^{140}\text{Ba}$  and  $^{40}\text{K}$ , as well as other interferences from the matrix: tetravalent Plutonium, Neptunium, Cerium and Ruthenium. Sr-Spec resin was used to concentrate the Strontium found in the samples.

The stable Strontium is used for determination of the chemical yield of the analysis and to correct the results, improving its accuracy.

Table 1 presents the values of three rounds of PNI and the evaluation of the results obtained at the laboratory.

The results of  $^{90}\text{Sr}$  analyses performed in these intercomparison exercises were evaluated by the IRD, according to:

- Mean (M): mean arithmetical simple, unweighted.
- Standard Deviation (D): The closer to zero the value, the better the performance achieved by the laboratory; for values over three, the analysis system is out of control.

$$D = \frac{(M - RV)}{\frac{RSD}{\sqrt{3}}} \quad (1)$$

- Coefficient of variation (CV): The lower the value, the better the repeatability of the analysis.

$$CV = \left( \frac{M}{SD} \right) 100\% \quad (2)$$

- Good interval of values, between the warning levels (WL): Values  $RV \leq \pm 2$  SDM. Where SDM is the Standard Deviation of Mean of Reference Value.

$$SDM = \frac{RSD}{\sqrt{3}} \quad (3)$$

- Acceptable range of values, between the control limits (CL): Values  $RV < \pm 3$  SDM.

**Table 1. Results of  $^{90}\text{Sr}$  determinations in PNI water samples**

Analysis	Value at Laboratory	Mean (M)	Standard Deviation (SD)	Reference Value (RV)	Reference Standard Deviation (RSD)	D*	CV*	WL*	CL*
April/2013	0.610 ± 0.061	0.657	0.057	0.620	0.093	0.68	9	In	In
	0.640 ± 0.064								
	0.720 ± 0.071								
December/2013	1.220 ± 0.149	1.240	0.018	1.310	0.200	0.60	1	In	In
	1.247 ± 0.152								
	1.254 ± 0.153								
April/2014	0.510 ± 0.051	0.518	0.008	0.540	0.081	0.46	1	In	In
	0.520 ± 0.051								
	0.525 ± 0.052								

\* D – Standard Deviation; CV – Coefficient of Variation; WL – Warning Levels; CL – Control Limits.

Table 1 above indicates that the laboratory results obtained in this work are acceptable regarding these criteria.

Table 2 presents the values of two urine samples of the intercomparison test organized by PROCORAD in 2012 and the evaluation of the results obtained by the laboratory.

**Table 2.  $^{90}\text{Sr}$  determinations in urine samples from PROCORAD 2012**

Sample	Value at Laboratory	Reference Value	Outlier	Deviation (%)
A	4.22 ± 0.13	4.10 ± 0.13	No	3
B	2.11 ± 0.06	2.05 ± 0.06	No	3

The results of  $^{90}\text{Sr}$  analyses performed in these ones of the intercomparison test were evaluated by PROCORAD, according to:

- Outlier: Not presenting outlier means that the results are within the limits.
- Deviation: This is calculated according to the reference values.

Table 2 above indicates that the laboratory results obtained are acceptable regarding these criteria.

The limit of detection for this technique was  $0.58 \text{ Bq.L}^{-1}$ , calculated using the formula proposed by Currie [8]:

$$L_d = \frac{2.71 + 3.29\sqrt{t \cdot R_b}}{60 \cdot t \cdot \text{Eff} \cdot Q} \quad (4)$$

Where  $R_b$  is the count rate in counts per minute (cpm) of the blank,  $\text{Eff}$  is the counting efficiency,  $t$  is the time counts, and  $Q$  is the quantity of sample.

The counting efficiency ( $\text{Eff}$ ) is obtained by:

$$\text{Eff} = \frac{R_{st} - R_b}{A_{st} \cdot 60 \cdot Y} \quad (5)$$

Where  $R_{st}$  is the count rate in cpm of the  $^{90}\text{Sr}$  standard,  $A_{st}$  is the activity of the standard (in Bq).

In order to validate the chemical procedure, in water and urine samples were analyzed using liquid scintillation technique. Results of analysis shown reveal good agreement between measured and assigned values for  $^{90}\text{Sr}$  for both intercomparison exercises that were showed in tables 1 and 2. A study with other reference materials will be held in the future to validate the different matrices that this methodology can be employed.

#### 4. CONCLUSION

The results showed that  $^{90}\text{Sr}$  analysis method by LSC has a good accuracy, and it is possible to validate the assay for determining the activity concentration of this radionuclide by analyzing water samples from the National Intercomparison Program (PNI) and the urine samples from the intercomparison test organized by PROCORAD.

It is known that  $^{90}\text{Sr}$  is a radioactive isotope of high importance due to its radiotoxicity and relatively long half life. It can migrate to the environment from nuclear reactors, therefore the methodology validation for its determination was of great importance. This methodology can be applied to control environmental, biological and food samples.

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