

## NEW METHOD FOR $^{90}\text{Sr}$ DETERMINATION IN LIQUID SAMPLES

A. ALVAREZ, N. NAVARRO, S. SALVADOR

Radiological Protection Division, CIEMAT-IMA,  
Avda Complutense 22, 28040 Madrid (Spain)

(Received December 30, 1994)

A method has been developed for measuring  $^{90}\text{Sr}$  activity in liquid samples. After concentrating strontium from the sample by coprecipitation with calcium phosphate, the residue is dissolved in 8N  $\text{HNO}_3$  and passed through an extraction chromatographic column (Sr.Spec) containing a new material that selectively retains strontium. This is eluted from the column with 0.05N  $\text{HNO}_3$  and counted by liquid scintillation. Measurement is performed using a double window method, that allows a rapid and single determination of  $^{90}\text{Sr}$ .

Strontium-90 is one of the most important fission products generated in nuclear operations. Its measurement has acquired considerable attention in environmental and personal monitoring programs, due to its long physical and biological half-life (28.6 and 49.3 years, respectively) and its accumulation in bone tissues since it follows the same metabolic behavior that calcium.

Both radionuclides  $^{90}\text{Sr}$  and its daughter  $^{90}\text{Y}$  are pure  $\beta$ -ray emitters ( $E_{\text{max}}$ : 546 keV and 2280 keV, respectively), and their determination has been traditionally made counting  $^{90}\text{Sr}/^{90}\text{Y}$  total  $\beta$ -activity in a proportional counter, after a radiochemical separation. This classical method has been based in the difference between solubility of calcium and strontium nitrates in concentrated nitric acid.<sup>1–3</sup> Such procedure permits the handling of large volume samples, it is very selective and provides good decontaminations for the majority of interferences. However, its main disadvantage is that requires working with fumant nitric acid, which gives off noxious fumes, which is very corrosive and presents fire hazard.

To overcome this disadvantage, alternative methods have been developed that include  $^{90}\text{Sr}$  separation by ion-exchange.<sup>4,5</sup> The main inconveniences of this isolation technique are laboriosity and complexity together with time consuming.

Recently, a new chromatographic extraction material has appeared, that allows selective strontium isolation in acid solution.<sup>6,7</sup> This new material, constituted by macrocyclic polyethers dissolved in aliphatic alcohols or ketones, is commercially available both as resins and columns. Its application to strontium radiochemical separation has notably improved the determination of this radionuclide. In this work the

application of this new material to the rapid separation of radiostrontium from liquid samples is described. Measurements were carried out by liquid scintillation spectrometry. Complications in counting owing to the ingrowth of  $^{90}\text{Y}$  were overcome by applying a double window method, that permits the  $^{90}\text{Sr}$  determination without waiting until radiochemical equilibrium has been reached or achieving theoretical calculus for  $^{90}\text{Y}$  ingrowth.

This method has been developed for the analysis of urine samples, within a monitoring programs for workers exposed to strontium and also for the analysis of aqueous samples.

### Experimental

*Reagents:* All the reagents used were of analytical grade. Calcium carrier ( $40 \text{ mg Ca} \cdot \text{ml}^{-1}$ ) was prepared from 205 g of  $\text{Ca}(\text{NO}_3)_2$  in one litre of deionized  $\text{H}_2\text{O}$ . The radioisotopes  $^{90}\text{Sr}/^{90}\text{Y}$  were obtained from CEA (France). The Sr.Spec columns were obtained from EICrom Industries, Inc. (USA). The liquid scintillator was from Instagel, Packard Co., USA.

*Equipment:* Beta-counting were performed with a Canberra Packard (Model 2500 TR) liquid scintillation spectrometer, using low potassium glass vials (Packard Co., USA).

*Preparation of samples:* Urine samples with volumes usually higher than one litre require a previous concentration, before chemical separation.  $^{90}\text{Sr}$  is coprecipitated as phosphate from the bulk urine sample using  $\text{Ca}^{2+}$  as carrier. The sample was placed in a glass beaker containing a magnetic stirrer. Following, 60 ml of concentrated  $\text{HNO}_3$  were added, and the beaker was placed into a water-bath, heating until the temperature 70–80 °C. Stirring continuously, 1 ml of concentrated  $\text{H}_3\text{PO}_4$ , 2 ml of  $\text{Ca}(\text{NO}_3)_2$  and 1 ml of Sr(II) were added, heating at constant temperature during half an hour. Then concentrated  $\text{NH}_3$  was added until calcium phosphate precipitate appeared carrying the strontium, and the sample was heated for 1 hour. The stirring bar was then removed and the precipitate was allowed to settle for at least 6 hours.

The supernatant liquid was decanted and transferred to a bottle, then centrifuged at 2500 rpm for 10 minutes. The supernatant liquid was discarded and the precipitate transferred to a glass beaker with three 5 ml portions of concentrated  $\text{HNO}_3$ . The beaker was heated to dryness on a hot plate. After that, several 10 ml portions of concentrated  $\text{HNO}_3$  were added, until the sample was free of organics. If the destruction of organic matter was not complete, the residue was calcined in a furnace at 500 °C.

The remaining residue was then dissolved in 10 ml of 8N  $\text{HNO}_3$ , and introduced in the chromatographic column (Sr.Spec).

*Sample elution:* The proposed method for the chromatographic separation is based on the publication of DIETZ and HORWITZ.<sup>8</sup> Prior to it, the column was rinsed successively with a few millilitres of 3N  $\text{HNO}_3$  and a few millilitres of 8N  $\text{HNO}_3$ . Following, the sample solution consisting of 10 ml of 8N  $\text{HNO}_3$  in which the residue remaining after precipitation was dissolved, was passed through the column. Then it was washed with three 5 ml portions of 8N  $\text{HNO}_3$ . Finally, strontium was eluted into a glass scintillation vial with a 5 ml aliquot of 0.05N  $\text{HNO}_3$ .

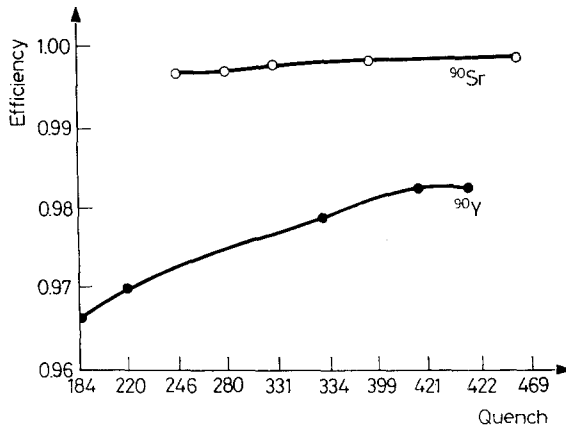


Fig. 1. Efficiency curves for  $^{90}\text{Sr}$  and  $^{90}\text{Y}$  obtained by CIEMAT/NITS calibration method

*Sample counting:* In a glass scintillation vial 14 ml of Instagel and 1 ml of 0.05N  $\text{HNO}_3$  containing the eluted strontium were added. Then the samples were counted for 30 minutes each using a double window method. Establishment of counting regions for  $^{90}\text{Sr}$  and  $^{90}\text{Y}$  was made taking into account the quench level of the sample. Previously, both radionuclides were calibrated using CIEMAT/NITS calibration method.<sup>9</sup> Radiochemically pure solutions of both radionuclides were obtained from a solution of  $^{90}\text{Sr}$  and  $^{90}\text{Y}$  in equilibrium. A set of  $^{90}\text{Sr}$  and  $^{90}\text{Y}$  standards with different level of quench were prepared from those pure solutions. Measurement of these standards allowed us to obtain the efficiency curves shown in Fig. 1. At the same time,  $^{90}\text{Sr}$  standards permitted us to establish the counting region for strontium (Region A). This was carried out taking into account the relation between the final point of the spectrum of these pure  $^{90}\text{Sr}$  standards and their quench level. Counting Region A for a particular sample is fixed by interpolation between the appropriate standards, those that bound quench level of the sample. Second counting Region (B) extends from the limit of Region A until the end of the spectrum.

Once fixed counting regions and calculated  $^{90}\text{Y}$  efficiencies in both regions for those standards that bound the sample, counting efficiencies for  $^{90}\text{Y}$  in the sample can be determined by interpolation.

Sample counting in both regions allows us to determine the activity in the sample using the following expressions applied in double window methods. As it is shown,  $^{90}\text{Sr}$  activity was determined subtracting contribution of  $^{90}\text{Y}$  in Region A to total counts in this region:

$$A(^{90}\text{Y}) = \frac{N_B}{E_B(^{90}\text{Y})} \quad (1)$$

where  $N_B$  – CPM in Region B,  
 $E_B(^{90}\text{Y})$  –  $^{90}\text{Y}$  efficiency in Region B;

$$A(^{90}\text{Sr}) = \frac{N_A - A(^{90}\text{Y})E_A(^{90}\text{Y})}{E(^{90}\text{Sr})} \quad (2)$$

where  $N_A$  – CPM in Region A,  
 $E_A(^{90}\text{Y})$  –  $^{90}\text{Y}$  efficiency in Region A,  
 $E(^{90}\text{Sr})$  –  $^{90}\text{Sr}$  efficiency.

## Results and discussion

The proposed method combined with liquid scintillation spectrometry, notably improves the traditionally used methods. The time for sample preparation is considerably reduced, with a good coprecipitation yield, never below 80–85%. This figure was calculated gravimetrically, weighting the  $\text{Sr}(\text{NO}_3)_2$  obtained after elution.

### *Elution curve*

Strontium was strongly retained from acid solutions on the Sr.Spec column. The corresponding elution curve was experimentally obtained using  $^{85}\text{Sr}$  as tracer which is a beta/gamma emitter with  $\gamma$ -emission at 513.9 keV (intensity = 99.2%). The eluted fraction containing strontium was collected in small fractions of 1 ml, and each vial was measured by  $\gamma$ -spectrometry. Figure 2 shows the results of this experiment. Almost all strontium was eluted in the first 3 ml of 0.05N  $\text{HNO}_3$ , without loss of strontium in the scrubbing elution.

A study of the main interferences was also performed. Ca, Ba and Ra, that belongs to the same chemical group as Sr, constitute the principal interferences. Volume

involved in strontium elution depends on the concentration of the acid solution utilized as mobile phase. Ca, Ba and Ra are removed from the column in the washing step with 8N  $\text{HNO}_3$ . Under these conditions strontium, that would need more 8N  $\text{HNO}_3$  volume to be eluted from the column, is completely isolated from the main interferences. In fact, elution of strontium was not observed in any case until at least 20 bed volumes (40 ml)

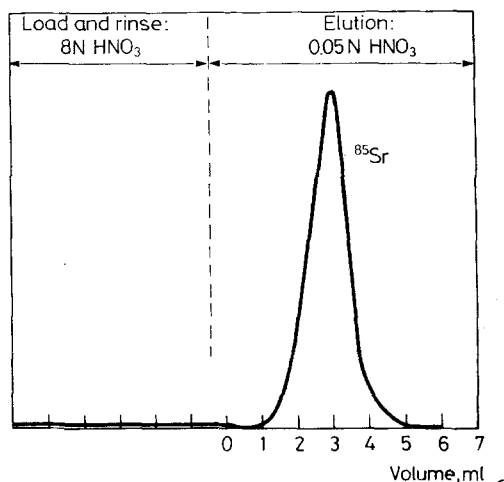


Fig. 2. Strontium elution curve

of loading/washing solution had been passed through the column, whereas Ca, Ba and Ra were entirely stripped from the column with 10 bed volumes (20 ml) of the same loading solution. Volume involved in strontium elution depends on the acidity of the nitric solution used as mobile phase. With the conditions studied, only 5 ml of 0.05N  $\text{HNO}_3$  were required for its complete elution from the column.

The experience has shown that  $^{137}\text{Cs}$  appears in many samples containing  $^{90}\text{Sr}$ . It is the most important radiochemical interference since it is also a  $\beta$ -emitter ( $E_{\text{max}}$ : 551 and 1173 keV) and its spectrum overlaps with strontium's one. Under the elution conditions that had been considered, complications appeared with samples containing high concentration of salts. In such cases, strontium was not retained strongly enough, being partly stripped from the column with the loading solution. In order to obtain its complete isolation from caesium, a sample dilution was performed before introducing the sample into the column. It was observed that with decreasing salt concentration, the retention of strontium on the column enhanced, allowing the separation of these radionuclides.

Yttrium-90 ingrowth since strontium is eluted from the column until its measurement, introduces a difficulty for the measurement by liquid scintillation spectrometry, since spectra of both radionuclides overlap in a certain zone. Figure 3 shows a characteristic spectrum from a  $^{90}\text{Sr}/^{90}\text{Y}$  solution.

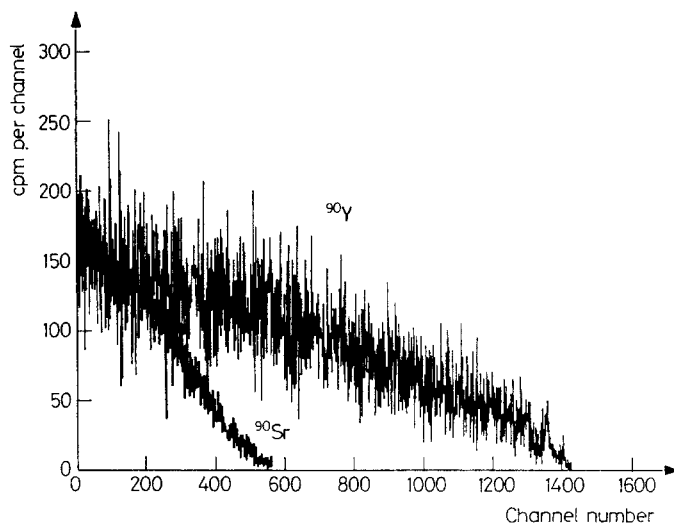


Fig. 3. Characteristic spectrum of a  $^{90}\text{Sr}/^{90}\text{Y}$  solution

As earlier exposed, previous workers have often resolved this spectral overlap by achieving mathematical approaches to calculate  $^{90}\text{Y}$  ingrowth or waiting a lengthy period of time before sample measurement, to assure that radiochemical equilibrium has been reached. On the contrary, the proposed method allows the measurement of the sample just after strontium separation, what represents a considerable time economizing in performing a radiostrontium determination.

#### *Limit of detection*

According with Currie criterium<sup>10</sup> the limit of detection (DL) is defined so that, if an amount of strontium equal to the DL exists in the sample, it will be detected with a 95% probability. Using the conditions proposed in the present work (i.e., a 11 volume sample, 85% chemical recovery, counting times of 30 minutes and assuming the counter background of 50 cpm in the entire spectrum), the minimum detectable amount for  $^{90}\text{Sr}$  would be  $0.12 \text{ Bq} \cdot \text{l}^{-1}$ . For the specific case of urine samples and assuming a human daily excretion of 1.4 litres, the minimum detectable amount calculated applying the

same criterium is  $8 \cdot 10^{-2} \text{ Bq} \cdot \text{l}^{-1} \cdot \text{day}^{-1}$ . Such value makes possible the application of this method for dosimetric purposes.

#### *Dosimetric application*

The presented method is adequate for  $^{90}\text{Sr}$  dosimetric control by urine analysis. The  $^{90}\text{Sr}$  Annual Limits of Incorporation (ALI) recommended by ICRP-54,<sup>11</sup> are  $7 \cdot 10^5 \text{ Bq}$  (class D) and  $1 \cdot 10^5 \text{ Bq}$  (class Y). In the case of a quarterly routine monitoring (90 days monitoring interval), the predicted activity as fraction of intake are  $3.4 \cdot 10^{-4}$  and  $1.7 \cdot 10^{-5} \text{ Bq}$  for class D and Y, respectively.

Considering an investigation level for routine monitoring according to the following expression;

$$IL_R = \frac{3}{10} \cdot \frac{ALI}{N} \quad N = 4 \quad (3)$$

the predicted activities in urine for this reference level would be  $17.8 \text{ Bq} \cdot \text{day}^{-1}$  (class D) and  $0.13 \text{ Bq} \cdot \text{day}^{-1}$  (class Y), in both cases above the limit of detection obtained with the proposed method.

### **Conclusions**

Sample preconcentration by strontium coprecipitation as phosphate, in combination with extraction chromatography using Sr.Spec column provide a simple and effective procedure for the separation of strontium from liquid samples. Liquid scintillation spectrometry combined with this procedure allows more rapid determinations, since avoids waiting until radioactive equilibrium has been reached or making calculations for  $^{90}\text{Y}$  ingrowth. The limit of detection obtained combining both methods, justify its application for  $^{90}\text{Sr}$  dosimetric control in routine monitoring programs by urine analysis.

The presented method has been successfully applied to  $^{90}\text{Sr}$  determination in urine and liquid samples, and it could be applied to any matrix with appropriate modifications.

\*

The authors wish to thank Dr. A. Grau CARLES for his assistance in this work.

### References

1. W. F. HILLEBRAND, G. E. F. LUNDELL, H. A. BRIGHT, J. I. HOFFMAN, *Appl. Inorg. Anal.*, 2nd ed., Wiley, New York, 1953.
2. N. H. FURMAN, *Scott's Standard Methods of Chemical Analysis*, Van Nostrand, New York, 1939.
3. H. H. WILLARD, E. W. GOODSPEED, *Ind. Eng. Chem. Anal. Ed.*, 8 (1936) 414.
4. H. L. VOLCHOCK, G. DEPLANQUE, *EML Procedure Manual*, 26th ed., HASL-300, Environmental Measurement Laboratory, U.S. Dept. of Energy, New York, 1983.
5. H. AMANO, N. YANASE, *Talanta*, 37 (1990) 585.
6. E. P. HORWITZ, M. L. DIETZ, D. E. FISHER, *Solv. Extr. Ion Exch.*, 8 (1990) 199.
7. E. P. HORWITZ, M. L. DIETZ, D. E. FISHER, *Solv. Extr. Ion Exch.*, 8 (1990) 557.
8. M. L. DIETZ, E. P. HORWITZ, D. M. NELSON, M. WAHLGREN, *Health Phys.*, 61 (1991) 871.
9. A. GRAU MALONDA, *Int. J. Appl. Radiation Isotopes*, 33 (1982) 371.
10. L. L. CURRIE, *Anal. Chem.*, 40 (1958) 586.
11. ICRP-54, *Individual Monitoring for Intakes of Radionuclides by Workers: Design and Interpretation*, *Annals of ICRP*, Vol. 19, No. 1-3, 1988.