

Determination of ^{94}Nb in radioactive wastes using extraction chromatography and gamma spectrometry

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Abstract A radiochemical methodology for the determination of ^{94}Nb in low-level radioactive wastes from nuclear power plant was proposed. Although ^{94}Nb is a strong gamma emitter, its concentration in radioactive waste samples is usually several orders of magnitude lower than that of other β - γ emitters, whose emissions interferes in the detection of the emission lines of ^{94}Nb . The procedure involves acid digestion, precipitation, cation exchange chromatography by using Amberlite IRA120 resin, extraction chromatography by using TEVA resin to isolate the Nb and the gamma spectrometry to its measurement. The chemical yield was 70% in average. Samples of evaporator concentrate and spent resin were analyzed. For the samples of the evaporator concentrate, the results obtained were below $L_D = 9.59 \times 10^{-4} \text{ Bq g}^{-1}$. For the spent resin an average result of $1.54 \times 10^2 \text{ Bq g}^{-1}$ was obtained.

Keywords Niobium · TEVA resin · Radioactive wastes · Extraction chromatography · Gamma spectrometry

Introduction

Final disposal of low and intermediate level (LLW and ILW) of radioactive waste have to meet certain requirements of regulations and one of them is the specification of the radionuclide inventory of nuclear power plants [1]. The safety planning for disposal takes into account especially long half-life radionuclides. For their control in waste packages, it is necessary to ensure compliance with the fixed waste acceptance criteria in order to avoid any potential impact of the radioactive contaminants on the environment of the repository site. Furthermore, ^{94}Nb enters the environment from the dismantling activities associated with nuclear reactor decommissioning [2]. A long postponement before decommissioning may represent the major contribution to the personnel exposure.

Many of the important long lived radionuclides contained in the radioactive waste are difficult to measure (DTM) from outside of the waste packages using non-destructive techniques because either they have low activities or are non-penetrating beta or alpha emitting nuclides (i.e. non-gamma emitters). In the case of ^{94}Nb for example, the difficulty is related to its low energy. Identification of these DTM nuclides requires methods that, in general, involve analysis of waste samples using complex chemical analysis to separate the various radionuclides for measurement.

The ^{94}Nb has a long half-life, 2.03×10^4 year and is a β - γ emitter, produced according to the reaction $^{93}\text{Nb}(n, \gamma)^{94}\text{Nb}$. The presence of relatively high levels of Nb in stainless steel (5–300 ppm) and Inconel (400–50,000 ppm) would lead to the production of significant amounts of the long lived ^{94}Nb in reactor core materials [3].

Although ^{94}Nb is a high energy γ -emitter with peaks in 871 and 703 keV [4], its concentration in radioactive waste samples is typically several orders of magnitude smaller

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than that of the other β - γ emitters, such as ^{60}Co and $^{110\text{m}}\text{Ag}$, normally present in this type of sample. This fact makes it difficult to measure by direct γ spectrometry in large aliquots of samples due to the high activity of these interfering radionuclides. Thus the separation and purification of these samples are required.

Niobium belongs to the fifth group of the elements in the periodic table, and exists in the four oxidation states from +II to +V being Nb(V) the most stable oxidation state of this element in aqueous solution. The Nb_2O_5 is the most stable oxide, which is very insoluble in common acids but dissolves in HF medium, forming the complex NbOF_5^{2-} [5]. The formation of this complex is the basis of some niobium separation processes such as, for example, the work presented by Espartero [6].

In this work, Espartero et al. [6] proposes a radiochemical separation method of $^{93\text{m}}\text{Nb}$ and ^{94}Nb from other β - γ emitters present in radioactive waste streams, based on the selective precipitation of niobium. The detection limits achieved were 8 times lower for ^{94}Nb and five times lower for $^{93\text{m}}\text{Nb}$ comparing to those obtained by direct γ -ray spectrometry without radiochemical separation. Osváth et al. [7] developed a radiochemical method for determination of Nb isotopes and the separation was based on the insolubility of Nb oxides and the retention of the fluoric complexes on anion exchange resin. The calculated limits of detection for ^{94}Nb without chemical separation were between 0.024 and 1.8 Bq mL^{-1} , depending on the sample composition, and after chemical separation was $6.3 \times 10^{-4} \text{ Bq mL}^{-1}$. Remenec et al. [3] used cation and anion exchange resins in the ^{94}Nb analysis in samples from parts of a dismantling nuclear reactor. The procedure was successful in the removal of $^{110\text{m}}\text{Ag}$, Co isotopes, ^{54}Mn , Fe and Ni isotopes. The ^{94}Nb was counted in a gamma spectrometer and the recoveries were $98 \pm 3\%$. In another work, Remenec et al. [8] studied the behaviour of ^{95}Zr and ^{95}Nb on a TEVA resin. It was investigated the behavior of zirconium and niobium isotopes in different acids, and the hydrofluoric acid was chosen as the best complexing reagent for the separation of zirconium and niobium at low concentrations of the acid (0.5 mol L^{-1}). Chemical recoveries of niobium and zirconium were in the range of 90–98%. The activities concentrations of ^{94}Nb were in the range of 10^1 – 10^3 Bq g^{-1} . Dulanská et al. [9] described a sequential method employing anion exchange resin or TEVA resin for the determination of ^{93}Zr , ^{94}Nb , ^{99}Tc and ^{126}Sn in radioactive wastes samples. For ^{94}Nb the average chemical recovery was 84%, using ^{95}Nb as tracer. Lee et al. [10] optimized a sequential procedure for the determination of $^{59/63}\text{Ni}$, ^{55}Fe , ^{90}Sr , ^{94}Nb and ^{99}Tc for various types of radioactive wastes, using anion exchange and extraction chromatography. The reliability of the procedure was evaluated by measuring the recovery of chemical carriers

added to a synthetic radioactive waste solution. For Nb the chemical yield was $95.3 \pm 1.9\%$, measured by ICP-AES (Inductively Couple Plasma Atomic Emission Spectrometer).

The lack of standard ^{94}Nb in the specialized market makes necessary the use of analytical alternative routes, for example the use of γ -emitters standards with energies close to the ^{94}Nb and similar chemical behavior. Espartero et al. [6] did not use any standard certificate for referencing his methodology, he used a Nb(V) carrier solution for the chemical yield calculations and Osváth et al. [7] used as a standard solution a mixture of ^{95}Zr and ^{95}Nb tracers. In the methodology proposed in this work, a certified niobium standard solution was used as a carrier and as a tracer for the chemical yield determination. The stable Nb was irradiated in a research reactor originating $^{94\text{m}}\text{Nb}$ ($t_{1/2} = 6.26 \text{ m}$, $E_\gamma = 871.09 \text{ keV}$, $I_\gamma (\%) = 0.5$) which was counted by gamma spectrometry.

The main objective of this work is to establish a methodology based on different procedures published in the specialized literature to determine the ^{94}Nb presence in low- and intermediate-level radioactive waste samples from Brazilian nuclear power plants.

Experimental

Reagents and apparatus

All reagents used were of analytical grade. The niobium standard solution, SRM 3137, came from NIST (National Institute of Standards & Technology) with a certified value of $9.986 \text{ mg g}^{-1} \pm 0.032 \text{ mg g}^{-1}$. The certified standard solutions of ^{60}Co ($35.441 \text{ Bq mL}^{-1}$) and ^{137}Cs ($747.572 \text{ Bq g}^{-1}$) were supplied by Instituto de Radioproteção e Dosimetria (IRD), Rio de Janeiro, Brasil. Cationic exchange resin (Amberlite IRA120) was purchased from Vetec. The TEVA resin, pre-packed in 2 mL columns as an extraction chromatographic material, is available from Eichrom Technologies, USA. The HPGe detector (Canberra, USA, 50% relative efficiency) was used for the gamma spectrometry analysis and the samples irradiation for posterior neutron activation analysis was performed in a Triga Mark 1 research reactor.

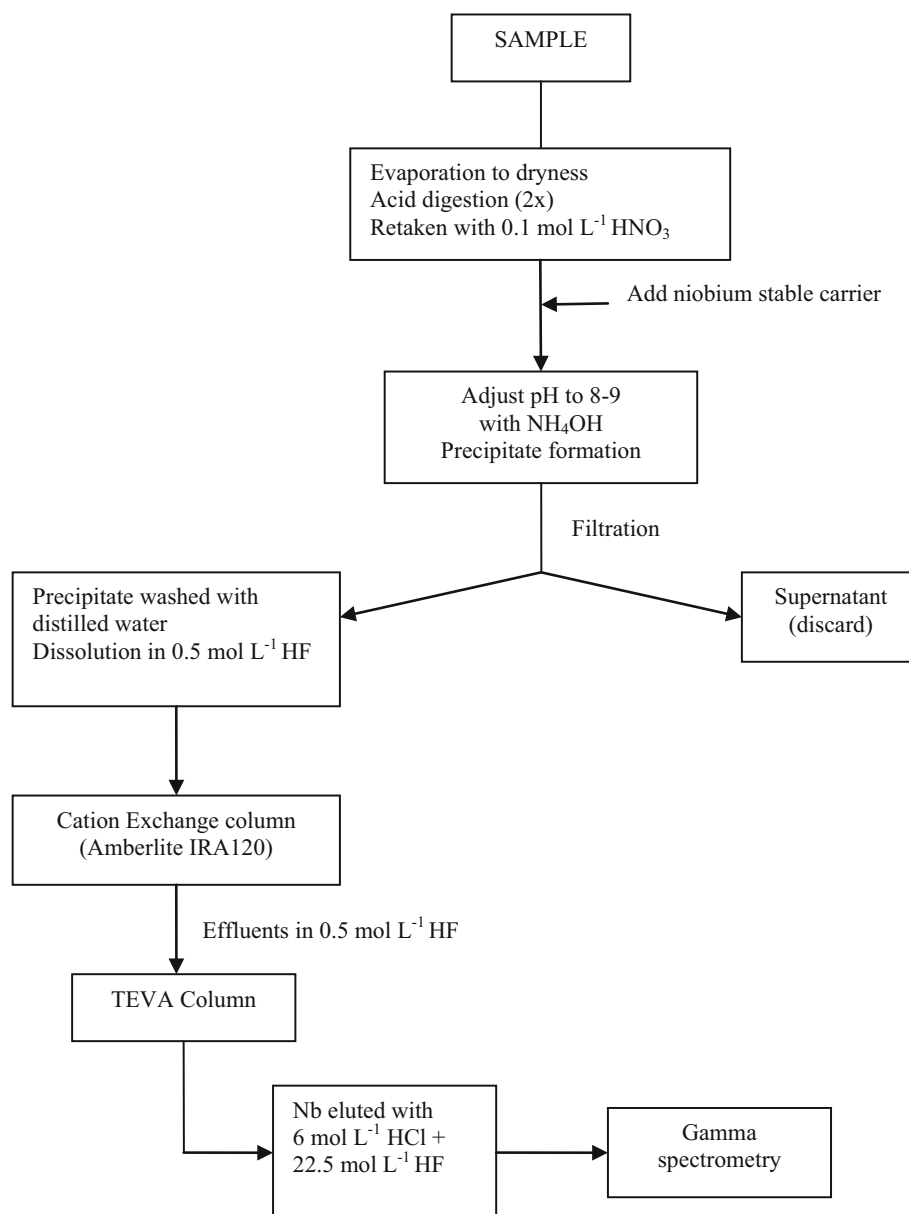
Methodology

The proposed methodology consisted primarily in the acid digestion of the sample and in the formation of insoluble niobium oxide precipitate by the use of a niobium carrier, based in the analytical procedure of Espartero et al. [6]. A cationic exchange resin [3], to remove $^{110\text{m}}\text{Ag}$ and Co isotopes and a TEVA extraction resin [8] to separate Nb

and Zr isotopes were employed in the process of separation and purification of the sample.

A flowchart of the procedure is shown in Fig. 1. An aliquot of 40 mL of the sample (evaporator concentrate and spent resin) was heated in a hot plate up to evaporation to dryness. Then an acid digestion was performed twice using 20 mL of concentrated nitric acid and 15 mL of 30% H_2O_2 . The residue was dissolved in 50 mL of 0.1 mol L^{-1} nitric acid solution with the addition of 1 mL of stable niobium carrier solution. The pH of the resulting solution was corrected to 8–9 with 25% ammonia hydroxide for the niobium oxide precipitation. The resulting precipitate was filtered in a Whatman 42 filter paper, washed with distilled water and retaken with 15 mL of 0.5 mol L^{-1} HF.

Fig. 1 Flowchart of ^{94}Nb separation and purification



The cationic exchange resin was packed in a 2 mL polypropylene column from Eichrom and then conditioned with 5 mL of 0.5 mol L^{-1} HF. The sample was loaded onto the column, which was rinsed with 2 mL of 0.5 mol L^{-1} HF. The eluates from the column were collected in a polyethylene vial and loaded onto a pre-packed TEVA resin which was conditioned with 10 mL of 0.5 mol L^{-1} HF. The column was rinsed twice with 10 mL of 0.5 mol L^{-1} HF. Niobium was eluted from the column with 20 mL of $6 \text{ mol L}^{-1} \text{ HCl} + 22.5 \text{ mol L}^{-1} \text{ HF}$ solution. After elution from the column the ^{94}Nb was immediately counted in the HPGe detector at 871 and 703 keV lines.

To calculate the yield of the process of separation and purification of ^{94}Nb , a simulated sample was prepared

containing Nb stable standard solution, ^{60}Co standard solution and ^{137}Cs standard solution. The Nb stable standard solution was used as a substitute for ^{94}Nb standard solution. An aliquot of this solution was irradiated, forming $^{94\text{m}}\text{Nb}$, which was measured by gamma spectrometry. The remaining solution was submitted to processes of separation and purification and an aliquot of the final solution was irradiated and measured by gamma spectrometry.

The irradiation of the aliquot was performed in the Triga Mark 1 reactor, with the formation of $^{94\text{m}}\text{Nb}$ by ^{93}Nb activation. The $^{94\text{m}}\text{Nb}$ was measured by gamma spectrometry in the HPGe detector at 871.09 keV line.

Results and discussion

The chemical yield of the process of separation and determination of ^{94}Nb , based on gamma spectrometry of $^{94\text{m}}\text{Nb}$ formed by neutron activation of ^{93}Nb , added to the sample as a tracer and a carrier (for the precipitate formation), was in a range of 65–75%. These values are comparable with those encountered in the literature. Espartero et al. [6]

reported a chemical yield ranging from 50 to 60% and Osváth et al. [11] founded values between 30 and 89%. The use of $^{94\text{m}}\text{Nb}$ obtained from irradiation of ^{93}Nb as a chemical yield monitor of the separation and purification process of niobium has not been reported yet in the literature.

The Lower Limit of Detection, L_D , was determined according to Currie [12] based on Eq. (1).

$$L_D = \frac{2.71 + 4.66(\sigma_b)}{T \cdot \text{Eff} \cdot Y \cdot \text{wt} \cdot 2.22}, \quad (1)$$

where L_D is the Lower Limit of Detection, σ_b is the standard deviation of background counting, T is the time of background counting, Eff is the efficiency of counting, Y is the chemical yield and wt is the weight of sample. For the evaporator concentrate samples analyzed the results obtained were below the L_D , $9.59 \times 10^{-4} \text{ Bq g}^{-1}$. Osváth et al. [7] obtained a L_D of $6.3 \times 10^{-4} \text{ Bq g}^{-1}$, a value very close to our result.

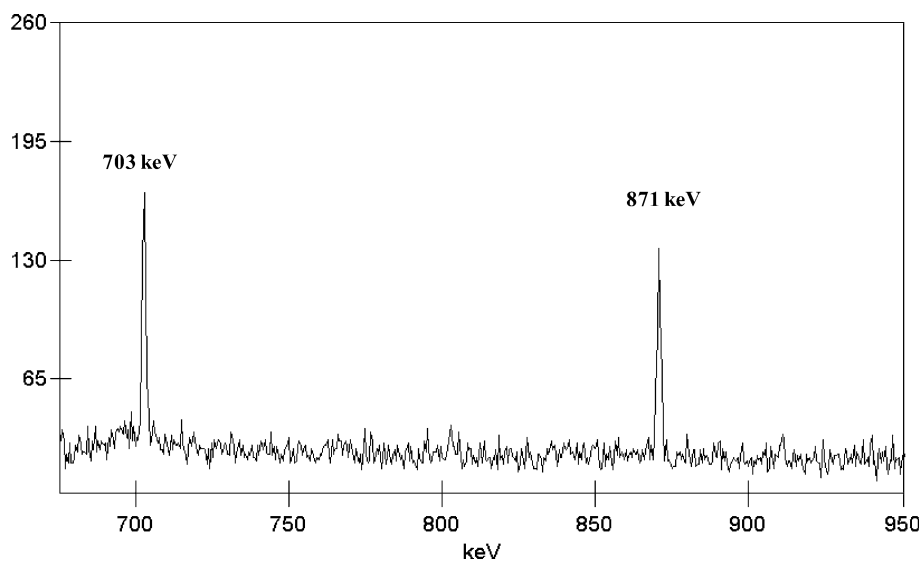
Table 1 shows the results for a spent resin sample experiments. These results refers to different aliquots of the same spent resin sample. The average result obtained was $(1.54 \pm 0.13) \times 10^2 \text{ Bq g}^{-1}$. The experiments were performed by varying the amount of stable Nb carrier added, sample 5 (with addition of 0.5 mL carrier solution) and sample 6 (with addition of 2.0 mL carrier solution) in order to verify whether the amount of the carrier affected the precipitate formation of niobium oxide and no significant differences were observed in the results. When comparing all the results shown in Table 1 it was not observed any discrepancy between the values obtained.

Figure 2 presents the gamma spectrum obtained from a radioactive waste sample with the two characteristic peaks of ^{94}Nb at 703 and 871 keV. It was not observed any other interfering peaks in the spectrum, confirming that the use of a cation exchange resin, Amberlite IRA 120 and an

Table 1 Results of ^{94}Nb obtained for spent resin samples

| Sample | Activity concentration (Bq g^{-1}) |
|--------|---|
| 01 | $1.42 \times 10^{+2}$ |
| 02 | $1.38 \times 10^{+2}$ |
| 03 | $1.72 \times 10^{+2}$ |
| 04 | $1.55 \times 10^{+2}$ |
| 05 | $1.51 \times 10^{+2}$ |
| 06 | $1.63 \times 10^{+2}$ |
| Mean | $(1.54 \pm 0.13) \times 10^{+2}$ |

Fig. 2 Gamma-ray spectrum of a radioactive waste sample after purification



extraction chromatographic resin, TEVA, were successful in the separation and purification of the analyzed radioactive samples.

Conclusions

From the results obtained, it was concluded that the radiochemical methodology presented was very successful for the separation and determination of ^{94}Nb in radioactive waste samples. The chemical yield obtained with values ranging from 65 to 75% are comparable with values found by Espartero et al. [6] and Osváth et al. [11]. The β - γ emitters that could interfere in the measurements of ^{94}Nb were effectively removed from the samples as showed by the gamma-ray spectrum.

The evaporator concentrate samples showed results below $L_D = 9.59 \times 10^{-4} \text{ Bq g}^{-1}$. This value is very close to the value reported by Osváth et al. [11], $6.3 \times 10^{-4} \text{ Bq g}^{-1}$.

The methodology proposed the use of $^{94\text{m}}\text{Nb}$ as a tracer to monitor the process of separation and purification and to determine the chemical yield. This approach has shown to be a good alternative to circumvent the unavailability of a certified standard solution of ^{94}Nb .

The methodology complements the characterization protocol of radioactive wastes from Brazilian nuclear power plants performed by our group as shown in previously published works [13–15]. The methodology is important because it is not restricted to our nuclear power plants and can be applied to other types of nuclear power plants, which may be useful since there are not many published works on the determination of ^{94}Nb in radioactive waste.

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