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Determination of ^{93}Zr in radioactive waste from nuclear power plants using Inductively Coupled Plasma Mass Spectrometry

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ABSTRACT

The zirconium isotope ^{93}Zr is a long-lived pure β-particle-emitting radionuclide produced from ^{235}U fission and from neutron activation of the stable isotope ^{92}Zr and thus occurring as one of the radionuclides found in nuclear reactors. Due to its long half-life, ^{93}Zr is one of the radionuclides of interest for the performance of assessment studies of waste storage or disposal. This paper describes the determination of ^{93}Zr in evaporator concentrate (EC) sample from nuclear power plant (PWR). A zirconium selective separation using liquid-liquid extraction and TRU column were used before the ICPMS measurement to remove isobaric interferences.[20-21] ^{93}Nb detection limit of 0.045 µg L^{-1} was obtained for ^{93}Zr determination by ICPMS technique.

Keywords: Zirconium; Evaporator Concentrate waste; TRU; ICPMS

1. INTRODUCTION

The long-term risk related to the disposal of low level radioactive wastes produced by Pressurized Water Reactor (PWR) nuclear power plants (NPP) is determined primarily by the presence of the long lived nuclides.[1-2] The zirconium isotope ^{93}Zr is a critical radionuclide for the low-level wastes (LLW) and intermediate-level wastes (ILW) disposal. It is a long-lived pure β particle emitting, with a maximum energy of 60 keV and a half-life of 1.61×10^6 years.[3] It is produced by nuclear fission and neutron activation of ^{92}Zr stable isotope that is a constituent of the structural components of nuclear reactors. After 1000 years, ^{93}Zr is the second contributor, after ^{99}Tc, of the fission products activity.[4] The control of long half-life radionuclides in waste packages is necessary to insure compliance of waste acceptance criteria, which have been formulated in order to avoid any potential impact of the radio contaminants on the environment of the repository site.[1-5]

According to the literature, the chemical behavior of zirconium is very complicated regarding the ionic species present in aqueous solutions and the possibility of hydrolysis, polymerization and coordination reactions, strongly dependents on physical-chemistry conditions of the zirconium solutions.[6] The chemical form and oxidation state of ^{93}Zr is very important for its separation from others pure β-particle- and β-γ- emitting radionuclides present in the LLW and ILW samples such as ^{54}Mn, ^{55}Fe, ^{60}Co, ^{63}Ni, ^{65}Ni, ^{65}Zn, ^{90}Sr, ^{90}Y, ^{94}Nb, ^{133}Ba, ^{137}Cs, ^{152}Eu and ^{241}Pu when using Liquid Scintillation Counting (LSC) measurements.[7]

In the Inductively Coupled Plasma Mass Spectrometry Technique (ICPMS) the most serious complication are often isobaric interferences leading to increased background count rates and degraded detection limits and resolutions. When measuring by ICPMS, liquid-liquid extraction and chromatography extraction can be used for isobaric interference reduction, mainly due to ^{93}Nb, ^{93m}Nb, ^{93}Mo nuclides.

Other techniques used for this kind of measurements are Thermal Ionization Mass Spectrometry (TIMS) and Multiple Collector-Inductively Coupled Plasma Mass Spectrometry (MC-ICPMS) which also requires a selective separation for the isotope to be studied.[8-9]

Chemical separations are always needed and especially when working with waste samples from nuclear power plants due to its very complex chemical and radiochemical characteristics.

Over the last decade, extraction chromatography (EXC) has emerged as a versatile and effective method for the separation of radionuclides from a wide range of sample types. Frequently, EXC is described as a technique that combines the selectivity of solvent extraction with the ease of operation of chromatographic methods.

Quemet et al. describe a radioanalytical method for zirconium determination based on separation and purification using UTEVA column and zirconium detection by TIMS.[8]

Osváth et al. describe a combined radioanalytical method for ^{93}Zr determination based on co-precipitation on iron (II)-hydroxide, separation and purification using UTEVA column and zirconium detection by ICP-MS and LSC. The results achieved were chemical yields over 65% (using ^{95}Zr tracer), limit of detection of 0.02 Bq L^{-1} and activity concentration of 0.2 and 0.8 Bq L^{-1} for two evaporation concentrates samples by ICPMS. For LSC they achieved activities below the minimum detectable activity (MDA), 0.061 Bq over a counting period of 60 min.[10-11]

Dulanská et al. describe a simple and rapid method of ^{93}Zr pre-concentration, separation and purification by using cation and anion exchange resins and zirconium detection by LSC. The results achieved were chemical yields over 76% (using ICP-OES) and MDA of 0.01 µg L^{-1}. In all analyzed samples they have not found ^{93}Zr activity and all results were below MDA.[12]

This paper presents the analytical procedure developed for the determination of ^{93}Zr concentration in evaporator concentrate (EC) waste samples from Brazilian nuclear power plants - Eletrobrás Termonuclear Enterprise located in Angra dos Reis city - using extraction chromatography and quadrupole ICPMS techniques

2. MATERIALS AND METHODS

2.1 Instrumentation

Measurements of ^{93}Zr and its main interferences were performed with an Inductively Coupled Plasma Mass Spectrometry, Elan DRCe from Perkin-Elmer. The operating conditions to ICPMS measurements were optimized daily. The instrumental parameters used in this work are summarized in Table 1.

Table 1. Instrumental parameters for the ICP-MS

Component/Parameter	Type/Value/Mode
Nebulizer	Meinhard concentric glass
Spray Chamber	Cyclonic spray
Triple Cone Interface Material	Nickel
Plasma Gas Flow	16.0 L.min^{-1}
Auxiliary Gas Flow	0.60 L.min^{-1}
Nebulizer Gas Flow	0.89 L.min^{-1}
Sample Uptake Rate	1 mL/min
Radio frequency power	1200 W
Integration Time	1500 ms
Replicates per sample	3
Mode of Operation	Standard

The ^{95}Zr and ^{94m}Nb measurements were carried out with HPGe detector 5019 with 50% relative efficiency and for ^{93m}Nb ($E_{x} =$ 16.61 keV, $I(\%)$ = 6.29 and 13.13 y half-life) and ^{93}Mo ($E_{x} =$ 16.61 keV, $I(\%)$ = 40.9 and 4.0 × 10^3 y half-life) interferences measurements were carried out with Ultra-Low Energy Ge detector GU0110, both with DSA-2000 coupled to microprocessor with Genie 2 K software from Canberra, USA.[13]

2.2 Materials, reagents and standards

All chemicals were analytical grade. All compounds used to prepare standard solutions were initially dissolved with deionized water obtained from a Milli-Q Model (Millipore make) to form stock solutions and serial dilutions were performed to obtain the analytical concentrations required.

The resin used in the selective extraction procedure was TRU extraction chromatography material supplied by Eichrom and the Dowex resin supplied by Sigma-Aldrich.[14-15] The characteristics of resins are shown in table 2.

Table 2. Characteristics of the resins

	Dowex resin	**Tru resin**
Inner diameter	11 mm	8 mm
Bed volume	3 mL	2 mL
Column length	80 mm	26 mm
Resin particle size	100-200 mesh	100-150 μ m
Resin mass	5.0 g	1.0 g

Due to the ^{93}Zr standard solutions is commonly not available in the market is necessary to use alternative procedures for its determination. In view of the similarity in ionization energies (6.63 eV for Zr and 6.76 eV for Nb) and mass/charge ratios the ^{93}Nb standard solution supplied by NIST was used for 93 m/z mass calibration and determination of ^{93}Zr concentration in matrices analyzed.[16-17]

2.3 Preparation of ^{95}Zr and ^{93}Nb solution

For selective extraction procedure, the ^{95}Zr standard solution was used to determine the recovery efficiency. The ^{95}Zr liquid solution was obtained from irradiation of ^{94}Zr (target nuclei), present in zirconium pure solution from Aldrich, in a TRIGA MARK I reactor. It was used a thermal neutron flux of 8.18×10^{11} n cm^{-2} s^{-1} for 8 h. Zirconium isotope ^{95}Zr is a γ emitting radionuclide, with energies of $E_\gamma = 756.7$ keV ($I_\gamma = 55.4\%$) and $E_\gamma = 724.2$ keV ($I_\gamma = 43.7\%$), and a half-life of 64.03 days [3]. The ^{95}Zr specific activity obtained through several aliquots tested was ranged from 22 up to 59 Bq g^{-1}.

^{95}Zr was used as tracer to determine the recovery efficiency of zirconium element during the selective extraction step. This tracer sample was counted on the HPGe gamma detector for 1800 seconds in a polyethylene vial containing 5 mL, positioned directly over the detector.

The ^{93}Nb standard solution was prepared with 5 % ultra-pure HNO_3. An aliquot of 250 µL was taken of 9.986 mg g^{-1} niobium standard solution and added to a 25 mL flask obtained a main solution of 0.1 mg g^{-1}. Through this main solution were prepared a calibration curve ranged from 0.2 – 200 µg/L.

2.4 Chemical purification of zirconium

After determination of zirconium recovery efficiency using the ^{95}Zr tracer solution, the selective extraction methodology was used in evaporator concentrate samples that is one representative matrices of LLW samples. These samples were from reactor primary coolant circuit and collected at the nuclear facilities for chemical preparation and instrumental analysis. According to Rodriguez et al., this matrix is very heterogeneous and therefore it was necessary to use this procedure for the total solubilization before ICPMS analysis.[18]

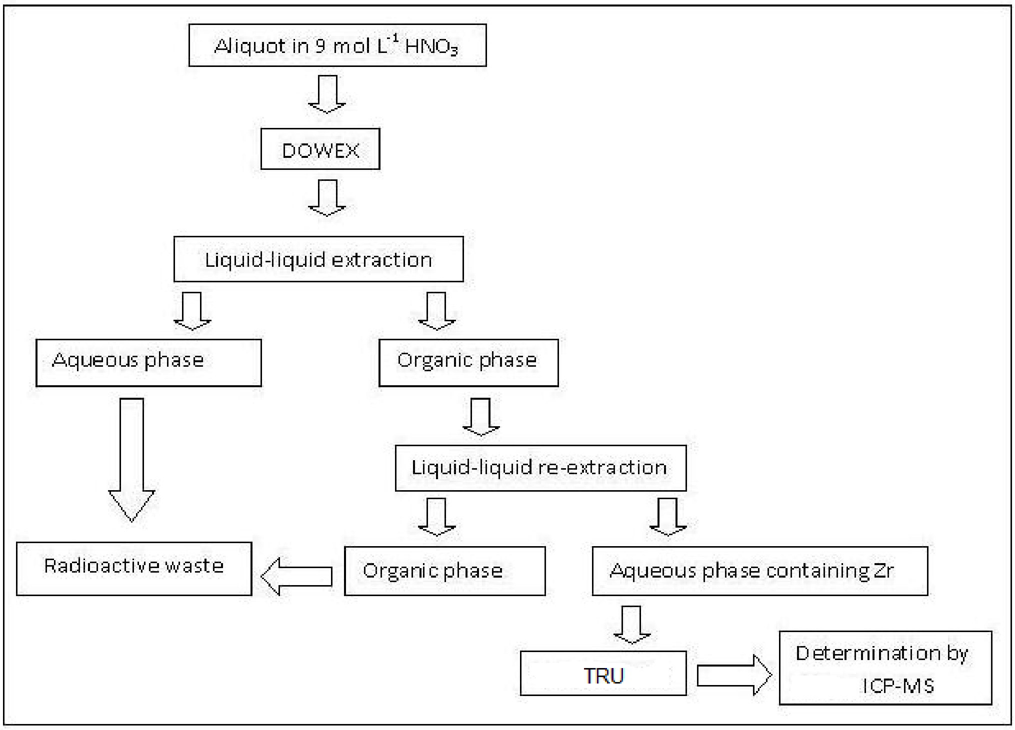
For evaporator concentrate two different samples were colected in duplicate (about 40 g). These samples were prepared in a Pt crucible and heated using a hot plate up to evaporation to dryness. After that, 20 mL of nitric acid (p.a. 65 %) and 15 mL de H_2O_2 (p.a. 35 %) were added into the crucible. The mixture was heated again up to evaporation to dryness. The solid obtained was calcined in an oven at 850 °C for 4 h. The residue was dissolved and for each step after addition of acid the mixture was heated up to evaporation to dryness: first, with 30 mL of 9 mol L^{-1} nitric acid, after, with 15 mL of HF. Finally, the solid resultant was dissolved using a hot plate in 20 mL of 9 mol L^{-1} nitric acid.

The solution, 20 mL in 9 mol L^{-1} nitric acid, is passed through the Dowex column (preconditioned by passing 50 mL of 9 mol L^{-1} HNO_3 solution) and passed through the column with 1 mL min^{-1} flow rate. The zirconium and other cations pass through the column except ^{241}Pu if present in the sample.[19] The column was washed with 50 mL 9 mol L^{-1} HNO_3 solution. This eluate was heated to dryness and 3 mL of 4 mol L^{-1} HCl/1 mol L^{-1} $AlCl_3$ solution was added. This solution was used for liquid–liquid extraction mixing 3 mL of 0.5 mol L^{-1} 1-(2-Thenoyl)-3,3,3-trifluoroacetone (TTA) in xylene that was carried out in a beaker under stirring for 8 min and then allowing the mixture to rest for 8 min. This procedure was repeated five times for complete extraction by TTA solution. At this step Ba, Co, Eu, Mn, Nb, Ni, Sr, Y and Fe were retained in the aqueous phase.

The zirconium present in the organic phase was back extracted into 15 mL of 0.5 mol L^{-1} HNO_3/0.5 mol L^{-1} HF aqueous solution using the same procedure of the first liquid–liquid extraction step. After that, the aqueous solution was heated to dryness and the final residue was dissolved in 3 mL of 4 mol L^{-1} HCl solution. This solution was put onto a column filled with TRU resin and passed through the column with 1 mL min^{-1} flow rate (TRU column was preconditioned for separation by passing 12 mL of 4 mol L^{-1} HCl solution). The column was washed with 12 mL of 2 mol L^{-1} HCl and this effluent was heated to dryness and taken up in a high purity 0.15 mol L^{-1} HNO_3 solution. The flowchart of the separation steps is shown in Fig. 1. The ^{93}Zr was determined in the final solutions obtained after separations by ICP-MS.

After zirconium selective separation, an aliquot of the sample was irradiated to verify the presence of ^{93}Nb and ^{93m}Nb interferences in ICMPS analysis. This checking was done through the neutron activation with ^{94m}Nb production and measurement in gamma spectrometry.

Figure 1- *The flowchart of the separation steps for Zirconium*



2.5 Limit of detection

The limit of detection for ^{93m}Nb and ^{93}Mo was based on Currie equations.[20-21]

$$L_d\,(Bq/L) = \frac{2.71 + 3.29\sqrt{t\,.\,R}}{t\,.\,E_{ff}\;.\,Q\,.\,60} \qquad \text{EQ. 1}$$

where R is the count rate in cpm of the blank, E_{ff} is the counting efficiency, Q is the sample quantity and 60 is the time conversion factor, seconds to minutes.

The ^{93}Nb limit of detection (LD) were obtained as 3×SD_0 of a series of ten replicate measurements of the calibration blank signal at the selected analytical masses, where SD_0 is the value of the standard deviation as the concentration of the analyte approaches 0, according to EPA Method 200.8 for the analysis of drinking waters.[22] We associated ^{93}Nb LD to the ^{93}Zr LD.

3. RESULTS AND DISCUSSION

The results shown are the average of duplicate results obtained with the analytical methodology established by using ICPMS technique and the limitations and advantages of this analytical route are discussed.

For zirconium determination by ICPMS, a set of tests was carried out on standard samples solution containing known quantities of ^{95}Zr in order to check the efficiency and reproducibility of the separation steps. The chemical yield obtained in this work for ^{95}Zr was over 65 % when used TRU resin.[23-24]

After irradiation, ^{95}Zr standard sample showed a count of 2656 cps. This tracer solution was measured before and after the extraction step in HPGe detector for the same time and geometry obtaining a final count of 1786 cps. Comparing the initial and final activities, the recovery yield of the Zr element was obtained.

As the niobium (^{93}Nb, ^{93m}Nb) and molybdenum (^{93}Mo) are the main interferences in zirconium determination when using ICP-MS, a sample aliquot obtained after TRU separation step was irradiated using a TRIGA Mark I nuclear reactor in order to evaluate the ^{93}Nb presence through ^{94m}Nb, that is an activation product, using gamma spectrometry measurement. The limit detection (LD) for ^{94m}Nb was 9.59×10^{-4} Bq.g^{-1} (8.12×10^{-14} µg L^{-1}). For the evaporator concentrate samples analyzed the results obtained were below the LD. The values obtained by Osváth *et al* was 6.3×10^{-4} Bq g^{-1} (5.34×10^{-14} µg L^{-1}) after radiochemical separation.[10]

Another sample obtained after TRU separation step were used for the ^{93m}Nb and ^{93}Mo interferences evaluation. The X-ray photopic for these radionuclides weren't observed after low energy gamma spectrometry analysis. The limit detection for ^{93m}Nb and ^{93}Mo was 3.89 × 10^{-6} Bq.g^{-1} (1.09 × 10^{-7} µg L^{-1}).

The ^{93}Nb limit of detection (LD) was 0.045 µg L^{-1} and we associated ^{93}Nb LD to the ^{93}Zr LD.

A final set of tests was carried out with two EC samples and their ^{93}Zr concentration are showed in table 3.

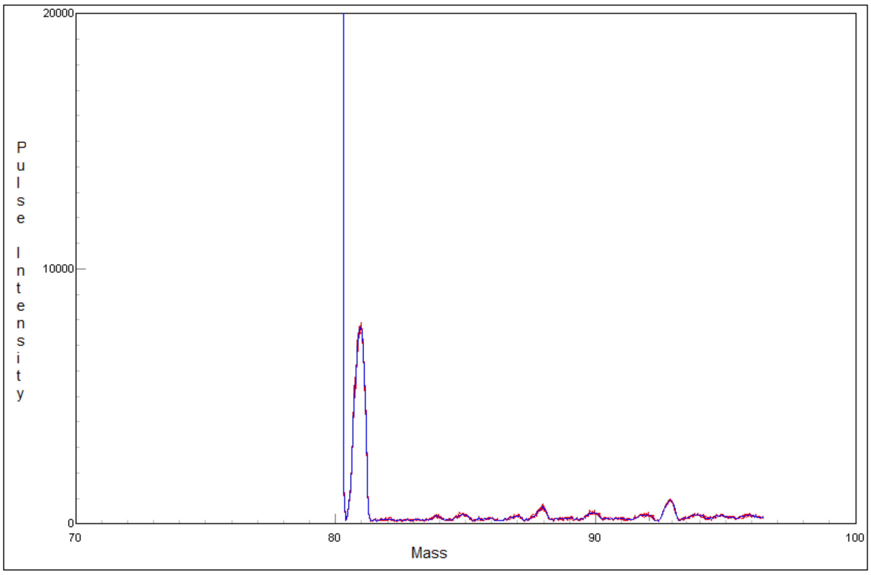
Table 3. ^{93}Zr concentration in

Samples	**^{93}Zr concentration (µg g^{-1})**	**Standard deviation**
EC 1	0,09	0,03
EC 2	0,93	0,03

Figure 2 shows the ICP-MS spectrum of ^{93}Zr waste solution after separation steps.

This spectrum refers to the selective extraction using Dowex and TRU resins and TTA solution. In this figure we can observe the peak referring to mass of ^{93}Zr.

Figure 2 – *ICP-MS spectrum of ^{93}Zr waste sample after separation steps*



4. CONCLUSION

Analytical methodologies have been proposed for ^{93}Zr determination in low level radioactive waste, evaporator concentrate samples, by ICP-MS technique.

For ICP-MS analysis a protocol was developed for chemical separation steps based on ^{95}Zr tracer and the recovery yield obtained was better than 65% which was also observed by Osváth.[11]

The ^{93}Nb utilization as a reference isotope for ^{93}Zr determination by ICP-MS is one option for calibration and simulation analysis in view of their similarity in ionization energies and mass/charge ratios.

The possible interferences caused by ^{93}Nb, ^{93m}Nb and ^{93}Mo mass/charge ratio were investigated using nuclear techniques in order to evaluate the results of separation methodologies adopted in this work.

Finally, the results obtained, considering the sensitivity of ICP-MS technique, were above the limit of detection calculated and they were very close to values obtained by Osváth.[10]

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