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RADIOCHEMICAL DETERMINATION OF ZIRCONIUM BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICPMS)

Thiago C. Oliveira[1], Roberto Pellacani G. Monteiro[2] and Arno Heeren de Oliveira[1]

[1]Departamento de Engenharia Nuclear (UFMG/DEN – MG)
Universidade Federal de Minas Gerais
Av. Presidente Antônio Carlos 6.627
31270-901 - Belo Horizonte, MG
tco@cdtn.br
heeren@nuclear.ufmg.br

[2]Centro de Desenvolvimento da Tecnologia Nuclear (CDTN/CNEN – MG)
Centro de Desenvolvimento da Tecnologia Nuclear
Av. Presidente Antônio Carlos 6.627
31270-901 - Belo Horizonte, MG
rpgm@cdtn.br

ABSTRACT

The zirconium isotope ^{93}Zr is a long-lived pure β-particle-emitting radionuclide thus occurring as one of the radionuclides found in nuclear reactors. It's produced from ^{235}U fission and from ^{92}Zr neutron activation. Due to its long half-life, ^{93}Zr is one of the interest radionuclides for assessment studies performance of waste storage or disposal. Measurement of ^{93}Zr is difficult owing to its trace level concentration and its low activity in nuclear wastes and further because its certified standards are not frequently available. The aim of this work was to apply a selective radiochemical separation methodology for ^{93}Zr determination in nuclear waste and analyze it by Inductively Coupled Plasma Mass Spectrometry (ICPMS). To set up the zirconium radiochemical separation procedure, a zirconium tracer solution was used in order to follow the zirconium behavior during the radiochemical separation. A tracer solution containing the main interferences, Ba, Co, Eu, Fe, Mn, Nb, Ni, Sr, and Y was used in order to verify the decontamination factor during separation process. The limit of detection of 0,039 ppb was obtained for zirconium standard solutions by ICPMS. Then, the protocol will be applied to low level waste (LLW) and intermediate level waste (ILW) from nuclear power plants.

1. INTRODUCTION

The long-term risk related to disposal of radioactive waste produced by PWR nuclear power plants is determined primarily by the presence of long lived nuclides [1, 2].

The control of long half-life radionuclides in waste packages is necessary to insure the respect of waste acceptance criteria that are fixed in order to avoid any potential impact of radio contaminants on the environment of repository site [1, 3].

The zirconium isotope ^{93}Zr is a critical radionuclide for low level waste (LLW) and intermediate level waste (ILW) disposal. It's a long-lived pure β particle emitting, with a maximum energy of 56 KeV and a half-life of 1.53 X 10^6 years [4]. It's produced by nuclear fission and neutron activation of the stable isotope ^{92}Zr 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 [5].

According to literature the chemical behavior of zirconium is very complicated regarding the ionic species present in aqueous solutions and the possibility of hydrolysis, polymerisation 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 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 [7]. Zirconium selective separation is necessary when using ICPMS or Liquid Scintillation Counting (LSC) techniques for ^{93}Zr measurements.

Further, due to low concentration of ^{93}Zr in LLW and ILW and because of its standard solutions is commonly not available in the market is necessary to use alternative procedures for its determination [8].

The aim of this work was to develop a zirconium determination by ICPMS in order to verify zirconium recovery and decontamination factor after a selective radiochemical separation method [9].

2. MATERIALS AND METHODS

2.1. Reagents and solutions

All chemicals were analytical grade; the hydrochloric acid, nitric acid, hydrofluoric acid, aluminum chloride, lithium nitrate and xylene were obtained from Merck and TTA was obtained from Riedel–de Haën. The Zr, Ba, Co, Eu, Fe, Mn, Nb, Ni, Sr and Y liquid standard solutions were obtained from SPEX CertiPrep.

All compounds used to prepare standard solutions were initially dissolved with deionised water to form stock solutions and serial dilutions were performed to obtain the analytical concentrations required.

The stable zirconium standard solution was used to determine the recovery efficiency and the Ba, Co, Eu, Fe, Mn, Nb, Ni, Sr and Y standard solution were used to determine the decontamination factor. ^{241}Pu recovery efficiency was determined using DOWEX resin and LSC counting according recent work [10].

2.2. Samples

Two synthetic matrices prepared based on chemical similarity of resin and filters wastes from Brazilian nuclear power plants were chosen to test the methodology.

2.3. Analytical techniques

Measurements of Zr and other elements were performed with Inductively Coupled Plasma Mass Spectrometry, X7 Quadrupole ICPMS from Thermo Scientific.

2.4. Radiochemical procedure

In order to check the separation step a simulated solution was prepared with appropriated quantities of Zr and the main interferences standard solutions for evaluation of chemical recovery yield and decontamination factor for them.

Separation procedure, to obtain free zirconium of interferences, comprises an extraction with Dowex resin, a liquid-liquid extraction with TTA in Xylene and a chromatography extraction with TRU or TEVA resins.

Selective extraction procedure was based on the process developed by Espartero 2002 [7] and Oliveira 2011 [9].

In the initial step of selective extraction, DOWEX resin was used to ^{241}Pu isotope separated [10].

Initial condition for DOWEX resin was the 3:2 HNO_3. DOWEX resin was preconditioned for separation by passing 25 mL of 3:2 HNO_3 solutions.

The second one, liquid–liquid extraction using TTA in xylene was used in order to separate the main interferences (Ba, Co, Eu, Fe, Mn, Nb, Ni, Sr and Y) of the Zr and it was back extracted into an aqueous acid solution.

Initial condition for liquid-liquid extraction was 2M HCl / 1M $AlCl_3$.

The third one, chromatography extraction TRU or TEVA resins was used to obtain free Zr of the interferences.

Initial condition for TRU and TEVA resins were the 4 M HCl and 8 M $LiNO_3$/0.01 M HNO_3 respectively. TRU column was preconditioned for separation by passing 12 mL of 4 M HCl solution and TEVA by passing 12 mL of 8 M $LiNO_3$/0.01 M HNO_3.

For TRU the Zr standard solution was heated to dryness and the final residue was dissolved in 4 M HCl solution. After that, 3 mL of this solution was put onto a column filled with TRU resin and passed through the column with 1 ml min^{-1} flow rate. The column was washed with 12 mL of 2 M HCl.

For TEVA the Zr standard solution was heated to dryness and the final residue was dissolved in 9 M HCl solution. After that, 3 mL of this solution was put onto a column filled with TEVA resin and passed through the column with 1 ml min^{-1} flow rate. The column was washed with 12 mL of H_2O.

The final solution containing Zr, Ba, Co, Eu, Fe, Mn, Nb, Ni, Sr and Y were measured by ICPMS.

Limit of detection of 0,039 ppb was obtained as $3*SD_0$, where SD_0 is the value of the standard deviation as the concentration of the analyte approaches 0.

3. RE4SULTS AND DISCUSSION

Tests were carried out on standard samples solution containing known amounts of Zr in order to check the efficiency and reproducibility of the separation steps. The chemical yield for Zr recovery was shown separately for each separation step in table 1:

Table 1: Zirconium recovery by ICPMS

Separation steps	Zr Recovery
1 - DOWEX ion exchange resin	better than 99%
2 - Liquid-liquid extraction	better than 97%
3 - TRU chromatography resin	~ 70%
4 - TEVA chromatography resin	~ 68%
5 -Complete extraction (DOWEX, Liquid-Liquid extraction and TRU)	~ 68%
6 -Complete extraction (DOWEX, Liquid-Liquid extraction and TEVA)	~ 65%

We also made tests with a standard samples solution containing known amounts of Zr and others interfering nuclides in order to check the decontamination factor of the separation steps. The decontamination factors for Ba, Co, Eu, Fe, Mn, Nb, Ni, Sr, Y for the same steps of table 1 were shown separately for each separation step in table 2:

A simulated waste samples (resin and filter) containing known amounts of zirconium and main interfering nuclides were used in order to check the Zr recovery and decontamination factor of the separation steps.

The results obtained with simulated waste samples, showed good agreement with results obtained by standard solution samples. The results obtained by this method prove to be able to measure zirconium in waste samples from nuclear-power plants.

Table 2: Main interfering decontamination factor

Separation steps	Ba	Co	Eu	Fe	Mn	Nb	Ni	Sr	Y
1	0%	0%	0%	0%	0%	86%	0%	0%	0%
2	75%	75%	69%	82%	99%	67%	78%	70%	62%
3	0%	0%	0%	72%	0%	72%	0%	0%	0%
4	26%	37%	35%	40%	44%	70%	37%	24%	36%
5	~75%	~75%	~69%	~99%	~99%	~99%	~78%	~70%	~62%
6	~99%	~99%	~99%	~99%	~99%	~99%	~99%	~94%	~98%

4. Conclusions

A chemical methodology was proposed for stable zirconium determination in synthetic samples by ICPMS. The protocol was developed on Zr synthetic solutions prepared with standard solutions for chemical recovery and decontamination factor evaluation.

Zirconium recovery yield obtained was better than 65% and decontamination factor obtained was better than 95%.

Waste samples from nuclear Power plants will be submitted to the same separation procedure.

This experiment showed a uniform behaviour and consistent results according to the found results by LSC.

TRU and TEVA resins showed good zirconium recovery. It is concluded that both resins may be used in the process of zirconium selective separation because other separation steps are performed before the separation step with resins.

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