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Determination of zirconium isotope composition and concentration for nuclear sample analysis using Thermal Ionization Mass Spectrometry

Alexandre Quemet*, Christophe Maillard, Alexandre Ruas

CEA, Nuclear Energy Division, RadioChemistry & Processes Department, F-30207 Bagnols sur Cèze, France

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ABSTRACT

A new Thermal Ionization Mass Spectrometry (TIMS) analytical procedure was developed to measure with high accuracy the zirconium isotope abundance and concentration without molybdenum correction in nuclear samples. A zirconium selective separation using UTEVA column was used before the TIMS measurement in order to remove all possible isobaric interferences (Mo, Y, Nb and Ru) in the solution. The separated solution was then deposited onto a filament previously outgassed for 4 h to reduce the molybdenum traces in the filament. Then, the filament was introduced into the TIMS source and was maintained for 4 h at a current of 5 A (ionization filament) and 1.2 A (evaporation filament) in order to eliminate all molybdenum trace present in the filament and in the sample. This methodology allowed the zirconium isotope abundance determination without using the molybdenum interference correction equation. The analytical results obtained with a natural solution after separation is in good accordance with the reference values: bias lower than 0.16% for the ^{90}Zr, ^{91}Zr, ^{92}Zr and ^{94}Zr isotope abundance, and a bias of ~0.8% for the minor isotope (^{96}Zr) were observed. This zirconium abundance determination methodology was used on three nuclear samples. Then, the calibration of a ^{91}Zr spike solution was performed by reverse isotope dilution using a SPEX standard zirconium solution. The zirconium concentration determination was then performed on the three nuclear samples by isotope dilution using the SPEX standard zirconium solution and the ^{91}Zr spike solution. The final uncertainties were estimated to be lower than 1%.

1. Introduction

Determination of zirconium concentration and isotope abundance is important for different applications such as life science [1], geology [2–6], environment [7], forensics [8] or nuclear field [9–13]. In nuclear applications, zirconium is used as a construction material in nuclear reactors [14] and is a fission product: the radioactive ^{93}Zr isotope is produced mainly by nuclear fission of uranium-235 in nuclear fuel. During the treatment and recycling of spent nuclear fuel, the first step is the shearing where the fuel rods are cut into small pieces. This step involves the separation between the spent fuel and the cladding material, made of zirconium alloy which has a low solubility in a nitric acid media [15]. The dissolution of the spent fuel is effective in hot nitric acid media. The apparition of dissolution fines, in particular of zirconium and molybdenum, can clog the dissolver during the dissolution process or affect the extraction process [16,17]. Thus, the accurate zirconium isotope analysis is required to determine its origin (construction material or fission product) and to understand the nuclear processes undertaken. Also, the accurate determination of the zirconium concentration is of prime interest for waste management.

Several studies for zirconium isotope measurement have been reported in literature. There are mainly two principal techniques used for this kind of measurement: multiple collector-inductively coupled plasma mass spectrometer (MC–ICP–MS) [2–4,9,10] and Thermal Ionization Mass Spectrometry (TIMS) [1,2,5,6,8,18–20].

TIMS is a reference technique for isotope measurement [21–23]. TIMS allows reaching isotope ratio with high measurement trueness and precision. Another advantage of the TIMS is the possibility to perform concentration determination with low uncertainty, better than 1%, thanks to the use of isotope dilution [2,19]. One of the major difficulties of zirconium measurements by TIMS is the low ionization efficiency of zirconium due to its high ionization potential (6.84 eV) [2]. Also, TIMS analysis requires an isobare pure fraction of the element of interest. Zirconium is mostly interfered by molybdenum. This is the reason why some separation methods

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* Corresponding author.
E-mail address: alexandre.quemet@cea.fr (A. Quemet).

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have been developed in order to extract or eliminate the molybdenum [24–30]. Some TIMS studies corrected mathematically the molybdenum interference by an interference correction equation [1,8,12,18]. Nevertheless in the nuclear industry, the molybdenum isotope abundance is generally unknown and varies from a sample to another making the use of the interference correction equation difficult.

This paper presents an analytical procedure developed for the zirconium isotope abundance and concentration determination using TIMS for nuclear samples containing a high amount of zirconium. After a brief description of the separation procedure on UTEVA resin, a detailed description of the methodology developed to obtain accurate zirconium isotope abundance without molybdenum interference correction equation is reported. The results obtained with a SPEX solution are discussed and compared with previous data found in the literature. The procedure was then applied to three nuclear samples in order to determine the non-natural isotope abundance. Also, the ^{91}Zr spike solution preparation and calibration are discussed. The zirconium concentrations in three nuclear samples were determined by isotope dilution in order to obtain the best accuracy.

2. Experimental

2.1. Materials, reagents and samples

All solutions were prepared using polypropylene flasks, except for the zirconium solutions, which were prepared in PFA vials.

4 M and 8 M nitric acid solutions were prepared by diluting high purity nitric acid (Merck, Suprapur) with deionized water (resistivity: 18.2 MΩ·cm).

For the separation protocol, a (4 M/0.1 M) $HNO_3/H_2C_2O_4$ mixture was prepared by diluting high purity nitric acid with deionized water and by weighing oxalic acid dihydrated (Fluka). A (7 M/1 M) HNO_3/HF mixture was prepared by diluting high purity nitric acid and hydrofluoric acid (Merck) with deionized water. A 1.5 M Al^{3+} solution was prepared to complex the fluoride present in some nuclear samples before the separation. This solution was prepared by dissolving aluminum nitrate (Merck) with deionized water. The UTEVA resin (Triskem) (100–150 μm particle size in 2 mL prepackaged columns) was used in the separation protocol in order to obtain a pure zirconium fraction.

A high precision balance (Mettler–Toledo) was used to prepare all the solutions.

2.1.1. Standard solutions

High purity zirconium and molybdenum standards were used to prepare the simulated solutions (Section 3.1.3). They were prepared from single element ICP SPEX solution (1000 mg L^{-1} ±0.5%, k = 2) diluted with appropriate amounts of 8 M nitric acid solution and deionized water in order to obtain a final solution at 4 M nitric acid.

For the first series of test of zirconium isotope composition (Sections 3.1.1 and 3.1.2), a solution at 5 μg μL^{-1} (±10%, k = 2) was prepared by evaporating 500 μL of the SPEX solution at 1000 mg L^{-1} and then redissolving it with 100 μL of 4 M nitric acid.

2.1.2. Preparation of the enriched ^{91}Zr solution

The zirconium spike solution was prepared by dissolving a ^{91}Zr enriched (95.30%) non-radioactive ZrO_2 powder provided by Eurisotop. The ZrO_2 powder was dissolved in a (7 M/1 M) HNO_3/HF mixture heated at 120 °C in a PFA vial during 2 h. The solution was agitated during the entire dissolution process. Once the dissolution was achieved, the solution was diluted in order to obtain a HNO_3 concentration of 4 M and a zirconium concentration around 10 μg g^{-1} (this solution is hereafter referred to as ^{91}Zr spike solution). The concentration of this ^{91}Zr spike solution was then determined with high accuracy by isotope dilution.

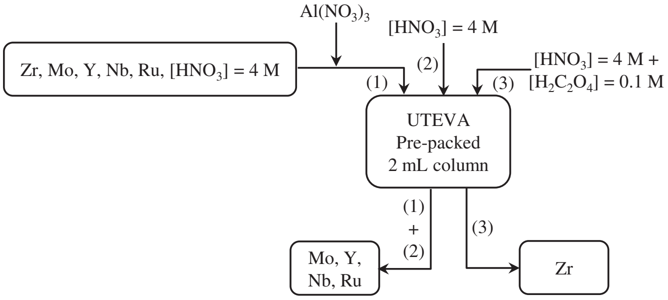

Fig. 1. Diagram of the separation procedure for Zr purification.

2.1.3. Particularity of the nuclear samples

The developed methodology was applied to three nuclear samples to determine the zirconium isotope abundance and concentration. These samples came from the dissolution of solids obtained in the dissolvers during the reprocessing of spent nuclear fuel.

These three samples, received in liquid form, were diluted with 8 M HNO_3 and deionized water in order to obtain a zirconium concentration around 100 mg L^{-1} with a HNO_3 concentration of 4 M. Sample 1 was the most challenging in terms of separation: the Mo/Zr concentration ratio was close to 2.5. Zr of sample 1 was essentially a fission product. Sample 2 had a Mo/Zr concentration ratio close to 0.03. Finally, the ratio was close to 1 for sample 3. Zr of samples 2 and 3 was essentially issued from the construction material. The other major elements in the samples were Na, B, U, Pu. Some lanthanides were also present in lower quantities. An ICP-OES analysis showed that the samples were free of other possible interfering elements for the zirconium isotope analysis such as yttrium (<25 mg L^{-1}) and ruthenium (<1 mg L^{-1}).

2.2. Separation procedure

The zirconium isotopes to consider are ^{90}Zr, ^{91}Zr, ^{92}Zr, ^{93}Zr, ^{94}Zr and ^{96}Zr. Zirconium is potentially interfered by the molybdenum isotopes ^{92}Mo, ^{94}Mo and ^{96}Mo, the radioactive yttrium isotope ^{90}Y, the niobium isotope ^{93}Nb and the ruthenium isotope ^{96}Ru. High accuracy zirconium isotope measurements by TIMS require a sample preparation to remove isobaric interferences. Therefore, a separation step conducted on a UTEVA column was necessary. The operating procedure developed in this work is summarized in Fig. 1.

The fluoride present in the sample was neutralized by the addition of a small quantity of Al^{3+} (molar ratio Al/F = 1). 5 mL of the zirconium sample at a concentration of about 100 mg L^{-1} (500 μg) was directly loaded on the column, previously conditioned with 5 mL of 4 M HNO_3. During this feeding step, the zirconium was fixed on the UTEVA resin. The column was then washed with 15 mL of 4 M HNO_3 in order to eliminate all interfering elements. Finally, the zirconium was eluted with 5 mL of (4 M/0.1 M) $HNO_3/H_2C_2O_4$ mixture. This solution was evaporated and redissolved with 100 μL of HNO_3 4 M in order to obtain a Zr concentration around 5 μg μL^{-1} (±20%, k = 2). 1 μL of this solution was then deposited onto the filament.

2.3. Instrumentation

Isotope measurements were performed on a Thermo Scientific Triton Thermal Ionization Mass Spectrometer, equipped with a glove box. The analyzer is a low resolution magnetic field (resolution around 400). The instrument used for the experiments is