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Rapid separation of zirconium using microvolume anion-exchange cartridge for ^{93}Zr determination with isotope dilution ICP-MS

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ABSTRACT

Estimating the risks associated with radiation from long-lived fission products (LLFP) in radioactive waste is essential to ensure the long-term safety of potential disposal sites. In this study, the amount of ^{93}Zr, a LLFP, was determined by ICP-MS after separating Zr from a spent nuclear fuel solution using a microvolume anion-exchange cartridge (TEDA cartridge). Zirconium in 9.4 M HCl was stably retained on the TEDA cartridge and readily eluted with 0.75 mL of a mixed solution of 9.4 M HCl and 0.01 M HF. The time taken to complete the Zr separation was 1.2 min. Almost all the other elements initially present in the spent nuclear fuel sample were removed, leading to accurate measurement of all six Zr isotopes (^{90}Zr, ^{91}Zr, ^{92}Zr, ^{93}Zr, ^{94}Zr, and ^{96}Zr). This demonstrated that the TEDA cartridge allowed highly selective separation of Zr regardless of its small bed volume of 0.08 cm^3. The concentrations of these isotopes were determined by an isotope-dilution method using a natural Zr standard that has a different isotopic composition from that of the spent nuclear fuel sample. The amount of ^{93}Zr in an initial spent nuclear fuel pellet was 1081 ± 79 ng per mg of ^{238}U. The measured concentrations of all Zr isotopes, as well as the isotopic composition, were consistent with values predicted using a burnup calculation code.

1. Introduction

Zirconium is generated by nuclear fission of U and Pu with high fission yields [1]. Around 3 kg of Zr per ton of U is present in spent nuclear fuel with a burnup of 30–40 GWd/t, which is typical for a commercial nuclear reactor [2]. Some Zr isotopes can also be generated through activation of the constituents of fuel claddings. Among these isotopes, ^{93}Zr, which has the longest half-life of 1.5 million years, has attracted much attention in terms of the long-term risk assessment of radioactive waste disposal. To ensure reliable estimation of the risks associated with ^{93}Zr radiation, accurate quantitation of its amount in radioactive waste is essential.

Spent nuclear fuel and its reprocessed waste, high-level radioactive waste (HLW), are common samples for ^{93}Zr determination since they contain sufficient amounts of this. Fuel debris along with highly contaminated peripheral construction materials (e.g., zircaloy cladding and concrete shielding) remaining after the accident at Fukushima Daiichi nuclear power station will surely comprise the majority of samples to be measured in subsequent years in Japan. Unlike in typical spent nuclear fuel and HLW, the concentration range of ^{93}Zr and its chemical composition in such samples can be variable and unpredictable. Accordingly, a versatile analytical method that is suitable for a wide variety of sample types is required.

The amount of ^{93}Zr can be measured by radiometry [3–8] or mass spectrometry [4,5,9–13]. Liquid-scintillation counting (LSC) is a commonly applied radiometric technique for measuring ^{93}Zr. For LSC, thorough removal of other beta-emitting nuclides and other potentially interfering nuclides, e.g., ^{55}Fe, ^{60}Co, ^{63}Ni, ^{93}Mo, ^{90}Sr, ^{90}Y, ^{99}Tc, ^{135}Cs, ^{137}Cs, ^{239}Np, and ^{241}Pu, is a prerequisite to achieving accurate measurement. A combination of several separation techniques, such as co-precipitation with BaZrF [4,8,10], liquid-liquid extraction using 2-thenoyltrifluoroacetone (TTA) [3,6] and *N*-Benzoyl-*N*-phenylhydroxylamine (BPHA) [4,10], and chromatographic separation using ion-exchange resins [4,8,10] and extraction chromatography resin (UTEVA® Resin) [7], have been applied to obtain a pure fraction of Zr. However, such separation procedures are time-consuming and generate a large volume of radioactive waste, which makes them labor-intensive. Even if a radiochemically pure fraction of Zr is obtained through these

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separation procedures, the measurement of ^{93}Zr at a low activity concentration is still challenging because of its low specific activity.

Inductively coupled plasma mass spectrometry (ICP-MS) is the most practical approach for measuring long-lived radionuclides [14]. Compared with other mass spectrometry techniques, ICP-MS is widely used in the field of radiochemical analysis because measurement by ICP-MS is relatively simple, highly-sensitive, and rapid.

ICP-MS is preferable to LSC in that it involves far fewer interfering nuclides. For ^{93}Zr, ^{93m}Nb (^{93} Nb) and ^{93}Mo are the only major potentially interfering nuclides. Considering that most of the previously proposed separation methods for ^{93}Zr [3–8,10] were intended for LSC (including those developed for both LSC and ICP-MS [4,10]), a separation method that is designed specifically for ^{93}Zr measurement with ICP-MS should greatly reduce the workload.

As expected from the extremely long half-life of ^{93}Zr, the amount of the daughter nuclide ^{93m}Nb (^{93}Nb) in radioactive waste is negligible, causing practically no interference. However, ^{93}Nb present in the environment can affect the detection at *m/z* 93 when a sample contains natural Nb. The nuclide ^{93}Mo, which is generated by activation of ^{92}Mo, is present as an impurity in fuel cladding and construction materials [15]. Accordingly, measurement of ^{93}Zr in irradiated materials is likely to be subject to interference from ^{93}Mo.

Chromatographic techniques with anion-exchange resin columns for Zr/Nb separation were reported [16–19]. The separation of Zr from Nb was conducted based on differences in the affinity of an anion-exchange resin. An anion-exchange resin has high affinity for both Zr(IV) and Nb (V) in highly concentrated HCl, whereas its affinity for Zr(IV) greatly decreases when a small amount of HF is added [16]. The difference between the affinities for Zr(IV) and Nb(V) is highest with around 9 M HCl/0.01 M HF [17]. When the concentration of HF is set lower than 0.01 M, the elution peak becomes broader [18]. Zr (IV) is also easily adsorbed by anion-exchange resin in dilute HF [19]. Dulanská et al. adsorbed Zr(IV) in 0.5 M HF and eluted with 35% HCl/dilute HF mixed solution [8].

For Zr/Mo separation, Schönbächler et al. reported that Zr, along with Ti, Mo, Te, Hf, and W, was adsorbed in an anion-exchange resin column with 4 M HF [20]. Then, Zr, Ti, and Hf were eluted with a mixed solution of 6 M HCl and 1 M HF, while only Mo remained on the column. Shimada et al. employed TEVA® resin to separate Mo from Zr and other coexisting elements [21]. As TEVA® resin has an extractant containing a quaternary ammonium group inside its pores, its separation properties are similar to those of a strongly basic anion-exchange resin. In 4 M HCl/0.1 M HF, Zr and Nb passed through the TEVA® resin, while Mo was retained.

As indicated in previous investigations on Zr/Nb and Zr/Mo separation, an anion-exchange procedure comprising Zr absorption with highly concentrated HCl and elution with a mixed solution of HCl and HF is suitable for simple separation of Zr from both Nb and Mo. In order to minimize the use of HF, 9 M HCl/0.01 M HF is preferable for Zr elution.

We developed a microvolume anion-exchange cartridge packed with a triethylenediamine (TEDA)-containing porous polymer disk [22]. TEDA is characterized by two anion-exchange groups (a combination of a tertiary amine and a quaternary ammonium) per molecule, resulting in a high anion-exchange capacity. TEDA is introduced into a polymer chain that is uniformly attached to the surface of the porous polymer (polyethylene) by graft polymerization, forming a high-density anion-exchange interfacial phase on its pore surface. This structure provides an ideal mass transfer field associated with a high contact efficiency of target ions, which enables rapid adsorption of ions at a high flow rate [22–27]. In our previous study, we applied the TEDA cartridge to Np/Am separation. Np in anionic form was stably retained on the TEDA cartridge in 9.4 M HCl/0.1 M HNO_3, while Am (Am^{3+}) passed through. The chemical yield for Np was 90% at a flow rate of 1.5 mL/min, which was 10 times faster than that for a conventional anion-exchange resin column (gravity flow). Thus, the TEDA cartridge appears to achieve rapid separation of Zr.

The objective of this study is to verify the practical performance of the TEDA cartridge with respect to Zr separation, which is expected to be more complicated than an anion/cation separation as in Np/Am separation [22]. For Zr separation, a clear difference in the affinity of the TEDA cartridge for Zr, Nb, and Mo, which are all present in anionic form, is important. We examined whether the TEDA cartridge is applicable to such chromatographic separation among these anions, irrespective of its small bed volume.

A spent nuclear fuel sample with a clear irradiation history was employed in this study. The nuclide composition and amount of ^{93}Zr in such samples are predictable with a burnup calculation code. To the best of our knowledge, there has been no measured data showing a clear relationship between the actual amount of ^{93}Zr in spent nuclear fuel and a theoretically predicted value. To ensure the reliability of the predicted values, the amount of ^{93}Zr in a spent nuclear fuel sample obtained through ICP-MS measurement was compared with that calculated theoretically.

2. Experimental

2.1. Reagents and standards

A natural Zr standard solution provided by Wako Pure Chemical Industries Ltd. was used as a spike for isotope dilution mass spectrometry. A rare-earth and U mixed standard (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Tm, U, Y, and Yb at 10 mg/L in 2 v/v% HNO_3) was supplied by High-Purity Standards. Other single-element standard solutions used for preparing a simulated sample solution and calibration standards were purchased from Wako Pure Chemical Industries Ltd. A ^{91}Zr-enriched metal standard (^{90}Zr: 5.99%,^{91}Zr: 89.2%, ^{92}Zr: 3.29%, ^{94}Zr: 1.30%, and ^{96}Zr: 0.23%) was obtained from Oak Ridge National Laboratory. About 2 mg of ^{91}Zr metal standard was dissolved in 0.2 mL of 1 M HNO_3/3 v/v% HF mixed solution and used for mass bias correction. HCl and HNO_3 supplied by TAMA Chemicals (AA-10 for HNO_3 and AA-100 for HCl), and HF supplied by Kanto chemical Co. Inc. (Ultrapur-100) used for chemical separation and dilution for ICP-MS measurement, were of ultrapure grade. Ultrapure water with a resistivity of 18.2 MΩ cm, purified with a Milli-Q system, was used throughout the experiments. To minimize contamination from labware, all PTFE beakers and polyethylene vials were immersed in 9.4 M HCl, 9.4 M HCl/0.01 M HF, and ultrapure water at 90 °C for 3 h before use.

2.2. TEDA cartridge and anion-exchange resin column

The TEDA cartridge was prepared by graft polymerization and subsequent chemical modifications of the pore surface of the porous polyethylene sheet (thickness: 2.0 mm, porosity: 75%, average pore size: 1.0 μm), according to the procedure described in our earlier publications [22–27]. The amount of anion-exchange group introduced into the sheet was 5.2 mmol/g sheet [22]. A 5.9 mmϕ disk with an effective volume of 0.08 cm^3 was cut from the prepared TEDA-containing sheet and then packed into an empty polypropylene cartridge (Bond Elut, volume: 1.0 mL) supplied by Agilent Technologies. The prepared cartridge was referred to as a TEDA cartridge. The TEDA cartridge was conditioned by loading pure water, 9.4 M HCl, 9.4 M HCl/0.01 M HF, 0.1 M HNO_3, and pure water again (1.0 mL each) immediately before loading sample solutions for removal of impurities. The flow rate was set at 1.5 mL/min by compressing air in the inner space of the cartridge using a syringe. To compare the separation performances with those of a conventional technique, strongly basic anion-exchange resin (AG®1 × 8, Bio-Rad Laboratories, Inc., wet bead size: 105–180 μm) was packed into a commercially available empty polypropylene column with an inner diameter of 5.0–5.5 mm. The wet bed volume was 1.0 mL. Based on our previous experiment, which demonstrated that an anion-exchange resin-packed column with a volume of 1 mL has sufficient