Zr/Nb isobar separation experiment for future ^{93}Zr AMS measurement

W.Lu¹, T. Anderson¹, M. Bowers¹, W. Bauder¹, P. Collon¹, W. Kutschera², Y. Kashiv¹,
J. Lachner², M. Martschini², K. Ostdiek¹, D. Robertson¹, C. Schmitt¹, M. Skulski¹, P.
Steier²

¹*Nuclear Science Laboratory (NSL), University of Notre Dame, Notre Dame, IN, 46628, USA*

²*Vienna Environmental Research Accelerator (VERA), University of Vienna, Austria*

^{93}Zr ($t_{1/2} = 1.6$ Ma) is mostly produced by the main s -process in low-to-intermediate mass AGB stars. Large uncertainty exists in the current $^{92}\text{Zr}(n,\gamma)^{93}\text{Zr}$ Maxwellian Average cross section. This could have significant impact on nucleosynthesis calculations. Large amounts of ^{93}Zr are also produced in nuclear reactors and pose long-term environmental radioactivity. Hence, measurement of ^{93}Zr by the AMS is important for both fields above. We report here on progress in the development of AMS method to measure ^{93}Zr . Compared with 98 MeV beam energy, Zr/Nb isobar position separation was improved using 155.2 MeV beam energy and Gas-Filled Magnet. Energy loss measurement with increased beam energy inside the detector indicates that higher beam energy can improve isobar energy loss separation. A chemical procedure to reduce the Nb content in Zr samples has been developed and tested. It reduces the ^{93}Nb content by a factor of 1000.

1. Introduction

Zirconium has five stable isotopes: ^{90}Zr , ^{91}Zr , ^{92}Zr , ^{94}Zr and ^{96}Zr . Among the unstable isotopes, ^{93}Zr has the longest half-life of 1.6 Ma [1] and is a pure β - emitter. The interest in ^{93}Zr stems from the following two fields. The first is nuclear astrophysics. Similar to stable Zr isotopes (except ^{96}Zr), ^{93}Zr is predominantly of s -process origin, with small contributions also from the r -process and other proposed nucleosynthesis processes, such as the α -process [2] and the νp -process [3]. The neutron numbers of the Zr isotopes, including ^{93}Zr , are equal or close to the neutron magic number 50 and so are located on the first s -process peak. For this reason, the $^{92}\text{Zr}(n,\gamma)^{93}\text{Zr}$ cross section at s -process temperatures is important for nucleosynthesis models. However, the uncertainties of the previous measurements (listed in the Table 1 of Lu et al. [4]) are up to 10%. In addition, all the previous measurements were made by the time-of-flight (TOF) method. Potentially, the neutron capture cross section could be measured by combining ^{92}Zr activation with measuring ^{93}Zr by AMS, as a complementary technique to the TOF method.

The second field is nuclear waste management. ^{93}Zr is present in a relatively large amount in nuclear waste from fission and neutron activation [5]. Measuring the ^{93}Zr abundance in nuclear waste is urgently needed in order to evaluate its long-term environmental impact. However, due to its long half-life and being a β - emitter, detecting ^{93}Zr by decay is extremely difficult. AMS, on the other hand, circumvents these limitations and could be suited for the measurements.

An alternative to storing nuclear waste in geological repositories is the transmutation of long-lived radionuclides. Takibaev et al. [6] have demonstrated using a fusion-driven neutron source with high-flux blanket to transmute ^{93}Zr to ^{94}Zr . Such a transmutation study needs accurate Zr neutron capture cross sections and an analytical method for measuring ^{93}Zr , for which AMS is well suited.

These applications require a reliable ^{93}Zr AMS detection method. However, earlier work on this topic is scarce due to the difficulties of detection development. The CIAE group started the AMS development of ^{93}Zr using a gas ionization chamber [7]. With the partial isobar separation, the claimed sensitivity for $^{93}\text{Zr}/\text{Zr}$ was below 10^{-10} (published in 2013 [8]). TU Munich group also spent great efforts on this development, during which different molecule forms (ZrF_4), isobar separation techniques (the passive absorber and the Gas-filled Analyzing Magnet System) were used [9]. Due to the fact that no ^{93}Zr is observed, an upper limit of 10^{-10} for detection was given through interpolation. We report here on the progress in developing the method at the NSL at the University of Notre Dame.

2. Review of the Previous Work

The previous work presented Zr/Nb isobar separation using a 98 MeV beam combined with Gas-Filled Magnet (GFM) and energy loss measurement at the NSL [4]. The NSL AMS facility is detailed in [4]. The key components are Multi-Cathode Source of Negative Ions by Cesium Sputtering (MC-SNICS), 11 MV FN tandem accelerator, Wien Filter (WF), Browne-Buechner spectrograph and Parallel Grid Avalanche Counter (PGAC), and four-anode Ionization Chamber (IC) detector system.

Using beam energy of 98 MeV, the position and energy loss of ^{93}Zr were not sufficiently separated from its stable isobar Nb (Figure 1). The residual Zr beam energy in the IC (point E in Figure 2) was much lower than the Zr Bragg peak in the isobutane gas (point A in Figure 2). In addition, energy measurement requires Zr ions be fully stopped inside the detector. It was found as well that due to insufficient isobar separation, it is necessary to chemically separate Zr from Nb contamination in the samples.

It was experimentally determined that zirconium oxide is better than zirconium metal and zirconium hydride as sample material. Zirconium is sputtered from the oxide as ZrO^+ , which suppresses Niobium sputtering (as NbO^+) [4]. When silver (the filler material) is mixed

with the cathode material, the typical ZrO^+ beam current is 1 μA . However, ^{109}Ag is an isobar of $^{93}\text{Zr}^{16}\text{O}$ ($m = 109$ amu) and hence interferes with ^{93}Zr measurement [4].

3. Current Work

Following the results of the earlier work, the current work focuses on three things: improving Zr/Nb isobar separation with higher beam energy, modifying the detector configuration for improved energy loss measurements with higher energy beam and developing an efficient chemical procedure for Nb reduction.

3.1. AMS Experimental Method

The results presented here were obtained using natural ZrO_2 blank (i.e., containing no ^{93}Zr) as the cathode material. No cathode filler was mixed into the ZrO_2 powder, as previous experiments have shown that even high purity C, Cu and Ag materials introduce additional Nb contamination. The $^{93}\text{Zr}/\text{Zr}$ ratio of the available ^{93}Zr enriched sample is $\sim 10^{-11}$. Since this ratio is below the currently achieved $^{93}\text{Zr}/\text{Zr}$ sensitivity, the ^{93}Zr position is extrapolated through the positions of the same energy $^{92,94}\text{Zr}$ in the spectrum.

It was pointed out that using higher energy may improve isobar separation [4]. Several particle energies higher than 98 MeV were tested in a number of follow-up experiments. For each energy, different GFM pressure and detector gas pressure combinations were tested. The beam energy available at the NSL is limited by the accelerator terminal voltage, charge state abundance after the stripper foil and the magnetic field strength. The highest Zr beam energy of 155.2 MeV was obtained with $q = +15$ charge state and the accelerator terminal voltage of 9.7 MV. The resulting particle transmission from the ion source to the detector is 0.01%. The results with 155.2 MeV beam energy, 2 Torr N_2 in the GFM, 3 Torr isobutane gas in the PGAC, and 9 Torr isobutane gas (limited by the pressure transducer used to regulate the IC gas pressure) in the IC, are presented in Figure 3.

With 155.2 MeV beam energy, the energy separation with the multi-anode IC of ^{93}Zr from ^{93}Nb is still small. This is probably due to the residual beam energy inside the IC (point D in Figure 2) being below the Bragg peak (point A in Figure 2). This significant energy reduction from 155.2 MeV incident energy (point B in Figure 2) is due to energy losses as the ion passes through the GFM Mylar window, GFM gas and two layers of Mylar windows in the existing detector configuration (ion passage in the GFM is shown in Figure 4). To enhance isobar energy loss separation, the beam energy inside the IC needs to increase. That was achieved by not using the GFM. This higher beam energy inside the IC requires higher gas pressure to fully stop the ions. Hence, a Mylar window supporting grid was made and added to the detector configuration (location indicated in Figure 4). And a 100 Torr pressure transducer replaced the original 10 Torr pressure transducer used for regulating the IC gas pressure. These modifications expanded IC pressure range to 50 Torr.

3.2. AMS Experiment Results and Discussion

The sample used was pure ZrO_2 without any conducting cathode filler. Cesium sputtering of the sample typically produces 400 nA current.

For 155.2 MeV beam energy, different GFM pressures (below 4 Torr) do not vary the degree of isobar position separation as much as it affects ion charge-exchange statistics in the GFM gas. But it changes the residual beam energy in the IC, thus influencing the degree of energy loss separation. With this beam energy and after ion energy loss in the GFM, Zr ions start with higher energy loss than Nb on the Bragg curve (cf. Figure 2). Additionally, the available highest IC gas pressure (10 Torr) is not sufficient to fully stop ions. Out of all the combinations, the overall best isobar separation occurs when the GFM was filled with 2 Torr gas. And in all 4 anodes, the largest energy loss separation between ^{93}Zr - ^{93}Nb happens in the first anode (dE1) (Figure 3).

Compared with the limited position separation with the 98 MeV beam energy (Figure 1), the interpolated ^{93}Zr - ^{93}Nb position separation in the GFM improved with the 155.2 MeV beam energy (Figure 3). The centroids of the position peaks are separated by about 50 channels (correspond to 1 cm along the PGAC). However, the Full-Width-Half-Maximum (FWHM) of the position peak is about 100 channels (correspond to 1.3 cm). The situation is similar for the energy loss difference. As a result, the ^{93}Nb region still overlaps to a large extent with the interpolated ^{93}Zr region. The peak widening is the result of energy straggling in both the foils and gas.

As pointed out earlier, the spectrograph was also run in Non-GFM mode to allow higher beam energy inside the IC, in order to explore isobar energy loss separation with higher energy. In this mode, there is no position separation between the isobars and only energy loss difference. As a result, the data are plotted as energy loss in one anode vs. energy loss in another anode. Energy signals of all anodes were amplified by the same factor, and were not changed in the course of experiment to study the energy loss process. The gas pressure inside the IC was changed from 15 Torr (beam not stopped inside the detector) to 30 Torr (beam almost fully stopped inside the gas volume) in 5 Torr steps. The 15 Torr and 25 Torr spectra for the first three anodes are shown in Figure 5. The data of the last anode (dE4) were excluded due to low signal/noise ratio. To avoid overcrowding Figure 5, only the ^{92}Zr and ^{93}Nb 1D energy peaks are plotted.

As shown in dE1 of Figure 5a, ^{93}Nb initially loses more energy than ^{92}Zr . This means that, under experimental conditions, the beginning section of ^{93}Nb Bragg curve is higher than that of ^{92}Zr . Then their Bragg curves cross and ^{92}Zr loses more energy (dE3 in Figure 5a). At 25 Torr, the crossover occurs in dE1, so ^{92}Zr and ^{93}Nb lose about the same energy (Figure 5b). From the relative energy loss differences in each anode at different IC gas pressures, we were able to qualitatively construct their Bragg curves (dashed lines in Figure 6) and compare them with SRIM calculations (solid lines in Figure 6). Figure 6 shows that the crossover of

the experimental Bragg curves happens ‘earlier’ than the theoretical calculation. Also, the ranges of the two ions in the IC are longer than predicted.

Comparison of the GFM and Non-GFM results at different energies indicates that isobar position separation in the GFM is achieved at a cost of energy loss measurement in the IC. However, with the available energy and existing setup at the NSL, Zr/Nb isobar cannot be fully separated in position. This means that such an isobar separation is more efficient by pure energy loss measurements. The Non-GFM result (Figure 7) shows that the maximum separation is achieved in dE3. Based on SRIM simulation, energy separation may improve at higher beam energy. In addition, the ions have relatively large energy straggling due to the two layers of Mylar windows in the detector. With only 1 atomic number difference between ^{93}Zr and ^{93}Nb , the straggling needs to be minimized, possibly through more homogenous windows. The insufficient isobar separation stresses the need for a higher resolution detector. We are currently in the process of building a 6 anode ionization chamber, which is expected to provide the required ^{93}Zr - ^{93}Nb separation.

3.3. Niobium Reduction Chemistry

Our earlier work has shown that Nb contamination in the Zr samples is high and needs to be chemically reduced [4]. In order to do that, we followed the chemical procedure developed by D.G. Graczyk of the Analytical Chemistry Laboratory, Chemical Science and Engineering Division, Argonne National Laboratory.

The separation procedure is based on anion exchange chromatography. Initially, Zr metal is dissolved in a HF-HCl acid mix. The Zr-containing solution is added onto a prepared Dowex AG column which is conditioned with the same HF-HCl acid mix. In this acidic environment, Zr ions travel faster down the column than Nb ions [10], which results in the Zr-containing eluent emerging first. The eluent is collected and the process can be repeated with fresh columns for further Nb reduction.

Next, reagents that were added during previous steps need to be removed. First, the fluoride in the eluent was expelled as BF_3 gas with boric acid. It was followed by boric acid removal as methyl borate by adding methanol and refluxing the methanol. Then, the Zr product was re-dissolved in sulfuric acid. Finally, the sample is precipitated with ammonia, collected and burned into ZrO_2 powder, to be used as the cathode material. A blank sample was prepared from Zr metal by the same procedure, except for column reduction.

3.4. AMS Measurement of Niobium Reduction Factors

The previous work showed that the isotopic selectivity of the NSL AMS facility is not sufficient to reject isotopic interference at ~ 90 amu region, whereas the Vienna Environmental Research Accelerator (VERA) Laboratory has demonstrated excellent isotopic selectivity. Therefore the measurement of Nb-chemical-reduction-factor through AMS took place at the VERA laboratory. A detailed VERA facility description can be found in [11]. Another work on separating ^{93}Zr from ^{93}Nb at 24 MeV using the VERA facility can be found in a paper by Martschini et al. (submitted to NIMB in 2014).

The chemical reduction factor was deduced by comparing the $^{93}\text{Nb}/^{90}\text{Zr}$ ratio of the blank sample to that of the Nb-reduced sample. The measured Nb chemical reduction factors are shown in Figure 8. The number of passages through the columns each sample went through is indicated in its legend. For the blank sample, the $^{93}\text{Nb}/^{90}\text{Zr}$ contamination level is measured to be 6×10^{-5} . In sample A, the $^{93}\text{Nb}/^{90}\text{Zr}$ contamination level is reduced to be 6×10^{-8} . The lower reduction factors of samples D, E, F and G is thought to be due to the Zr metal contamination with Nb in the machining process. We conclude that a reduction factor of 1000 is achievable with this chemical procedure.

4. Conclusions and Outlook

Based on the new experimental results, it appears that higher beam energy will improve both ^{93}Zr - ^{93}Nb GFM position separation and energy loss measurement. The degree of attainable GFM position separation in the NSL facility is expected not to be sufficient for ^{93}Zr AMS measurement. At the same time, the Non-GFM experimental results show that it will be possible to separate the two isobars based solely on differences in energy loss. However, this will require a dedicated high energy resolution detector and minimizing energy straggling. A 6 anode small ionization chamber has been designed and built for this purpose, and will be used independent of the PGAC detector. Thin Silicon Nitride foils will be used in this detector instead of the Mylar windows to reduce energy loss and straggling. In this configuration, the Zr beam energy inside the detector could be very close to its Bragg peak. This detector enables the study of the Zr Bragg curve in more detail, as our preliminary results showed that the shape of the experimental Zr Bragg curve deviates from that simulated with SRIM. In addition, the upgrade of the NSL low energy injection system is expected to improve isotopic selectivity by at least an order of magnitude. Combined with the Nb reduction chemistry, we expect to reach a detection limit of $^{93}\text{Zr}/\text{Zr} \sim 10^{-10}$.

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Figure 1. dE1 vs. position spectrum of $E_{\text{beam}} = 98$ MeV (Figure 4b in [4]). The dotted ellipse is the expected ^{93}Zr region. The solid ellipse is the ^{93}Nb region.

Figure 2. The plot shows the Bragg curves for 200 MeV ^{93}Zr and ^{93}Nb beam in 30 Torr isobutane gas calculated with SRIM. The inset shows the Bragg curves for 500 MeV ^{93}Zr and ^{93}Nb beam in 30 Torr isobutane gas calculated with SRIM. The energies of ^{93}Zr and ^{93}Nb in the plot fall approximately within the grey region of the inset. Point A is the ^{93}Zr Bragg peak (~ 160 MeV) in isobutane. Point B corresponds to 155.2 MeV ^{93}Zr . Point C to E are the residual ^{93}Zr energies inside the IC in experimental conditions: point C is the residual energy (~ 97 MeV) for 155.2 MeV Zr beam using the PGAC and IC combination in the Non-GFM (cf. Figure 7); point D is the residual energy (~ 59 MeV) for 155.2 MeV Zr beam in the GFM (cf. Figure 3); point E is the residual energy (~ 28 MeV) for 98 MeV Zr beam in the GFM (cf. Figure 1).

Figure 3. dE1 vs. position spectrum of $E_{\text{beam}} = 155.2$ MeV in the GFM. The GFM was filled with 2 Torr N_2 gas. The PGAC was filled with 3 Torr isobutane gas. The IC was filled with 9 Torr isobutane gas. The expected location of ^{93}Zr (dash ellipse) was extrapolated from the locations of ^{92}Zr (dot ellipse) and ^{94}Zr (dash dot ellipse).

Figure 4. Beam path in the GFM and the existing detector. Not to scale. The GFM and detector Mylar windows are each $2.54 \mu\text{m}$ thick. The window supporting grid between the PGAC and IC is a new addition to the configuration.

Figure 5. The energy loss spectra of 155.2 MeV ^{92}Zr (black line) and ^{93}Nb (red dotted line) in the first 3 anodes of the IC with various IC pressures, in Non-GFM mode. All signal gains are the same. The IC pressure was 15 Torr in (a), 25 Torr in (b).

Figure 6. Solid lines: SRIM simulation of the Bragg curves of ^{93}Zr and ^{93}Nb inside the IC in the Non-GFM mode. Beam energy is 155.2 MeV. Ions pass two layers of Mylar windows in the detector before entering IC gas volume (cf. Figure 4). The IC is filled with 25 Torr isobutane. Dashed lines: qualitative interpretation of the energy loss from the experimental result (Figure 5).

Figure 7. dE1 vs. dE3 of 155.2 MeV beam in the Non-GFM mode. The IC is filled with 25 Torr isobutane gas. The black ellipse indicates the ^{93}Nb region. The orange dotted ellipse indicates the ^{92}Zr region. The red dot dash ellipse indicates the ^{94}Zr region. The purple dash ellipse is the expected ^{93}Zr position.

Figure 8. The Nb reduction factor of different samples after the chemical reduction procedure. Each sample started with a small Zr metal shave machined from the same Zr rod, followed the chemical procedure detailed in 3.3 and turned into ZrO_2 powder. The number of passages through the columns each sample went through is indicated in the legend.

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