Precise half-life measurement for the ground state of ^{94}Nb

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The half-life of the ground state of ^{94}Nb has been remeasured by a combination of multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) for the determination of the isotope ratio ^{94}Nb/^{93}Nb and γ-ray spectrometry for the determination of ^{94}Nb activity. The resulting value, $(2.04 \pm 0.04) \times 10^4$ yr, is in agreement with the latest literature value of $(2.03 \pm 0.16) \times 10^4$ yr [R. P. Schuman and P. Goris, J. Inorg. Nucl. Chem. **12**, 1 (1959)] within uncertainty limits, but has a much reduced uncertainty.

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I. INTRODUCTION

In nucleosynthesis of natural elements, the monoisotopic element Nb was produced mostly by the slow neutron capture process (*s* process) via the decay of the long-lived radioactive nuclide ^{93}Zr ($T_{1/2}$ = 1.5 million years). ^{93}Nb can be used to discriminate between intrinsic and extrinsic asymptotic giant branch (AGB) stars [1]. An accurate half-life of ^{94}Nb is required in the study of nucleosynthesis of naturally occurring elements because of its position in the weak *s*-process path.

With an uncomplicated decay mode [2], ^{94}Nb has been selected by International Atomic Energy Agency (IAEA) as one of the γ-ray decay data standards for detector calibration and other applications [3]. So, it is essential to have an accurate half-life value of ^{94}Nb.

The recently developed niobium-containing zirconium alloy exhibits excellent burn-up characteristics, making it an ideal material for the pressure tubes in some reactors and the cladding of most light water reactors because of its long-term corrosion resistance and favorable mechanical properties. A half-life value of ^{94}Nb with sufficient accuracy is therefore required in radioactive waste management and reactor decommissioning.

In our studies on AMS measurement of ^{92}Nb, a unique nuclide in cosmophysics as one of the four most accurate *p*-process extinct chronometers and the only "shielded" *p*-process nuclide, an absolute method had to be used due to the lack of a ^{92}Nb standard sample. In order to evaluate the feasibility and accuracy of the absolute Accelerator Mass Spectrometry (AMS) method, ^{94}Nb, produced by reactor neutron activation on ^{93}Nb and standardized for ^{94}Nb/Nb by multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS), was used as the reference in the absolute AMS measurement of ^{92}Nb.

Taking the advantage of the simple and well established decay scheme of ^{94}Nb and sophisticated HPGe γ-ray spectrometry, the specific activity of ^{94}Nb was determined. Combining the ^{94}Nb/Nb isotope ratio with the specific activity of ^{94}Nb, a new value of the half-life of ^{94}Nb was obtained with unprecedented accuracy. This enables the quantification of the atom ratio ^{94}Nb/Nb simply by HPGe γ-ray spectrometry.

II. EXPERIMENT

A. Production of ^{94}Nb by ^{93}Nb(n,γ) reaction

Several grams of high-purity niobium powder (99.99%), packaged and sealed in an aluminum can (5 mm in inner diameter and 6 mm high), were irradiated for 200 h in a thermal column of the swimming pool research reactor at CIAE. The thermal neutron flux at the sample position was about 10^{11} n cm^{-2} s^{-1}.

After six months of cooling, all of the metastable states of niobium 94 (^{94}Nb^m, $T_{1/2}$ = 6.26 min) and other short-lived nuclides had decayed. The specific activity and the isotopic abundance ratio of ^{94}Nb/Nb in the samples were then measured by HPGe γ-ray spectrometry and MC-ICP-MS, respectively.

B. Measurement of ^{94}Nb specific activity

For the γ-spectrum measurement, 94.83 mg of the irradiated niobium powder was weighed by a microbalance and packaged in a polyethylene bag (5 mm × 5 mm).

The sample was measured by a low-background anti-Compton γ spectrometer, consisting of a coaxial HPGe detector [model GEM-10020(P), ORTEC corporation, USA; FWHM 1.88 keV and relative efficiency 115.7% for 1332 keV γ rays] as the main detector surrounded by a well-type anticoincidence detector group composed of a suite of annular and cylindrical NaI(Tl) scintillation detectors.

A full energy efficiency curve was established at the sample position of 30 cm from the top surface of the main detector by a series of standard γ sources (^{57}Co, ^{137}Cs, ^{60}Co, ^{152}Eu, and ^{182}Ta) with relative standard uncertainties in activities of less than 1%, certified by the National Institute of Metrology of China.

As shown in Fig. 1, the decay scheme of ^{94}Nb [2], two prominent γ rays with energies of 702.6 and 871.1 keV are emitted in cascade following the β^- decay of ^{94}Nb to the ground state of ^{94}Mo. A γ-ray spectrum was taken on the anti-Compton HPGe detector at the sample position of 30 cm

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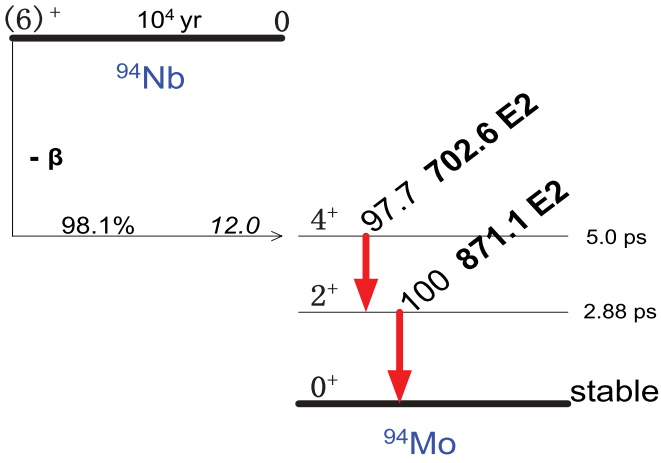

FIG. 1. (Color online) Decay scheme of ^{94}Nb.

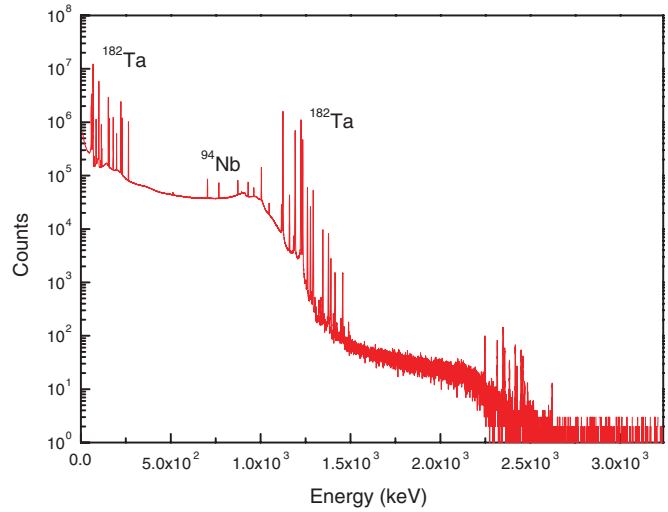

FIG. 2. (Color online) The full view of the γ-ray spectrum.

from the surface of the main detector, to make coincidence losses of the cascade γ rays negligible.

The currently recommended values of the emission probabilities of 702 and 871 keV γ rays [3], applied in following calculation, and the detection efficiencies from the above mentioned efficiency curve are listed in Table I.

A full view γ-ray spectrum of a ^{94}Nb sample is presented in Fig. 2. It shows that the main interferences in the activity determination came from the Compton continuum of the impurity ^{182}Ta. Fortunately, the peaks of the interested γ rays are still quite clear and prominent, as presented in Fig. 3.

The spectrum was acquired by 116000 s counting. The net peak areas of 702.6 and 871.1 keV were obtained after the dead time corrections.

The resulting specific activity of ^{94}Nb is given in Table II.

C. Measurement of ^{94}Nb/Nb

For the isotope ratio determination, several milligrams each of the irradiated and the unirradiated niobium powder samples were respectively weighed and dissolved with nitric acid plus hydrofluoric acid. After the removal of fluorine, the solution was adjusted to about 1 mg/L niobium in 2% nitric acid medium.

The isotopic ratios of ^{94}Nb/^{93}Nb in both irradiated and unirradiated (blank) samples were measured by a set of MC-ICP-MS (Isoprobe^{TM}, GV corporation, U.K.). The intensive events of ^{93}Nb were measured on Faraday collectors with static mode. The sparse events of ^{94}Nb and impurities with $A = 94$ were recorded by the Daly-photomultiplier ion counting system. The resulting $^{94}A/^{93}$Nb values from 12 independent measurements for each of an unirradiated and two irradiated samples are listed in Tables III and IV, respectively.

For the unirradiated sample, the ions with $A = 94$ were contributed by ^{94}Zr$^+$, ^{94}Mo$^+$, and the molecular ion ^{93}Nb^{1}H$^+$. For the irradiated sample, in addition to the same contributors as for the unirradiated sample, ^{94}Nb$^+$ is a dominate contributor of all nuclides with $A = 94$.

In the data analysis, the underlined data in Tables III and IV were rejected because they are outside of the confidence interval. The average isotope ratio of $^{94}A/^{93}$Nb in the two irradiated samples was calculated to be $^{94}A/^{93}\text{Nb} = (1.1228 \pm 0.0064) \times 10^{-5}$, with a relative standard deviation (RSD) of 0.57%. Subtracting the ratio of $^{94}A/^{93}$Nb of the unirradiated sample from that of the irradiated sample, the isotopic ratio of ^{94}Nb to ^{93}Nb, ^{94}Nb/^{93}Nb, was preliminarily obtained to be $(7.412 \pm 0.106) \times 10^{-6}$ with a relative standard deviation of 1.43%.

Because there was no ^{94}Nb standard available for mass spectrometry, the standard reference material SRM 987 (strontium carbonate, isotopic standard, National Institute of Standards & Technology, USA) certified for the isotopic ratios of ^{86}Sr to ^{88}Sr and ^{84}Sr to ^{88}Sr, was used to correct for instrumental mass bias and the efficiency ratio between Daly and Faraday detectors. The certified and measured (uncorrected for efficiency and cup ratio) values for the strontium isotopic abundance ratios were compiled in Table V.

TABLE I. Emission probabilities and detection efficiencies of 702 and 871 keV γ rays.

Energy (keV)	Efficiency	Rel. unc.	Emission probability	Rel. unc.
702.63	0.0005811	0.7%	0.99815	0.006%
871.11	0.0004878	0.7%	0.99892	0.003%

TABLE II. Calculation for specific activity of ^{94}Nb.

Energy (keV)	Net peak area	Rel. unc.	Activity	Rel. unc.	Avg. specific activity
702.63	355966	0.37%	5.29 kBq	0.8%	55.68 ± 0.32 Bq/g
871.08	297797	0.44%	5.27 kBq	0.8%	

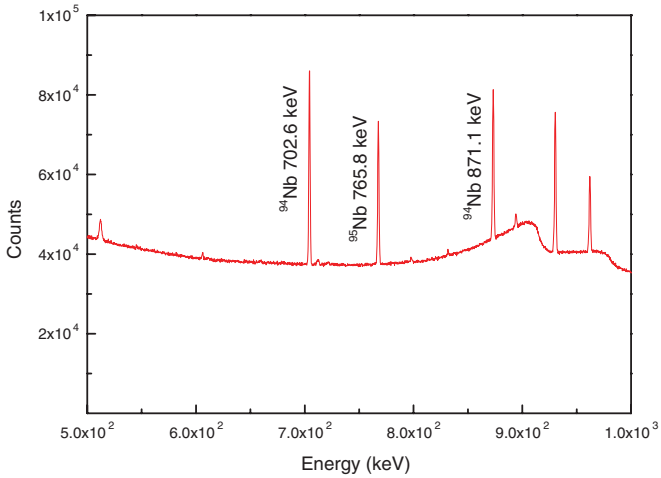

FIG. 3. (Color online) The local zoom of the γ-ray spectrum.

The correction factors for the mass bias and Daly-Faraday gain, β and K, were respectively obtained by Eqs. (1) and (2) to be $\beta = -3.020$ and $K = 1.114$:

$$\beta = \ln((N_{\mathrm{Sr86}}/N_{\mathrm{Sr88}})_{\mathrm{certified}}/(N_{\mathrm{Sr86}}/N_{\mathrm{Sr88}})_{\mathrm{measured}})/\ln(86/88), \quad (1)$$

$$K = (N_{\mathrm{Sr84}}/N_{\mathrm{Sr88}})_{\mathrm{certified}}/(N_{\mathrm{Sr84}}/N_{\mathrm{Sr88}})_{\mathrm{measured}}/(86/88)^{\beta}, \quad (2)$$

where $N_{\mathrm{Sr86}}/N_{\mathrm{Sr88}}$ and $N_{\mathrm{Sr84}}/N_{\mathrm{Sr88}}$ are the isotopic ratios of ^{86}Sr/^{88}Sr and ^{84}Sr/^{88}Sr, respectively.

The corrected ^{94}Nb/^{93}Nb is $(7.994 \pm 0.128) \times 10^{-6}$ calculated by Eq. (3),

$$(N_{\mathrm{Nb94}}/N_{\mathrm{Nb93}})_{\mathrm{corrected}} = K \times (94/93)^{\beta} \times (N_{\mathrm{Nb94}}/N_{\mathrm{Nb93}})_{\mathrm{uncorrected}}, \quad (3)$$

TABLE III. Results of $^{94}A/^{93}$Nb for an unirradiated sample.

Cycle	Daly[a]	Faraday[a]	$^{94}A/^{93}$Nb
1	2.860×10^{-5}	7.606	3.760×10^{-6}
2	2.937×10^{-5}	7.643	3.843×10^{-6}
3	2.912×10^{-5}	7.548	3.858×10^{-6}
4	2.889×10^{-5}	7.515	3.844×10^{-6}
5	2.866×10^{-5}	7.568	3.786×10^{-6}
6	2.841×10^{-5}	7.556	3.760×10^{-6}
7	2.851×10^{-5}	7.560	3.771×10^{-6}
8	2.921×10^{-5}	7.539	3.875×10^{-6}
9	2.915×10^{-5}	7.518	3.877×10^{-6}
10	2.803×10^{-5}	7.463	3.756×10^{-6}
11	2.878×10^{-5}	7.481	3.847×10^{-6}
12	2.978×10^{-5}	7.538	3.950×10^{-6}
	Average isotope ratio		3.816×10^{-6}
	RSD (%)		1.29

[a]Beam intensities on both Daly and Faraday cups are in volts.

where $(N_{\mathrm{Nb94}}/N_{\mathrm{Nb93}})_{\mathrm{uncorrected}}$ and $(N_{\mathrm{Nb94}}/N_{\mathrm{Nb93}})_{\mathrm{corrected}}$ represent the ratios of ^{94}Nb/^{93}Nb before and after correction, respectively.

III. RESULTS

A. Half-life

The half life was calculated by Eq. (4) to be $(2.04 \pm 0.04) \times 10^4$ yr:

$$T_{1/2} = (N_{94}/N_{93}) \div A_{\mathrm{SP}} \times (1/93) \times R \times \ln 2, \quad (4)$$

where A_{SP} is specific activity of ^{94}Nb in the irradiated sample, $A_{\mathrm{SP}} = A/\varepsilon/\gamma$ $(55.68 \pm 0.32\ \mathrm{Bq/g})$, with A being the average counting rate of the 702.6 (or 871.3) keV full-energy peak for a 1 g sample, ε the full-energy peak efficiency for 702.6 (or

TABLE IV. Results of $^{94}A/^{93}$Nb for two irradiated samples.

Cycle	Sample 1			Sample 2		
	Daly[a]	Faraday[a]	^{94}A/^{93}Nb	Daly[a]	Faraday[a]	$^{94}A/^{93}$Nb
1	7.060×10^{-5}	6.344	1.113×10^{-5}	1.030×10^{-4}	9.188	1.120×10^{-5}
2	7.193×10^{-5}	6.342	1.134×10^{-5}	1.028×10^{-4}	9.106	1.129×10^{-5}
3	7.046×10^{-5}	6.362	1.108×10^{-5}	1.012×10^{-4}	9.077	1.115×10^{-5}
4	7.082×10^{-5}	6.308	1.123×10^{-5}	1.037×10^{-4}	9.107	1.138×10^{-5}
5	6.933×10^{-5}	6.297	1.101×10^{-5}	1.055×10^{-4}	9.254	1.140×10^{-5}
6	7.083×10^{-5}	6.241	1.135×10^{-5}	1.037×10^{-4}	9.214	1.126×10^{-5}
7	6.953×10^{-5}	6.254	1.112×10^{-5}	1.048×10^{-4}	9.213	1.137×10^{-5}
8	7.038×10^{-5}	6.250	1.126×10^{-5}	1.023×10^{-4}	9.131	1.120×10^{-5}
9	6.965×10^{-5}	6.243	1.116×10^{-5}	1.026×10^{-4}	9.138	1.122×10^{-5}
10	6.952×10^{-5}	6.272	1.108×10^{-5}	1.025×10^{-4}	9.118	1.124×10^{-5}
11	6.929×10^{-5}	6.227	1.113×10^{-5}	1.026×10^{-4}	9.036	1.135×10^{-5}
12	6.867×10^{-5}	6.191	1.109×10^{-5}	1.040×10^{-4}	9.102	1.142×10^{-5}
	Average isotope ratio		1.116×10^{-5}			1.129×10^{-5}
	RSD (%)		0.97			0.80

[a]Beam intensities on both Daly and Faraday cups are in volts.

TABLE V. Certified and measured Sr isotopic ratios of the SRM 987.

Certified isotope ratio	$^{88}Sr/^{86}Sr$	8.37861 ± 0.00325
	$^{87}Sr/^{86}Sr$	0.71034 ± 0.00026
	$^{84}Sr/^{86}Sr$	0.05655 ± 0.00014
Measured isotope ratio (uncorrected)	$^{88}Sr/^{86}Sr$	8.98110 ± 0.00790
	$^{87}Sr/^{88}Sr$	0.08187 ± 0.00012
	$^{84}Sr/^{88}Sr$	0.00526 ± 0.00001

871.3) keV γ rays at 30 cm source-detector distance, and γ the emission probability of 702.6 (or 871.3) keV γ rays in the decay of ^{94}Nb. N_{94}/N_{93} is the isotopic ratio of ^{94}Nb to ^{93}Nb [$(7.994 \pm 0.128) \times 10^{-6}$], and R is the Avogadro constant.

B. Uncertainties

The total uncertainty of the ^{94}Nb half-life consists of the uncertainties in the specific activity, A_{SP}, and the isotope abundance ratio, N_{94}/N_{93}, as detailed in Table VI.

The uncertainty in specific activity was mainly contributed by peak counting statistics and efficiencies, which were calibrated by a set of standard sources certified by the National Institute of Metrology of China with relative standard uncertainties of less than 1%. The uncertainties in the efficiencies of 702 and 871 keV γ rays were estimated to be lass than 0.7%, taking advantage of the locations of the two γ rays being at the linear region of the efficiency curve (in log-log scale). The summing effect of the γ-ray cascades of interest (702 and 871 keV) is negligible due to the total efficiencies of 702 and 871 keV γ rays being smaller than 0.1% at the counting position 30 cm from the top surface of the detector.

In the mass spectra measurement, the relative statistic uncertainty was 1.5%, estimated by the relative standard deviation of multiple measurements. The main contributors of systematic uncertainty are the difference in the interference of $A = 94$ for the irradiated and nonirradiated Nb samples, and the normalization for mass bias and Daly-to-Faraday efficiency ratio by NIST SRM. For the former, $^{94}Nb^m$ produced by the reaction of ^{93}Nb(n,γ) decays with a branching ratio of 0.6% and a half-life of 3.26 m directly to ^{94}Mo, which causes the $^{94}A/^{93}$Nb ratio for the irradiated sample to be a little higher than that for the nonirradiated one. The relative uncertainty caused by this additional ^{94}Mo was estimated based on the cross sections of the ^{93}Nb$(n,\gamma)^{94}Nb^m$ reaction and the branching ratio of $^{94}Nb^m$ decay to ^{94}Mo to be less than 0.01%. For the latter, the uncertainties introduced in the corrections for mass bias and Daly-to-Faraday efficiency ratio were estimated to be about 0.01% and 0.2%, respectively.

TABLE VI. Uncertainty budget.

	Uncertainty item	Relative Standard Uncertainty (RSU)(%)
Activity measurement	Peak area	0.3
	Sample mass	0.01
	γ-ray branching uncertainty	<0.01
	Efficiency	0.7
	Sample self-absorption and geometrical correction	<0.01
Isotope ratio measurement	Statistics	1.5
	Mass bias correction	0.01
	Correction in Daly-Faraday gain ratio	0.2
	SRM 987	0.3
	Interference correction	<0.01
Total relative standard uncertainty in half-life of ^{94}Nb		1.8

TABLE VII. ^{94}Nb half-life values so far determined.

$T_{1/2}$ (yr)	Standard uncertainty (yr)	Time	Reference
>0.01	No information	1948	[8]
5×10^4	No information	1952	[7]
2.2×10^4	0.5×10^4	1953	[6]
2.7×10^4	0.4×10^4	1955	[5]
2.03×10^4	0.16×10^4	1959	[4]
2.04×10^4	0.04×10^4	2011	This work

IV. DISCUSSION

A summary of the $T_{1/2}$ (^{94}Nb) so far determined experimentally is presented in Table VII.

All previous measurements were made more than a half century ago, when neither sophisticated mass spectrometry nor modern high-resolution HPGe γ-ray spectrometry was invented. That severely limited the measurement precision. In addition, no international or national standards were used to guarantee the traceability of the values obtained in those measurements. That made the accuracy of those values unreliable. Evaluation values published in *Table of Isotopes*, 8th edition in 1996 [2] and more recently by Woods in 2007 [3] were all based on those values, and therefore unsatisfactory in both accuracy and precision.

In this work, high-purity Nb samples with Zr and Mo contents of <1 mg/kg each were used. The burn-up losses of ^{94}Mo and ^{94}Zr in the irradiated sample are therefore negligible. There is essentially no difference in the interference from the formation of the molecular ions $^{93}NbH^+$ between unirradiated and irradiated samples. Thus, a subtraction of $^{94}A/^{93}$Nb in the unirradiated sample from that in the irradiated one eliminated all isobaric and molecular interferences and resulted in the net ^{94}Nb/^{93}Nb in the irradiated sample.

With a combination of the high-energy resolution of the HPGe spectrometer and the high sensitivity of MC-ICP-MS, the new half-life value of ^{94}Nb, $(2.04 \pm 0.04) \times 10^4$ yr, was obtained with a much reduced uncertainty and clearer traceability.

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