Precision measurement of the half-life of $^{90\text{m}}\text{Nb}$ and $^{99\text{m}}\text{Tc}$

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Summary. We have produced $^{90\text{m}}\text{Nb}$ and $^{99\text{m}}\text{Tc}$ in the reactions of $^{\text{nat}}\text{Zr}(p, xn)^{90\text{m}}\text{Nb}$ and $^{100}\text{Mo}(\gamma, n)^{99\text{m}}\text{Mo}$, followed by disintegration to $^{99\text{m}}\text{Tc}$, respectively, and measured the half-lives of these nuclides by using a reference source method. In order to determine the short half-lives of $^{90\text{m}}\text{Nb}$ precisely, an on-line gas-jet system has been employed. As a result, the half-lives of these nuclides were determined with good precision on the order of magnitude of 0.1%.

1. Introduction

It was reported that the decay constants of the some dozen of nuclides from ^7Be to ^{235}U were changed with changing environmental factors such as chemical state [1]. Several studies have measured the half-life of ^7Be with various chemical states in recent years to investigate the effects of environmental condition on the decay constant [2, 3]. On the other hand, it is well known that the decay constants of $^{90\text{m}}\text{Nb}$ and $^{99\text{m}}\text{Tc}$ are also affected by its chemical environment. Almost all $^{90\text{m}}\text{Nb}$ and $^{99\text{m}}\text{Tc}$ nuclei decay via a 2.3-keV transition from the 124.7-keV level to the 122.4-keV level in ^{90}Nb and a 2.2 keV from the 142.7 keV to the 140.5 keV in ^{99}Tc [4], respectively. Because of the high internal conversion coefficient and low transition energy, the probability of the transition is expected to vary with changes in the chemical form affecting the electron density at the nucleus.

However, the variation measurements of decay constants of $^{90\text{m}}\text{Nb}$ and $^{99\text{m}}\text{Tc}$ were carried out with only a few kinds of the chemical forms and indicate some different results [1]. The goal of our research is to clarify the effects of chemical structure on the decay constants of $^{90\text{m}}\text{Nb}$ and $^{99\text{m}}\text{Tc}$. It is difficult that the observation of the variation of the decay constant because that is on the order of magnitude of 0.1% [1]. In the present study, the half-lives of $^{90\text{m}}\text{Nb}$ and $^{99\text{m}}\text{Tc}$ have been precisely measured by using a reference

source method. In order to determine the short half-lives of $^{90\text{m}}\text{Nb}$ in various chemical states precisely, we have employed an on-line gas-jet system.

2. Experimental procedure

2.1 Measurement for the half-life of $^{99\text{m}}\text{Tc}$

The isotope $^{99\text{m}}\text{Tc}$ was produced in the nuclear reaction $^{100}\text{Mo}(\gamma, n)^{99\text{m}}\text{Mo}$, followed by disintegration to $^{99\text{m}}\text{Tc}$. A sample of about 5 mg of enriched ^{100}Mo was enclosed in a quartz tube for bremsstrahlung irradiation. The irradiation was carried out with the electron linear accelerator at Tohoku University. The accelerator was operated at an electron energy of 50 MeV with a mean current of around 0.1 mA. The ^{100}Mo target was placed in close contact with the back of a platinum converter and cooled with running tap water during the 8 h irradiation.

After the irradiation, the ^{100}Mo target was dissolved in 1 mL of 7 M (mol/dm³) HNO_3 and then heated to dryness. The residue was dissolved in a few drops of 7 M NH_3aq and then added 0.1 M HCl to adjusted to neutral pH. The solution was passed through an anion exchange resin column (Dowex 1×8 , 200–400 mesh, 5.5 mm $\varnothing \times 40$ mm) to eliminate Tc from the Mo solution.

To allow the decay of ^{99}Mo ($T_{1/2} = 66.0$ h) and the growth of $^{99\text{m}}\text{Tc}$, the purified Mo solution was left to stand for about 22 h after the end of the purification of the Mo solution. The solution containing $^{99\text{m}}\text{Tc}$ was passed through an anion exchange resin column (Dowex 1×8 , 200–400 mesh, 5.5 mm $\varnothing \times 40$ mm) to adsorb the Tc isotopes. The resin was washed with 8 mL of 1 M HCl to remove Mo isotopes from Tc fraction. The Tc isotopes were eluted from the column with 12 mL of 7 M HNO_3 . The decontamination factor of the anion exchange process was confirmed to be 400–800 by γ -ray spectrometry of ^{99}Mo . The solution was heated to dryness and adjusted to 0.12 M KCl solution. The solution was passed through an alumina column (Wako Pure Chemical Industries, Ltd., 300 mesh, 5.5 mm $\varnothing \times 40$ mm) to reduce the content of ^{99}Mo . The alumina column procedure was repeated twice using a fresh column each time. Additionally, the Tc isotopes was purified by the anion exchange column

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procedure, the alumina column procedure (three times), and the anion exchange column procedure in this order. The purified Tc solution was finally adjusted to 7 M HNO₃ solution and divided into several fractions. 500 µg per a counting source of ^{99g}Tc was added to the purified solution as carrier. The Tc isotopes were changed its chemical form to prepare counting sources.

To prepare pertechnetate sources, the Tc fraction were heated to dryness and then the residue was dissolved in 0.7 M KCl solution. The solution was evaporated to dryness on a glass plate and then coated with paraffin.

The sulfide of heptavalent technetium Tc₂S₇ was precipitated from the Tc fraction adjusted to 2 M HCl by bubbling hydrogen sulfide at about 80 °C. The precipitate was collected on an alumina membrane filter of Anodisc 25 (pore size, 0.02 mm, Whatman Co., Ltd.), heated to dryness, and coated with paraffin.

The two samples of KTcO₄ and Tc₂S₇ were set in an automated sample changer [2] and placed alternately in front of a high-purity (HP) Ge detector at intervals of 1800 s. The 140.5-keV γ rays from ^{99m}Tc were measured for real time of 1750 s at each data point. The procedures were repeated over at least 42 h ($T/T_{1/2} > 7$). A ¹³⁷Cs source was attached to near the HP-Ge detector as a reference source to correct for influential factors for determination of half-life such as pile-up effect. The dead-time of measurement system was less than 16% at the beginning of the measurement. The internal clock time of the computer for data acquisition was constantly calibrated by a time-standard signal distributed via a long-wave radio transmission station in Japan.

2.2 Measurement for the half-life of ^{90m}Nb

The isotope ^{90m}Nb was produced in the nuclear reaction ^{nat}Zr(*p*, *xn*)^{90m}Nb with a 14 MeV proton beam delivered from the RIKEN K70 AVF Cyclotron. Five ^{nat}ZrO₂ targets of about 100 µg cm⁻² thickness were prepared by electrodeposition onto an 810 µg cm⁻² aluminum backing foil. The targets were placed in a gas-jet chamber at intervals of 8 mm. The beam intensity was about 8 µA. The 14 MeV proton beam entered the target stack at an energy of 13.8 MeV. The reaction products recoiling out of the targets were stopped in the helium gas, attached to KCl aerosol particles generated by sublimation of KCl powder at 640 °C, and continuously transported to the chemistry laboratory.

In order to determine the nuclide included in the reaction products, the reaction products were collected on a glass filter for 180 s and assayed by γ-ray spectrometry with a HP-Ge detector. The accumulation of γ-ray spectrum for 1 min was started 1 min after the end of aerosol collection and then repeated 30 times successively.

Next, the reaction products were deposited on a polyethylene terephthalate film to measure the half-life of ^{90m}Nb in 20 M HF. After deposition for 30 s, they were dissolved in 20 M HF and subjected to γ-ray spectrometry. The accumulation of γ-ray spectrum for 6 s was started within 1 min after the end of the aerosol deposition and then repeated 15 times successively. In order to achieve adequate statistical precision, the procedure was repeated 120 times. The half-lives of ^{90m}Nb were determined by the reference source method using ¹³⁷Cs as a reference source.

2.3 Derivation of half-life

The half-life of ^{90m}Nb and ^{99m}Tc was determined based on a reference source method [5]. The ratio $R(t)$ is given by the following equations:

$$R(t) = \frac{C_{\text{sample}}^0(t)}{C_{\text{ref}}^0(t)}, \quad (1)$$

$$C^0(t) = \frac{\lambda N}{(1 - e^{-\lambda t_R})} \frac{t_R}{t_L}, \quad (2)$$

where $C_{\text{sample}}^0(t)$ and $C_{\text{ref}}^0(t)$ are count rates of a sample and a reference source at the beginning of each data acquisition, respectively. N is the net counts in the objective peak. t_R and t_L are real time and live time, respectively. Using the slope of the graph $\ln R(t)$ vs. time a_{slope} , the half-life of the radionuclide in the sample T_{sample} is described in the following equation:

$$T_{\text{sample}} = \frac{1}{1/T_{\text{ref}} - a_{\text{slope}}/\ln 2} \quad (3)$$

where T_{ref} is the half-life of the reference source, namely ¹³⁷Cs ((11018.3 ± 9.5) d [6]).

3. Results and discussion

3.1 The half-life of ^{99m}Tc

A typical γ-ray spectrum for a KTcO₄ sample measured for 1750 s is shown in the Fig. 1. In all γ-ray spectrum obtained, the ^{99m}Tc γ line at $E_\gamma = 140.5$ keV and ¹³⁷Cs γ line at $E_\gamma = 661.5$ keV can be observed as two prominent peaks. No peaks were seen at around $E_\gamma = 181$, 739.5, and 777.9 keV which are the expected energy regions for ⁹⁹Mo, followed by disintegration to ^{99m}Tc.

If the activity ratio $A(\text{Mo})/A(\text{Tc})$ is smaller than about 10^{-6} at the beginning of the measurement, the activity of ⁹⁹Mo has no influence on the determination the half-life of ^{99m}Tc. Unfortunately, the amount of ⁹⁹Mo in the counting sample was not determined exactly because it was too small to detect. However, ^{99m}Tc was isolated from ⁹⁹Mo by using three anion exchange column processes. The decontamination factor of one anion exchange process is expected

Fig. 1. A typical γ-ray spectrum for a KTcO₄ sample measured for 1750 s.

Fig. 2. A typical exponential curve for the $R(t)$ obtained using a least-squares fitting procedure (a) and their residuals (b).

to be 400–800 described above. $A(\text{Mo})/A(\text{Tc})$ at after the 22 h growth time of $^{99\text{m}}\text{Tc}$ is approximately 1. Therefore, $A(\text{Mo})/A(\text{Tc})$ is expected to be smaller than 10^{-6} by the three anion exchange column processes. Additionally, we carried out five alumina column processes to eliminate ^{99}Mo from $^{99\text{m}}\text{Tc}$ completely.

In Fig. 2, a typical exponential curve for the $R(t)$ obtained using a least-squares fitting procedure and their residuals are plotted as a function of time. The residuals of the fit of all the data remain within the limit of approximately 1%. For the samples of KTcO_4 , the measurements were repeated several times using several detectors. The results were summarized in Fig. 3. The uncertainty is given by the uncertainty of the slope of the straight line fitted to the logarithm of $R(t)$ and the uncertainty of the half-life of ^{137}Cs (0.09% [6]) used as a reference source. The half-life values have the possibility to include random errors besides statistical errors [7]. The random errors are estimate to be 0.09% from the deviation of the values in Fig. 3. As a results, the half-life of $^{99\text{m}}\text{Tc}$ with the chemical form of KTcO_4 is determined to be (6.0016 ± 0.0053) h, which is in good agreement with recent values of other authors which were measured with the chemical form

Fig. 3. The half-life of $^{99\text{m}}\text{Tc}$ with the chemical state of KTcO_4 .

Fig. 4. Relative differences in the decay constant of $^{99\text{m}}\text{Tc}$ between TcO_4^- and Tc_2S_7 forms.

of pertechnetate ((6.0072 ± 0.0010) h in normal saline solution [8] and (6.0071 ± 0.0021) h in NaTcO_4 [5]).

Relative differences in the decay constant of $^{99\text{m}}\text{Tc}$, $\{\lambda(\text{TcO}_4^-) - \lambda(\text{Tc}_2\text{S}_7)\} / \lambda(\text{Tc}_2\text{S}_7)$ obtained from this work and the previous researches [9, 10] are plotted in the Fig. 4. The previous values are not consistent with each other within 2σ . Our result is consistent with the value reported by Mazaki *et al.* [10] within 1σ although the error of our value is larger than that of the previous values. Repetitive experiments by using the present methods will allow us to obtain good statistics and further information on the variation of decay constant of $^{99\text{m}}\text{Tc}$ with changing its chemical form.

3.2 The half-life of $^{90\text{m}}\text{Nb}$

A γ -ray spectrum for the glass filter sample is shown in Fig. 5. The spectrum is obtained as the sum of the first five spectra. The γ peaks of $^{90\text{g}}\text{Nb}$ ($T_{1/2} = 14.6$ h), $^{90\text{m}}\text{Nb}$, $^{52\text{m}}\text{Mn}$ (21.1 min), $^{54\text{m}}\text{Co}$ (1.48 min), ^{64}Ga (2.63 min), and $^{91\text{m}}\text{Y}$ (49.7 min) are observed in the spectrum. The γ peak of $^{90\text{m}}\text{Nb}$ at 122 keV is clearly separated from the peak of $^{90\text{g}}\text{Nb}$ at 133 keV, which is the closest to that of $^{90\text{m}}\text{Nb}$. No

Fig. 5. A γ -ray spectrum measured 300 s after the 180-s aerosol collection.

Fig. 6. Half-life values obtained in the present study (a) and its histogram (b). The solid line in (b) shows the Gaussian fit to the data.

serious background was observed in the γ -ray spectrum for determination of the half-life of ^{90m}Nb .

In the measurement of 20 M HF solution samples, only γ -rays from $^{90m,g}\text{Nb}$ and 511-keV line were observed. The half-life values of ^{90m}Nb obtained in the present study and its histogram are shown in Fig. 6. The half-life of ^{90m}Nb in 20 M HF solution has been determined to be (18.97 ± 0.04) s, which include 0.11% of a statistical error and 0.09% of a random error. The random error is assumed to be same as that of the Tc experiments. Note that this half-life is determined in a chemical form, probably NbF_7^{2-} , while the accepted value (18.81 ± 0.06) s [11] was determined by weighted average from the half-life of ^{90m}Nb with various chemical forms. Further work is underway to clarify the variation of the half-life of ^{90m}Nb with changing chemical form.

4. Conclusion

We have produced ^{90m}Nb and ^{99m}Tc in the $^{\text{nat}}\text{Zr}(p, xn)^{90m}\text{Nb}$ and $^{100}\text{Mo}(\gamma, n)^{99}\text{Mo}$, followed by disintegration to ^{99m}Tc ,

respectively. The half-lives of these nuclides were determined with good precision on the order of magnitude of 0.1%, namely (6.0016 ± 0.0053) h for ^{99m}Tc in KTcO_4 and (18.97 ± 0.04) s for ^{90m}Nb in 20 M HF solution. Additionally, relative difference in the decay constant of ^{90m}Tc between KTcO_4 and Tc_2S_7 form have been determined to be $(32.4 \pm 3.3) \times 10^{-4}$, which is consistent with the value reported by Mazaki *et al.* within 1σ . The present system will allow us to measure the half-life of ^{90m}Nb and ^{99m}Tc with various chemical states.

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