

〈Technical Note〉

INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY FOR THE DETERMINATION OF ^{237}Np IN SPENT NUCLEAR FUEL SAMPLES BY ISOTOPE DILUTION METHOD USING ^{239}Np AS A SPIKE

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A determination method for ^{237}Np in spent nuclear fuel samples was developed using an isotope dilution method with ^{239}Np as a spike. In this method, inductively coupled plasma mass spectrometry (ICP-MS) was taken for the ^{237}Np instead of the previously used alpha spectrometry. ^{237}Np and ^{239}Np were measured by ICP-MS and gamma spectrometry, respectively. The recovery yield of ^{237}Np in synthetic samples was $95.9\pm 9.7\%$ (1S, n=4). The ^{237}Np contents in the spent fuel samples were 0.15, 0.25, and 1.06 $\mu\text{g}/\text{mgU}$ and these values were compared with those from ORIGEN-2 code. A fairly good agreement between the measurements (m) and calculations (c) was obtained, giving ratios (m/c) of 0.93, 1.12 and 1.25 for the three PWR spent fuel samples with burnups of 16.7, 19.0, and 55.9 GWd/MtU, respectively.

KEYWORDS : Neptunium-237, Spent Nuclear Fuel, Isotope Dilution Method, Gamma Spectrometry, Inductively Coupled Plasma Mass Spectrometry

1. INTRODUCTION

Transuranic elements, such as Np, Pu, Am, and Cm, in spent nuclear fuel are important for fuel characterization [1,2], burnup credit [3,4,5,6], and the management of radioactive wastes [7] and are used for code validation through which the amount of nuclides produced or decayed during neutron irradiation is predicted. For the determination of ^{237}Np in spent nuclear fuel samples, the selection of an appropriate tracer is required depending on the detection technique, such as alpha spectrometry or mass spectrometry, as ^{237}Np has a very low specific activity owing to its long half life (2.14×10^6 y), which controls the sample amounts according to the detection method and the type of tracer. Generally, the determination of ^{237}Np in environmental samples has been performed by alpha spectrometry, inductively coupled plasma mass spectrometry (ICP-MS), thermal ionization mass spectrometry, and neutron activation gamma spectrometry using ^{235}Np ($t_{1/2}=396.1\text{d}$, α) [8], ^{236}Np ($t_{1/2}=5000\text{y}$, β) [9, 10] and ^{239}Np ($t_{1/2}=2.35\text{d}$, β , γ) [11] as tracers. The method used for environmental samples is relatively simple compared to that used for radioactive

materials, especially spent nuclear fuel samples. The spent fuel includes many radio-nuclides, which require cumbersome sample pretreatments, and an individual separation should be performed prior to the measurement, especially for alpha-emitting nuclides. For the spent fuel samples, the tracers ^{235}Np and ^{236}Np can also be used even though a small amount of these nuclides, equivalent to about 0.01% of ^{237}Np as an activity base, is already contained in the spent fuels with a burnup of 50 GWd/MtU and 5 years of cooling time. However, they have some limitations in their use since they are not available in our laboratory. ^{239}Np cannot be used as a tracer since a considerable amount of ^{239}Np as an activity base is already included in the spent fuel itself.

In this case, another method should be used as an alternative. Thus, an isotope dilution method for the determination of ^{237}Np in a spent fuel sample using ^{239}Np as a spike was previously developed in our laboratory, in which ^{237}Np was detected by alpha spectrometry and ^{239}Np by gamma spectrometry [12,13]. However, this method has a weak point showing a high measurement uncertainty owing to too low an alpha specific activity of ^{237}Np and a

high gamma specific activity of ^{239}Np for a given sample amount, which causes too low an activity ratio of $^{237}\text{Np}/^{239}\text{Np}$. This ratio is used as one of the terms in the equation related to the isotope dilution method.

In this work, inductively coupled plasma mass spectrometry (ICP-MS) was taken for the measurement of ^{237}Np instead of alpha spectrometry to reduce measurement errors caused by the too low alpha activity of ^{237}Np because ICP-MS has a higher sensitivity, lower measurement uncertainty, and more convenience in measurement compared to alpha spectrometry. This method was applied to PWR spent fuel samples and the ^{237}Np contents were determined. The measured values were compared with the values calculated using the ORIGEN-2 code [14].

2. EXPERIMENTS

2.1 Reagent and Apparatus

The standard solution of ^{243}Am (North America Scientific Inc) was used for ^{239}Np as a spike as ^{243}Am enters a radioequilibrium state with ^{239}Np after a certain time depending on the half lives of the two nuclides. The standard solution of ^{237}Np for ICP-MS was obtained from the Damri company of France (CEA). An anion exchanger (AGMP-1 x 8, 100-200 mesh size) was obtained from Bio-Rad Laboratories, USA. A disposable polyethylene column filled with an anion exchanger (7 mm id x 70 mm h) was used. Inorganic acids such as hydrochloric acid and nitric acid used for the sample treatments were the products of an extra pure grade from the Junsei Company, Japan and GR from Merck Company, Germany, respectively. Hydroxylamine-hydrochloride and hydriodic acid used for the reduction of Pu and Np, and elution of Pu, respectively, were of GR grade from Merck Company. Radiation shielded inductively coupled plasma atomic emission spectroscopy (ICP-AES), used for the determination of uranium in the sample solutions, was an IRIS-HS model from Thermo Jarrell Ash, USA. The inductively coupled plasma mass spectrometer (ICP-MS) used for the determination of ^{237}Np was a Finnigan Mat, Element model from Finnigan, Germany.

2.2 Sample Preparations

Three PWR spent fuel samples with burnups of 16.7-55.9 GWd/MtU were taken from a nuclear power plant in Korea (Table 1). The initial concentration of ^{235}U was 4.51wt% and the cooling time for the spent fuel samples was 3.2 years. A small piece of each specimen (~ 0.5g) was dissolved in (1+1) nitric acid under a reflux condenser in a chemical hot cell. A mother solution was diluted to ~ 0.2 $\mu\text{gU/mL}$, and an appropriate amount of the diluted solution was sent to a glove box using a pneumatic transfer. The uranium content in the diluted solutions was determined by a radiation-shielded ICP-AES followed by a neptunium separation.

Table 1. Spent Fuel History

Samples	GWd/MtU	^{235}U ini. wt%	Irradi., day	Cooling, y	Fuel soln $\mu\text{g/g-soln}$
SF1	16.7	4.51	1425	3.2	216.0
SF2	19.0	4.51	1425	3.2	259.7
SF3	55.9	4.51	1425	3.2	236.1

2.3 Separation and Measurements

Two appropriate amounts of diluted sample solutions, equivalent to ~10 μgU each, were taken as the "sample" and "spiked sample." The solution for the "spiked sample" was spiked with 30 Bq of ^{239}Np (^{243}Am). The two sample solutions were treated with HNO_3 and HCl on a hot plate two or three times repeatedly. The residue was dissolved by 3 mL of 0.05 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ -0.1M HCl and left overnight to obtain Pu(III) and Np(IV). Finally, prior to the separation, the sample solutions were made in a medium of 9M HCl -0.1M HNO_3 . In this step, Pu(III) is oxidized to Pu(IV). Two anion exchange columns were prepared for the "sample" and "spiked sample." The treated sample solutions were loaded onto each column. The following steps were conducted according to the procedure shown in Fig. 1 [15]. The Np fraction was collected by an elution of 12 mL of 4 M HCl after the elution of Pu with 12 mL of 9 M HCl -0.1 M HI . The collected fraction of Np was evaporated on a hot plate, and the medium was changed into nitrate form using c-HNO_3 . The gamma activities of ^{239}Np were measured as soon as possible after separation, and the ^{237}Np amounts were measured by ICP-MS. Finally, the ^{237}Np contents in the sample solutions were obtained through an isotope dilution equation using the ratios of $^{237}\text{Np}/^{239}\text{Np}$ in the "sample" and "spiked sample," respectively.

3. RESULT AND DISCUSSION

3.1 Method Validation

First, two calibration curves for ^{239}Np and ^{237}Np were obtained through gamma spectrometry and ICP-MS spectrometry, respectively. The gamma activities of ^{239}Np were measured at 277.86 KeV for 3, 6, 15, and 30 Bq for 5000 sec. The gamma spectrum of ^{239}Np has a number of peaks at energies of around 90 to 300 KeV, as shown in Fig. 2. In this study, the peak at 277.86 KeV was selected for measurements because this peak has the highest energy and a relatively high branching ratio (14.1%). The peaks at about 100 KeV with high peak intensities were not taken owing to a high background effect. The calibration curve showed a good linearity ($\gamma^2=0.992$) as shown in Fig. 3. However, it revealed a limitation for an amount of less than 5 Bq of ^{239}Np , which showed a relatively higher measurement uncertainty (RSD>15%). For the ^{237}Np by ICP-

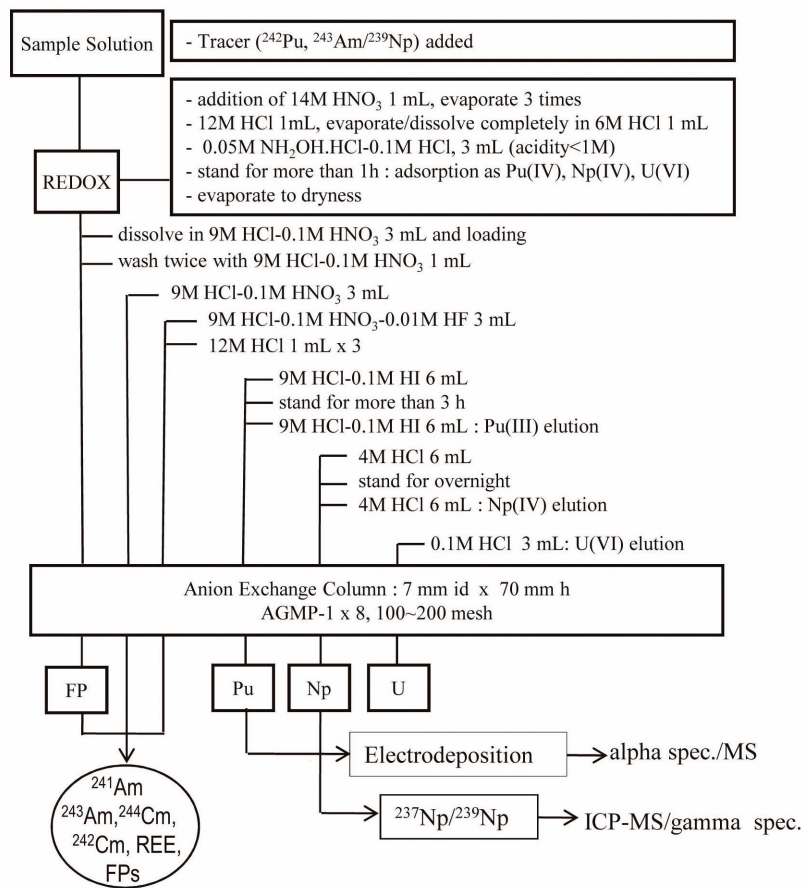


Fig. 1. Separation of Actinides from Fission Products.

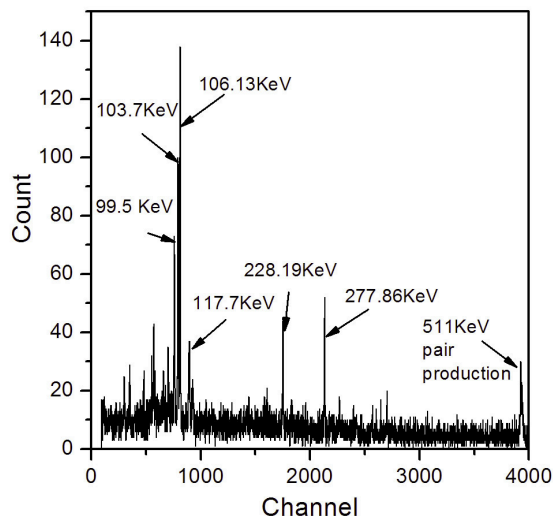


Fig. 2. Gamma Spectrum of ^{239}Np Separated from ^{243}Am and Electrodeposited, 15Bq, LT=5000sec

MS, the calibration curve also expressed a good linearity ($\gamma^2=0.998$) within a range of 0.1 to 1 $\mu\text{g}/\text{mL}$ (Fig. 3). The recovery yields for ^{237}Np were measured from a synthetic sample including 10 ng of ^{237}Np and 30 Bq of ^{239}Np . In

this experiment, 30 Bq of ^{239}Np was additionally added as a spike. The recovery yield for ^{237}Np from the synthetic sample was $95.9\pm 9.7\%$ (Table 2), which was obtained from the data of ^{237}Np and ^{239}Np using equation (1) after

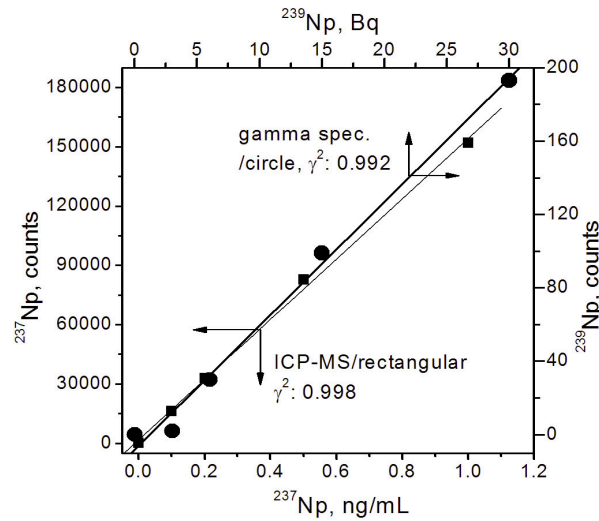


Fig. 3. Calibration Curves for ^{237}Np and ^{239}Np . Rectangular: ^{237}Np by ICP-MS, Circle: ^{239}Np by Gamma Spectroscopy

the measurements by ICP-MS and gamma spectrometry, respectively. The gamma activity of ^{239}Np was measured within as short a time as possible (<5-8h) after separation from ^{243}Am owing to its short half life ($t_{1/2}=2.35\text{d}$). Thus, decay corrections were made for the time interval between the end of the separation and the start of the measurement, and during the measurement time using equations (2) and (3), respectively. Finally, the measured activity (Bq) of ^{239}Np was converted into weight (ng) using a specific activity of ^{239}Np ($1.27 \times 10^{-7} \text{ ng/Bq}$).

$$Cx = Ct \left(\frac{mt}{mx} \right) \left(\frac{Mx}{Mt} \right) \left(\frac{Rt - Rm}{Rm - Rx} \right) \left(\frac{\sum x Ri}{\sum t Ri} \right) \quad (1)$$

$$f_1 = \exp \{ +\lambda_A (t_S - t_E) \} \quad (2)$$

$$f_2 = \lambda_{AtG} / \{ 1 - \exp(-\lambda_{AtG}) \} \quad (3)$$

where Cx is the concentration of ^{237}Np in the sample solution, Ct is the concentration of ^{239}Np in the spike solution, mx is the sample weight, mt is the weight of the spike solution added, Mx is the average molecular weight of Np in the mixture of the sample and spike solution, Mt is the average molecular weight of Np in the spike solution, Rt is the ratio of $^{237}\text{Np}/^{239}\text{Np}$ in the spike solution, Rm is the ratio of $^{237}\text{Np}/^{239}\text{Np}$ in the mixture, Rx is $^{237}\text{Np}/^{239}\text{Np}$ in the sample solution, $\sum x Ri$ is $(^{237}\text{Np}/^{239}\text{Np} + ^{239}\text{Np}/^{239}\text{Np})$ in the sample solution, and $\sum t Ri$ is $(^{237}\text{Np}/^{239}\text{Np} + ^{239}\text{Np}/^{239}\text{Np})$ in the spike solution. In addition, f_1 , f_2 are the correction factors for the decay times from the end of the separation to the beginning of the measurement, and during the measurement time, respectively. Also, λ_A is a decay constant ($0.693/t_{1/2}$) of the analyte, t_S is the start time for the measurement, t_E is the end time of the separation, and t_G is the total measurement time.

Table 2. Recovery Yield of ^{237}Np from the Synthetic Samples by an Isotope Dilution Mass and Gamma Spectrometry

Cat	Added(ng)	Found(ng)	Recov.(%)
S1	10	9.1	
S2	10	8.7	
S3	10	9.7	
S4	10	10.9	
average	10	9.6	95.9±9.7(1S)

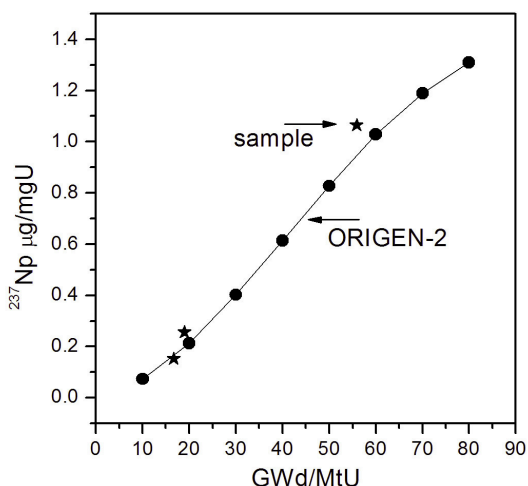
* Sample: ^{237}Np 10ng+ ^{239}Np 30Bq, spike: ^{239}Np 30Bq

3.2 Determination of ^{237}Np in the Spent Fuel Samples

The contents of ^{237}Np in the spent fuel samples were determined using an isotope dilution method, as mentioned above. The measured values of ^{237}Np were 0.15, 0.25, and 1.06 $\mu\text{g}/\text{mgU}$ for SF1, SF2 and SF3, respectively (Table 3) and were compared with those predicted by a calculation using the ORIGEN-2 code. The measurement values (m) agreed with the calculation values (c) as a ratio (m/c) of 0.93, 1.12, and 1.25, respectively, within about 10% difference on average. Fig. 4 shows a correlation curve between the measurement and the calculation as a function of burnup. In the literature reporting ^{237}Np content in spent nuclear fuels, the measurement values of ^{237}Np obtained from the PWR spent fuel from the Takahama-3 reactor were found to be in good agreement to within 4% difference at a high burnup (30-47.25 GWd/MtU) and showed a range of 34.2-71.8% of differences at a low burnup (7- 28.9 GWd/MtU) compared to the calculated values [16]. The contents of ^{237}Np in the MOX fuel irradiated up to 120 GWd/MtU in the Mark-II reactor of JOYO in Japan were greatly biased from the calculated values [17]. From these results a higher deviation of the measurement from the calculation was observed in low burnup and MOX fuel. This means

Table 3. The Contents of ^{237}Np in Spent Fuel Samples (unit: mg/mgU)

Sample	GWd/MtU	^{237}Np /meas.	^{237}Np /cal.	m/c
SF1	16.7	0.15	0.16	0.93
SF2	19.0	0.25	0.20	1.25
SF3	55.9	1.06	0.95	1.12
Average				$1.1 \pm 0.16(1S)$

Fig. 4. Correlation of ^{237}Np between Measurements and Calculations in the Spent Fuel Samples. Star: Samples, Circle: ORIGEN-2

that the deviation increases as the content of ^{237}Np goes down and the fuel type is more complicated. In this work, the measurement values showed a fairly good agreement (~10% difference on average) with the calculated values compared to other works. However, it is difficult to find a correlation between the deviation and the fuel burnup owing to a lack of data.

4. CONCLUSION

In this work, ICP-MS was taken for the determination of ^{237}Np in spent nuclear fuel samples instead of alpha spectrometry in the previously developed isotope dilution method. Two calibration curves for ^{237}Np and ^{239}Np were established by using ICP-MS and gamma spectrometry, respectively, for the verification of the measurement values. Finally, this method was applied to the three PWR spent nuclear fuel samples after a recovery yield test from the synthetic samples. The result showed that the measurement values agreed with the calculated values within an acceptable error range.

In the future, this method will be validated using the ^{237}Np data obtained through other methods and will also be used further to contribute to the buildup of ^{237}Np database in the spent nuclear fuels.

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