

## **Examination of analytical method of rare earth elements in used nuclear fuel**

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### 1. Introduction

Various fission products (FPs) such as neodymium (Nd) and samarium (Sm) and actinides such as uranium (U) and plutonium (Pu) exist in used nuclear fuel (UNF). Amounts of these elements in UNF strongly depend on initial composition, initial enrichment of uranium and irradiation history of fuel. Burnup value is the most important parameter and indispensable for safety evaluation of fuel materials since it characterizes nuclide composition of UNF. Detail operational data of a reactor is necessary to calculate burnup value by computational codes, but such data is not sufficiently available. Therefore, it is required to measure amounts of U, Pu and Nd in UNF for the purpose of the evaluation of burnup value.

Japan Atomic Energy Agency (JAEA) has performed to develop an analytical method to measure of burnup value and amounts of U, Pu and Nd in UNF. The method employs the isotope dilution method (IDM) using mixed spike and the thermal ionization mass spectrometry (TIMS) so that measured burnup value is accurate enough to be used as input data of burnup calculation.

On the other hand, there are several isotopes in FPs that have large neutron absorption cross sections. The existence of those isotopes in UNF greatly affects the reactivity and criticality in a reactor. Those are sorts of rare earth elements and expected to be taken into account as burnup credit in criticality safety evaluation of UNF. Therefore, it is required to evaluate amounts of those isotopes by burnup calculation more accurately. It is necessary to compare the calculated value with that obtained by measurement in order to confirm the correctness and reliability of these codes, i.e. to validate these codes. However, these important fission products are rare earth elements so that there are few available experimental data because of the difficulty of the measurement.

So, we studied improvement of the JAEA's method to obtain the analytical data of

these rare earth elements.

## 2. Study of the improvement of the analytical method

### 2.1. Conventional separation scheme

In rare earth elements, some isotopes of gadolinium (Gd), Sm and europium (Eu) have particularly large neutron absorption cross sections. It is difficult to measure those isotopes because some of them have same mass numbers. Therefore, fine chemical separation is required before measurement by the mass spectrometry.

In the conventional JAEA's method using an anion exchange resin for separation of U, Pu and Nd, rare earth elements such as Gd, Sm and Eu except Nd are wasted without being separated [1]. The conventional separation scheme is shown in Fig.1. Neodymium can be separated from other rare earth elements due to faster elution of Gd, Sm and Eu than Nd, although they are eluted with same eluate of 0.3 M HNO<sub>3</sub>-80% CH<sub>3</sub>OH. As for Gd, Sm and Eu, these elements cannot be separated from one another because their elution rates are almost same.

We examined to separate these elements mutually by adding a new separation process of Gd, Sm and Eu into the conventional method.

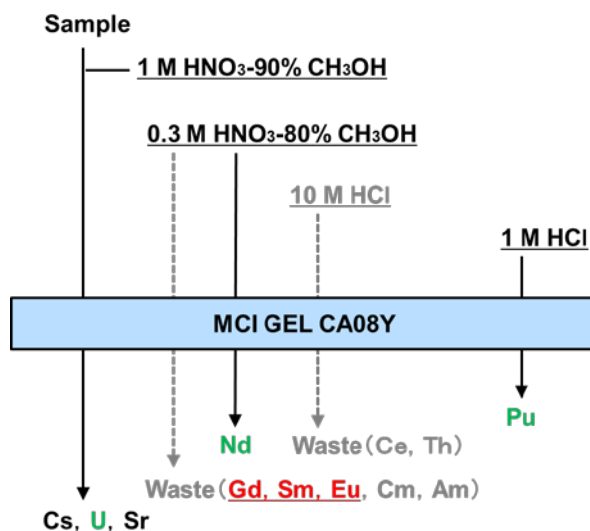


Fig.1 The conventional scheme developed in JAEA

### 2.2. Experimental apparatus

In the conventional method, a quartz column is used for separation. The column has an inner diameter of 3 mm and a height of 90 mm, which allows to load a small amount of resin with enough height for separation. Temperature must be maintained constant during elution because elution performance of an anion exchange resin is easily

influenced by change of temperature. Therefore a thermostatic bath is used to maintain constant temperature. The experimental apparatus is shown in Fig.2.

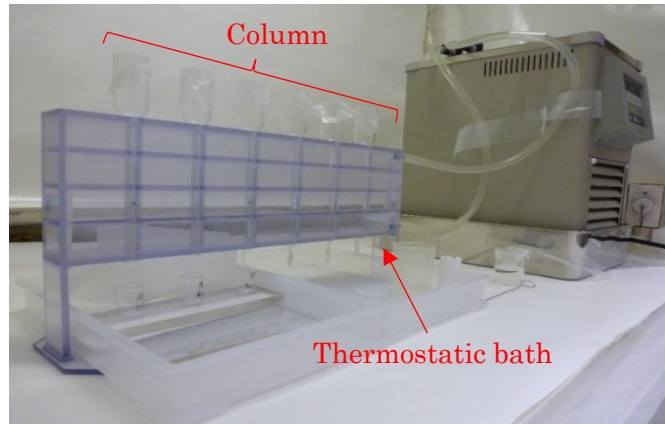


Fig.2 Appearance of experimental apparatus

### 2.3. Reagents

The reagents were used in experiment as follows:

- Anion exchange resin as MCI GEL CA08Y was particle size 25 $\mu$ m
- Nitric acid as TAMAPURE was of ultra-pure grade
- Hydrochloric acid as TAMAPURE was of ultra-pure grade
- Methanol was of LC/MS grade
- Stable isotopes of  $^{149}\text{Sm}$ ,  $^{151}\text{Eu}$  and  $^{155}\text{Gd}$  were obtained from Oak Ridge National Laboratory, USA.

### 2.4. Condition of separation experiment

Elution behavior of each element for the anion exchange resin changes by conditions such as nitric acid concentration, methanol concentration and column temperature [2]. Goal of this study was to find a specific combination of them where Gd, Sm and Eu could be separate from one another. The column temperature is maintained constant because it is already known that temperature change has significant influence on elution behavior of other elements and such influence on U, Pu and Nd must be prevented. Then, three concentrations of nitric acid listed in Table 1 were tried to observe separation behavior.

Table 1. Condition of separation experiment

Volume of the anion exchange resin	0.35 mL
Amounts of samples	$^{149}\text{Sm}$ : about 200 pg $^{151}\text{Eu}$ : about 150 pg $^{155}\text{Gd}$ : about 350 pg

Temperature	26 °C
Eluate concentrations	1) 0.6 M HNO <sub>3</sub> -80% CH <sub>3</sub> OH 2) 0.7 M HNO <sub>3</sub> -80% CH <sub>3</sub> OH 3) 0.8 M HNO <sub>3</sub> -80% CH <sub>3</sub> OH

### 2.5. Separation of Gd, Sm and Eu

The CA08Y resin was washed with the nitric acid and the hydrochloric acid. Then this resin was loaded into the three columns to make their height 50 mm. And 1 M HNO<sub>3</sub>-90% CH<sub>3</sub>OH was loaded to condition the resin.

Samples in Table 1 were mixed and evaporated. The nitric acid was added to dissolve the mixed sample. Subsequently, the methanol was added to the sample. This sample solution was stirred and loaded into the column.

Each concentration eluate more than 25 mL was fed into each column. Effluent was collected 1 mL by 1 mL. These effluent samples were measured with HR-ICP-MS (ELEMENT2 : Thermo Fisher Scientific) .

### 2.6. Result and discussion

Measurement result and elution behavior are shown in Table 2 and Fig.3 respectively.

Table 2. Measurement result of eluate in each acid concentration

Eluate(mL)	Recovery (%)								
	0.6 M HNO <sub>3</sub> -80% CH <sub>3</sub> OH			0.7 M HNO <sub>3</sub> -80% CH <sub>3</sub> OH			0.8 M HNO <sub>3</sub> -80% CH <sub>3</sub> OH		
	<sup>149</sup> Sm	<sup>151</sup> Eu	<sup>155</sup> Gd	<sup>149</sup> Sm	<sup>151</sup> Eu	<sup>155</sup> Gd	<sup>149</sup> Sm	<sup>151</sup> Eu	<sup>155</sup> Gd
1	0.0	0.1	0.0	0.0	0.1	0.0	0.0	0.2	0.4
2	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.3	0.1
3	0.0	0.1	0.4	0.0	0.3	0.3	0.0	0.1	0.1
4	0.0	1.1	9.2	0.0	0.0	37.5	0.1	0.3	2.8
5	0.0	0.2	79.0	0.0	0.1	58.7	0.0	0.1	70.0
6	0.0	47.1	0.4	0.0	2.3	3.5	0.0	0.0	28.0
7	0.0	38.1	0.1	0.0	53.0	0.3	0.0	2.2	1.5
8	0.0	3.2	0.3	0.0	39.1	0.2	0.0	27.5	0.1
9	0.3	1.0	0.6	0.0	3.2	0.2	0.0	44.6	0.1
10	18.9	0.2	0.1	0.2	0.5	0.1	0.0	15.6	0.0
11	43.0	0.1	0.0	5.1	0.1	0.1	0.0	2.0	0.5
12	28.1	0.0	0.0	29.2	0.1	0.1	0.1	0.2	0.0
13	6.3	0.1	0.0	42.5	0.2	0.1	1.5	0.0	0.0
14	1.0	0.1	0.0	19.7	0.1	0.0	8.9	0.0	0.0
15	0.2	0.0	0.0	3.5	0.0	0.0	23.4	0.0	0.0
16	0.1	0.0	0.0	0.6	0.2	0.1	33.1	0.1	0.0
17	0.0	0.0	0.0	0.2	0.0	0.1	20.0	0.1	0.0
18	0.1	0.2	0.1	0.1	0.0	0.0	7.3	0.1	0.0
19	0.1	0.2	0.1	0.1	0.0	0.0	1.2	0.1	0.1
20	0.0	0.0	0.0	0.1	0.1	0.0	0.3	0.1	0.0
21	0.1	0.1	0.1	0.0	0.1	0.0	0.1	0.2	0.1
22	0.0	0.1	0.0	0.0	0.1	0.0	0.0	0.1	0.0
23	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0
24	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0
25	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.1	0.0

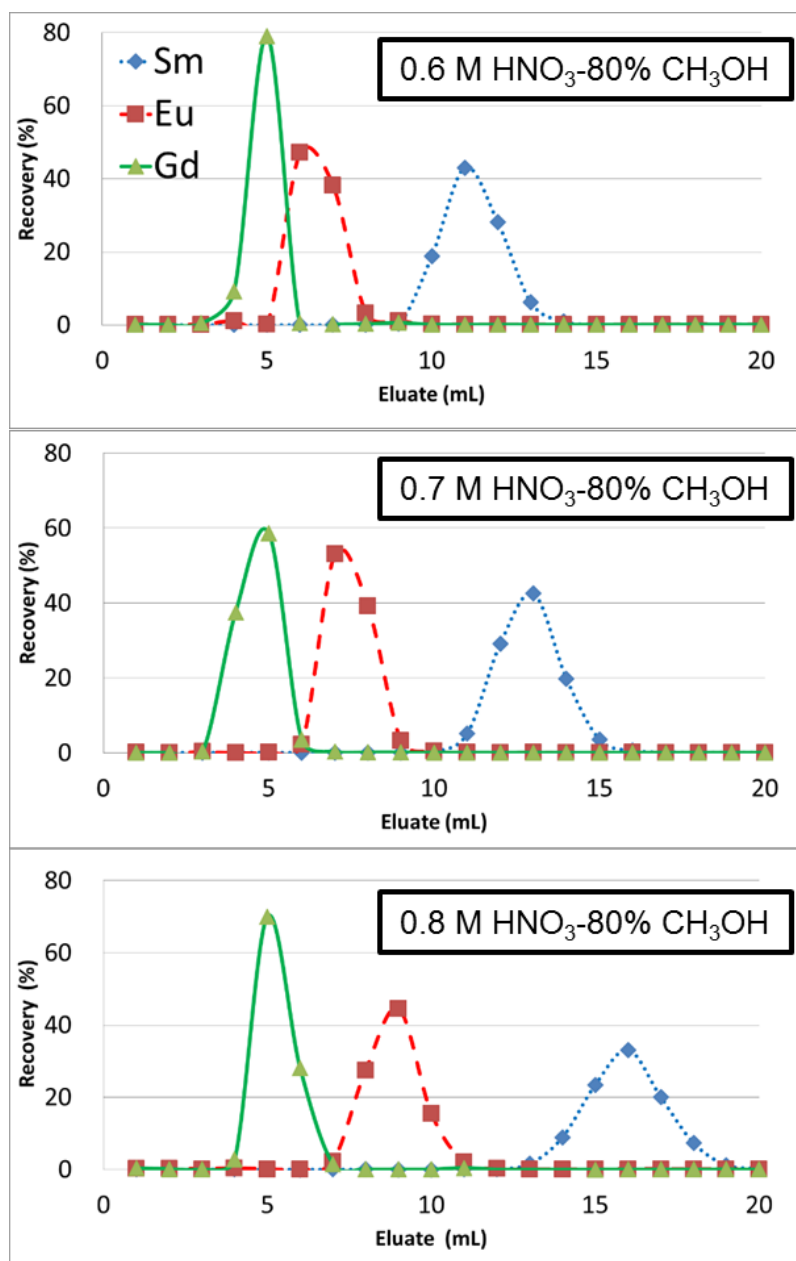


Fig.3 Elution behavior of Gd, Sm and Eu in each acid concentration

In this study, the elution behavior of Gd did not change significantly for different acid concentrations of eluate. Elution timings of Sm and Eu were delayed when the acid concentration of eluate was higher. Figure 3 shows that the eluate of 0.6 M HNO<sub>3</sub>-80% CH<sub>3</sub>OH was not adequate to separate Gd and Eu. Although the eluate of 0.7 M HNO<sub>3</sub>-80% CH<sub>3</sub>OH was able to separate Gd, Sm and Eu, the peaks of Gd and Eu were close. On the other hand, the eluate of 0.8 M HNO<sub>3</sub>-80% CH<sub>3</sub>OH was able to separate each element completely with peaks of Gd and Eu divided far enough.

Based on these results, it was determined that the optimum acid concentration among three different concentrations for the separation of Gd, Sm and Eu was 0.8 M HNO<sub>3</sub>-80% CH<sub>3</sub>OH.

### 3. Evaluation of the improved analytical method

#### 3.1. The separation scheme of new method

Figure 4 shows the new scheme that includes the separation process of the rare earth elements described in the previous section. In the conventional method, after uranium is collected in effluent of 1 M HNO<sub>3</sub>-90% CH<sub>3</sub>OH, eluate of 0.3 M HNO<sub>3</sub>-80% CH<sub>3</sub>OH is fed into the column to elute Nd. In the new method, the separation process of the rare earth elements with 0.8 M HNO<sub>3</sub>-80% CH<sub>3</sub>OH is added between those elution processes of U and Nd. Therefore, it is necessary to confirm the added process does not have significant influence on elution of Nd and Pu which are separated after the rare earth elements.

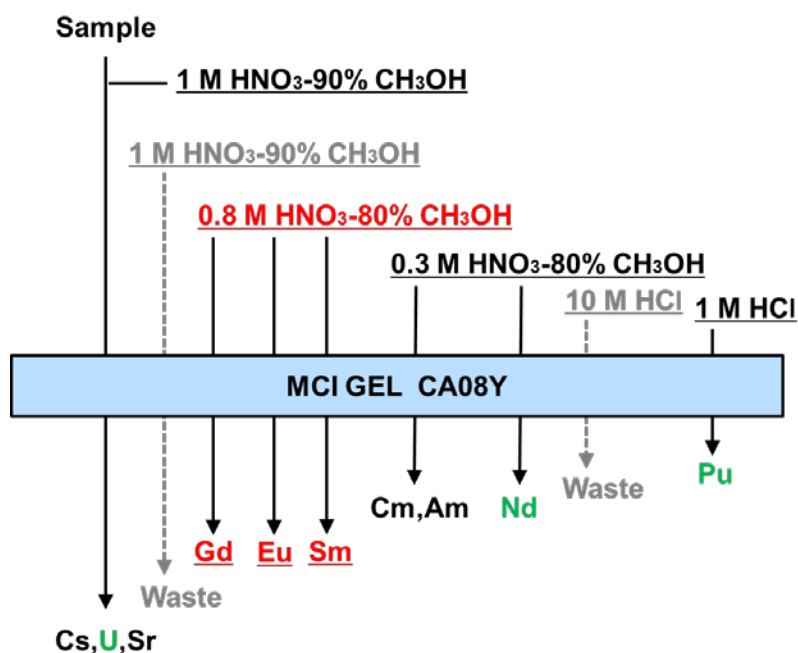


Fig.4 The new scheme that includes the separation process of the rare earth elements

#### 3.2. Condition of experiment for confirmation of new scheme

In this experiment, samples including U, Pu and Nd were used to confirm the added process does not have significant influence on elution of these element.

Details of condition are listed in Table 3.

Table 3. Condition of experiment for confirmation of new scheme

Volume of the anion exchange resin	0.35 mL
Amounts of samples	$^{233}\text{U}$ : about 2 $\mu\text{g}$ $^{242}\text{Pu}$ : about 50 ng $^{150}\text{Nd}$ : about 20 ng $^{149}\text{Sm}$ : about 200 pg $^{151}\text{Eu}$ : about 150 pg $^{155}\text{Gd}$ : about 350 pg
Temperature	26°C

### 3.3. Procedure of experiment for new scheme

The CA08Y resin was prepared in the same way described in section 2.5.

Samples in Table 3 were mixed and evaporated. Then 1 M hydroxyl ammonium chloride was added and evaporated to adjust Pu valence. Subsequently, the nitric acid and the methanol were added to the sample. This sample solution was stirred and loaded into the column.

Each concentration eluate was fed into each column. Then each effluent sample was measured with HR-ICP-MS.

### 3.4. Result and discussion

Measurement results are shown in Table 4 and Table 5.

Table 4. Measurement result with the conventional method and the new method

	The conventional method		The new method		Difference (%)
	Amounts of isotopes (ng)	Recovery (%)	Amounts of isotopes (ng)	Recovery (%)	
$^{233}\text{U}$	1158	57.9	902	45.1	-12.8
$^{242}\text{Pu}$	29.8	59.5	20.8	41.5	-18.0
$^{150}\text{Nd}$	13.1	65.4	14.6	73.0	+7.6

Table 5. Measurement result of the rare earth elements with the new method

Fractions	Recovery (%)		
	$^{155}\text{Gd}$	$^{151}\text{Eu}$	$^{149}\text{Sm}$
Gd	104.9	28.1	< 1
Eu	< 1	85.7	1.3
Sm	< 1	< 1	96.9



Table 4 shows that the analytical values obtained by the new method and the conventional method were almost same. We confirmed that the newly added separation process did not interfere with separation of Nd. And Table 5 shows that the new method were able to separate Gd, Sm and Eu.

#### 4. Conclusion

It is necessary to measure amounts of the rare earth elements that are important in criticality safety evaluation of UNF. For this purpose, we examined validity of the new method that adding the new separation process of the rare earth elements into the conventional JAEA's method for measurement of U, Pu and Nd.

It is confirmed that Gd, Sm and Eu can be separated finely from one another by adding a new separation process using another eluate to the conventional method of separation of U, Pu and Nd. Analytical values obtained by the new method and the conventional method are almost same for U, Pu and Nd, which means the added operation does not interfere with separation of them. With this new method, it has become possible to obtain isotopic composition data of UNF including the rare earth elements. These data will contribute the validation and improvement of burnup calculation codes. We plan to apply the new method on UNF to analyze U, Pu, Nd and the rare earth elements.

#### Acknowledgements

The authors are grateful to J. Ohtomo, N. Suzuki, S. Ichimura, H. Hosomi and S. Nemoto for their assistance in the experiment.

#### References

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