

Separation of Pu and Nd from Uranium Matrix by Equilibrated Cation Exchanger for Burnup Measurement of Irradiated Nuclear Fuel

Kih Soo Joe, Jung Suk Kim, Young Shin Jeon,
Sun Ho Han, and Tae Yoon Eom

Korea Atomic Energy Research Institute,

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조사후핵연료의 연소도 측정을 위한 동적이온교환체에 의한 우라늄 매트릭스로부터 Pu 및 Nd의 분리

조기수 · 김정석 · 전영신 · 한선호 · 엄태윤

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Abstract

Ion chromatographic method has been applied for burnup measurement of irradiated nuclear fuel by dynamic system using 1-octanesulfonate as a cation exchanger and α -hydroxyisobutyric acid as an eluant. A number of elution techniques were evaluated for the optimum separation of plutonium, uranium and neodymium. These elements were individually separated and collected by gradient elution between 0.05 M and 0.40 M of α -hydroxyisobutyric acid in a single column, and finally determined by isotope dilution mass spectrometry. The burnup data from this method were compared with those from conventional anion exchange method. The results showed a good agreement within 3.5 % of difference between two methods.

요 약

조사후핵연료의 연소도측정에 1-octanesulfonate 를 양이온 교환체로 사용하고 α -hydroxyisobutyric acid를 용리액으로 사용하는 동적계의 이온크로마토그래피를 적용하였다. Pu, U 및 Nd의 최적 분리조건을 찾기위해 용리조건들을 변화하였다. 이들 원소들을 α -hydroxyisobutyric acid 용리액을 0.05 M과 0.40 M을 혼합시키는 기울기용리법으로 개별 분리한후 분취하여 동위원소희석 질량분석법으로 각각 정량하였다. 본 방법에 의해 구한 연소도 값을 기존의 음이온교환수지법에 의한 값과 비교한 결과 3.5 % 차이 이내에서 두 값이 서로 일치하였다.

1. Introduction

Chemical analyses of fission products, actinide elements and fission gases are required to support

post-irradiation examination of nuclear fuel. Determination of uranium, plutonium and neodymium is specifically necessary for burnup measurement by chemical method. For this work

these monitors are separated by ion exchange method after dissolution of fuel in a hot cell and determined by isotope dilution mass spectrometry. Anion exchanger has been used for the separation of neodymium with a mixture of nitric acid-methanol as an eluant, and for the separation of uranium and plutonium with nitric acid and hydriodic acid, respectively [1, 2]. However, this method is laborious and time-consuming in operation with two column system. This system has also liabilities to problems for application to high performance liquid chromatography due to shrinkage and swelling of resin by pressure variation, and gas bubbling inside the resin by organic solvent. Cassidy et al. successfully applied high performance liquid chromatography to the determination of lanthanum in uranium-thorium oxide fuel for burnup measurement without mass spectrometry [3].

In this work high performance liquid chromatography using 1-octanesulfonate as an equilibrated cation exchanger was applied to the separation of plutonium and neodymium in an irradiated PWR fuel on a single column without group separation. The isotope ratios of each element separated were measured by mass spectrometry followed by burnup calculation.

In order to increase the peak distance between plutonium and uranium elements chemical reduction treatment was tried to reduce the plutonium species before injection.

2. Experimental

HPLC system :

HPLC system consisting of a base column (Supelcosil LC-18, 150(L) × 4.6 mm(ID), 10 μm pore size, Supelco Inc.), an injection valve (Rheodyne 7126, Rheodyne Co.), a solenoid switching valve (Cole-Parmer Instrument CP# N-0367-7230) and a UV/Vis detector (M481, Waters Co.) was installed inside a plastic glove box. A

solvent delivery pump (Spectra-Physics, SP 8800), an integrator (SP4270, Spectra-Physics) and a syringe pump (LC-5000, ISCO) were connected with the system outside the glove box as shown in Figure 1. Color developing reagent delivered from the syringe pump and eluate from the separating column were mixed in a mixing tee and delivered to the detector. Each element separated was collected using solenoid valve and sent to a mass spectrometer (Cameca, TSN 206 SA, France) for isotopic ratio measurements.

Reagents :

A mixture of α-hydroxyisobutyric acid (α-HiBA, Aldrich Co.) and 1-octanesulfonate (Aldrich Co.) was made in solution. This solution was used as an eluant after filtered with 0.45 μm membrane. 0.5% of Arsenazo III (2,2-[1,8-dihydroxy-3,6-disulfo-2,7-naphthalene-bis-(azo)]dibenzene arsonic acid) (Merck GR) solution was used for coloring reagent. Neodymium standard solution was made by dissolution of Nd₂O₃ (Spex Industry Co.) in nitric acid. This solution was diluted for chromatography and mass spectrometry. Plutonium and uranium spike solution were made by dissolving PuO₂ (Pu-242) and UO₂ (U-233)

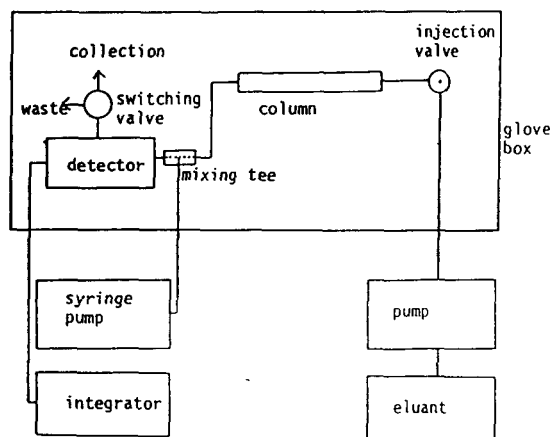


Fig. 1. Schematic Diagram of Chromatographic System for the Separation of Pu, U and Nd

from ORNL in nitric acid, and standardized by mass spectrometry using Pu-239 and U-238 standard solution, respectively. Synthetic solution of lanthanides was prepared by dilution of stock solutions of 1000 ppm in each lanthanide from Spex Industry Company.

Sample preparation :

0.5~2.5 gr of an irradiated fuel (Table 1) was weighed and dissolved in (1+1) HNO₃ under reflux for 10 hours in a lead shielded line. The solution was filtered and diluted to ~100 ppm of uranium (~1 ppm of plutonium and ~0.05 ppm of neodymium) in distilled water. Two portions of the diluted solution were taken. One portion was used for sample preparation and another was subjected to spike solution. These solutions were transferred to a glove box by pneumatic system for chromatography. Both samples were slowly dried on a hot plate at low temperature and redissolved in dilute nitric acid.

Separation procedure :

Dynamic system using 1-octanesulfonate as a

Table 1. History of Irradiated Nuclear Fuel Used for Burnup Measurement

sample no	G23N1-3	G23N1-5	4-B
% of U-235	3.21	3.21	2.93
burnup estimated (MWD/MTU)	40000	40000	1000
irradiation time, yr	4.33	4.33	0.25
sample taken, gr	0.76	0.48	2.03
nitric acid (1+1) added, gr	112.346	90	112.091
solution taken, gr	1.190	1.081	2.026
diluted soln with water, gr	51.874	39.078	67.815

burnup estimated : calculated by "CODE MANUAL MEDIUM" [4]

cation exchanger was applied on C₁₈ reversed phase column[3]. Each of the three elements, plutonium, uranium and neodymium, was individually separated with discontinuous gradient technique between 0.05 M and 0.40 M of α -HiBA mixed with 0.01 M of 1-octanesulfonate maintaining pH 3.80. Absorption was measured at 651 nm for the detection by post-column reaction with Arsenazo III coloring reagent. The eluant and the color forming reagent were maintained at a flow rate of 1.0 mL/min. and 0.5 mL/min., respectively. Distance between detector and collection point (switching valve) was minimized down to about 5 cm with a dead volume of 0.03 mL. About 0.5~1.0 mL of the eluate was collected corresponding to each component peak appeared on the recorder.

3. Results and Discussion

Dynamic ion exchange system has an advantage to adjust an effective ion exchange capacity by controlling the concentration of modifier in the eluant (Figure 2). The rapid mass transfer on the charged layer enhanced the column efficiency to get sharp peak in this system as well. α -HiBA was used as a complexing agent because it has given a good result in lanthanide separations [5]. Variation of α -HiBA concentrations was tried to

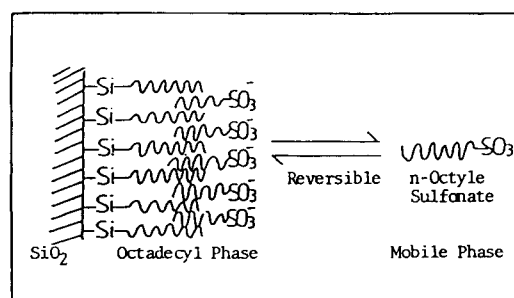


Fig. 2. Equilibrated Cation Exchanger of 1-Octanesulfonate on C₁₈ Reversed Phase

get an optimum separation condition. In Figure 3 eleven lanthanides were individually separated by isocratic elution from a synthetic solution. This neodymium fraction was used for burnup monitor in the irradiated fuel. Uranium peak was overlapped with the lanthanides heavier than neodymium in case that the uranium concentration was over 2000 times of neodymium (Figure 4). This ratio of uranium over neodymium concentration was close to that of the irradiated fuel. In this chromatogram plutonium and neodymium were separated from uranium matrix. However, the plutonium peak was so close to the uranium that the plutonium fraction could be contaminated with the uranium. Therefore, gradient elution was performed in a concentration range from 0.05 M to 0.40 M of α -HiBA.

Individual separation of plutonium, uranium and neodymium from synthetic solution was shown in Figure 5. Contamination of uranium in neody-

mium fraction did not give any problem for neodymium determination by mass spectrometry. The uranium contamination in the plutonium fraction might be occurred and interfered in plutonium determination by mass spectrometry. However, it did not cause any serious problem in this work because of its negligible contribution to the burnup calculation.

The actinide elements such as neptunium, americium, curium, and californium may be interfered in the determination of uranium and plutonium [6-8]. Americium and curium are eluted

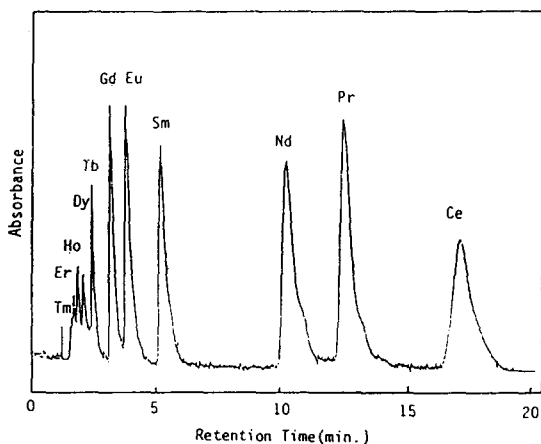


Fig. 3. Separation of Lanthanides on Equilibrated Cation Exchanger by α -HiBA Eluant
 Column : C_{18} Reversed Phase (15 \times 0.46 cm, id)
 Eluant : 0.01 M 1-Octanesulfonate/0.19 M α -HiBA pH 3.80
 Flow Rate : 1.0 mL/min.
 Detection : Arsenazo III, 651 nm by Post Column Reaction
 Sample : 20 μ L of 2 ppm Each Lanthanide

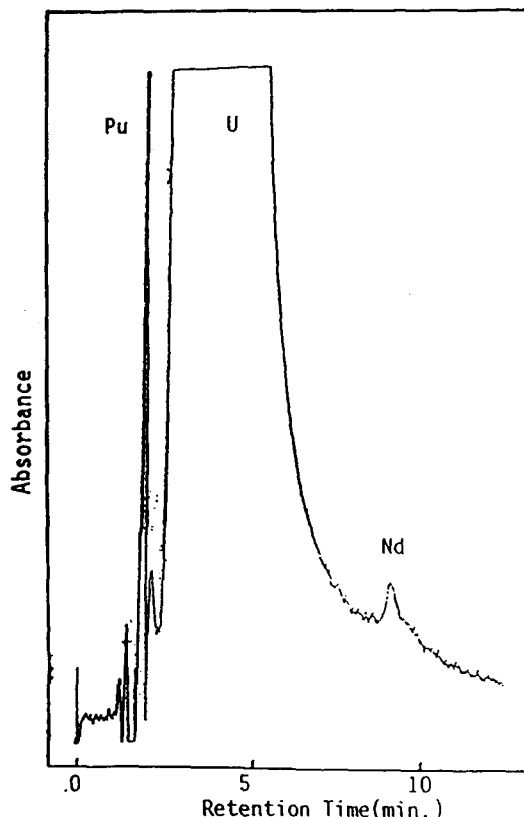


Fig. 4. Separation of Pu, U and Nd on Equilibrated Cation Exchanger by α -HiBA Eluant
 Eluant : 0.01 M 1-Octanesulfonate/0.225 M α -HiBA Eluant, pH 3.80
 Sample : 20 μ L of 1 ppm, 2000 ppm and 1 ppm in Pu, U and Nd Each
 Others : Same as in Fig. 3

with an uranium fraction in α -HiBA eluant [7-11], but these elements give no interferences in uranium determination by mass spectrometry (Table 2). Neptunium and californium were supposed to be overlapped with plutonium or uranium fraction in separation [6, 10]. However, californium does not give any isobaric problem to the determination of these elements. The only in-

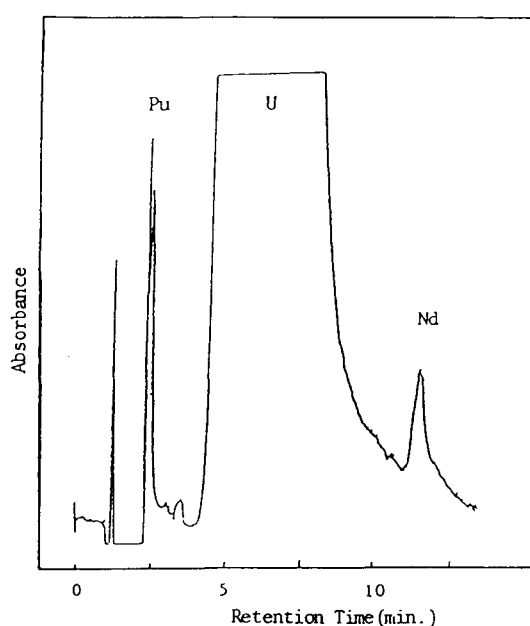


Fig. 5. Separation of Pu, U and Nd from Synthetic Mixture

Column : C₁₈ Reversed Phase (15 × 0.46 cm, 10 μ m)

Eluant : α -HiBA Gradient in 0.01 M of 1-Octanesulfonate, pH 3.80

Flow Rate : 1.0 mL/min.

Detection : Arsenazo III, 651 nm, by Post Column Reaction

Sample : 20 μ L of 1 ppm Pu, 2,000 ppm U and 1 ppm Nd in Mixture

Gradient Condition :

Time, min	% of α -HiBA	
	0.05 M	0.40 M
0 - 5.0	80	20
5.1-15.0	50	50
15.1-20.0	0	100

terfering element is neptunium which has many isotopes from 233 to 240 in a mass number. Fortunately the amount of each nuclide except Np-237 is very small (10^{-4} ~ 10^{-15} g/ton compared to 10^2 ~ 10^3 g/ton of Pu isotope) after 4 years of cooling time. Np-237 is not overlapped with the isotopes of plutonium or uranium (Table 2). Consequently the actinide elements were not considered to be problem for the determination of uranium, plutonium and neodymium in chromatography and mass spectrometry for the burnup measurement.

As seen in Fig. 6 plutonium, uranium and neodymium from the irradiated PWR fuel were individually separated by α -HiBA gradient elution. The fractions of each element were collected and determined by mass spectrometry. The isotope ratios of the sample and spiked sample were measured. Plutonium fractions were supposed to be contaminated by uranium component due to higher intensity ratios of Pu-238 to Pu-239 in samples than in calculation (Table 2). This phenomenon seems to be memory effect in the column caused by high concentration of uranium.

Table 2. Amount of Heavy Nuclides Calculated

mass no	U	Pu	Np	Am	Cm
233	2.2×10^{-3}		5×10^{-7}		
235	5.4×10^3				
236	4.2×10^3		5.8×10^{-4}		
237			5.8×10^2		
238	9.3×10^5		1.9×10^{-7}		
239		2.3×10^2	1.5×10^{-4}		
240		5.1×10^3	9.2×10^{-15}		
241		2.6×10^3		5.8×10^2	
242		1.2×10^3		5.8×10^{-5}	4.1×10^{-2}
243		7.0×10^2		5.8×10^2	5.9×10^{-1}
244					5.4×10^1
245				5.8×10^{-16}	2.6×10^0
246				5.8×10^{-21}	4.2×10^{-1}

unit : gr/MTU burnup : 40000 MWD/MTU

cooling time : 4 years calculation : ORIGEN II code

initial heavy metal : 1 metric ton

Samarium isotopes(144, 148 and 150 in a mass number) may be interfered in neodymium determination if contaminated. This effect was not considered in this work, because the peaks at 147 and 149 in a mass number were not detected in mass spectrometry. Arsenazo III coloring reagent was also proved to be no effect in mass spectrometry. Table 3 showed the burnup data calculated using the isotope ratios by the Nd-148 method[12]. The result was in a good agreement within 3.5 % of difference between this method and conventional anion exchange method.

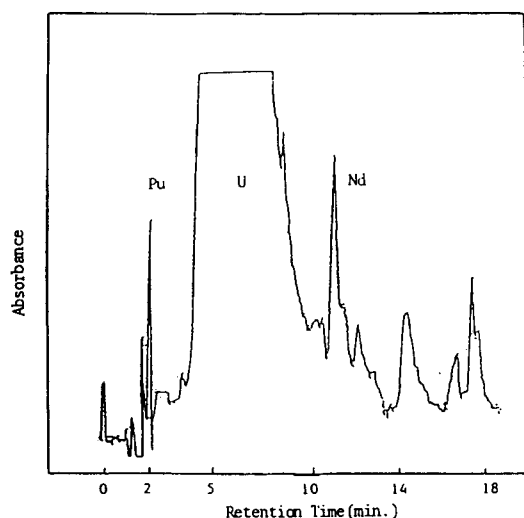


Fig. 6. Separation of Pu, U and Nd from Irradiated PWR Fuel

Sample : 20 μ L of G23N1-3 Solution

Other Conditions : Same as in Fig. 5

Table 3. Comparison of Burnup Determined Between Anion Exchange and Ion Chromatographic Method

Sample	Anion Exchange (A)	Ion Chromatography (B)	Diff.(%) (A-B) 100/A
G23N1-3	40876.0	39444.2	3.50
G23N1-5	40236.6	39660.5	1.43
4-B	470.0	—	—

unit : MWD/MTU

4. Conclusion

Dynamic system using equilibrated cation exchanger was proved to be better in convenience compared to a conventional anion exchange method for the separation of burnup monitors in an irradiated fuel. But uranium contamination to plutonium fraction may be occurred by direct injection of fuel solution without a group separation. This problem will be overcome by increasing the peak distance between two elements with an injection after controlling the proper oxidation states of the elements. This experiment is going on for the further development.

References

1. ASTM E321-75, Part 45(1975).
2. R.M. Abernathy, G.M. Matlack and J.E. Rein : IAEA-SM-149/37(1972).
3. C.H. Knight, R.M. Cassidy, B.M. Recoskie, and L.W. Green, *Anal. Chem.*, **56**, 474-478(1984).
4. Winter et al., "CODE MANUAL MEDIUM", KWU Technical Report U6 512/88/e 331 a.
5. D.J. Barkley, Marcia Blanchette, R.M. Cassidy and S. Elchuk, *Anal. Chem.*, **58**, 222-2226(1986).
6. Authur E. Matell and Robert M. Smith, "Critical Stability Constants", Vol 3, plenum press, N.Y. (1977).
7. S. Specht, B.O. Schutz, H.J. Born, *J. Radioanal. Chem.*, **21**, 167-176(1974).
8. Cornelius Keller, "The Chemistry of the Trans-uranium Elements", Kernchemie in Einzeldarstellungen Vol 3, Verlag Chemie Gmbh, (1971).
9. G.R. Choppin and R.J. Silva, *J. Inorg. Nucl. Chem.*, **3**, 153(1956).
10. H. Louise and D.C. Hoffman, *J. Inorg. Nucl. Chem.*, **3**, 243-247(1956).
11. D. Ishii, A. Hirose and Y. Iwasaki, *J. Radioanal. Chem.*, **46**, 41-49(1978).
12. ASTM E321-79, Part 45(Reapp. 1985).