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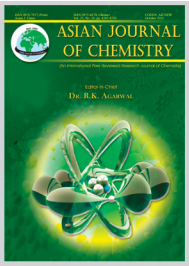

Determination of Uranium, Plutonium, Neodymium, Gadolinium and Their Isotopes in UO_2-Gd_2O_3 Spent Nuclear Fuels†

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Determination of U, Pu, Nd, Gd and their isotopes in UO_2-Gd_2O_3 spent nuclear fuels by isotope dilution mass spectrometry has been studied. The spent fuel samples were dissolved in 8 M HNO_3 at 90 ºC for 16 h under reflux. This method involves two sequential anion exchange resin (AG 1X8 and 1X4) separation procedures and a Gd purification procedure with a cation exchange resin (AG 50WX8) separation. Each fraction isolated was analyzed by thermal ionization mass spectrometry. The contents of U, Pu, Nd, Gd and their isotopes (^{234}U, ^{235}U, ^{236}U, ^{238}U, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu, ^{143}Nd, ^{144}Nd, ^{145}Nd, ^{146}Nd, ^{148}Nd, ^{150}Nd, ^{152}Gd, ^{154}Gd, ^{155}Gd, ^{156}Gd, ^{157}Gd, ^{158}Gd and ^{160}Gd) in the spent fuel samples were determined by isotope dilution mass spectometric method (IDMS) using quadruple spikes (^{233}U, ^{242}Pu, ^{150}Nd and ^{158}Gd). The results obtained from IDMS were applied to burnup determination as a destructive method using ^{148}Nd isotope monitor.

Key Words: Uranium, Plutonium, Neodymium, Gadolinium, UO_2-Gd_2O_3, IDMS.

INTRODUCTION

One of the important parameters required for studies of a nuclear fuel is burnup, which is the number of fission per 100 heavy nuclide atoms (mass ≥ 232) initially present in the fuel. However, usually the fuel burnup is expressed in amount of energy taken out per ton of fuel, *e.g.*, gigawatt days per metric ton (GWD/MtU). Various methods have been developed to measure a burnup both by non-destructive and by destructive techniques. The destructive method, which is based on the determination of specific nuclides, *e.g.*, U, Pu and ^{148}Nd by a chemical analysis after an appropriate separation of the heavy elements and a monitoring of the fission product, is widely used as a reference method to measure the burnup of a spent fuel[1-7]. Gadolinium is added to the UO_2 fuel in the form of Gd_2O_3. The purpose of adding Gd to the uranium oxide is based on the high neutron capture cross section of the isotopes ^{155}Gd and ^{157}Gd of 61000 barns and 254000 barns, respectively[8]. The excess reactivity of the fuel is restrained by these isotopes in the initial phase of the irradiation cycle and released by the end of the cycle, when the two Gd isotopes are transformed by neutron capture. In order to obtain an adjustment of the existing design codes to the real behaviour of the fuel under irradiation, it is necessary to ascertain the depletion characteristics of the neutron absorbing Gd isotopes and their influence on fissioning, transformation and formation of fuel nuclides, experimentally. Nuclear fuel in a reactor undergoes the variation in its isotopic composition, that is, depletion of the fissile isotopes initially present, buildup of heavy elements and buildup of fission products. In order to check the consistency of the post-irradiation analysis results, the correlations between the parameters of the spent nuclear fuels such as concentration of heavy elements and fission products, ratios of their isotopes and total and fractional burnup have been studied[9-14]. These correlations can be used to identify reactor fuel information and to estimate the burnup and Pu content. Some of these correlations may also be useful for safeguards purposes.

The aim of the present work is to determine the U, Pu, Nd, Gd and their isotopes for the samples from irradiated UO_2-Gd_2O_3 fuel rod and to compare the results for the validity of the methods. In this paper, all the experiments were described for determination of the isotope compositions of U, Pu, Nd and Gd after their separation by ion exchange separation techniques from the fuel samples, determination of the elements in the spent fuel by isotope dilution mass spectrometric method using ^{233}U, ^{242}Pu, ^{150}Nd and ^{158}Gd as spikes.

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EXPERIMENTAL

Certified ^{233}U (99.470 atom%), ^{150}Nd (96.13 atom%) and ^{158}Gd (97.53 atom%) spikes were obtained from Oak Ridge National Laboratory (ORNL). The spike solutions were prepared by dissolving the oxides in HNO_3 (1+1)-0.01 M HF. NBL CRM 129 U_3O_8 powder (New Brunswick Laboratory) and a uranium standard solution (Spex Industries Inc.) were used as a reference standard material for uranium. The standard solutions of neodymium and gadolinium were obtained from AccuTrace and Spex Industries Inc. Certified ^{242}Pu spike solution (99.9033 atom%, IRMM-044) was obtained from the Institute for Reference Materials and Measurements (Table-1). The UO_2-Gd_2O_3 fuel used in this work was irradiated in a power reactor for 1425 days and then cooled for 2 years for post irradiation analyses. The isotopic compositions of U, Pu, Nd and Gd separated from irradiated UO_2-Gd_2O_3 fuel samples were determined using a Finnigan MAT 262 mass spectrometer.

TABLE-1
ISOTOPIC COMPOSITIONS OF THE CERTIFIED SPIKES FOR IDMS

Spike	Isotope	Atom%
^{233}U	U-233	99.4700
	U-234	0.1660
	U-235	0.0640
	U-236	0.0150
	U-238	0.2820
^{242}Pu	Pu-238	0.0009
	Pu-239	0.0826
	Pu-240	0.0108
	Pu-241	0.0009
	Pu-242	99.9033
	Pu-244	0.0015
^{150}Nd	Nd-142	0.7700
	Nd-143	0.3900
	Nd-144	0.8800
	Nd-145	0.3400
	Nd-146	0.8400
	Nd-148	0.6600
	Nd-150	96.1300
^{158}Gd	Gd-152	<0.0200
	Gd-154	0.0500
	Gd-155	0.2500
	Gd-156	0.4600
	Gd-157	0.8800
	Gd-158	97.5300
	Gd-160	1.8300

Basic processes in the PIE analytical laboratory for the determination of U, Pu, Nd and Gd and their isotopes are shown in Fig. 1. The spent fuel sample having been precisely weighed was placed into a 100 mL dissolution flask of the dissolution apparatus. The fuel sample was refluxed for 16 h with *ca.* 30 mL of 8 M HNO_3 without a catalyst. The dissolved fuel solution was weighed and an aliquot was diluted with 8 M HNO_3 with the aid of an calculation code for an estimation of the nuclide contents in the spent fuel. An aliquot of the diluted fuel solution was placed in a capped vial and transferred from the shielded facility into a glove box.

Chemical separation was carried out for both the unspiked and the spiked sample solutions in the same experimental conditions in a glove box without any heavy shieldings. Two portions were subjected to a determination of the U, Pu, Nd and Gd isotopes in the sample with and without a spike addition followed by the sequential anion and cation exchange separation procedures detailed in Fig. 2. Isotopic compositions of U, Pu, Nd and Gd in each fraction that had been isolated and concentrated were measured by using a thermoionization mass spectrometer (TIMS). Each sample solution of U, Pu, Nd and Gd in the range of μg to ng was loaded onto a triple rhenium filament and then measured. The mass discrimination bias factor and the contribution of natural Nd for all the Nd isotopes measured were corrected[1].

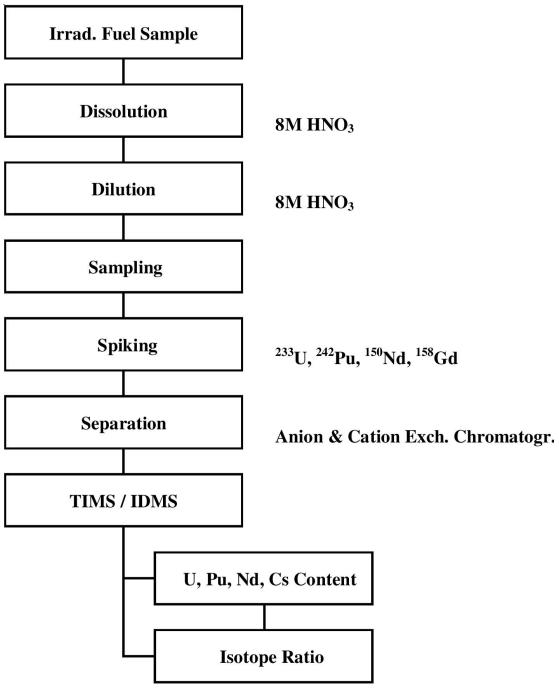

Fig. 1. Basic processes in PIE analytical laboratory

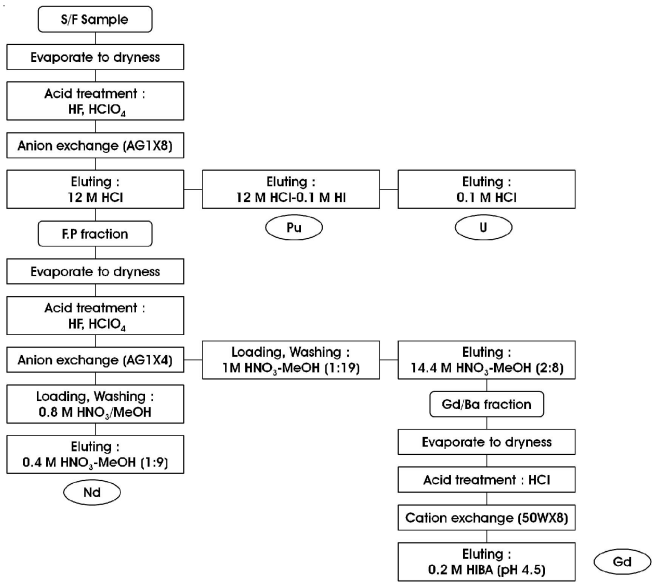

Fig. 2. Analytical scheme for the U, Pu, Nd and Gd separation

RESULTS AND DISCUSSION

Separation procedure: In previous works[2-4], a series of experiments on the separation of U, Pu and some fission product (Nd, Cs, *etc*.) using the spent fuels from reactors of various types were performed. We found the satisfactory chromatographic separation of these elements could be achieved. In the present work, the separation of U, Pu, Nd and Gd from the UO_2-Gd_2O_3 spent fuel solutions was carried out in a glove box by three sequential anion and cation exchange separation procedures as shown in Fig. 2. Prior to load on the first column, treatment with small amount of 1 M $HClO_4$ was used to assure all the Pu in Pu(VI) state because Pu(VI) is more strongly adsorbed on an anion exchange resin as negatively charged chloride complex form. Elution of the Pu with 12 M HCl-0.1 M HI and the U with 0.1 M HCl was performed satisfactorily and no further purification was needed. The Am and Np were not appeared in the Pu and U portions and the complete separation was identified from the mass spectrometry. The adsorption of the rare earths from nitric acid-methanol solutions has been studied using strongly basic anion exchange resins[15,16]. Distribution coefficients were a function of both the volume percentage of alcohol and of the nitric acid concentration. The rare earths were eluted from a column in order of decreasing atomic number. A series of preliminary experiments on the separation of Nd and Gd in nitric acid-methanol system was performed using the prepared solution with suitable simulated fission product elements. Elution of the Nd with 0.4 M HNO_3-MeOH (1:9) was performed satisfactorily without additional purification steps. Fig. 3 shows the elution of Gd from simulated fission products with 14.4 M HNO_3-MeOH (2:8) after washing with 1 mL of 1 M HNO_3-MeOH (1:19) on column with AG 1X8. The separation factors for adjacent rare earths relative to Gd, *i.e.*, Eu-Gd and Gd-Dy were 1.50 and 0.63, respectively.

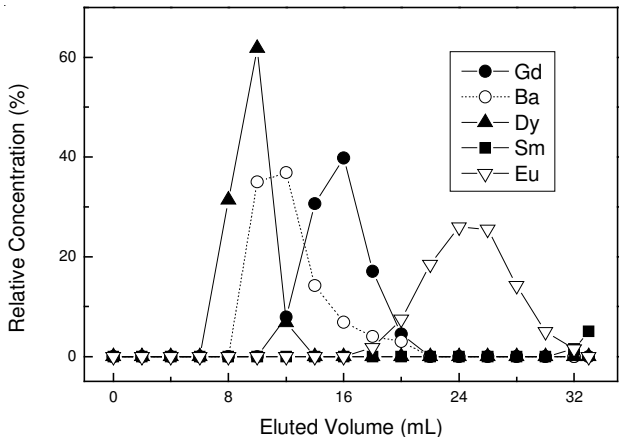

Fig. 3. Elution of Gd from simulated fission products

However, the presence of an isobar BaO in the Gd fraction can introduce a bias in the ^{152}Gd and ^{154}Gd determination, because ^{136}Ba and ^{138}Ba are naturally occurring isotopes and also formed in the fission processes. This fraction was therefore evaporated to dryness and redissolved in 1 mL of 4 M HCl. The solution dissolved in 0.5 mL of 0.2 M α-hydroxyisobutyric acid (α-HIBA) was loaded onto a third cation exchange resin column (Dowex AG 50WX8, 200-400 mesh, H^+ form, 0.4 i.d. × 7.5 cm) and then the Gd was eluted with 7 mL of 0.2 M α-HIBA. Fig. 4 shows the elution of Gd from Ba with 0.2 M α-HIBA on column with AG 50WX8. The Gd fraction was heated to dryness with a few drops of c-HNO_3 to decompose the α-HIBA before the introduction into a mass spectrometer.

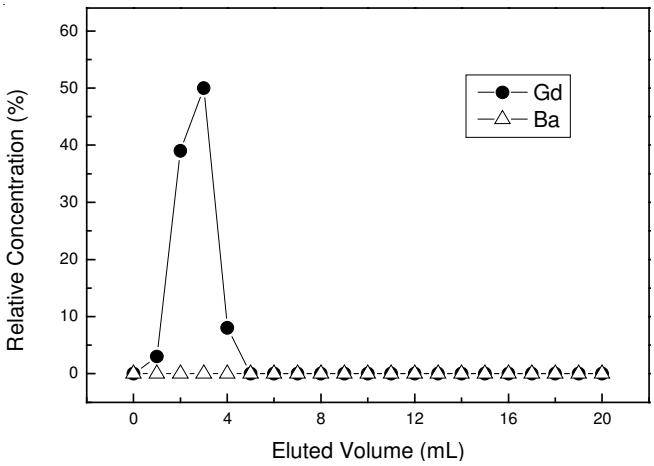

Fig. 4. Elution of Gd from Ba with 0.2 M HIBA (pH 4.5) on column AG 50WX8

Determination of the isotopic composition: The isotopic compositions of a spent fuel depend on the nature of that fuel and on the conditions of its irradiation. A detailed knowledge of these quantities is useful for the reactor work as well as for the effective utilization of a nuclear fuel. Isotopic compositions of U, Pu, Nd and Gd in each fractions isolated, followed by the separation procedures in Fig. 2, were measured by the thermoionization mass spectrometer (TIMS). In this work, all the measured average ratios of Nd were corrected for a mass discrimination and the contribution of a natural contamination, so as to achieve a high accuracy for the burnup measurement[1-4]. After the mass spectrometric measurement of each portion isolated from the spiked and unspiked sample solutions, the concentrations of U, Pu, Nd and Gd in the sample solutions were determined by the isotope dilution method (IDMS). For example, the content of Gd in a spent fuel sample can be calculated as follows:

$$Cs = Ct\cdot(Gt/Gs)\cdot(Ms/Mt)\cdot[(Rt-Rm)/(Rm-Rs)]\cdot(\Sigma s\ Ri/\Sigma t\ Ri)$$

where Cs: Concentration of Gd in spent fuel sample (μg Gd/mL); Ct: Concentration of ^{158}Gd spike solution (μg Gd/mL); Gs: Volume taken of spent fuel sample (mL); Gt: Volume taken of ^{158}Gd spike solution (mL); Ms: Mean atomic weight of spent fuel sample; Mt: Mean atomic weight of ^{158}Gd spike solution; Rt: Ratio of two basic isotopes in ^{158}Gd spike solution; Rm: Ratio of two basic isotopes in mixture of ^{158}Gd spike solution and spent fuel sample; Rs: Ratio of two basic isotopes in spent fuel sample; Σs Ri: Sum of all isotopes for a basic isotope in spent fuel sample; Σt Ri: Sum of all isotopes for a basic isotope in ^{158}Gd spike solution.

A major advantage of IDMS is that a quantitative recovery of the elements concerned is not required. Tables 2-4 show the isotopic compositions of U, Pu and Nd in the UO_2-Gd_2O_3 spent fuel samples measured by the TIMS, respectively. Table-5 also

TABLE-2
ISOTOPIC COMPOSITIONS OF THE U SEPARATED FROM THE UO_2-Gd_2O_3 SPENT FUEL SAMPLES

Isotope	Atom %		
	B-1	B-2	B-3
U-234	0.009 ± 0.002	0.011 ± 0.002	0.007 ± 0.002
U-235	0.430 ± 0.012	0.473 ± 0.004	0.528 ± 0.006
U-236	0.209 ± 0.004	0.404 ± 0.008	0.194 ± 0.007
U-238	99.373 ± 0.042	99.113 ± 0.032	99.275 ± 0.026

TABLE-3
ISOTOPIC COMPOSITIONS OF THE Pu SEPARATED FROM THE UO_2-Gd_2O_3 SPENT FUEL SAMPLES

Isotope	Atom %		
	B-1	B-2	B-3
Pu-238	2.001 ± 0.025	3.070 ± 0.020	1.479 ± 0.027
Pu-239	56.914 ± 0.020	48.233 ± 0.032	59.337 ± 0.032
Pu-240	24.488 ± 0.012	25.204 ± 0.020	23.923 ± 0.014
Pu-241	11.609 ± 0.010	14.209 ± 0.016	11.178 ± 0.008
Pu-242	4.988 ± 0.010	9.284 ± 0.040	4.084 ± 0.004

TABLE-4
ISOTOPIC COMPOSITIONS OF THE Nd SEPARATED FROM THE UO_2-Gd_2O_3 SPENT FUEL SAMPLES

Isotope	Atom %		
	B-1	B-2	B-3
Nd-143	20.123 ± 0.034	18.068 ± 0.017	21.339 ± 0.043
Nd-144	32.144 ± 0.061	33.918 ± 0.041	31.055 ± 0.083
Nd-145	17.062 ± 0.032	15.900 ± 0.018	17.291 ± 0.027
Nd-146	16.801 ± 0.031	18.043 ± 0.016	16.603 ± 0.026
Nd-148	9.219 ± 0.019	9.353 ± 0.015	9.182 ± 0.021
Nd-150	4.561 ± 0.019	4.718 ± 0.012	4.530 ± 0.018

TABLE-5
ISOTOPIC COMPOSITIONS OF THE Gd SEPARATED FROM THE UNSPIKED AND SPIKED UO_2-Gd_2O_3 SPENT FUEL SAMPLES

Isotope	Atom %		
	Nat. Abund.	Unspiked	Spiked
Gd-152	0.20	0.1594	0.4047
Gd-154	2.18	1.6238	1.1800
Gd-155	14.80	0.1637	0.0910
Gd-156	20.47	36.3138	26.5774
Gd-157	15.65	0.0362	0.2590
Gd-158	24.84	40.8140	54.6534
Gd-160	21.86	20.8890	16.8345

shows the isotopic compositions of Gd in the unspiked and spiked sample prepared from a UO_2-Gd_2O_3 spent fuel. The isotopic compositions of natural Gd added to the UO_2 fuel in the form of Gd_2O_3 were changed by the depletion characteristics of the neutron absorbing Gd isotopes (^{155}Gd and ^{157}Gd) during irradiation. Table-6 shows the contents of U, Pu, Nd, Gd and their isotopes in a UO_2-Gd_2O_3 spent fuel sample determined by IDMS. The quantity (14.823 μg) of Gd in the sample calculated from amount of Gd_2O_3 added to the UO_2 fuel is within a deviation of 3.3 %, with that (14.322 μg) obtained by the experimental method (IDMS).

The relationships between isotope ratios and burnup values and correlations between isotope themselves provide an excellent basis for determining the internal consistency and hence the reliability of the data by chemical methods. In this work, the U, Pu, Nd and Gd isotope ratios and burnup values measured from three UO_2-Gd_2O_3 and three UO_2 spent fuel samples irradiated in the same fuel assembly of a power reactor are applied for correlation check due to linearity or nonlinearity. Figs. 5 and 6 show the dependencies of the total burup values in GWD/MtU against the isotope ratios of the ^{242}Pu/^{240}Pu and ^{146}Nd/^{145}Nd determined experimentally for the spent fuel samples. A correlation between the isotope compositions of U and Pu, *e.g.* the ^{236}U/^{235}U atom ratio against the ^{240}Pu/^{239}Pu atom ratio is shown in Fig. 7. The results plotted were in agreement with good linearity.

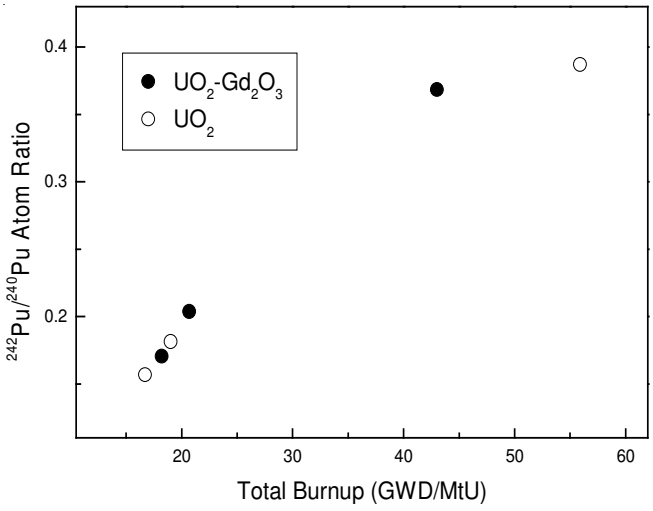

Fig. 5. Dependency of ^{242}Pu/^{240}Pu atom ratio on total burnup

TABLE-6
QUANTITIES OF U, Pu, Nd, Gd AND THEIR ISOTOPES IN A UO_2-Gd_2O_3 SPENT FUEL SAMPLE DETERMINED BY ISOTOPE DILUTION MASS SPECTROMETRY

U		Pu		Nd		Gd	
Isotope	μg	Isotope	μg	Isotope	μg	Isotope	μg
U-234	0.017	Pu-238	0.087	Nd-143	0.299	Gd-152	0.022
U-235	0.752	Pu-239	1.374	Nd-144	0.564	Gd-154	0.227
U-236	0.645	Pu-240	0.721	Nd-145	0.266	Gd-155	0.023
U-238	159.527	Pu-241	0.408	Nd-146	0.304	Gd-156	5.150
–	–	Pu-242	0.268	Nd-148	0.160	Gd-157	0.005
–	–	–	–	Nd-150	0.082	Gd-158	5.863
–	–	–	–	–	–	Gd-160	3.039
Total	160.9407	Total	2.859	Total	1.675	Total	14.330

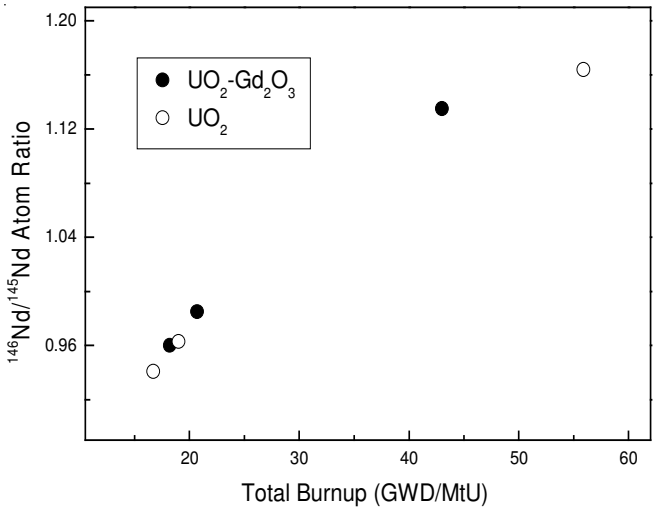

Fig. 6. Dependency of $^{146}Nd/^{145}Nd$ atom ratio on total burnup

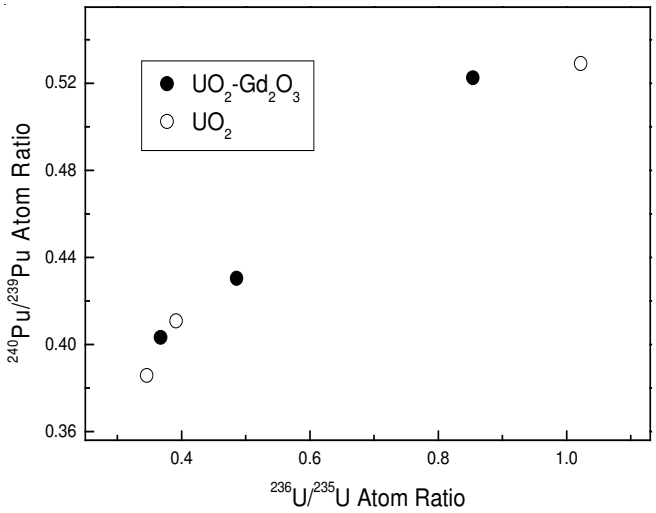

Fig. 7. Dependency of $^{240}Pu/^{239}Pu$ atom ratio on $^{236}U/^{235}U$ atom ratio

Conclusion

The contents of U, Pu, Nd, Gd and their isotopes in the spent UO_2-Gd_2O_3 fuel samples can be simultaneously determined by the isotope dilution mass spectrometric method by using the quadruple spikes. Several correlations between U, Pu, Nd and Gd isotope ratios with burnup values measured experimentally from the spent fuel samples can be applied in order to check the consistency of the post-irradiation analysis results. These isotope patterns provide information on the real irradiation characteristics which are necessary for evaluating a fuel's performance in a reactor.

REFERENCES

1. Annual Book of ASTM Standards 12.02, E321-96 (reapproved 2005) (2005).
2. J.S. Kim, Y.S. Jeon, S.D. Park, S.H. Han and J.G. Kim, *J. Nucl. Sci. Technol.*, **44**, 1015 (2007).
3. J.S. Kim, Y.S. Jeon, S.D. Park, B.C. Song, S.H. Han and J.G. Kim, *Nucl. Eng. Technol.*, **38**, 301 (2006).
4. J.S. Kim, S.H. Han, M.Y. Suh, K.S. Joe and T.Y. Eom, *J. Korean Nucl. Soc.*, **21**, 277 (1989).
5. P. De Regge, De Huys, R. Boden and C. Ballaux, IWGFPT/31, 23 (1989).
6. J. Krtil, F. Sus and A. Hermann, *Radiochem. Radioanal. Lett.*, **48**, 209 (1981).
7. P. De Regge and R. Boden, *J. Radioanal. Chem.*, **35**, 173 (1977).
8. N.R. Daly, Advances in Mass Spectrometry, Heyden & Son Ltd. (London), Vol. 7A, p. 499 (1978).
9. H. Graber, G. Hofmann and R. Berndt, IAEA-SM-260/84, 443 (1983).
10. W. Smulek, R.K. Al-Dabbagh, K. Goroncek and M. Borkowski, *J. Radioanal. Nucl. Chem.*, **121**, 385 (1988).
11. J. Krtil, F. Sus, V. Bulovic, E. Klosova, J. Rocek and Z. Maksimovic, *Radiochem. Radioanal. Lett.*, **50**, 79 (1982).
12. W. Smulek, J. Kritil, F. Sus, V. Bulovic and E. Klosova, *Radiochem. Radioanal. Lett.*, **50**, 299 (1982).
13. J. Krtil, F. Sus, V. Bulovic, E. Klosova, V. Kuvik and Z. Maksimovic, *Radiochem. Radioanal. Lett.*, **49**, 49 (1981).
14. J.S. Kim, *J. Korean Nucl. Soc.*, **29**, 327 (1997).
15. S. Usuda and N. Kohno, *Sep. Sci. Technol.*, **23**, 1119 (1988).
16. S. Usuda, *J. Radioanal. Nucl. Chem. Art.*, **111**, 399 (1987).