Journal of Radioanalytical and Nuclear Chemistry, Articles, Vol. 91/1 (1985) 17–24

DETERMINATION OF ACTINIDE NUCLIDES IN WATER SAMPLES FROM THE PRIMARY CIRCUIT OF A RESEARCH REACTOR

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(Received June 11, 1984)

Primary coolant samples from a research reactor have been analyzed for ^{239,240}Pu, ^{238}Pu, ^{238}U, ^{237}Np and ^{239}Np. The determination of ^{237}Np and ^{238}U was carried out with the help of isotope dilution neutron activation analysis with ^{239}Np or ^{238}Np as tracer. For determination of ^{239,240}Pu and ^{238}Pu alpha spectroscopic isotope dilution analysis with ^{238}Pu as tracer was used. ^{239}Np was determined with the help of isotope dilution analysis using ^{238}Np as tracer. Nuclides were isolated by chemical separation on anionite resin. Before measurement, Pu isotopes were electrolytically deposited on stainless steel plates. Activity ratios referred to ^{238}U were reported. They are helpful for identification of the sources of actinide activity in reactor effluents.

Introduction

The primary coolant of nuclear reactors contains a variety of radionuclides formed by activation of water and by activation of reactor materials. Activity detected is also due to contamination of reactor coolant systems, contamination of the fuel cladding and due to failure in fuel cladding. For correlation of clad failure characterization and localization methods, there is a need for high accuracy in analytical determination as well as in gaseous and nonvolatile radionuclides.

To get more information about the origin of radioactivity found in the effluent, the analytical determination of actinide concentration and actinide concentration ratios is necessary. These measurements are applicable for instance to examine test fuel elements for the production of fission products, where the burnup is characteristically different from those normally used. For the detection of a direct contact between fuel and water through a failure in fuel cladding (macro leakages), there is a necessity for the determination of actinide activity ratios.

Actinide determinations in reactor water are described elsewhere,[1,2] however, the recovery of separations was not mentioned. The aim of our work is to point out the

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usefulness of isotope dilution analysis for determination of actinides in a concentration range which can expected to be very low. With the help of this technique it will be possible to watch the analytical procedure in order to increase the accuracy of analytical values.

Experimental and results

Sampling

Samples of primary coolant water were taken by the operator in a bypass of the primary circuit of a research reactor. They were kept in polyethylene bottles, the volume was 1 – 2 l.

Neptunium – 239

^{239}Np was determined using isotope dilution analysis with ^{238}Np as a tracer, therefore 10 – 20 ml water samples with the added ^{238}Np tracer (2 – 10 cps = 200 to 1000 Bq) were evaporated. The separation was carried out with anionite resin (SBW) in NO_3^- form. The procedure is shown in Fig. 1.[3] Valency states Np(IV), Pu(III) and U(VI) achieved by addition of 0.3 ml 2.2N $Fe(NH_2SO_3)_2$ and 0.1 ml 5N $NH_2OH \cdot HCl$ were necessary before separation. Gamma spectroscopic measurements were carried out by a multichannel analyzer in connection with a Ge(Li) detector (50 cm^3). The photopeaks at 105 keV, 228 keV, 278 keV for ^{239}Np, and 985 keV and 1028 keV (including the 1026.5 keV peak) for ^{238}Np were used for calculation of the count rates. Figure 2 shows the gamma spectra of 1 ml individual primary coolant water sample without separation (a) and 10 ml separated neptunium fraction (b). The recovery was 80 to 90%.

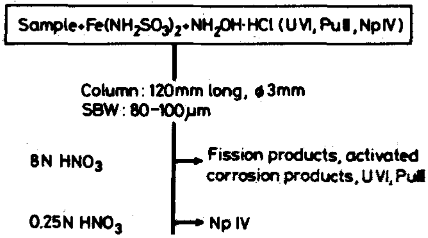

Fig. 1. Separation of neptunium by anion exchange

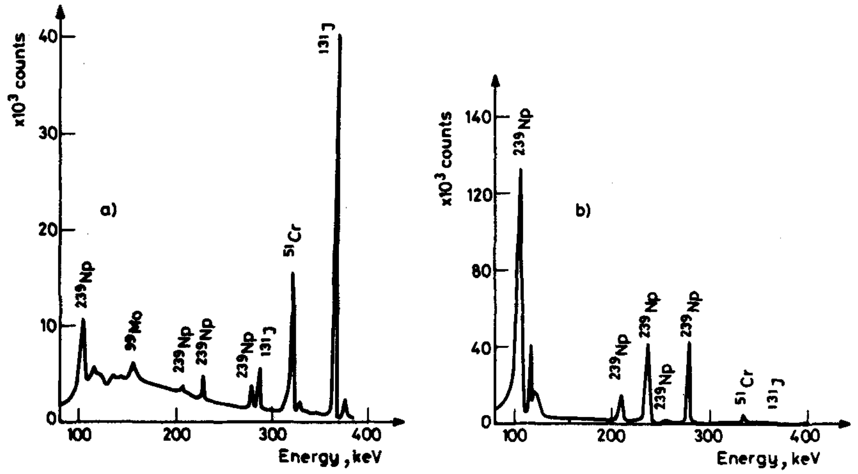

Fig. 2. Gamma spectra of ^{239}Np, (a) nonseparated, (b) separated from reactor water

Uranium

For determination of uranium, samples of 10 – 100 ml water were evaporated in quartz ampoules in several portions by gentle heating under an IR lamp. The irradiation was carried out with a neutron flux of $2 - 3 \cdot 10^{13}$ n · cm^{-2} · s^{-1} in an irradiation time of about 100 hours to give ^{239}Np after the reaction

$$^{238}U\,(n, \gamma)\,^{239}U \xrightarrow{\beta^-} {}^{239}Np.$$

The irradiated samples were dissolved in 10N HNO_3, and ^{238}Np tracer was added. The separation and the measurement of neptunium was carried out using the same procedure as described for ^{239}Np. Table 1 shows the uranium values obtained from two water samples, taken at different times. The procedure for one example is described.

Neptunium – 237

^{237}Np was determined using 50 – 200 ml water samples; ^{238}Np or ^{239}Np was added as tracer. Separation of neptunium before irradiation was carried out (see Fig. 1) within a certain range of recovery (40–60%). The neptunium fraction was irradiated after the decay of ^{238}Np, using the same conditions as those used in determination of uranium. After the $^{237}Np\,(n, \gamma)\,^{238}Np$ reaction ^{238}Np is

Table 1

Uranium determination in reactor water. Irradiation: 2 – 3 · 10^{13} n · cm^{-2} · s^{-1}, 92 hours; addition of 2.34 ng ^{237}Np as tracer – ca. 1000 Bq ^{238}Np; measurement: 50 cm^3 Ge(Li) detector; amount of the sample: 95.768 g

Energy, keV	106	210	230	278	985	1028
U-standard (101.33 ng), cps	168.39	10.95	30.89	33.27	–	–
Np-tracer (2.34 ng), cps	–	–	–	–	6.53	6.20
Sample+tracer, cps	54.4	3.4	10.35	10.75	3.45	3.45
Recovery, %				Mean:	53.8	
Recovery corrected, cps	101.16	6.32	19.24	19.98	–	–
U-amount, ng	59.24	54.97	55.62	61.65		
Water sample (26 January 1984):			604.3 pg ± 120 pg		uranium	
Water sample (17 March 1983):			351.0 pg ± 70 pg		uranium	

Table 2

^{237}Np determination in reactor water by isotope dilution activation analysis

1. Separation before irradiation. Amount of the sample 53.427 g water; addition of 1.17 ng ^{238}Np as tracer: – ca. 1000 Bq ^{238}Np

Energy, keV	985	1028
Sample + tracer, cps	0.72	0.73
^{238}Np tracer, cps	1.19	1.31
Recovery, %	Mean:	58.1

2. Separation after irradiation and determination of the amount of ^{237}Np

Energy, keV	106	210	230	278	985	1028
Sample – nonseparated, cps	17.95	1.10	3.65	3.65	2.27	2.12
Sample – separated, cps	10.94	0.61	2.17	1.71	–	–
Recovery, %	Mean:	55.70%				
^{237}Np standard, 5.4825 ng/cps	–	–	–	–	18.49	20.53
^{237}Np amount, ng					1.208	1.016
^{237}Np in reactor water:					20.81 ∓ 5 pg	

produced. The amount of ^{237}Np in the ^{238}Np tracer did not exceed 20% of the amount of ^{237}Np in the sample in order to avoid additional appreciable errors. If there was a necessity, separation of neptunium was repeated after irradiation. The calculation of ^{237}Np activity is described in detail in Reference 8. The ^{237}Np analysis is shown in Table 2.

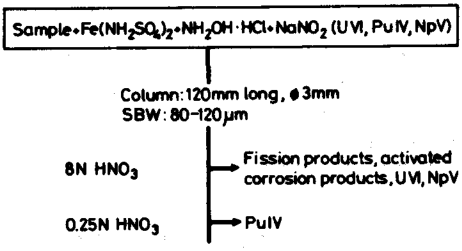

Fig. 3. Separation of plutonium by anion exchange

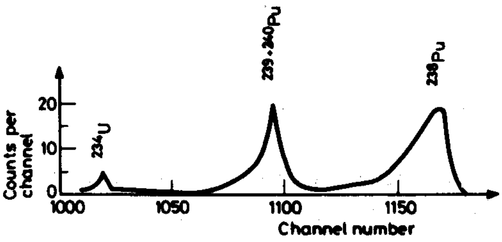

Fig. 4. Alpha-spectrum of the plutonium fraction separated from reactor water

Plutonium

^{239,240}Pu and ^{238}Pu were determined in reactor water samples (1 – 2 l) after separation by anion exchange,[4] using the procedure shown in Fig. 3. Two subsamples were prepared, one which contains ^{236}Pu as tracer and one, which did not contain tracer. Before separation the valency states Pu(IV), Np(V) and U(VI) were achieved by addition of 0.3 ml 2.2N $Fe(NH_2SO_3)_2$ and 0.3 ml 0.5N $NaNO_2$. Preparation of counting samples for alpha spectroscopy was carried out using electrolytic deposition.[5,6] Alpha activity was measured by a Si(Li) detector (177 mm^2 surface) connected with a multichannel analyzer. No discrimination is possible between ^{239}Pu and ^{240}Pu by means of alpha spectroscopy. The alpha energies were evaluated as a sum at 5.155 MeV, 5.143 MeV, 5.105 MeV, 5.168 MeV, 5.123 MeV for ^{239,240}Pu and 5.499 MeV, 5.456 MeV, 5.358 MeV for ^{238}Pu. An alpha spectrum

Table 3
Alpha-spectroscopic determination of the ratio $^{239,240}Pu/^{238}Pu$ in reactor water

Sample	m_T/m_P	$\frac{A_T}{Bq \cdot g^{-1}}$	Peak energy, MeV	cps/g	$\frac{239+240}{238}$
Without tracer	–	–	5.166	0.031	0.6
Without tracer	–	–	5.480	0.051	
With tracer	0.000103	9.491	5.166	0.0011	0.012
With tracer			5.480	0.0915	
$A_{Pu239,240} = 0.015 \mp 0.03$ Bq					

of a separated plutonium fraction of an individual water sample without tracer is shown in Fig. 4. ^{234}U activity is due to a trace amount of uranium in the plutonium fraction. Table 3 shows the values for plutonium activity, calculated with the help of the equation for isotope dilution analysis.[7]

Treatment of analytical values

Activity ratios for the various actinide nuclides referred to the activity of ^{238}U or ^{238}Pu are given. The frequency distribution of the concentration values was checked with the chi-square test at the 95% confidence level are of the order of 30% at the concentration values around 10 pg/l and 20% at the concentration level of 100 pg/l.

Discussion

Actinide activities in primary coolant are less important than the corresponding activity ratios for interpretation of actinide measurements. Column 2 of Table 4 contains activity ratios referred to ^{238}U of the nuclides quoted in Column 1. The activity ratios are compared with those found in a power plant spent fuel solution, Column 3. These values are taken from our previous investigations of a spent fuel solution with 2% ^{235}U starting enrichment and 1.37% fima.[8,11] Columns 4 and 5 contain activity ratios referred to ^{238}Pu for water of a power plant (Column 4) foun in Reference 1 compared with our values for water of the research reactor (Column 5).

From the activity ratios referred to both ^{238}U and ^{238}Pu it is recognizable that they depend on the ^{235}U enrichment in fuel used. (The ^{235}U starting enrichment

Table 4
Activity ratios of actinide nuclides observed in primary coolant water and in spent fuel samples

Nuclide	Activity ratio $^{238}U = 1$		Activity ratio $^{238}Pu = 1$	
	RFR – water	Power plant spent fuel	Power plant water	RFR – water
^{238}U	1 ·	1	–	$3.0 \cdot 10^{-4}$
^{239}Np	$35.8 \cdot 10^{6}$	–	–	$1.1 \cdot 10^{4}$
^{237}Np	0.93	0.44 ·	–	$2.7 \cdot 10^{-4}$
^{238}Pu	$0.34 \cdot 10^{4}$	$0.86 \cdot 10^{3}$	1	1
$^{239,240}Pu$	$0.20 \cdot 10^{4}$	$1.52 \cdot 10^{3}$	1.3	0.6

of fuel elements in the research reactor is about one order of magnitude higher than that of those used in a power plant).

The main source of ^{237}Np and ^{238}Pu is the following reaction chain proceeding from ^{235}U:

$$^{235}U\,(n, \gamma)\,^{236}U \xrightarrow{\beta^-} {}^{237}Np\,(n, \gamma)\,^{238}Np \xrightarrow{\beta^-} {}^{238}Pu.$$

This is reflected by the higher activity ratios for ^{237}Np and ^{238}Pu observed in RFR water (Column 2) than in spent fuel solution of a power plant (Column 3), and by the difference of the ratio $^{239,240}Pu : {}^{238}Pu$ for power plant water (Column 4) and for the RFR water (Column 5). Moreover, the ratio of $^{239,240}Pu : {}^{238}U$ is significant for burnup of spent fuel.[9]

To give a rough estimation of the activity ratio $R_c = A_{Np^{239}} / A_{U^{238}}$ in the investigated reactor water, we use the equation for ^{238}U activation:

$$R_c = (\sigma\, \Phi_{th} + I \cdot \Phi_{epi})\, SD \cdot \lambda_{238}^{-1},$$

$$\text{where} \quad SD = \sum_j (1 - e^{-\lambda_{239} t_{Bj}})\, e^{-\lambda_{239} t_{Aj}}.$$

The following values are used to estimate the activity ratio R_c for activation of uranium in the reactor core:[10]

$\Phi_{th} = 8 \cdot 10^{13}\ n \cdot cm^{-2} \cdot s^{-1}$,
$\Phi_{epi} = 2.4 \cdot 10^{12}\ n \cdot cm^{-2} \cdot s^{-1}$,
$I = 2.80 \cdot 10^{-22}\ cm^{-2}$,
$\sigma = 2.7 \cdot 10^{-24}\ cm^{2}$,
$\lambda_{238} = 4.85 \cdot 10^{-18}\ s^{-1}$.

The saturation and decay factor SD for ^{239}Np was calculated from the irradiation periods SD = 0.65. Hence, it follows that $R_C/R_C = 7.8 \cdot 10^7$. From this rough estimation it is to be seen that the most of the ^{238}U amount was activated in the core of the research reactor at a neutron flux density of about $8 \cdot 10^{13}$ n $\cdot$ cm^{-2} $\cdot$ s^{-1}, if we compare this calculated ratio with the observed ratio found by activity measurement of ^{239}Np (Table 4).

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