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Anion-Exchange Separation of Nd and the Transplutonium Elements in Spent Nuclear Fuels for Burn-up Determination

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Abstract

Three methods of anion-exchange separation of Nd, Am, and Cm from spent nuclear fuel samples for destructive burn-up measurements with nitric acid–methyl alcohol mixed media have been developed. The first method was developed for the routine analysis of Nd by isotope dilution mass spectrometry to separate Nd from Am and Cm as well as from major fission products, U and Pu, on a conventional anion-exchange resin with 1 *M* HNO_3–90% CH_3OH and 0.5 *M* HNO_3–80% CH_3OH media at ambient temperature. The second method quantitatively separates Nd, Am, and Cm using a fine resin and a 0.5 *M* HNO_3–80% CH_3OH medium at a considerably slower flow rate at ambient temperature. The third method is a more rapid separation: the preliminary separation of irradiated U at elevated pressure is followed by the sequential elutions of Nd, Am, and Cm at elevated temperature and pressure.

INTRODUCTION

A stable isotope, ^{148}Nd, and the sum of Nd isotopes are excellent fission monitors of ^{235}U and ^{239}Pu. After chemical purification, the Nd isotopes have been determined by the IDM method (isotope dilution mass spectrometry) as a standard method of burn-up measurement (*1–4*). The sum of Nd isotopes may be determined by an elemental analysis such as ICP emission spectroanalysis. The radioactive isotope, ^{147}Nd ($T_{1/2}$: 10.98 d), could also be used as a fission monitor in test fuels of short irradiation (*5*). Quantitative separation of Nd is necessary in such a case.

Measurements of the main transplutonium nuclides ($^{241\text{-}243}$Am and $^{242\text{-}244}$Cm) in spent fuels are required for evaluation of accurate burn-up and the amounts of alpha-waste (*6*), and for studying isotope correlations among them (*7*, *8*). They have been also determined by alpha-activity measurements and mass spectrometry.

We have determined such isotopes and some other important ones radiochemically for burn-up measurements by sequential ion-exchange separation (*9–11*). Several ion-exchange steps are required to purify Nd, and the process takes a few weeks. In the ASTM method (*1*), U and Pu are separated from the main fission products, and Nd is finally purified from Am and Cm by anion exchange with nitric acid–methyl alcohol mixed media. However, the separated Nd, Am, and Cm could not be obtained quantitatively.

One of the authors has investigated the anion-exchange behavior of the transplutonium elements in nitric acid–methyl alcohol mixed media at elevated temperatures from the point of view of separating the short-lived nuclides produced by heavy-ion bombardments of U or Pu targets (*12–14*). The anion-exchange system has been applied to rapid mutual-separation of the light lanthanoids from La to Pm (*15*). In such a separation system, elevating the temperature serves to improve the effectiveness of rapid separation, while separation factors among the rare earth and transplutonium elements increase with decreasing temperature (*12*).

This paper presents three anion-exchange separation procedures that are effective for the separation of Nd and the transplutonium elements in spent nuclear fuels with nitric acid–methyl alcohol mixed media. The first one was developed for IDM determination of Nd (Procedure I), the second one was for quantitative separation (Procedure II), and the third one was for a more rapid separation (Procedure III).

EXPERIMENTAL

Materials

Table 1 shows the respective anion-exchange resins, columns, and eluents used for Procedures I, II, and III. For the rapid separation of Procedure III, a pressurized ion-exchange apparatus was employed (*16*). The rapid separation of U and Pu was performed by using 0.25 mL MCI GEL CA08B resin (crosslinking, 8%; particle size, 16 ± 2 μm).

TABLE 1
Resin, Column, and Eluent Used to Separate Nd, Am, and Cm

	Procedure I	Procedure II	Procedure III
Resin:	BIORAD AG 1 × 4	MCI GEL CAO6Y	MCI GEL CAO8S
Crosslinking	4%	6%	8%
Particle size	−400 mesh	23.5 ± 4 μm	11 ± 2 μm
Column:	Glass	Glass	Teflon
Size	ϕ4 mm × 8 cm	ϕ4 mm × 4 cm	ϕ1 mm × 5.7 cm
Volume	1 mL	0.5 mL	0.05 mL
Eluent	1 *M* HNO_3–90% CH_3OH 0.5 *M* HNO_3–80% CH_3OH	0.5 *M* HNO_3–80% CH_3OH	0.01 *M* HNO_3–90% CH_3OH

Preparation of Sample Solution

A mixture of spent fuel specimens (burn-up: 20–30 GWd/t) and the fission products containing ^{147}Nd was used as samples. After reduction-oxidation treatment to change the oxidation states of Pu to Pu(IV), the residues were redissolved with small amounts of concentrated HNO_3 solution. The solution was mixed with a 10-fold volume of C_2H_5OH (see Fig. 1), and an appropriate portion of the solution (which should contain less than a few milligrams of U) was transferred to a resin column.

Recommended Separation Procedures

Procedures I, II, and III are outlined in Figs. 1, 2, and 3, respectively. If the sequential separation of U and Pu is necessary, preliminary group-

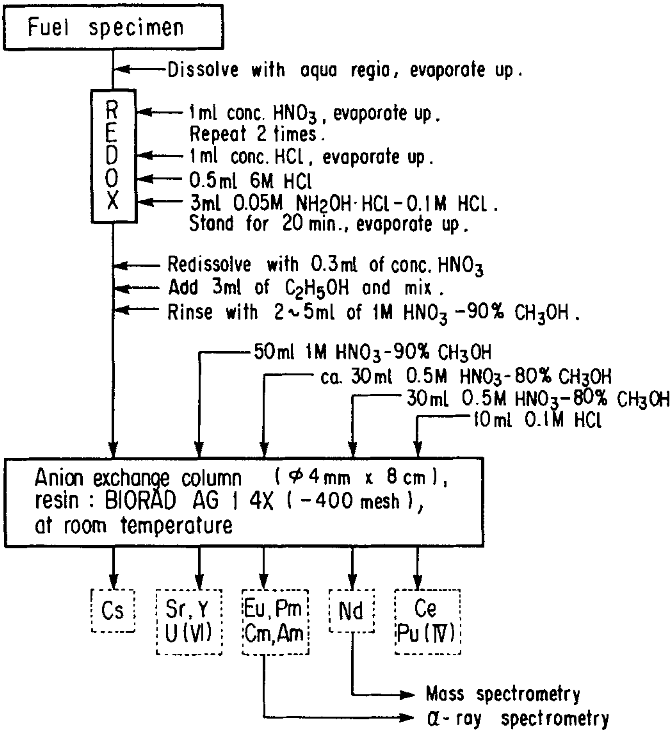

FIG. 1. Procedure I (separation of Nd for IDM determination).

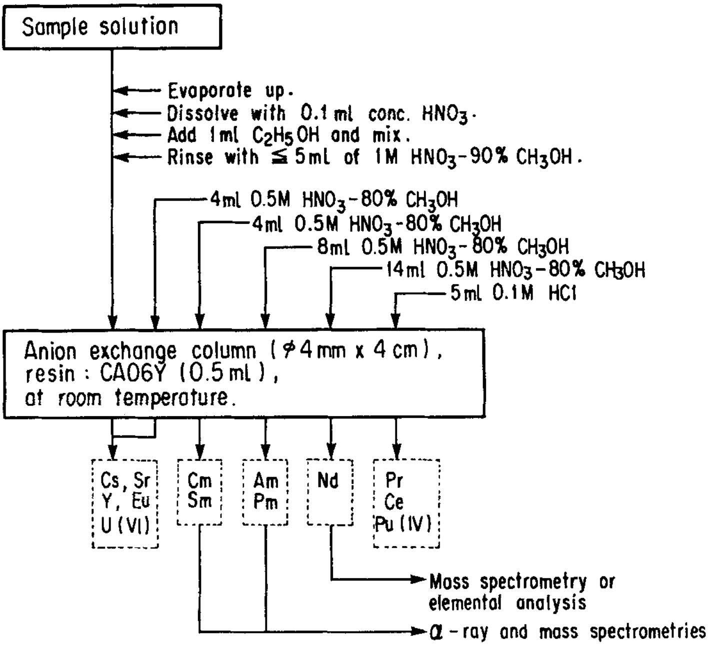

FIG. 2. Procedure II (quantitative separation).

separation of FP, U, and Pu is performed by anion exchange with HCl solution (9). The rapid group-separation procedures by anion exchange with aqueous HNO_3 solution at elevated pressure are also given in Fig. 3. In such a case, the FP fraction of the group separation is fed to the Nd purification process.

Activity Measurement

A drop of effluent was placed at appropriate intervals on a Ta disk (φ24 mm × 0.05 mmt) in order to obtain the elution curves. After evaporating the solution, the alpha-, beta-, and gamma-activities were measured on the disks with a Si-surface-barrier and Ge(Li) detectors.

RESULTS AND DISCUSSION

Separation of Nd for IDM Determination

Figure 4 shows the elution curves obtained by using a conventional anion-exchange resin, BIORAD AG 1×4. After passing the sample

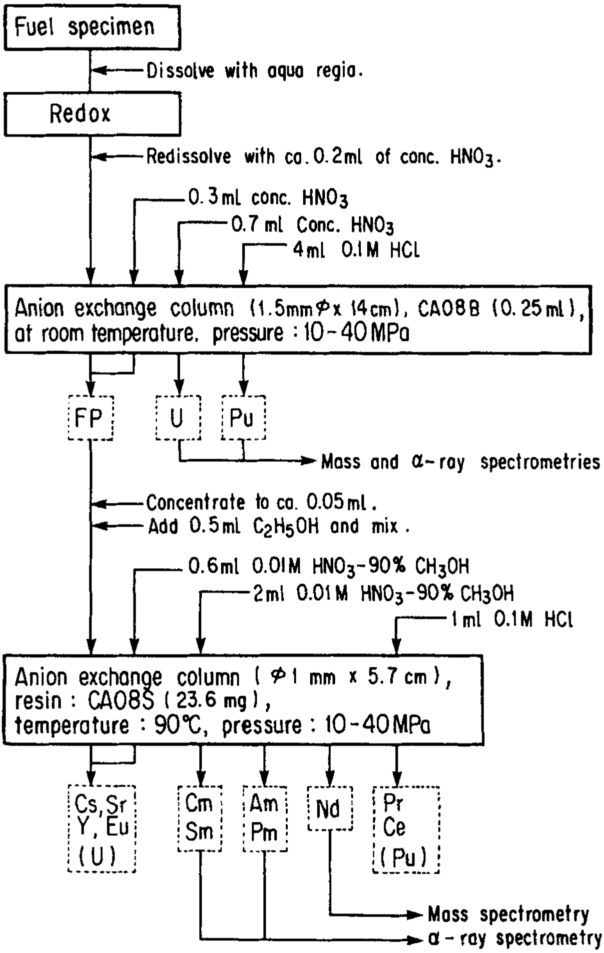

FIG. 3. Procedure III (rapid separation).

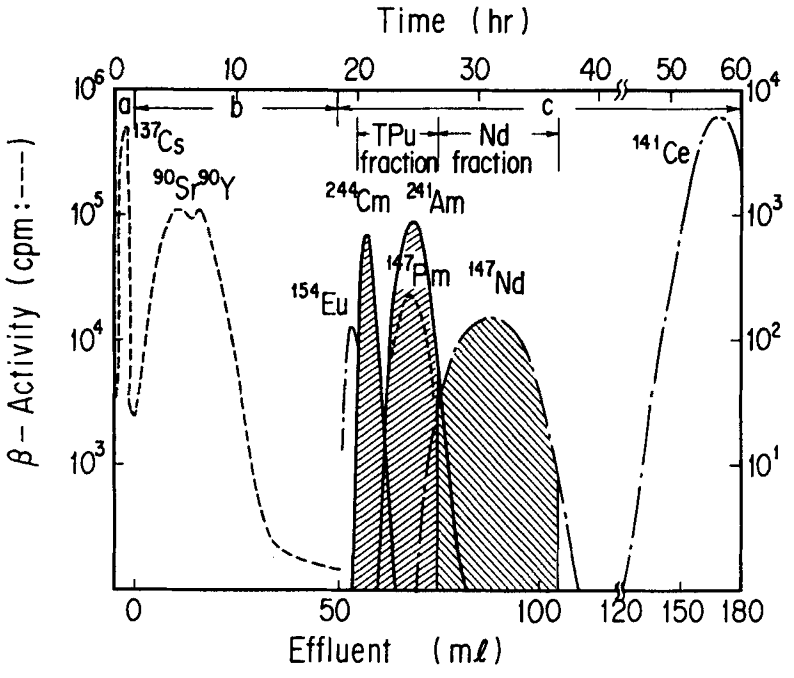

FIG. 4. Separation of Nd, Am, and Cm on the conventional anion-exchange resin at ambient temperature and pressure. Resin: BIORAD AG 1 × 4 (1 mL). Column bed: ϕ4 mm × 8 cm. a: Sample solution (0.3 mL concentrated HNO_3 + 3 mL C_2H_5OH) and wash solution (2 mL of 1 *M* HNO_3-90% CH_3OH). b: 50 mL of 1 *M* HNO_3-90% CH_3OH. c: 130 mL of 0.5 *M* HNO_3-80% CH_3OH. Flow rate: ~0.4 cm/min.

solution through the column, the inner walls of the column were rinsed with 2-5 mL of 1 *M* HNO_3-90% CH_3OH, and ^{134,137}Cs was passed immediately through the column. ^{90}Sr-Y and U(VI) were eluted from the column with 50 mL of 1 *M* HNO_3-90% CH_3OH medium. Then ^{154}Eu, ^{244}Cm, ^{241}Am + ^{147}Pm, ^{147}Nd, and ^{144}Ce were eluted in that order with the 0.5 *M* HNO_3-80% CH_3OH medium. The effluent from 5 to 25 mL was taken as the Am-Cm fraction.

Neodymium was recovered in the next 30 mL of effluent with considerable yield, being monitored by the gamma-activity of ^{147}Nd. If ^{147}Nd was not present, the elution position of Nd was predicted by monitoring the alpha-activity of ^{241}Am or the beta-activity of ^{147}Pm. Although the Nd fraction crossed over by 5-10% of Pm + Am and some other nuclides, such as ^{95}Zr and ^{103,106}Ru, the separation from Ce and Sm, which disturbed the IDM determination of Nd, was complete. After Nd elution, Pr, Ce, and Pu(IV) can be washed out of the column with 0.1 *M* HCl or 0.1 *M* HNO_3 solution.

On the basis of the above results, the steps of Procedure I for the IDM determination of Nd are given in Fig. 1. Neodymium and Am + Cm samples were prepared by evaporating the fractions for IDM measurement and alpha-ray spectrometry. Since U and Pu are recovered in the Sr and Ce fractions, respectively, it is possible to take U and Pu for IDM without further separation of U and Pu. It took about 3 days to do the Nd separation, but the procedures are simple and several samples can be treated in parallel, which is very suitable for routine burn-up measurements.

Quantitative Separation of Nd, Am, and Cm

Figure 5 shows chromatograms of the rare earth and transplutonium elements obtained by using a fine resin, MCI CAO6Y, at ordinary temperature and pressure. It is necessary to transport the whole sample with a minimum amount of 1 *M* HNO_3–90% CH_3OH to the column for quantitative separation. The flow rate was so slow (~0.09 cm/min) that the ion exchanges always attained equilibrium and the relevant elements could be separated effectively. Caesium, Te, Sr, Y, Np, U(VI), and Eu were eluted first from the column with 4 mL of 0.5 *M* HNO_3–80% CH_3OH; Cm and Ba were eluted next with 4 mL of the eluent (Cm fraction); and Am + Pm were eluted with the succeeding 8 mL fraction of the eluent (Am fraction). After eluting Am + Pm, Nd was eluted with 10 mL of the same eluent. More than 99.9% of ^{147}Nd activity was recovered in the Nd fraction. Activities of the neighboring rare earths were not detected in the Nd fraction when it was slightly contaminated by the activities of ^{95}Zr and ^{103,106}Ru. By further elution with the same eluent, Pr and Ce were effectively separated. In addition to ^{147}Nd and ^{141,144}Ce identified by gamma-ray spectrum analysis, ^{143}Pr was detected by beta-activity measurements. Plutonium(IV) absorbed on the resin column was eluted with 0.1 *M* HCl.

Table 2 summarizes the relative separation factors of Y and light rare earth elements to Nd compared with those in the literature (*17*, *18*). The separation factors agreed with the reported data at room temperature. Separation factors between the two elements at room temperature are larger than those at elevated temperature (*12*, *15*).

This procedure, shown in Fig. 2 as Procedure II, enables one to make quantitative separation of Nd, Am, and Cm from irradiated U samples.

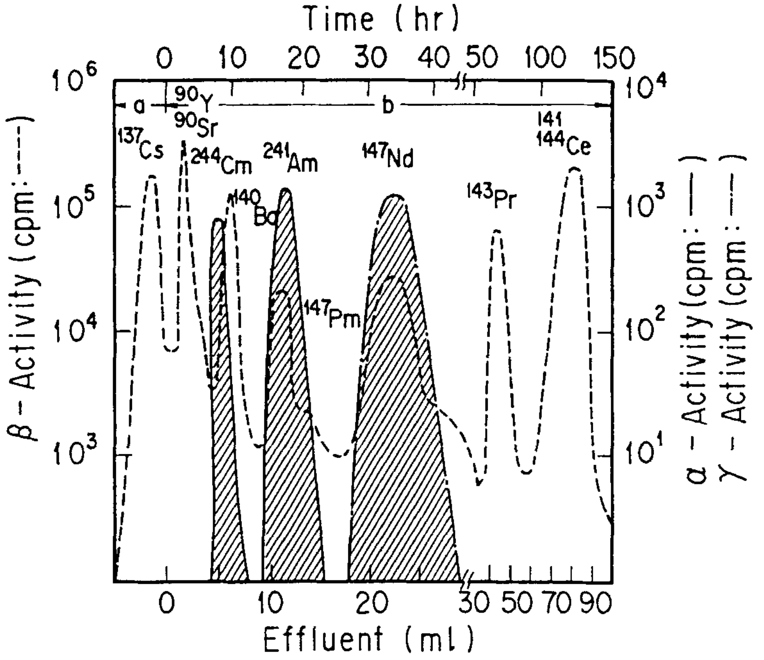

FIG. 5. Quantitative separation of Nd, Am, and Cm on the fine resin at ambient temperature and pressure. Resin: CAO8Y (0.5 mL). Column bed: ϕ4 mm × 4 cm. a: Sample solution (0.1 mL concentrated HNO_3 + 0.9 mL C_2H_5OH). b: 100 mL of 0.5 *M* HNO_3-80% CH_3OH. Flow rate: ~0.09 cm/min.

Although it takes about 2 days to isolate Nd, it is possible to determine the sum of Nd isotopes. Alpha-ray spectrometry of the Am and Cm fractions results in quantitative determinations of the alpha-active nuclides.

Rapid Separation

The rapid separation of the light lanthanoids, including Nd, Am, and Cm, has been reported (*15*). In this paper the sequential rapid separation by anion exchange is examined. Figure 6 shows an elution for the initial separation of irradiated U with concentrated HNO_3 at elevated pressure and ambient pressure. The volume of effluents and the elapsed time are indicated as the bottom and top abscissas, respectively. After 0.2 mL of the sample solution was charged, Nd and other main fission products

TABLE 2
Separation Factors Relative to Nd

Eluent	Y	Eu	Cm	Pm	Am	Nd	Pr	Ce	La	Ref.
0.5 *M* HNO_3–80% CH_3OH at ambient temperature	0.07	0.16	0.23	0.49	0.52	1	1.94	3.44	5.4	This work
0.5 *M* HNO_3–80% CH_3OH at 90°C	0.1	0.28	0.40	0.66	0.71	1	1.56	2.23	3.0	Usuda et al. (*15*)
0.01 *M* HNO_3–90% CH_3OH at 90°C	0.1	0.25	0.38	0.60	0.70	1	1.62	2.55	3.7	Usuda et al. (*17*)
10% 1 *M* HNO_3 + 90% CH_3OH at ambient temperature	0.03	0.09	—	(0.38)	—	1	2.2	3.72	6.5	Faris et al. (*17*)
10% 5 *M* HNO_3 + 90% CH_3OH at ambient temperature	0.02	0.12	—	—	—	1	1.84	2.72	—	Korkisch et al. (*18*)

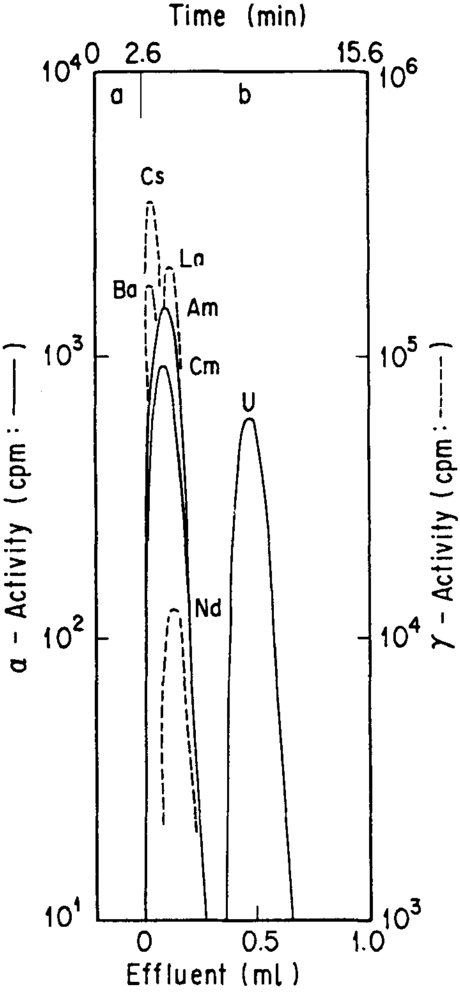

FIG. 6. Elution for rapid initial separation of irradiated U. Resin: CAO8B (0.25 mL). Column bed: ϕ1.5 mm × 14 cm. a: Sample solution (0.2 mL concentrated HNO_3). b: 1 mL concentrated HNO_3. Flow rate: ~4.4 cm/min.

were passed through the column with 0.3 mL of concentrated HNO_3 (FP fraction) and then U was eluted in 0.5 mL of the solution. Plutonium was recovered with 0.1 *M* HCl or 0.1 *M* HNO_3.

The FP fraction was concentrated to about 0.05 mL, and 0.5 mL C_2H_5OH was added to the solution. The mixture was transfered to a small column packed with 0.05 mL CAO8S. Figure 7 shows the elution curves for rapid separation of Nd, Am, and Cm at 90°C. The volume of effluents and the elapsed time are also indicated. Caesium, Te, Sr, Y, Ba, and Eu were washed with 0.6 mL of the initial 0.01 *M* HNO_3-90% CH_3OH eluent. Then Cm (+ Sm), Am + Pm, and Nd were developed with 2 mL of the solution. Cross contaminations in appropriate fractionations were within 1%.

The entire rapid separation procedures are given in Fig. 3 as Procedure III. The time required to separate Nd was less than 1 h. The procedures are quite adequate for an automated operation. If the separation of Nd

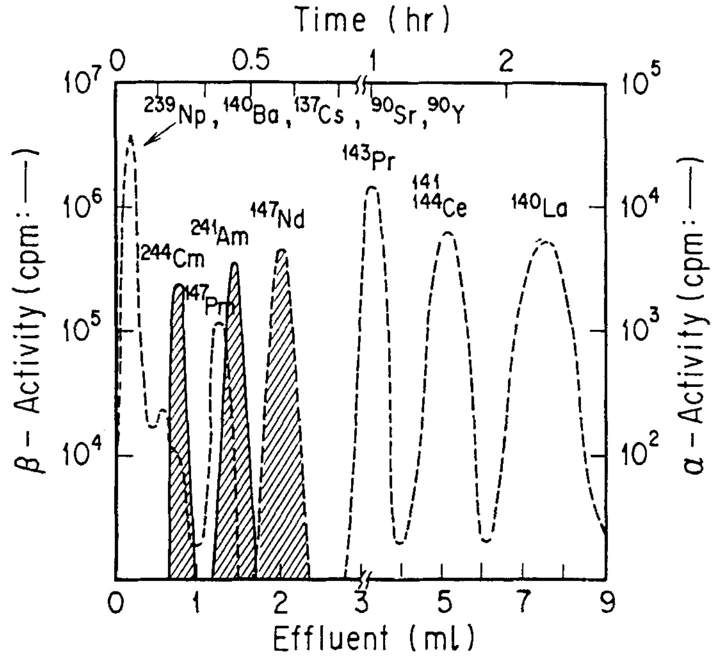

FIG. 7. Rapid separation of Nd, Am, and Cm at 90°C. Resin: CAO8S (23.6 mg). Column bed: 1 mmϕ × 5.7 cm. Sample solution: 0.05 mL concentrated HNO_3 + 0.5 mL C_2H_5OH. Eluent: 9 mL of 0.01 *M* HNO_3-90% CH_3OH. Flow rate: ~7 cm/min.

from a milligram amount of irradiated U is necessary in a one-column operation, the column volume should be 0.25 mL (*15*).

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