

## Radiochemical measurement of $^{237}\text{Np}$ in a solution of mixed radionuclides: Experiences in chemical separation and alpha-spectrometry

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A radiochemical procedure is described for the measurement of 0.1 Bq  $^{237}\text{Np}$  in a solution containing similar activity concentrations of Th, U, Pu and Am as well as activity concentrations of  $^{60}\text{Co}$ ,  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  one hundred times higher. A tracer of  $^{239}\text{Np}$  (milked from  $^{243}\text{Am}$ ) was used as an isotopic spike for chemical yield determination. The relationship between gamma-counting geometries for ampoule (liquid) and  $\text{NdF}_3$  (solid)  $^{239}\text{Np}$  sources was established so that Np chemical yields could be measured by a comparative method. Efficiencies of alpha-spectrometers for  $^{237}\text{Np}$  in  $\text{NdF}_3$  sources were measured by a bootstrap technique. Two sets of experiments were designed and used to test out the procedure.

### Introduction

Neptunium-237 ( $T_{1/2} = 2.14 \cdot 10^6$  y) is an anthropogenic, long-lived radionuclide produced in nuclear reactors by successive neutron capture of  $^{235}\text{U}$  to  $^{237}\text{U}$  followed by beta-decay of  $^{237}\text{U}$  ( $T_{1/2} = 6.75$  d),  $^{235}\text{U}(\text{n},\gamma)^{236}\text{U}(\text{n},\gamma)^{237}\text{U}(\beta^-) \rightarrow ^{237}\text{Np}$ , and by fast neutron reactions<sup>1,2</sup> with  $^{238}\text{U}$ ,  $^{238}\text{U}(\text{n},2\text{n})^{237}\text{U}(\beta^-) \rightarrow ^{237}\text{Np}$ . It is also produced directly by alpha-decay of  $^{241}\text{Am}$  ( $T_{1/2} = 432$  y). Thermonuclear weapons in which natural uranium is used to increase the explosive yield<sup>3</sup> similarly generate  $^{237}\text{Np}$  by the fast neutron  $^{238}\text{U}(\text{n},2\text{n})^{237}\text{U}(\beta^-) \rightarrow ^{237}\text{Np}$  pathway.<sup>4</sup> Irradiation of separated  $^{237}\text{Np}$  by thermal neutrons makes  $^{238}\text{Pu}$  for thermo-electric power generators through the  $^{237}\text{Np}(\text{n},\gamma)^{238}\text{Np}(\beta^-) \rightarrow ^{238}\text{Pu}$  channel.<sup>2</sup> Neptunium-237 enters the environment by way of releases from nuclear fuel reprocessing facilities (e.g., Sellafield discharges into the Irish Sea)<sup>5</sup> and atmospheric testing of thermonuclear devices.<sup>4,6</sup> In its most stable oxidation state of Np(V), the neptunyl ion,  $\text{NpO}_2^+$ , is very soluble and is expected to be very mobile in aquatic environments.<sup>5</sup> Numerous measurements of  $^{237}\text{Np}$  in environmental samples have been carried out.<sup>6–11</sup> The increasing availability of mass spectrometers capable of measuring sub-nanogram amounts of  $^{237}\text{Np}$  has encouraged studies of the biogeochemistry of neptunium.<sup>4,5,11</sup>

The present interest in measuring  $^{237}\text{Np}$  originated from the need to verify its activity concentration in a liquid solution mixture of actinide and non-actinide radionuclides. This mixture was prepared by quantitative gravimetric dilution of NIST radioactivity standards and other liquid solutions with accurately known radioactivity concentrations that had been measured at NIST. Such mixed radionuclide solutions are used for performance testing programs of radioanalytical

laboratories to gauge their traceability to NIST.<sup>12</sup> In this particular case, the 10 g mixture contained  $^{60}\text{Co}$ ,  $^{90}\text{Sr}$ ,  $^{137}\text{Cs}$ ,  $^{230}\text{Th}$ ,  $^{234}\text{U}$ ,  $^{238}\text{U}$ ,  $^{237}\text{Np}$ ,  $^{238}\text{Pu}$ ,  $^{240}\text{Pu}$  and  $^{241}\text{Am}$  with activity concentration ranges of 100 to 300 Bq/g for the first three nuclides and 1 to 3 Bq/g for the actinides. The gamma-emitting  $^{60}\text{Co}$  and  $^{137}\text{Cs}$  concentrations were measured by accurately weighing three 2 g (i.e.,  $2.00 \pm 0.01$  g) aliquots of the mixture into individual glass ampoules, flame-sealing them, and comparing their associated gamma-ray net photopeak counting rates on a high-purity germanium crystal detector gamma-ray spectrometer system with those of similarly-produced 2 g liquid sources of the original  $^{60}\text{Co}$  and  $^{137}\text{Cs}$  SRMs in identical counting configurations. The  $^{90}\text{Sr}$  activity concentration was measured in weighed aliquants (approx. 0.1 g) to each of which was added a known mass of stable Sr carrier, followed by radiochemical separation and purification of the Sr fraction. Chemical recovery of the Sr was determined by weighing the final dried  $\text{SrCO}_3$  precipitate, which was subsequently mounted. The beta-radioactivity of the  $^{90}\text{Sr}$  together with that of its ingrowing daughter  $^{90}\text{Y}$  was measured on gas-flow proportional counters that had been calibrated with similar  $^{90}\text{Sr} (^{90}\text{Y})$  sources of known activity. The activity concentrations of alpha-emitting  $^{230}\text{Th}$ ,  $^{234}\text{U}$ ,  $^{238}\text{U}$ ,  $^{238}\text{Pu}$ ,  $^{240}\text{Pu}$  and  $^{241}\text{Am}$  analytes were determined by taking weighed aliquants (approx. 0.1 g) of the mixture, adding known amounts of alpha-emitting tracers of  $^{229}\text{Th}$  (for  $^{230}\text{Th}$ ),  $^{232}\text{U}$  (for  $^{234}\text{U}$  and  $^{238}\text{U}$ ),  $^{242}\text{Pu}$  (for  $^{238}\text{Pu}$  and  $^{240}\text{Pu}$ ) and  $^{243}\text{Am}$  (for  $^{241}\text{Am}$ ), chemically separating and purifying individual elements, and preparing final “weightless” sources by electro-deposition onto stainless steel disks. Alpha-spectrometric measurements with high-purity silicon detectors resolved the signals from individual nuclides, and the activity (and hence, activity concentration)

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of each analyte was calculated by comparison of its spectral peak intensity with that of the tracer in the same spectrum.

The situation for  $^{237}\text{Np}$  presented a difficult analytical case. The low intensity, low energy gamma-ray emissions of  $^{237}\text{Np}$  and its  $^{233}\text{Pa}$  daughter ( $T_{1/2}=27.0$  d) were not visible above the Compton continuum produced by the intense photon emissions of  $^{137}\text{Cs}$  (662 keV) and  $^{60}\text{Co}$  (1173 and 1332 keV), which had 100-fold higher activity concentrations than  $^{237}\text{Np}$ . No other long-lived, alpha-emitting isotope of Np existed that could be used as a tracer in the same manner that  $^{229}\text{Th}$  was used for  $^{230}\text{Th}$ , etc., as described previously for alpha-spectrometric determinations of Th, U, Pu and Am nuclides. The use of  $^{236}\text{Pu}$  as a non-isotopic, alpha-emitting tracer for  $^{237}\text{Np}$ <sup>13</sup> was considered to be unsatisfactory for our purposes because (1) it depended upon the non-fractionation of Np and Pu throughout all of the chemical operations taking place to separate and purify a joint Np-Pu fraction, and (2) a  $^{236}\text{Pu}$  solution whose concentration was known with sufficient accuracy was not available. Tracer  $^{242}\text{Pu}$  could not be used in place of  $^{236}\text{Pu}$  because the energies of its alpha-emissions are not totally resolved from those of  $^{237}\text{Np}$  under the usual measurement conditions. These considerations led us to investigate using beta-emitting  $^{239}\text{Np}$  ( $T_{1/2}=2.3565$  d) as an isotopic tracer for chemical recovery determination of  $^{237}\text{Np}$ , which would be chemically separated and measured with alpha-spectrometers. Our objective was to determine how accurately and precisely we could measure the  $^{237}\text{Np}$  activity concentration using a method based on  $^{239}\text{Np}$  and calibrated alpha-spectrometers, keeping in mind the suitability of such a method for our verification needs and possible application to more complex (e.g., environmental) samples.

## Experimental

### *Efficiency calibration of alpha-spectrometers for $^{237}\text{Np}$*

A "bootstrap" method was used to perform efficiency calibrations of alpha-spectrometers (EG&G Ortec Model Octete PC with 450 mm<sup>2</sup> high purity silicon detectors) for sources made by co-precipitation of  $^{237}\text{Np(IV)}$  with 50  $\mu\text{g}$  of  $\text{Nd}^{3+}$  from dilute acid solution as  $\text{NdF}_3$ . Accurately weighed amounts (0.05–0.06 g) of NIST SRM4341 Liquid Standard,<sup>14</sup> [ $^{237}\text{Np}$ ]=97.0 Bq/g ( $\pm 1.28\%$ ,  $k=3$ ), were added to 4 ml of 1M  $\text{HNO}_3$  and 50  $\mu\text{g}$  of  $\text{Nd}^{3+}$  carrier (0.5 ml) in each of three small plastic tubes. Then 0.05 g of sulfamic acid crystals,  $\text{NH}_2\text{SO}_3\text{H}$ , and 0.05 g of Mohr's salt crystals,  $(\text{NH}_4)_2\text{Fe}^{\text{II}}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , were dissolved in the 1M

$\text{HNO}_3$  solution to destroy nitrite and adjust to  $^{237}\text{Np(IV)}$ . After 5 minutes, 1 ml of 48% HF was added to precipitate the 1st  $\text{NdF}_3(^{237}\text{Np}^{\text{IV}})$ . After at least 1/2 hour, the suspension was filtered by a 5 ml plastic syringe onto a 93  $\mu\text{g}$   $\text{NdF}_3$  substrate-loaded, paper membrane filter (Millipore VCWP, 0.1  $\mu\text{m}$  porosity, 25 mm) in a plastic holder. Filtrate, washings and syringe/holder rinses were evaporated and combined in a PFA plastic beaker, then dissolved in 3 ml of 1M  $\text{HNO}_3$ . The cycle of co-precipitation and filtering was repeated twice more to produce 2nd and 3rd  $\text{NdF}_3(^{237}\text{Np}^{\text{IV}})$  sources. The 1st, 2nd and 3rd sources of the three paper filter sets were mounted onto plastic disks and measured in the same alpha-spectrometer to determine their relative activities. In a similar manner, three sets of 1st, 2nd and 3rd  $\text{NdF}_3(^{237}\text{Np}^{\text{IV}})$  sources were prepared by vacuum filtration on polypropylene membrane filters (Pall-Gelman Metricel M5PU025, 0.1  $\mu\text{m}$  porosity, 25 mm) but without  $\text{NdF}_3$  substrate and measured in the same alpha-spectrometers.

### *Relative efficiency calibration of gamma-spectrometer for $^{239}\text{Np}$ sources*

The final purified Np fractions containing both  $^{237}\text{Np}$  and  $^{239}\text{Np}$  were to be prepared as  $\text{NdF}_3(\text{Np})$  co-precipitation sources for alpha-spectrometry but also were to be measured for  $^{239}\text{Np}$  with a high-purity Ge gamma-spectrometer (Princeton Gamma-Tech Model no. NIGC23 SD) in order to assess the Np chemical recovery. From the original  $^{239}\text{Np}$  tracer solution (see next section for details of preparation), weighed aliquants would be added to each sample and blank, and one aliquant would be taken as a comparator. In order to avoid any losses of tracer, the comparator would consist of 5 g ( $5.00\pm 0.01$  g) of original  $^{239}\text{Np}$  tracer solution transferred to a standard 5 ml NIST glass ampoule and flame-sealed. It was, therefore, necessary to relate the  $^{239}\text{Np}$  counting geometries of the 5 g solution in the glass ampoule and the plastic disk-mounted  $\text{NdF}_3$  sources. This was done by first preparing four  $\text{NdF}_3(^{239}\text{Np})$  sources on paper filters, mounting and measuring them several times in a reproducible geometry. Afterwards, these  $\text{NdF}_3(^{239}\text{Np})$ -loaded filters were carefully detached from the plastic disks, digested, evaporated and re-dissolved in 2M  $\text{HNO}_3$ . Successive 2M  $\text{HNO}_3$  additions provided a quantitative transfer to a standard NIST glass ampoule with a final solution weight of  $5.00\pm 0.01$  g. These four ampoule sources were then measured several times in a reproducible geometry on the same gamma-spectrometer before the  $^{239}\text{Np}$  activity decayed away. The average decay-corrected net 278 keV photoppeak counting rates for corresponding  $\text{NdF}_3$  and ampoule sources were calculated and compared.

### Preparation of $^{239}\text{Np}$ tracer

$^{239}\text{Np}$  in radioactive equilibrium with about 20 kBq of its  $^{243}\text{Am}$  ( $T_{1/2}=7380$  y) parent was separated and purified according to the method described by LA ROSA et al.<sup>15</sup> with the modifications that (1) 10 mg of  $\text{Ni}^{2+}$  carrier was used in place of 10 mg of  $\text{Nd}^{3+}$  carrier and (2) 10M NaOH was used in place of concentrated  $\text{NH}_4\text{OH}$  in all instances where it occurred in the procedure. In essence, the strong retention of  $\text{Np(IV)}$  stabilized by iodide in 9M HCl on AG 1-X4 anion-exchange resin formed the basis of the  $^{239}\text{Np(IV)}$  separation from  $^{243}\text{Am(III)}$ , which was not retained under the same conditions. Freshly precipitated  $\text{Ni(OH)}_2$  carried  $\text{Am(III)}$  and  $\text{Np(IV)}$  tracers as efficiently as  $\text{Nd(OH)}_3$ . Nickel has advantages over Nd: (1) traces of  $\text{Ni}^{2+}$  remaining in the anion-exchange column during elution of  $^{239}\text{Np(IV)}$  with 0.1M HF–0.1M  $\text{HNO}_3$  do not form an insoluble precipitate with fluoride like  $\text{NdF}_3$ , which can “trap”  $^{239}\text{Np}$ , and (2) chemical separation of  $^{243}\text{Am}$  from Ni carrier, if desired, is much easier than from Nd carrier. After two successive anion-exchange columns, the purified  $^{239}\text{Np}$  was obtained in 50 ml of 2M  $\text{HNO}_3$  solution containing dilute HCl and small amounts of  $\text{HBF}_4$  and  $\text{H}_3\text{BO}_3$ . 5 g ( $5.00\pm 0.01$  g) of this solution were transferred to a NIST standard borosilicate glass ampoule, flame-sealed and used as a comparator. The remaining  $^{239}\text{Np}$  solution was divided into six approximately equal weighed portions, which were added to a set of five mixed radionuclide solution ( $^{237}\text{Np}$ ) samples (approx. 0.1 g each) and one blank sample (no radionuclides). The set of  $^{239}\text{Np}$ -spiked samples and blank was immediately subjected to the radiochemical separation procedure for Np, as discussed below.

### Radiochemical Np separation procedure

Two sets of mixed radionuclide samples and blanks were analyzed at different times. The radiochemical separation scheme for the 2nd set is illustrated in Fig. 1. Radiochemical equilibration of  $^{237}\text{Np}$  and  $^{239}\text{Np}$  was induced in the first step by adjusting both to  $\text{Np(IV)}$  with  $\text{Fe(II)}$  in dilute acid.  $\text{Np(IV)}$  was co-precipitated twice with  $\text{NdF}_3$  from 7–8M  $\text{HNO}_3$  leaving  $\text{U(VI)}$  and non-actinides in solution.  $\text{KMnO}_4$  was later used to oxidize Np to  $\text{Np(VI)}$ , which did not co-precipitate with  $\text{NdF}_3$ ; this afforded a positive separation from  $\text{Th(IV)}$  and  $\text{Am(III)}$ , which did co-precipitate with  $\text{NdF}_3$ . The separation scheme for the 1st set did not include this  $\text{KMnO}_4$  oxidation to  $\text{Np(VI)}$  and had strong evidence for  $^{230}\text{Th}$  contamination in the final  $\text{NdF}_3$  alpha-

spectrometry sources (see Results and Discussion section). An EiChrom TEVA® extraction chromatography column provided a final separation of  $\text{Np(IV)}$  from  $\text{Pu(III)}$  and  $\text{Nd}^{3+}$  carrier as well as from traces of Th and Am. Co-precipitation with  $\text{Ni(OH)}_2$  was used to concentrate the  $\text{Np(IV)}$  to a conveniently small volume just prior to the  $\text{NdF}_3(\text{Np})$  source preparation since  $\text{Ni(II)}$  does not precipitate in acidic HF medium.

## Results and discussion

### Efficiency calibration of alpha-spectrometers for $^{237}\text{Np}$

For the six sets of  $\text{NdF}_3(^{237}\text{Np})$  sources (3 sets paper filters and 3 sets plastic filters, 18 sources in total), the  $^{237}\text{Np}$  activity ratios ranged from 0.016 to 0.032 for the 2nd source to the 1st source, and from 0.0010 to 0.0040 for the 3rd source to the 1st source. Assuming that activity losses were negligible, the fraction of the total  $^{237}\text{Np}$  activity co-precipitated in the 1st  $\text{NdF}_3(^{237}\text{Np})$  was taken to be  $\{1\text{st}/(1\text{st}+2\text{nd}+3\text{rd})\}$ , ranging from 0.968 to 0.982. All of the 1st  $\text{NdF}_3(^{237}\text{Np})$  sources were then measured on 3 different alpha-detectors, and it was found that the paper filter sources appeared to display less dispersion than the plastic ones. The paper filter/syringe filtration source preparation method was adopted on the basis of this nominally smaller dispersion and its speedier, easier technique. Efficiency calibration measurements with the 3 paper filter sources were made on 6 different detectors for the two experiments, and the results are presented in Table 1. The average efficiencies of the six detectors for  $^{237}\text{Np}$  were between 23.0% and 24.6% for the source position closest to the detector.

### Relative efficiency calibration of gamma-spectrometer for $^{239}\text{Np}$ sources

The results of the measurements of the four  $\text{NdF}_3$ -ampoule  $^{239}\text{Np}$  source sets on the gamma-spectrometer are given in Table 1. The 278 keV gamma-ray photopeak of  $^{239}\text{Np}$  was chosen because of its energy (attenuation not sensitive to slight differences in source thickness and glass ampoule wall thickness), its relatively high intensity, and its location in a comparatively flat baseline region of the gamma-ray spectrum. From the decay-corrected net 278 keV photopeak rates of  $\text{NdF}_3$  and ampoule sources (2 measurements of each source), the ampoule/ $\text{NdF}_3$  geometry ratios were calculated for each pair. The average and standard deviation of the four ratios are 0.5364 and 0.0017, respectively (Table 1).

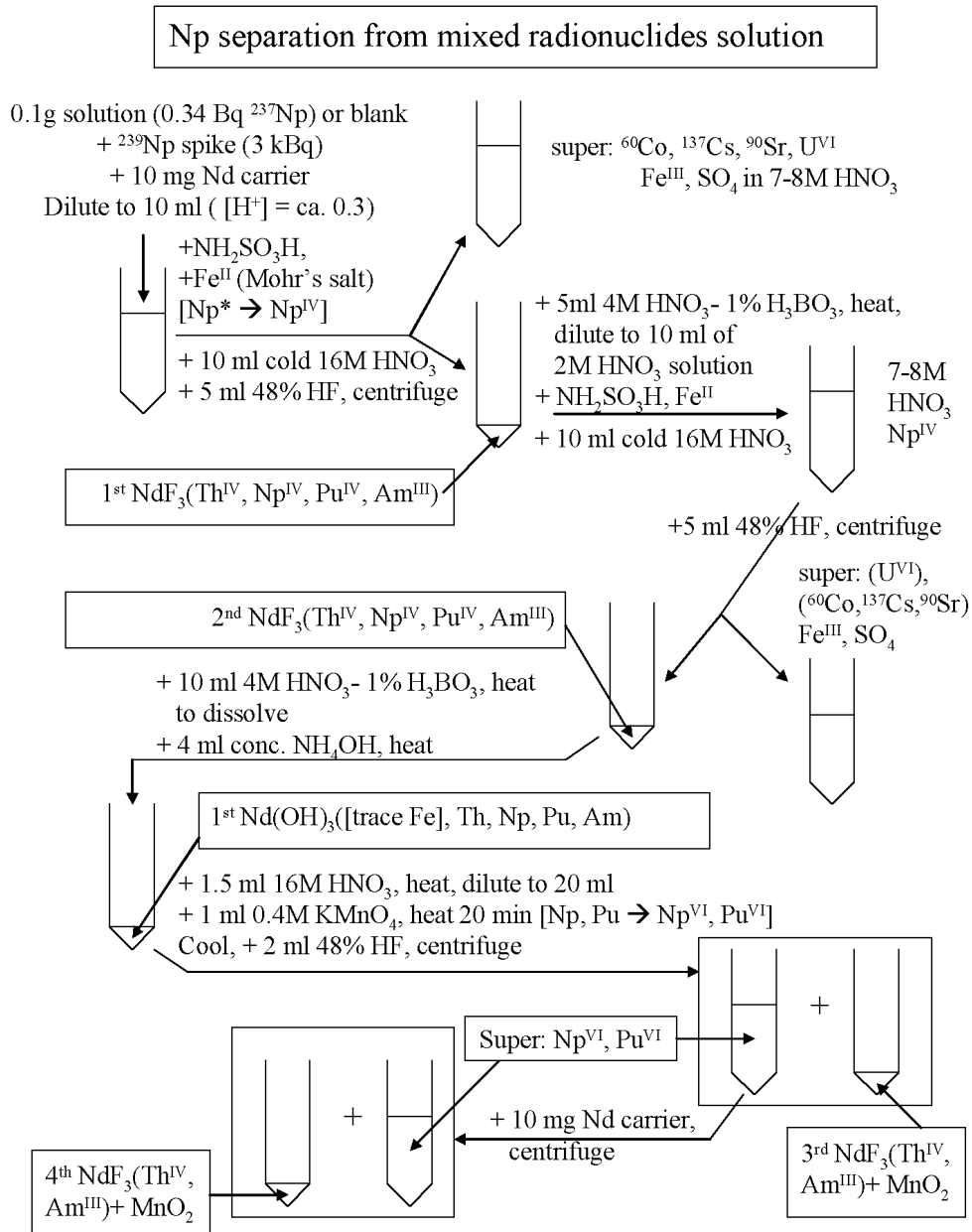


Fig. 1a. Scheme of radiochemical separation procedure for Np from a solution of mixed radionuclides. (Part 1)

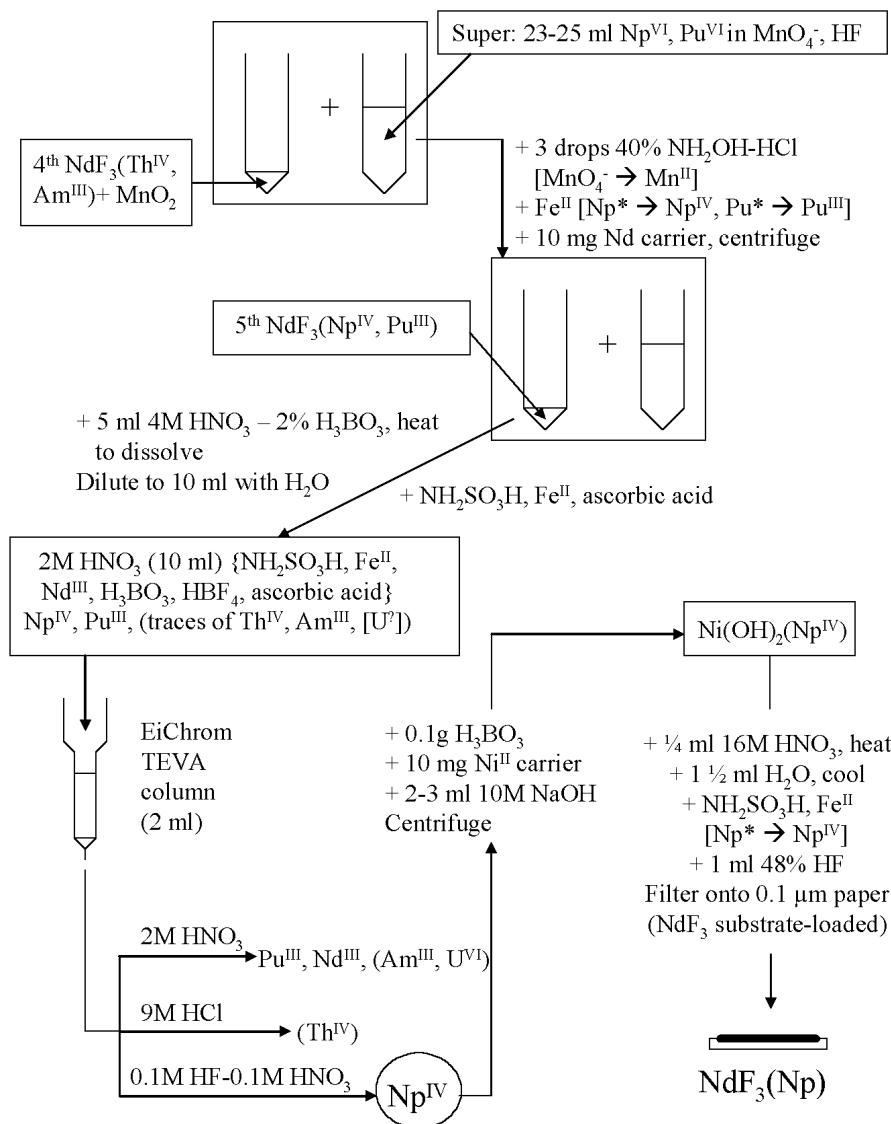


Fig. 1b. Scheme of radiochemical separation procedure for Np from a solution of mixed radionuclides. (Part 2)

### Preparation of $^{239}\text{Np}$ tracer

Purity of the separated  $^{239}\text{Np}$  from  $^{243}\text{Am}$  parent was checked in the batch prepared for determining the relative ampoule/ $\text{NdF}_3$  efficiency calibration. One of the  $\text{NdF}_3(^{239}\text{Np})$  sources (No. 3), which represented about 25% of the total  $^{239}\text{Np}$ , was measured in an alpha-spectrometer for 10,000 seconds. No alpha-counts were observed in the  $^{243}\text{Am}$  energy region (5.2 to 5.4 MeV), and only 1 count in the entire spectrum. Assuming this one count was really due to  $^{243}\text{Am}$  and an alpha-detection efficiency of 24%, the maximum  $^{243}\text{Am}$  amount in the total  $^{239}\text{Np}$  batch was calculated to be  $<0.002$  Bq. Starting with 20,000 Bq of  $^{243}\text{Am}$  ( $^{239}\text{Np}$ ),

this represents a fraction of  $<10^{-7}$ , suggesting that  $<10^{-5}\%$  of the original  $^{243}\text{Am}$  contaminates the purified  $^{239}\text{Np}$ .

The recovery of the  $^{239}\text{Np}$  from the two-column milking procedure was estimated to be 50 to 70%. Direct gamma-measurements of the AG 1-X4 anion-exchange columns before and after stripping with 0.1M HF-0.1M  $\text{HNO}_3$  indicated incomplete removal of the  $^{239}\text{Np}$  for both 1st and 2nd columns. Perhaps a more effective strip solution could be found, but the simplicity of the dilute HF- $\text{HNO}_3$  and subsequent complexation of fluoride by  $\text{H}_3\text{BO}_3$  must be weighed against the introduction of other reagents that might complicate the milking procedure.

*Analytical results for the  $^{237}\text{Np}$  concentration in the radionuclide mixture*

Table 2 presents the experimental results for the  $^{237}\text{Np}$  concentration in the mixed radionuclide solution for the 1st and 2nd experiments. In the 1st set, all of the five individual determinations are considerably higher than the accepted value, leading to an average value that is biased about 9% too high. A close examination of the alpha-spectra showed that there was evidence of  $^{230}\text{Th}$  contamination from the shape of the lower energy part of the  $^{237}\text{Np}$  alpha-signal. This made sense chemically as well. Th(IV) would have accompanied Np(IV) in all the  $\text{NdF}_3$  precipitations, and was separated from Np(IV) only when 10M HCl eluted Th from the TEVA column (Np retained). Apparently a significant fraction of Th was not eluted with 20 ml of 10M HCl, but did elute

with the Np with 0.1M HF–0.1M  $\text{HNO}_3$ . In the 2nd experimental set, an additional step oxidizing Np to Np(VI) with  $\text{KMnO}_4$  followed by two  $\text{NdF}_3$  precipitations was introduced; this was designed to give a better Th-Np separation, leaving Np(VI) in the supernatant solution while Th(IV) co-precipitated efficiently with the  $\text{NdF}_3$ . The 2nd set results give an average that is only 2% higher than the accepted value and a slightly smaller dispersion than for the 1st set. This suggests that elimination of the  $^{230}\text{Th}$  had now been achieved. However, the 2nd set Np chemical recoveries were significantly lower than for the 1st set. As seen in Fig. 2, the alpha-spectrum of a Np source from the 2nd set is very clean; there is no indication of U contamination, and the  $^{238}\text{Pu}$  and  $^{240}\text{Pu}$  signals are very small compared to that of the  $^{237}\text{Np}$ .

Table 1. Efficiency calibrations for alpha ( $^{237}\text{Np}$ ) and gamma ( $^{239}\text{Np}$ ) spectrometers

Detector No.	$\text{NdF}_3(^{237}\text{Np})$ source No.	Start date of counting	Value	$^{237}\text{Np}$ efficiency <sup>1</sup>	
				Unc	Unwtd ave ( <i>n</i> )
Alpha-spectrometry					
11	1	13 May 05	(0.2117)*	(0.0017)	
11	1	17 Oct 05	0.2257	0.0016	
11	2	19 Dec 05	0.2323	0.0008	
11	3	15 Dec 05	0.2313	0.0008	0.2297 ± 0.0036 (3)
12	1	10 May 05	0.2428	0.0009	
12	1	05 Dec 05	0.2365	0.0008	
12	1	20 Dec 05	0.2360	0.0006	
12	2	17 Oct 05	0.2408	0.0015	
12	3	06 Dec 05	0.2414	0.0008	0.2395 ± 0.0030 (5)
13	1	06 Dec 05	0.2446	0.0009	
13	2	10 May 05	0.2498	0.0008	
13	2	05 Dec 05	0.2420	0.0007	
13	3	17 Oct 05	0.2459	0.0015	0.2456 ± 0.0033 (4)
14	1	14 Oct 05	0.2382	0.0006	
14	2	06 Dec 05	0.2389	0.0008	
14	2	23 Dec 05	0.2427	0.0023	
14	3	10 May 05	0.2428	0.0008	
14	3	05 Dec 05	0.2381	0.0007	0.2401 ± 0.0024 (5)
15	1	07 Dec 05	0.2308	0.0007	
15	2	11 May 05	0.2395	0.0007	
15	2	14 Oct 05	0.2381	0.0005	
15	3	12 May 05	0.2355	0.0008	
15	3	09 Dec 05	0.2354	0.0004	0.2359 ± 0.0033 (5)
16	1	19 Dec 05	0.2315	0.0008	
16	2	12 May 05	0.2388	0.0009	
16	2	16 Dec 05	0.2346	0.0015	
16	3	11 May 05	0.2349	0.0007	
16	3	14 Oct 05	0.2333	0.0005	0.2346 ± 0.0027 (5)
Gamma-spectrometry					
			Ampoule/ $\text{NdF}_3$ relative efficiency ( $^{239}\text{Np}$ , 278 keV)		
K	1		0.5371	0.0069	0.5364 ± 0.0017 (4)
K	2		0.5359	0.0094	
K	3		0.5343	0.0077	
K	4		0.5381	0.0042	

<sup>1</sup> The  $^{237}\text{Np}$  efficiency values are calculated from measurements of 1st  $\text{NdF}_3(^{237}\text{Np})$  sources, dividing alpha signal rate (counts/s) by  $^{237}\text{Np}$  activity (Bq) in source, and “Unc” reflects only the statistical counting uncertainty. The “Unwtd ave (*n*)” column gives the unweighted average of the efficiency ± unweighted standard deviation of the distribution for *n* values. The value with asterisk (\*) was excluded.

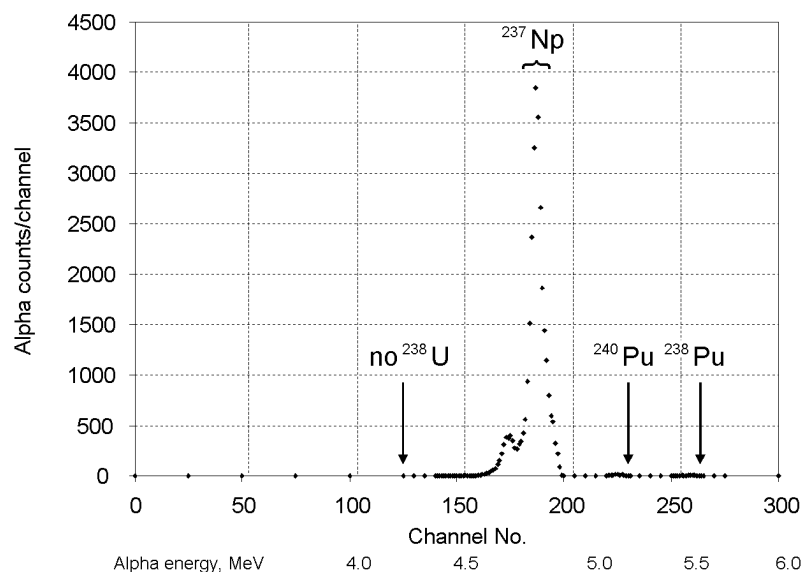


Fig. 2. Example of an alpha-spectrum from a separated  $\text{NdF}_3$  ( $^{237}\text{Np}$ ) source of the 2nd experimental set

Table 2. Results of  $^{237}\text{Np}$  determinations using  $^{239}\text{Np}$  tracer<sup>1</sup>

Sample No.	Np chemical recovery, <sup>2</sup> %	$^{237}\text{Np}$ activity concentration, <sup>3</sup> Bq/g
1st Experiment		
1	$72 \pm 2$	$3.81 \pm 0.18$
2	$79 \pm 2$	$3.81 \pm 0.18$
3	$80 \pm 2$	$3.72 \pm 0.16$
4	$89 \pm 4$	$3.61 \pm 0.22$
5	$87 \pm 2$	$3.59 \pm 0.17$
Blank	$54 \pm 1$	–
	Unwtd ave =	$3.71 \pm 0.21$
2nd Experiment		
A	$35 \pm 1$	$3.48 \pm 0.13$
B	$54 \pm 2$	$3.62 \pm 0.13$
C	$32 \pm 1$	$3.50 \pm 0.11$
D	$54 \pm 2$	$3.42 \pm 0.12$
E	$32 \pm 1$	$3.43 \pm 0.14$
Blank	$19 \pm 1$	–
	Unwtd ave =	$3.49 \pm 0.16$
	Accepted value =	$[3.412 \pm 0.029]^4$

<sup>1</sup> Radiochemical measurements of  $^{237}\text{Np}$  activity concentration in a mixed radio-nuclide solution. All uncertainties are approximately 95% ( $k=2$ ) confidence level.

<sup>2</sup> Np chemical recovery from gamma-spectrometry measurements of  $^{239}\text{Np}$  278 keV  $\gamma$ -ray in  $\text{NdF}_3(\text{Np})$  sources relative to ampoule comparator source.

<sup>3</sup> Activity concentration of  $^{237}\text{Np}$  in Bq per gram of mixed radionuclide solution. The uncertainty of individual values ( $k=2$ ) was combined from counting statistics, alpha- and gamma-spectrometry uncertainty components. “Unwtd ave” is the unweighted average  $\pm 2$  standard deviation uncertainty ( $k=2$ ) of data distribution.

<sup>4</sup> Accepted value is calculated from the  $^{237}\text{Np}$  activity concentration of NIST SRM4341 and the gravimetric dilution factor.

## Conclusions

This method has demonstrated that it can give results very close to the accepted value, but a small bias cannot be excluded at this time. Additional experiments would be useful to determine if the apparent bias persists. Improvements in the Np chemical recovery, in both the

milking and the main radiochemical procedures, would certainly be desirable and might lead to a reduction in the  $^{239}\text{Np}$  activity of spike used. Drawbacks of the present procedure are the necessity of milking a very active (20 kBq)  $^{243}\text{Am}$  source, the short half-life of  $^{239}\text{Np}$ , required calibrations and source measurements on both alpha- and gamma-spectrometry systems, and

extensive chemical operations typically extending over 3 days. Advantages are the ability to follow the Np chemical separation steps with gamma-emitting  $^{239}\text{Np}$  tracer, no reliance on  $^{236}\text{Pu}$  as a tracer for both Np and Pu, and a greater flexibility in designing the Np radiochemical procedure with an isotopic tracer.

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