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Measurement of ^{237}Np in environmental water samples by accelerator mass spectrometry

Miranda J. Keith-Roach,*†[a] J. Philip Day,[a] L. Keith Fifield[b] and Francis R. Livens[a]

[a] *Department of Chemistry, University of Manchester, Manchester, UK M13 9PL*
[b] *Department of Nuclear Physics, Australian National University, Canberra, ACT 0200, Australia*

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Accelerator mass spectrometry (AMS) was used to measure ^{237}Np in environmental water samples extracted from Irish Sea sediments. The samples were of limited volume (~700 ml) and of low activity (0.06–0.79 mBq l^{-1}; 2.30–30.3 pg l^{-1}). AMS proved to have the required sensitivity for measuring these samples, and was in principle capable of measuring much smaller amounts, as low as 0.4 μBq (3.9×10^7 atoms). However, the background level in the procedural blanks showed that there was a systematic low level ^{237}Np contamination of each sample, arising from the ^{239}Np yield monitor used in the separations procedure, which effectively increased the detection limit of these analyses.

Introduction

Neptunium is becoming an increasingly important component of nuclear waste as the nuclear fuel cycle develops.[1] It has an extremely long half-life (2.14×10^6 years) and thus has a low specific activity, but because of this longevity and in-growth from its parent ^{241}Am and grandparent ^{241}Pu it will be one of the greatest dose-deliverers to humans over time.[2] The low activities present in the environment have meant that it has been of less *immediate* concern to humans than the other transuranium elements, Pu and Am, and it has therefore been studied to a lesser extent. Moreover, it is difficult to measure typical environmental levels through conventional α-counting methods. However, the study of Np in the environment is now of increasing interest because of its relatively high mobility, its in-growth in the environment and the time-scales involved.

The activity of Np in the contaminated estuarine sediments close to Sellafield, UK, has been found to be fairly low, typically 10–100 Bq m^{-2},[2,3] but these levels are still potentially high enough to measure the remobilisation of Np into the solution phase. This is of interest in terms of the mobility and redistribution of Np, especially as it is seen as the most mobile transuranic element. It has a relatively low distribution coefficient in the marine environment, approximately 10^3–10^4 l kg^{-1},[4,5] and this is thought to be due to its existence in the oxidised v state, as the neptunyl ion (NpO_2^+).[5]

Until the development of double-focusing sector field ICP-MS, accelerator mass spectrometry (AMS) was the only technique that had been shown to be capable of measuring microbecquerel activities of ^{237}Np.[6,7] In this study, AMS was used to measure the ^{237}Np content of a series of interstitial water samples from the Esk Estuary, Cumbria, UK, and to assess the performance of the method. The samples were collected monthly for 13 months to measure changes in Np concentrations in solution over a yearly cycle.

† Present address: Department of Nuclear Safety, Risø National Laboratory, 4000-Roskilde, Denmark. E-mail: Miranda.keith-roach@risoe.dk; Tel: +45 4677 4911; Fax: +45 4677 4193.

Experimental

Sampling and laboratory methods

The sampling technique was described in detail by Keith-Roach *et al.*[8] Briefly, sediment porewater samples were collected from the same location in north-west England each month using *in situ* ceramic porous cup samplers. The samples were acidified in the field with concentrated HNO_3 and stored in plastic bottles for transport to the laboratory, where they were maintained at 4 °C. Sub-samples (50 ml) were taken for stable element analysis, and the transuranics were sequentially separated from the remainder of the sample (~700 ml). Analytical-reagent grade reagents were used at all times.

It has been demonstrated that samples with sufficiently high Pu and Np concentrations can be digested, diluted and measured directly by ICP-MS, using an on-line chromatographic column to separate the Pu and Np from U.[9] However, low specific activity environmental samples require preconcentration of the actinides and removal of the bulk matrix elements prior to any form of mass spectrometry. The procedure used in this study is described below.

The Np yield monitor used was ^{239}Np, which was freshly milked from its parent ^{243}Am prior to each chemical separation. The method employed was based on that of Yamamoto *et al.*,[1] using several kBq of ^{243}Am (AEA Technology, Harwell, UK). The yield monitor was prepared in a laboratory designated as a Controlled Area under the UK Ionising Radiations Regulations because of the relatively high activity of the Am stock. The parent solution was passed through two consecutive anion-exchange columns to maximise the separation of the daughter from the parent isotope. The ^{239}Np fraction was made up to a standard geometry and γ-counted for 30 min on a hyper-pure Ge detector (50% relative efficiency), shielded with Cu/Cd lined Pb to reduce the background. The absence of a signal at 74.7 keV indicated essentially complete ^{243}Am removal.

The subsequent procedures, described below, were all carried out in a dedicated low-level laboratory. The ^{239}Np solution was made up to volume in a 50 ml calibrated flask, and aliquots of accurately known activity (~500 Bq) were added to the samples and procedural blank (one procedural blank was

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analysed with each batch of samples). The samples were heated down with HNO_3 (d = 1.42; 10 ml per 100 ml of sample) to destroy any traces of organic matter. The residue was dissolved in the minimum volume of water and concentrated HNO_3 was added to reduce the pH to < 1; typically, final volumes were 150 ml. The transuranic elements were then removed from solution through an iron oxy-hydroxide coprecipitation in the presence of sulfite. The floc was isolated by centrifugation at 2000 rpm for 10 min, and then dissolved in HCl (d = 1.18; 20 ml). This solution was taken to dryness over 2–3 h, and the residue was dissolved in 9 M HCl (30 ml).

Neptunium was separated from the matrix elements and other transuranic elements through an ion-exchange method adapted from Hursthouse.[10] The Np fraction was reduced to < 30 ml and made up to standard geometry for γ-counting. The chemical yield was assessed from the γ-counting rates before and after Np extraction, making allowance for decay of ^{239}Np. The samples were then prepared for AMS by adding ^{242}Pu internal standard (1.01 mBq; 1.73×10^{10} atoms; certified standard, NPL, UK), Fe (4 ml, 1000 ppm BDH certified AA standard) and HNO_3 (d = 1.42; 5 ml) and taking to dryness on a hot-plate. The dry sample was dissolved in de-ionised water (10 ml) and HNO_3 (d = 1.42; 5 ml) and again taken to dryness. When the samples were completely dry, the hot-plate was turned on to full power (~350 °C) and the samples were heated very strongly for 30 min to oxidise the Fe. The samples were allowed to cool and then the Fe_2O_3, containing the Np and Pu internal standard, was transferred to a container. On two occasions, an aliquot of the yield monitor was prepared directly for AMS analysis to compare the amount of ^{237}Np in the yield monitor with that in the associated procedural blank. Two standards, containing known amounts of Pu and Np, were also prepared to assess the relative formation efficiencies of Pu and Np ions in the AMS ion source, and an Fe_2O_3 blank was prepared to determine the matrix/machine background.

The samples were analysed by AMS at the Australian National University, Canberra, using the methodology described by Fifield *et al.*[7] Prior to measurement, the samples were heated at 800 °C for 8 h in a porcelain crucible in a muffle furnace. Approximately 3 mg of Fe_2O_3 were then intimately mixed with about 1 mg of Al powder [Alfa (Johnson Matthey), Cat. No. 11067, < 325 mesh, purity 99.5%], prior to compaction into standard copper sample holders for AMS. The holders were placed in a 32-position sample wheel for insertion into the ion source.[11]

The AMS technique

Negative NpO^- and PuO^- ions are produced by sputtering the sample with a Cs^+ beam in a commercial ion source (MC_SNICS; Multi-Cathode Source of Negative Ions by Caesium Sputtering, National Electrostatics, Middleton, WI, USA). These ions are pre-accelerated to 130 keV before magnetic mass analysis, which is set to select mass 253 or 258 for $^{237}NpO^-$ or $^{242}PuO^-$, respectively. The selected ions then enter the 14 UD accelerator, which further accelerates them to the high voltage terminal at 5 MV. Electrons are stripped from the ions in an 80 cm long canal containing oxygen gas at a pressure of ~0.004 Torr. These high energy charge-changing collisions with the stripper gas also destroy any molecular interferences present in the beam.[12] The now positively charged atomic ions are then accelerated back to ground potential where a large analysing magnet selects the ^{237}Np or ^{242}Pu ions in the 7+ charge state with energies of ~40 MeV. These ions are then identified and counted individually in a longitudinal field ionisation chamber, operated with propane at a pressure of 100 Torr. The energy resolution of AMS for 40 MeV ^{237}Np ions is 2.8%, which adequately resolves $^{237}Np^{7+}$ from any molecular fragments in lower charge states which happen to pass the final magnetic analysis.[7]

Switching between ^{237}Np and ^{242}Pu is accomplished by changing the magnetic field in the first mass-analysis magnet, while at the same time changing the accelerating voltage in order to be able to pass both species around the final analysing magnet without changing its field. Samples are typically counted for 1 min at mass 242 (^{242}Pu) and 5 min at mass 237 (^{237}Np) for as many times as is necessary, always ending with a ^{242}Pu measurement. Standards of known amounts of ^{237}Np and ^{242}Pu in Fe oxide were run periodically to give the relative counting efficiencies for Np and Pu, allowing quantitative measurement of the amount of Np in each sample.

Results and discussion

The relative counting efficiency of Np/Pu was found to be 0.74 ± 0.03 in this case, within the error of 0.77 ± 0.03 found in an earlier study.[7]

Results for the interstitial water samples are presented in Table 1. Table 1 includes results from the comparison of the two yield monitors and the associated procedural blanks. Note that the Np content of both the samples and the blanks has been corrected to a 100% chemical yield, and that the amount of Np in the procedural blank of each batch has been subtracted from the amount of Np in the samples. The latter is justified below.

The uncertainties quoted are 1σ errors, including contributions from counting statistics, chemical yield and blank subtraction.

Table 1 shows that the average count rate from the ^{242}Pu internal standard varies from sample to sample, ranging from 510 to 1980 counts min^{-1}. Furthermore, the count rate from a given sample was not constant over time. It did, however, change linearly, since even when the count rate changed by 50% or more between successive ^{242}Pu measurements, the Np/Pu ratio always agreed within error with the ratio obtained when the source output was more stable. This also demonstrates that the Pu and Np respond in the same way when there are any changes in the beam. It is an advantage of the AMS technique that samples can be analysed more than once, giving excellent confidence in the final set of results.

The iron oxide blanks gave 2.4 and 0.2 counts min^{-1} on two occasions, showing that the matrix contains negligible ^{237}Np, and that there is minimal cross-contamination between samples in the AMS ion source.

The procedural blanks, however, which were prepared alongside each batch of three samples, contain significant and variable amounts of Np, which decreased 23-fold over the course of this study. It seemed unlikely that this was the result of random laboratory contamination during the extraction and purification of ^{237}Np from the samples because these procedures were performed in a dedicated low activity laboratory. The ^{239}Np yield monitor, on the other hand, was prepared in a radiochemical laboratory, and so contamination seemed more likely to occur in this part of the procedure. As shown in Table 1, the ^{237}Np content of yield monitors 1 and 2 and the associated procedural blanks provide strong evidence that the contamination was being introduced through the yield monitor itself. In both cases the yield monitor is clearly providing the majority of the ^{237}Np observed in the procedural blank, although there is a suggestion that the procedural blank may contain a small ~4 μBq contribution from the remainder of the procedure. The first possibility was that the ^{237}Np arose from the milking procedure, since the ^{243}Am parent stock solution contains some ^{241}Am ($t_{½}$ = 433 years), which is the parent of ^{237}Np. The amount, however, is far from sufficient to explain the levels of contamination observed, as can be seen from the following considerations.

The $^{241}Am/^{243}Am$ activity ratio of the ^{243}Am parent solution as measured by γ-spectrometry was 0.018. Since the ^{243}Am activity of the solution was 3 kBq, ^{237}Np will build up in the solution at the rate of 4.7×10^6 atoms d^{-1}. Before the initial milking, the stock solution had stood for over 1 year, but as can be seen from Table 2, even this would account for only 20 μBq, or 10%, of the 200 μBq of ^{237}Np observed in the procedural blank A. Subsequent regular milking should have reduced the ^{237}Np contribution to fewer than 10^7 atoms or 0.1 μBq. We therefore have to conclude that the ^{237}Np contamination arises from preparing the yield monitor in the radiochemical laboratory rather than from the ^{243}Am stock solution itself. The general decrease in contamination with time may be due to improved handling procedures or the increased time interval from when ^{237}Np work was carried out in the laboratory. Supporting evidence for this conclusion was provided by an additional experiment in which a ^{243}Am solution, which had not been milked for 5 months, was milked twice with an interval of 2 d between milkings. AMS samples were prepared from each of these and the ^{237}Np was measured. It was found that the sample prepared from the earlier milking contained 40% *less* ^{237}Np than the later sample, a finding that is consistent with random laboratory contamination. The measured yields of ^{239}Np from these milkings implied that at most 5% of any in-grown ^{237}Np could have been washed into the second elution.

Knowing now that the radiochemical laboratory contributes a measurable ^{237}Np background, it should be possible to refine the procedures for preparation of the ^{239}Np yield monitor to reduce the ^{237}Np contribution to suitably low levels. Nevertheless, when measuring at the microbecquerel level, it will be important to ensure that the ^{243}Am stock solution has been decontaminated of Np a few days before the preparation of a yield monitor solution. It is worth noting that it would be possible to dispense with the ^{239}Np yield monitor and with the ^{242}Pu spike if suitably pure ^{236}Np ($t_{½} = 1.5 \times 10^5$ years) were available because it could fulfil the double role of chemical yield monitor and AMS normalisation isotope.

Although the contamination introduced *via* the yield monitor is significant, it will be the same for all samples and procedural blank in a given batch, since aliquots of the milked solution are used as the yield monitor. Further, the samples in this study have ^{237}Np levels which are comfortably above the level of contamination and hence the ^{237}Np content of each sample can be estimated reliably by subtracting the associated procedural blank value.

In the absence of yield monitor contamination, real samples prepared in our low-level laboratory should be quantifiable at activities around 10 μBq, using 3σ of the 4 μBq difference observed between yield monitors and procedural blanks. The detection limit of the AMS system itself is much lower than this; for example, the count rates for ^{237}Np in analysing blank Fe_2O_3 targets were 2.4 and 0.2 counts min^{-1} (mean = 1.3 counts min^{-1}). These counts were almost certainly due to real ^{237}Np ions as the result of cross-contamination from much higher level samples in the same wheel since AMS is essentially a background-free technique, requiring positive identification of every ion. If, however, 3σ of the mean background is taken as the minimum detectable signal, then 3.3 counts min^{-1} above the 1.3 counts min^{-1} background constitutes a real signal. The variability in ion source output, as monitored by the count rate from the ^{242}Pu internal standard, makes it difficult to put an absolute activity on this, but in the best case, sample 1, a ^{237}Np count rate of 2605 counts min^{-1} was observed from a sample containing 3.08×10^{10} atoms of Np (316 μBq) before yield correction and so, here, 3.3 counts min^{-1} is equivalent to 3.9×10^7 atoms of Np, or 0.40 μBq. This is much lower than the detection limit of quadrupole ICP-MS (4×10^{10} atoms).[13] Lower limits of detection have been demonstrated for ideal standard solutions with an optimised double-focusing sector field ICP-MS instrument,[6] but have not yet been achieved for real samples, which may be subject to some interference from ^{238}U at mass 237 in ICP-MS. There will be U even in low-level samples that have been subject to lengthy radiochemical separations, from trace contamination of laboratory reagents. As mentioned above, AMS measurement requires positive identification of every ion and is therefore much less vulnerable to interferences.

The ultimate sensitivity of AMS is controlled by ion source output and efficiency of sample utilisation. Using sample 1 again as a best case scenario, the ^{237}Np counting rate would be 8.2 counts min^{-1} μBq^{-1}, which corresponds to a sensitivity of 1 count per 0.024 μBq Np (2.34×10^6 atoms; 9.21×10^{-16} g)

Table 1 AMS results[a]

Batch	Sample	Np/counts min^{-1}	Pu/counts min^{-1}	Yield (%)	Np in sample/ ($\times 10^{10}$ atoms)	Np in sample/ μBq	Net Np in sample/μBq	Np activity/ μBq l^{-1}
	Iron oxide blank	2.4	2.4					
	1×10^{10} atoms Np std.	221.8	522.5		1	103 ± 5		
A	Sample 1	2605	1980	70.3	4.38	450	249	350 ± 45
	Sample 2	624.0	614.4	71.4	3.34	340	141	190 ± 25
	Sample 3	1716	1034	71	5.46	560	359	560 ± 30
	Procedural blank A	846.6	621.8	81	1.96	200 ± 10		
B	Sample 4	1259	1145	77.2	3.33	340	173	280 ± 20
	Sample 5	1929	1418	77.6	4.09	420	171	230 ± 15
	Sample 6	1017	901.5	73.8	3.58	370	199	230 ± 20
	Procedural blank B	645.6	1124	81.2	1.64	170 ± 5		
C	Sample 7	463.2	966.9	70	1.6	160	139	150 ± 10
	Sample 8	416.4	542.7	75.2	2.39	250	220	230 ± 10
	Sample 9	558.6	870.9	68.3	2.19	230	199	220 ± 10
	Procedural blank C	69.0	865.8	75.3	0.248	25 ± 2		
D	Sample 10	109.8	756.9	73.8	0.475	49	37	62 ± 5
	Sample 11	1774	666.3	76.7	8.1	830	819	1200 ± 50
	Procedural blank D	45.0	1029	79.4	0.118	12 ± 1		
E	Sample 12	1304	813.3	67.7	5.52	5700	533	790 ± 30
	Sample 13	878.4	535.2	76.5	5.01	510	480	760 ± 35
	Yield monitor 1	148.8	1225	100	0.28	29 ± 1		
	Procedural blank E	78.6	600.6	92.3	0.329	33 ± 2		
	Yield monitor 2	9.25	510.4	100	0.047	4.8 ± 1		
F	Procedural blank F	30.6	929.1	83.6	0.084	8.6 ± 1		
	Iron oxide blank	0.2	2					

[a] The net count-rate for a sample is calculated by subtracting the procedural blank associated with the relevant batch. Sample 5 had 1.48 × more yield monitor added, so 1.48 × the procedural blank value was subtracted.

Table 2 Calculations of ^{237}Np in-growth over time in the ^{243}Am stock solution

Ageing time/d	^{237}Np (atoms)	^{237}Np/μBq
2	9.3×10^{6}	0.095
150	7.0×10^{8}	7.2
300	1.4×10^{9}	14.4
450	2.1×10^{9}	21.6

in a 5 min counting interval. Since a sample containing 4 mg of iron will run for at least 1 h, the ultimate sensitivity would be 1 count per 4 nBq Np (3.9×10^{5} atoms; 1.5×10^{-16} g).

Procedural blank F can be used as an example of an accurate, low-level measurement. We saw a typical count-rate signal for the ^{242}Pu internal standard, and could measure 7.2 μBq (before yield correction) with a 9% analytical error in 5 min. Therefore, these Np measurements were well within the capability of AMS. This method has the potential to analyse very low-level samples of limited volume, provided that the yield monitor can be prepared in a laboratory that is not used for other ^{237}Np work.

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