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The production of Neptunium-236g

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ABSTRACT

Radiochemical analysis of ^{237}Np is important in a number of fields, such as nuclear forensics, environmental analysis and measurements throughout the nuclear fuel cycle. However analysis is complicated by the lack of a stable isotope of neptunium. Although various tracers have been used, including ^{235}Np, ^{239}Np and even ^{236}Pu, none are entirely satisfactory. However, ^{236g}Np would be a better candidate for a neptunium yield tracer, as its long half-life means that it is useable as both a radiometric and mass spectrometric measurements. This radionuclide is notoriously difficult to prepare, and limited in scope. In this paper, we examine the options for the production of ^{236g}Np, based on work carried out at NPL since 2011. However, this work was primarily aimed at the production of ^{236}Pu, and not ^{236g}Np and therefore the rate of production are based on the levels of ^{236}Pu generated in the irradiation of (i) ^{238}U with protons, (ii) ^{235}U with deuterons, (iii) ^{236}U with protons and (iv) ^{236}U with deuterons. The derivation of a well-defined cross section is complicated by the relevant paucity of information on the variation of the ^{236m}Np:^{236g}Np production ratio with incident particle energy. Furthermore, information on the purity of ^{236g}Np so produced is similarly sparse. Accordingly, the existing data is assessed and a plan for future work is presented.

1. Introduction

1.1. Chemical yield tracers

In selecting an isotope dilution tracer a number of requirements should be met (Harvey and Lovett, 1984):

- The tracer must exhibit the same chemical behaviour as the analyte, and thus the tracer should be same element as the analyte,
- The tracer should not interfere with the measurement of the analyte and it is thus preferable to measure both the analyte and tracer by the same technique, or that the tracer does not register in the analyte measurement (and vice versa), and
- That chemical equilibrium between the tracer and analyte should be established at the earliest possible point in the analysis. This requires that the tracer should be added as soon as possible in the analysis and (for solids) employ total dissolution.

Furthermore, one should also consider that:

- The tracer should not be initially present in the samples being analysed, since using nuclides present in the samples being analysed complicates analysis,
- The tracer should be pure and not introduce contamination into samples being measured, especially the analyte. This puts a stringent purity requirement on the tracer that may differ for mass spectrometry and radiometric measurements, and
- The tracer activity should be traceable to national or international standards, although this may not be necessary where the yield can be determined by comparative measurements, such as γ emitting tracers.

This constrains the choices available for a suitable neptunium tracer. Bearing in mind the difficulty of obtaining a neptunium chemical yield tracer and the data quality requirements for such measurements, it may be possible to employ a plutonium yield tracer, such as ^{236}Pu (for example; Maxwell et al., 2011; Thakur and Mulholland, 2012). This approach is indeed acceptable (and has been very successful) for measurements where a higher level of uncertainty may be tolerated. However, there is always the risk of speciation of neptunium and plutonium during analysis and this

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may be especially so in solid matrices. For high precision work, including measurements for forensic purposes, it is essential that the tracer is a neptunium isotope. There are a number of neptunium isotopes that could potentially be employed, and these are set out in Table 1 (DDEP, ENSDF).

The practical candidate neptunium isotopes are ^{235}Np, ^{236g}Np and ^{239}Np, of which only ^{236g}Np is really suitable for mass spectrometry (^{235}Np has an activity of ~52 kBq/ng). Neptunium-236g has been produced intermittently, although much of it as a by-product of the production of ^{236}Pu (Efurd et al., 1991). Since 2009, as part of NPL's work to maintain regular supplies of ^{236}Pu, irradiation of various uranium isotopes has been carried out at the University of Birmingham, with chemical separation and measurement work carried out at NPL.

1.2. The low-lying structure of the odd–odd nucleus ^{236}Np

The spin and parity of low-lying states in odd–odd nuclei (i.e., radionuclides with a single unpaired proton and neutron) are determined by the vector, angular momentum coupling of the two unpaired particles (Gallagher and Moszkowski, 1958).

The radionuclide ^{236g}Np is of interest both as a long-lived odd–odd isotope and as a chemical yield tracer. The parallel and anti-parallel couplings of the final unpaired proton and neutron in this nucleus gives rise to two competing states with the same internal, single-particle configuration, which have assigned spin/parity $I^{\pi} = (6^-)$ and (1^-) respectively. The higher-spin, 'high-K' coupling has been established as the ground state of this prolate deformed nucleus and decays with a half-life of 1.55×10^5 years. The anti-parallel coupling of the Nilsson orbitals gives rise to the metastable, but considerably shorter-lived $I^{\pi} = K^{\pi} = (1^-)$ state, which has an evaluated decay half-life of 22.5 h. Both of these states decay to excited states in ^{236}U (by electron capture) and ^{236}Pu (by β^- decay). The spin/parity of the decaying state has been established by the identification of electromagnetic transitions from high spin ($I^{\pi} = 6^+$) and low-spin ($I^{\pi} = 2^+$) states respectively which are populated in the daughter nuclei. The excitation energy difference between the $I^{\pi} = 6^-$ ground state and $I^{\pi} = 1^-$ excited state has not been experimentally established to date but evaluations suggest an energy difference of the order of 60 keV. This energy difference would give a direct measurement of the Nilsson orbital dependent proton-neutron residual interaction in this nucleus.

The odd–odd nucleus ^{236}Np has 93 protons and 143 neutrons and has an assigned ground state spin/parity of $I^{\pi} = (6^-)$ (Sood and Sheline, 1987). This is thought to arise from the maximum $K^{\pi} = 6^-$ projected angular-momentum coupling (where $K = \Omega_p + \Omega_n$) of the proton [642]5/2$^+\uparrow$ and neutron [743]7/2$^-\uparrow$ Nilsson orbitals (Gorman and Asaro, 1970). In the Nilsson orbital nomenclature, Ω is the single-particle angular momentum of the unpaired particle and is equal to $\Lambda \pm \Sigma$ where Λ is the orbital angular momentum projection on to the nuclear axis of symmetry and Σ is the intrinsic nucleon spin = ½ħ (Walker and Dracoulis, 1999). The anti-parallel coupling of the same two orbitals $K = [\Omega_p - \Omega_n] = [5/2^+ – 7/2^-] = 1^-$ is thought to give the underlying structure of the first excited state of this nucleus (Browne and Tuli, 2006; Herzberg and Cox, 2011). Although the relative excitation energy between the two couplings in ^{236}Np has not been definitively determined, the most recent nuclear data evaluation for the $A = 236$ isobars suggests that the low-spin coupling lies approximately 60 keV above the long lived ground state. This is consistent with the expected Gallagher-Moszkowski coupling rules in deformed nuclei (Sood and Sheline, 1987).

The decay of the long-lived, high-spin coupling, ground state in ^{236}Np (^{236g}Np, $t_{½}$: 1.55(8) × 10^5 years, DDEP) proceeds by both β^- decay to ^{236}Pu and by electron capture to ^{236}U (Browne and Tuli, 2006; Bé et al., 2011) with a branching ratio of approximately 13% and 87% for the two branches respectively. The data used in this paper is from the data in DDEP, evaluated in 2009, and this half-life data is dependent on one source (Lindler et al., 1981). The value quoted in ENSDF ($1.53(5) \times 10^5$ years) is taken from an earlier evaluation (Browne and Tuli, 2006), which considers a number of published values. It is not clear why the later evaluation uses only the data from Lindler's paper; in a recent review (Kellett, 2012) no additional requirement for half-life data was noted. The assigned spin and parity of the ground state for ^{236}Np is consistent with the observed K-forbidden decays (Sood et al., 2009) to the spin 6 ground-state rotational band states, and their subsequent decay by characteristic E2 γ-rays of energies 158.35 and 160.33 keV to $I^{\pi} = 4^+$ states in the ^{236}Pu and ^{236}U daughter nuclei respectively (Ahmad et al., 1983). There is also a small (<0.2%) α decay branch which has been inferred but not directly observed.

The first excited state in ^{236}Np (^{236m}Np, $t_{½}$: 22.5(4) hours, DDEP) and, like the proposed $K^{\pi} = 6^-$ ground state, decays by β^- and electron capture to ^{236}Pu and ^{236}U respectively. The branching ratio for the competing decay branches from the ^{236m}Np state are listed as 50(3)% for each decay mode in the most recent nuclear data sheets evaluation (Browne and Tuli, 2006). This majority of the decay strength from the ^{236m}Np state decays directly to the

Table 1
Better known neptunium isotopes.

Nuclide	Half life	Production route	Comments
^{234}Np	4.4 days	^{233}U(*d*,*n*) ^{234}U(*p*,*n*) or (*d*,2*n*) ^{235}U(*p*,2*n*) or (*d*,3*n*) ^{236}U(*p*,3*n*) or (*d*,4*n*) ^{238}U(*p*,5*n*) or (*d*,6*n*)	Unlikely to be able to produce by this route, due to scarcity of suitably pure target material. Separation of ^{234}Np needs to carried out relatively quickly, in the presence of large amounts of fission products.
^{235}Np	396.1 days	^{234}U(*d*,*n*) ^{235}U(*p*,*n*) or (*d*,2*n*) ^{236}U(*p*,2*n*) or (*d*,3*n*) ^{238}U(*p*,4*n*) or (*d*,3*n*)	Unlikely to be able to produce by this route, due to scarcity of suitably pure target material. Production is possible by all these routes, although the irradiation of ^{235}U or ^{236}U are preferred as this avoids the formation of ^{237}Np. The decay mode ^{235}Np (EC/β^+) means that measurement is not straightforward.
^{236m}Np	22.5 h	^{235}U(*d*,*n*) ^{236}U(*p*,*n*) or (*d*,2*n*) ^{238}U(*p*,3*n*) or (*d*,4*n*) ^{237}Np(γ,*n*)^{236m}Np ^{237}Np(*n*,2*n*)^{236m}Np	The short half-life of this nuclide is too short to be practical. It is, however, a route to the production of ^{236}Pu.
^{236g}Np	1.55 × 10^5 years	^{235}U(*d*,*n*) ^{236}U(*p*,*n*) or (*d*,2*n*) ^{238}U(*p*,3*n*) or (*d*,4*n*) ^{237}Np(γ,*n*)^{236m}Np ^{237}Np(*n*,2*n*)^{236m}Np ^{240}Am(α)^{236g}Np	The half-life and decay mode (β^-/γ) of this isotope make it suitable for mass spectrometry or radiometric determination. The ratio of formation to^{236m}Np is not well defined. Production by these routes are worthless, without subsequent isotope separation. The branching ratio for α decay is ~2 × 10^{-7}, and this route is therefore impractical.
^{238}Np	2.102 days	^{238}U(*p*,*n*) or (*d*,2*n*)	It is possible to use ^{238}Np as a yield tracer (β^-/γ emitter), but the short half-life and especially the production route make it impractical.
^{239}Np	2.358 days	^{238}U(*n*,γ) ^{243}Am decay	Similar comments to ^{238}Np apply, although the alternative production route, via decay of ^{243}Am make this more attractive and this isotope is commonly used as a yield tracer

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