

Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy.

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Rapid Measurements of Neptunium Oxidation States Using Chromatographic Resins

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The Savannah River Site's (SRS) H-Canyon facility uses ceric ammonium nitrate (CAN) to separate impure neptunium (Np) from a high sulfate feed stream. The material is processed using a two-pass solvent extraction purification which relies on CAN to oxidize neptunium to Np(VI) during the first pass prior to extraction. Spectrophotometric oxidation-state analyses normally used to validate successful oxidation to Np(VI) prior to extraction were compromised by this feed stream matrix. Therefore, a rapid chromatographic method to validate successful Np oxidation was developed using Eichrom Industries' TRU and TEVA® resins. The method was validated and subsequently transferred to existing operations in the process analytical laboratories.

Introduction

Recently, the Savannah River Site's (SRS) H-Canyon facility started processing neptunium (Np) solutions which are less pure than typically encountered using existing process equipment. The impure neptunium solutions are subjected to a two-pass solvent extraction purification to decontaminate plutonium from the neptunium. The first pass is an oxidizing flowsheet using cerium (IV) as ceric ammonium nitrate (CAN) to oxidize

the neptunium to the hexavalent oxidation state. A second pass is performed using a ferrous sulfamate (FS) process.

Historically, successful oxidation of Np-bearing solutions in the Canyon was rapidly confirmed using spectroscopic methods analyzing UV/Visible spectroscopy: Np(V) strongly absorbs, whereas Np(IV) and Np(VI) have weak absorption bands^{1,2,3}. However, the concentration of Np is too low relative to the concentrations of other impurities in these impure solutions to enable accurate spectroscopic measurements.

The Savannah River National Laboratory (SRNL) was asked by SRS's H-Canyon to develop a method to measure Np extractability, i.e., to roughly measure the percent of Np(VI) following the cerium (IV) oxidation strike. The goal of the method was to validate 90% +/- 20% of the radioactive neptunium was in the Np(VI) oxidation state. This method would be used to validate that the oxidation to the hexavalent state had occurred, and that the first pass extraction would be successful. Due to a required 8-hour turn-around time for results, the method developed by SRNL had to be rapid. The 8-hour turn-around time also required the method be transferable to a different existing laboratory due to its proximity to the Canyon. The required on-line date for the method necessitated that the method easily transfer into the current operations of the existing process laboratory.

A method was quickly established using two commercially available chromatographic resins, Eichrom Industries TRU and TEVA®. Eichrom TRU resin is an extraction chromatographic material in which the extractant system is octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide (CMPO) dissolved in tri-n-butyl phosphate (TBP). Eichrom TEVA's extractant system is based on an aliphatic quaternary amine (Aliquat

336). Under high nitric acid conditions, TRU resin will extract actinides in the +3, +4, and +6 oxidation states⁴, TEVA will extract actinides in the +4 oxidation state⁴. Neptunium (V) will not be retained by either system⁴.

Experimental

The method was designed using Eichrom Industries' 2-mL pre-packed resin cartridge systems. The 2-mL bed volumes have a working capacity of approximately 4 milligrams of actinide. Small aliquots of sample (0.1 mL) were diluted with 10 mL of 1.0N nitric acid; two such dilutions were prepared for independent separation schemes.

One dilution was introduced to an Eichrom TRU cartridge which was pre-conditioned with 10mL of 1.0N nitric acid. The loaded TRU cartridge was then rinsed once with 20mL 1.0N nitric acid. Flow rates for all steps were 1 drop/second. The effluent and rinse solution, which contained Np(V), were combined and analyzed by low energy gamma spectroscopy to quantify the Np(V). Np(IV) and Np(VI) were also quantified by low energy gamma spectroscopy via direct analysis of the cartridge.

The second dilution of the sample was introduced to an Eichrom TEVA® cartridge which was pre-conditioned with 10mL of 1.0N nitric acid. The loaded TEVA® cartridge was then rinsed once with 20mL 1.0N nitric acid. Flow rates for all steps were 1 drop/second. Np(IV), which was extracted by the cartridge, was quantified by low energy gamma spectroscopy via direct analysis of the cartridge.

Aliquots of untreated sample were also analyzed by low energy gamma spectroscopy.

The ratio of Np(V) to Np(IV + VI) was determined using the direct aliquot analysis and the analysis of the effluent/rinse from the TRU cartridge. The ratio of the Np(IV) and Np(VI) was determined by analyzing the two cartridges. The combination of both data sets allowed the ratio of Np(IV), Np(V), and Np(VI) to be determined.

^{233}Pa , which is the daughter of ^{237}Np , is present in varying relative concentrations in any mixture containing ^{237}Np . Both of these nuclides emit 87keV gamma rays, thus leading to varying degrees of interference from ^{233}Pa in the ^{237}Np measurement. Since the primary (87keV) gamma emission from ^{237}Np is not easily de-convoluted from its daughter's 87keV emission, the analytical method relied on the measurement of the 29keV ^{237}Np gamma emission. The low energy of this emission necessitated a low energy gamma spectroscopy system. A low-energy gamma spectrum of ^{237}Np is depicted in Figure 1.

Thin beryllium or carbon composite windowed high purity germanium detectors were utilized for all of the analysis. All of the detectors were 2000 mm² windowed vertical detectors. The detectors had varying Ge crystal depth, so the same detector was used for all stages of a particular sample's experiment. The direct aliquot of sample and the sample of effluent/rinse from the TRU cartridge were generated as 25-mL samples in a 250-mL polyethylene bottle. The bottles were centered directly on the protective cover of the thin-windowed detector prior to analysis. The cartridges were triple-bagged and counted directly. These cartridges were analyzed using a 2-inch spacer to raise the sample from the detector face; thus minimizing any geometry effects arising from inconsistent positioning the cartridges above the detector.

As a result of the limited time available for the method development (~3 weeks), only several experiments were feasible to validate the method. Three experiments were quickly designed to provide proof of concept within the required schedule. Initially, a set of three different Np samples was generated using purified Np product (Np Stock A) from the Canyon. The Np in this product, which contained aged, purified Np in the +4, +5, and +6 oxidation states, was predominantly Np(V). A portion of Stock A was reduced to Np(IV) using ferrous sulfamate (Stock A(FS)). Another portion of Stock A was oxidized to Np(VI) using cerium (IV) in the form of ceric ammonium nitrate to mimic the processing conditions (Stock A(CAN)). The success of the oxidation and reduction was verified using spectroscopic methods (Figure 2). Each sample was analyzed using the proposed chromatographic method for verifying oxidation state once.

A second experiment was carried out utilizing an impure Np solution (Np Stock B) which had not yet been processed in the Canyon. One sample of Stock B was analyzed untreated. One sample of Stock B was oxidized to Np(VI) using cerium (IV) in the form of ceric ammonium nitrate to mimic the processing conditions (Stock B(CAN)). Also, an additional sample of Stock A was treated with ceric ammonium nitrate, generating another Np(VI) sample (Stock A(CAN)). Each sample was analyzed in triplicate using the proposed chromatographic method for verifying oxidation state.

A final experiment was designed to gather more information. This experiment included additional aliquots of Stock A(CAN) and Stock A(FS). Stock A was also subjected to treatment with hydrazine to generate a purer Np(V) surrogate sample prior to analysis. Stock B and Stock B(CAN) were also analyzed. Each sample was analyzed in triplicate using the proposed chromatographic method for verifying oxidation state.

Results and Discussion

Calculation for % Np(V) of Np(total):

$$\%Np(V) = \frac{Np(\text{measured from TRU effluent/rinse})}{Np(\text{measured from original aliquot})} * 100\%$$

Calculation for % Np(VI) of Np(total):

$$\%Np(VI) = \frac{Np(\text{measured from TRU cartridge}) - Np(\text{measured from TEVA cartridge})}{Np(\text{measured from TRU cartridge})} * \{1 - \%Np(V)/100\} * 100\%$$

Calculation for % Np(IV) of Np(total):

$$\%Np(IV) = (1 - \%Np(V)/100 - \%Np(VI)/100) * 100\%$$

Table 1: Results from Measurements with Relatively Pure Np Stock

Material	Oxidation State	Measured Oxidation State (N=1)		
		Np(IV)	Np(V)	Np(VI)
Stock A	Np(V)	0.37%	93.6%	5.99%
Stock A(FS)	Np(IV)	101.7%	0.86%	-2.56%
Stock A(CAN)	Np(VI)	1.44%	3.26%	95.3%

The results of the first test indicate the experimentally determined oxidation state using the resin method agrees with the expected oxidation state. The Np (V) sample was

measured to be 93.6% Np(V), the Np (VI) sample was measured to be 95.3%Np(VI) and the Np (IV) sample was measured to be 101.7% Np(IV).

Table 2: Results from Measurements with Impure Np Stock

Material	Oxidation State	Measured Oxidation State (N=3)		
		Np(IV)	Np(V)	Np(VI)
Stock B		Mean=15.8% %RSD=34.1	Mean=58.4% %RSD=6.19	Mean=25.8% %RSD=10.8
Stock B(CAN)	Np(VI)	Mean=3.87% %RSD=23.9	Mean=1.64% %RSD=16.7	Mean=94.5% %RSD=0.941
Stock A(CAN)	Np(VI)	Mean=3.28% %RSD=63.7	Mean=1.16% %RSD=57.2	Mean=95.5% %RSD=2.87

Results from actual tank samples of impure Np-containing solution (Stock B) contained 25.8% of the ²³⁷Np in the +6 oxidation state. After oxidation with cerium (IV), the measured percentage of ²³⁷Np as Np(VI) rose to 94.5%. Results from the processed Np solution (Stock A), after oxidation using cerium (IV), also indicated a high Np(VI) content (95.5%).

Table 3: Results from Final Measurements

Material	Oxidation State	Measured Oxidation State (N=3)		
		Np(IV)	Np(V)	Np(VI)
Stock B		Mean=30.8% %RSD=6.94	Mean=21.8% %RSD=0.95	Mean=47.4% %RSD=3.87

Stock B(CAN)	Np(VI)	Mean=2.76% %RSD=16.4	Mean=0.87% %RSD=1.76	Mean=96.4% %RSD=0.48
Stock A(CAN)	Np(VI)	Mean=1.95% %RSD=39.1	Mean=11.6% %RSD=94.5	Mean=86.5% %RSD=11.7
Stock A(FS)	Np(IV)	Mean=94.6% %RSD=2.40	Mean=2.05% %RSD=3.732	Mean=3.40% %RSD=68.3
Stock A (Hydrazine)	Np(V)	Mean=23.7% %RSD=14.6	Mean=75.2% %RSD=7.36	Mean=1.07% %RSD=194

Results from this experiment again showed that untreated Np-containing tank samples (Stock B) were low in Np(VI), with an average Np(VI) percentage of 47.4%. Results also showed that upon treatment with cerium (IV), these Np-containing tank samples increased Np(VI) content from 47.4% to 96.4%. Results from the Np-product samples which were treated with ferrous sulfamate (Stock A(FS)) to reduce the Np(V) to Np(IV) confirmed that reduction had been successful. The Np(IV) content Stock A was 0.37% (Experiment 1) while the Np(IV) content of Stock A(FS) was 94.6%. The test attempting to shift the equilibrium in pure Np-product (Stock A) to 100% Np(V) using hydrazine indicated that the treated sample (Stock A (hydrazine)) actually had less Np(V). It appears that hydrazine reduced some Np(V) to Np(IV). The Stock A (CAN) had some breakthrough in the Np(V) effluent, resulting in some lower than expected (VI) percentages averaging around 86.5%.

In all cases there exists the possibility of a reduction in Np as it passes through the resin bed, which may bias the measured Np(IV) slightly high. However, the tests of the

samples which have been oxidized to Np (VI) established that such an effect would be minor; in the order of several percent.

Conclusions

The experiments successfully provided proof of concept. The resin chromatography method coupled with low energy gamma spectroscopy can reliably validate the oxidation of Np to Np(VI) in solutions of impure Np-bearing tank material following treatment with CAN. This method was successfully carried out by the SRS support analytical laboratories to determine Np extractability for the SRS H-Canyon neptunium campaigns. While the method is not intended to be a substitute for spectrophotometric methodology, it was successfully established as a rapid, reliable alternative when sample matrices compromise the spectrophotometric result.

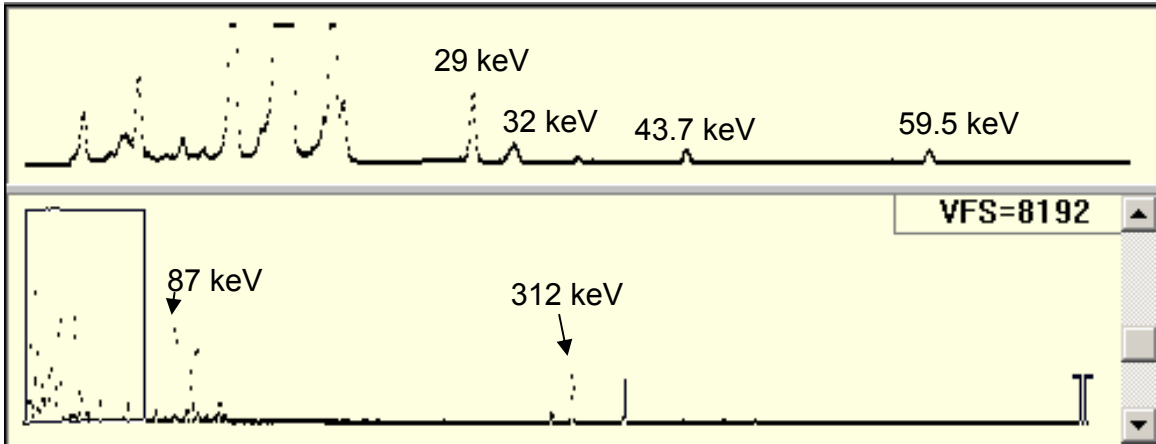
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Figure 1. Low Energy Gamma Spectrum of Neptunium-bearing Canyon Process Sample
Obtained Using a Be-windowed Semiplanar High Purity Germanium Detector

Figure 2. UV-Vis Spectra of Neptunium Test Solutions with Valence States Adjusted to
Np(IV), Np(V), and Np(VI).



Np Spectra

