

# Development of Halide and Oxy-Halides for Isotopic Separations

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**October 2014**

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Title: *Development of Halide and Oxy-Halides for Isotopic Separations*

Principal Investigator: Leigh R Martin (INL)

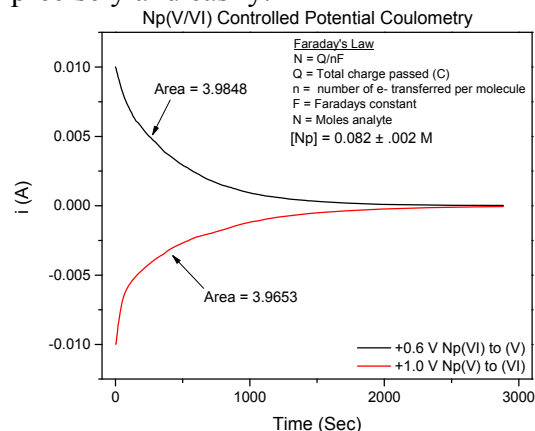
Co-Investigators: Aaron Johnson (INL), Jana Pfeiffer (INL), Martha Finck (INL)

### General description of the project including objectives and purpose.

The goal of this project was to synthesize a volatile form of Np for introduction into mass spectrometers at INL. Volatile solids of the 5f elements are typically those of the halides (e.g.  $\text{UF}_6$ ), however fluorine is highly corrosive to the sensitive internal components of the mass separator, and the other volatile halides exist as several different stable isotopes in nature. However, iodide is both mono-isotopic and volatile, and as such presents an avenue for creation of a form of Np suitable for introduction into the mass separator. To accomplish this goal, the technical work in the project sought to establish a novel synthetic route for the conversion  $\text{NpO}_2^+$  (dissolved in nitric acid) to  $\text{NpI}_3$  and  $\text{NpI}_4$ .

### Summary of the scientific or technical progress achieved during the life of the project.

Np exhibits a rich REDOX chemistry in acidic aqueous solutions. As such, it can exist in the +3 through +6 oxidation states when dissolved in nitric acid. In the +5 and +6 states Np exists as a linear dioxocation,  $\text{NpO}_2^+$  and  $\text{NpO}_2^{2+}$ ; however the presence of oxygen in these oxidation states may limit their usefulness as precursors into the mass separator. Due to this, the initial aims of the project were to understand how to successfully control the oxidation of Np in solution to create pure +3 or +4 oxidation states. Chemical methods have often been employed to adjust the oxidation state of Np, however the desirability of a high purity material free of impurities led researchers to the use of electrochemical methods to control the REDOX behavior of Np. Electrolytic methods do not require the addition of any special reagents, and its selectivity for the specific oxidation state can be controlled through adjustment of the electrolysis potential precisely and easily.

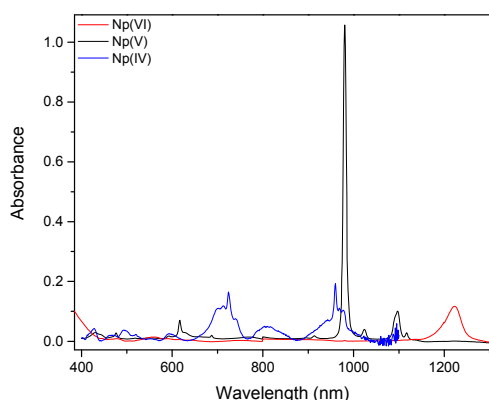


**Figure 1.** Controlled potential coulometric determination of total [Np]. Np oxidation state controlled in the +5 or +6 oxidation state by applying +0.6 or +1.0 V respectively. Experiments performed with a Pt gauze working electrode, Pt wire CE, and Ag/AgCl reference electrode in 1 M  $\text{HNO}_3$ .

In addition to oxidation state control, through application of Faraday's Law, the total concentration of Np in solution can be determined through the  $\text{NpO}_2^+/\text{NpO}_2^{2+}$  REDOX couple. Figure 1 summarizes this result. A constant potential of 0.6 or 1.0 V was used to cycle between Np +5 and +6 respectively. The total current passed through the sample as a function of time was recorded (Figure 1). Integrating the area under the peak gives the parameter Q from Faradays Law ( $Q=nFN$ ), with F being Faraday's constant, and n being 1 for the 1 electron transfer process. From this simple equation the total moles of Np (N) can be easily calculated and the total molar concentration of Np was determined to a high precision. The results of this study are applied to the remaining electrochemical studies. As the total

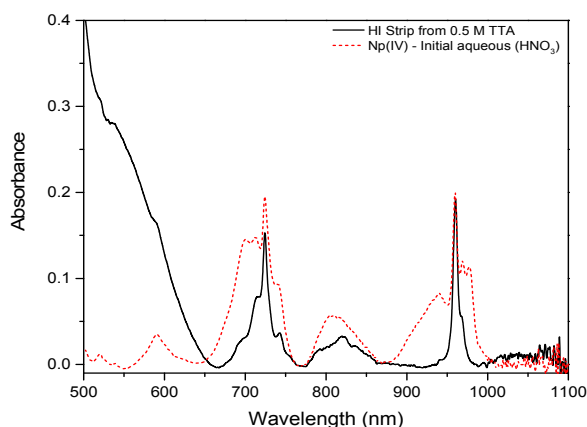
moles of Np is now known to high precision, Faraday's law can be used to determine total electrons transferred for reduction of  $\text{NpO}_2^+$  to  $\text{Np}^{4+}$  and  $\text{Np}^{3+}$ , giving a higher degree of confidence in the preparation of Np in these oxidation states.

Methods to prepare pure amounts of  $\text{Np}^{4+}$  and  $\text{Np}^{3+}$  via electrolysis were subsequently investigated. When using a platinum electrode, prior literature suggest that  $\text{NpO}_2^+$  is reduced to  $\text{Np}^{4+}$  through an adsorbed hydrogen atom on the electrode surface at a potential of  $-0.02 \sim -0.12$  V. This reduction proceeds via  $\text{NpO}_2^+ + \text{Pt-H} + 3\text{H}^+ \rightarrow \text{Np}^{4+} + 2\text{H}_2\text{O} + \text{Pt-}$ . A fraction of the  $\text{Np}^{4+}$  produced in this potential range is reduced to  $\text{Np}^{3+}$ . This  $\text{Np}^{3+}$  in solution can then reduce  $\text{NpO}_2^+$  by  $\text{NpO}_2^+ + \text{Np}^{3+} + 4\text{H}^+ \rightarrow 2\text{Np}^{4+} + 2\text{H}_2\text{O}$ . Application of these equilibrium were used to determine the methods by which pure  $\text{Np}^{4+}$  and  $\text{Np}^{3+}$  can be prepared. In this work, a constant potential of  $-0.10$  V was applied to a solution of  $4.1$  mM Np in  $1.0$  M  $\text{HNO}_3$  and was allowed to proceed for approximately 200 minutes. During this time, a peak maximum in the current-time curve was observed which is due to the competing reduction equilibrium discussed previously. The species present in solution post electrolysis were examined via absorbance spectroscopy. Through this analysis, it was determined that post-electrolysis a mixture of  $\text{Np}^{3+}$  and  $\text{Np}^{4+}$  existed in solution, with no remaining  $\text{NpO}_2^+$  or  $\text{NpO}_2^{2+}$ . Methods for complete conversion of this  $\text{Np}^{3+}/\text{Np}^{4+}$  mixture into their pure components were then examined. By applying a positive potential of  $+0.10$  V for approximately 20 minutes, the  $\text{Np}^{3+}$  was quantitatively oxidized to  $\text{Np}^{4+}$ . Applying a negative potential of  $-1.2$  V was shown to produce pure  $\text{Np}^{3+}$  from the mixture. However, this reaction only proceeds with the evolution of hydrogen gas, and  $\text{Np}^{3+}$  was found unstable in air. Research targeted  $\text{Np}^{4+}$  species from this point on until the inert atmosphere glovebox is operational at the RCL facility. Conversion strategies were standardized and verified for creation of purified quantities of  $\text{Np}^{4+}$ ,  $\text{NpO}_2^+$ , and  $\text{NpO}_2^{2+}$  which were confirmed via absorbance spectroscopy (Figure 2).



**Figure 2.** Absorbance spectra displaying purified  $\text{Np}^{4+}$ ,  $\text{NpO}_2^+$ , and  $\text{NpO}_2^{2+}$ . Spectra for  $\text{NpO}_2^+$  and  $\text{NpO}_2^{2+}$  were recorded using a Varian Cary-6000i spectrometer equipped with optics in the NIR range, while  $\text{Np}^{4+}$  was recorded on a Varian Cary-60, however there are no observable peaks above 1100 nm.

Once the electrochemical techniques were understood for the production of  $\text{Np}^{4+}$ , conversion strategies to create  $\text{NpI}_4$  were investigated. It was theorized that this compound could be created via solvent extraction.  $\text{Np}^{4+}$  in nitric acid solution was extracted by equal volume of  $0.5$  M thenoyltrifluoroacetone (TTA) in toluene. The  $\text{Np}^{4+}$  was extracted into this organic phase, whereby it maintained its  $+4$  oxidation state as confirmed by absorbance spectroscopy. The Np was subsequently stripped into purified  $7$  M hydroiodic acid, where its absorbance spectra were then recorded. The results of this study are shown in Figure 3. This figure shows that the oxidation state is retained throughout the solvent extraction and strip procedure. Also, the spectra of  $\text{Np}^{4+}$  in  $\text{I}^-$  vs  $\text{NO}_3^-$  media show major differences which confirms changes of the coordination environment around the Np metal center. This is initial confirmation of the successful synthesis of  $\text{NpI}_4$  in solution.



**Figure 3.** Absorbance spectra of  $\text{Np}^{4+}$  in nitric acid before extraction with TTA and following the strip into purified HI.

**Brief statement describing how the project benefited the DOE national security missions (energy resources, nuclear security, environmental quality, and science), and if applicable, the missions of other federal agencies.**

Developing a reliable synthetic route for the production of solid  $\text{NpI}_4$  species will provide a form of Np suitable for introduction into a mass spectrometers to at higher efficiencies to reduce sample losses, particularly when sample masses are limited. Increasing the efficiency of sample introduction via modifying the chemical species introduced into mass spectrometry systems will reduce the mass of sample necessary for analysis. This is extremely important for analyzing radioactive isotopes. .

**Relevant Peer-Reviewed Publications (project to date): Include full citation including authors, title, publication, volume/issue, page # and date published. If not yet published, include status (Submitted, accepted, in press)**

**Relevant presentations (project do date): Include author(s), title, conference, location, date.**

1. Jana K. Pfeiffer, Martha R. Finck, and Leigh R. Martin. Electrochemical Reduction and Subsequent Extraction of Neptunium for  $\text{NpI}_4$  Production. 38<sup>th</sup> Actinide Separations Conference, Albuquerque, NM, May 10-14.