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SPECTROPHOTOMETRY OF NEPTUNIUM IN NITRIC ACID SOLUTIONS

Andrew J. Johnson and Glenn A. Shepherd

Abstract. Studies have been made of the effect of varying nitric acid concentrations in neptunium solutions on the oxidation states of neptunium present. Spectrophotometric methods were used to determine the proportions of neptunium(IV), (V), and (VI) present in nitric acid solutions varying between one and ten normal (1 $\underline{N}$ and 10 $\underline{N}$). Absorption spectra of both the neptunium(IV) and (VI) complexes with nitrate have been identified and are given. (Appropriate Roman numerals are used to denote valences of the materials.)

INTRODUCTION

The different valence states of neptunium (Np) can be qualitatively differentiated by their ultraviolet-visible-near infrared absorption spectra.¹ This has been the basis for the quantitative spectrophotometric determination of neptunium methods used elsewhere² and at Rocky Flats. During the development of these methods in the laboratory, it was noted that the nitric acid (HNO_3) concentration is a critical parameter for accurate analysis. A change in acid concentration affects the absorbance of the analytical absorption bands used, indicating possible complex formation.

The complexing behavior of Np in HNO_3 solutions has been investigated by Ryan³ and Keder.⁴ Ryan, in working with quadrivalent actinides, confined his investigations to quadrivalent Np. The work of Keder with Np(IV) and (VI) was done in a nitric acid-perchloric acid mixture using a tributyl phosphate-xylene extraction.

The current work, in addition to repeating some of Ryan's investigations with Np(IV), also covers the HNO_3 complexes of Np(V) and (VI). While Keder worked only with 0.1 $\underline{N}$ to 4.0 $\underline{N}$ HNO_3 solutions, the

complexing behavior of Np in HNO_3 solutions up to 10 $\underline{N}$ was investigated in this study.

The investigation included study of the effect of a varying concentration of HNO_3 in solutions containing the (IV), (V), and (VI) valence states of Np. The complexing effect of nitrate could be observed and would aid in understanding the ion-exchange behavior of Np in HNO_3 solutions.

SUMMARY

An investigation was undertaken to determine the effect of varying HNO_3 concentrations on the oxidation states of Np. Such information has considerable importance in determining the chemistry of Np in analytical and separation procedures. The behavior of Np in solvent extraction, carrier precipitation, and ion-exchange processes is dependent upon the valence state of the Np under the existing conditions.

Spectrophotometric methods were employed to determine the proportions of Np(IV), (V), and (VI) present in HNO_3 solution varying in concentrations from 1 $\underline{N}$ to 10 $\underline{N}$. Since the different valence states of Np can be differentiated by their absorption spectra, the complexing effects of the nitrate ion can be observed. Thus, an understanding of the ion-exchange and the solvent-extraction behavior of neptunium in nitric acid solutions may be achieved.

Molar ($\underline{M}$) absorptivities were calculated using the absorbances found for the major absorption band of each of the species at varying HNO_3 concentrations. The bands used were as follows:

Np(IV) — 960 millimicrons (μm)

Np(V) — 980 μm

Np(VI) — 1230 μm

The experimental data indicated the following:

1. A decrease in the concentration of the quadrivalent neptunium (Np^{4+}), pentavalent neptunium (NpO_2^+), and the hexavalent (NpO_2^{++}) ions, as the concentrations of the HNO_3 were increased.

¹C. F. Metz and G. R. Waterbury. "The Transuranium Actinide Elements." I. M. Kolthoff, P. F. Elving, and E. B. Sandell, Editors. *Treatise on Analytical Chemistry*. Part II, 9.232. Interscience, New York. 1962.

²C. A. Colvin. "Spectrophotometric Determination of Neptunium Using 1.23-Micron Sexivalent Absorption Peak." *Analytical Chemistry*, 35:806. 1963.

³J. L. Ryan. "Species Involved in the Anion-Exchange Absorption of Quadrivalent Actinide Nitrates." *Journal of Physical Chemistry*, 64:1375. 1960.

⁴W. E. Keder. "Neptunium Complex Ion Species Extracted from Nitric Acid-Perchloric Acid Mixtures by Tributyl Phosphate." *Journal of Inorganic Nuclear Chemistry*, 16:138. 1960.

2. At 5.5 $\underline{N}$ HNO_3 , most of the uncomplexed Np(IV) had disappeared.
3. Above 6 $\underline{N}$ HNO_3 , only the spectrum of the Np(IV) complex was visible.
4. Over the 1 to 4 $\underline{N}$ HNO_3 range, the molar absorptivity of the Np(IV) , 1.23 micron-band remained constant.
5. The formation of a nitrate complex with Np(V) was not observed in the HNO_3 solutions above 3 $\underline{N}$.
6. Apparently the Np(V) was reduced by disproportionation to Np(IV) , since only the spectrum of this specie was visible.

EXPERIMENTAL

Equipment: A Cary-14, ratio-recording spectrophotometer was used to record the 400 to 1400 $\text{m}\mu$ -spectral region. The instrument used a tungsten-lamp source with a 1P28 detector in the ultraviolet-visible region and a PbS detector in the near-infrared. Standard rectangular 1-centimeter (cm) silica cells were used for samples.

Conditions of the Experiment: Two different sets of conditions were used and will be fully described. In the first set, redox (oxidation-reduction) agents were employed to adjust the initial valence state of the neptunium for the spectrophotometric standards. The second set employed no redox agents, other than the HNO_3 solution in which the valence states were measured.

Preparation of the Standards: A stock solution containing 4.8 grams per liter (g/l) Np was used to prepare the Np(IV) , (V), and (VI) standard solutions. Three 10-milliliter (ml) portions of this solution were evaporated to incipient dryness and redissolved in appropriate oxidizing or reducing reagents to give 10-ml master solutions of the neptunium-valence state desired.

Np(IV) – The stock-solution residue was redissolved in 5 ml of concentrated HCl (hydrochloric acid) and 0.1 gram $\text{NH}_2\text{OH}\cdot\text{HCl}$ (hydroxylamine hydrochloride).

Np(V) – The stock-solution residue was redissolved in 5 ml of 1 $\underline{N}$ HNO_3 and 1 ml of H_2O_2 (hydrogen peroxide).

If a precipitate formed, the solution was heated until clear.

Np(VI) – The stock-solution residue was redissolved in 1 ml of concentrated HNO_3 and 0.1 ml of 0.5 $\underline{M}$ ceric nitrate.

The above master solutions were diluted to a final volume of 10 ml with 1 $\underline{N}$ HNO_3 . A spectral scan of each master solution showed that only the desired neptunium-valence state was present. From each master solution, a series of standards were prepared containing one ml of the master solution and 9 ml of 1, 2, 3, 4, 5, 6, 7, 8, and 10 $\underline{N}$ HNO_3 . Each standard, therefore, contained 0.48 g/l Np . The concentration of the HNO_3 was the variable.

Results Obtained on the Standards: The absorption spectra of the standards were recorded over the 400 to 1400 $\text{m}\mu$ spectral range. An HNO_3 solution of the same normality as that of the neptunium-containing sample solution was used in the reference beam. This negated any interference of the nitric acid spectrum in the neptunium spectrum. Spectral scans were made within 2 hours of the standard preparation.

Molar absorptivities were calculated using the absorbances found for the major absorption band of each of the species at each different nitric acid concentration. The bands used were as follows:

Np(IV) – 960 $\text{m}\mu$ ⁵

Np(V) – 980 $\text{m}\mu$ ⁶

Np(VI) – 1230 $\text{m}\mu$ ⁷

Figure 1 shows the effect of increasing HNO_3 concentration on the molar absorptivities of these bands. The curves thus indicated the decrease in the concentration of the uncomplexed Np^{+4} , NpO_2^+ , and NpO_2^{++} as the HNO_3 concentration was increased.

The curve for Np(IV) decreased rapidly, until at about 5.5 $\underline{N}$ HNO_3 concentration most of the uncomplexed Np(IV) had disappeared. Spectral scans of solutions containing higher concentrations of HNO_3 showed only the spectrum of the hexanitrate complex.⁸ Examinations of the spectra of the Np(IV) solutions indicated that all the spectra were composed of a combination

⁵ C. F. Metz and G. R. Waterbury. *Loc. cit.*

⁶ *Ibid.*

⁷ C. A. Colvin. *Loc. cit.*

⁸ J. L. Ryan. *Loc. cit.*

FIGURE 1. The Effect of Increasing Nitric Acid (HNO_3) Concentration on the Molar Absorptivities of Free Neptunium(IV), (V), and (VI) in Nitric Acid Solutions.

of only two basic spectra: the uncomplexed Np(IV) and the hexanitrate complex. No complexes containing fewer than six nitrate groups were detected.

The absorption of the Np(V) , 980- μ band also decreased rapidly with an increase in the HNO_3 concentration of the solutions. In the 3 N HNO_3 solution, some of the Np(V) had been reduced to Np(IV) and the spectrum of the Np(IV) complex was visible. Above 6 N HNO_3 , only the spectrum of the Np(IV) complex was visible.

Unlike the Np(IV) and Np(V) curves, the molar absorptivity of the Np(VI) , 1.23- μ band remained constant over the 1 to 4 N HNO_3 concentration range. Above this HNO_3 concentration, there was a slow decrease in molar absorptivity with increasing nitric acid concentration.

Sample Preparation: The effect of the acid concentration on the HNO_3 solution of Np containing no added

reducing or oxidizing agent was next studied. A 10-ml aliquot of a stock solution containing 0.48 g/l Np was evaporated to dryness and redissolved in 1 N HNO_3 . One-ml aliquots of this master solution were then diluted to 10 ml with 1, 2, 3, 4, 5, 6, 7, 8, 10, and 13 N HNO_3 .

Results: The spectra of the sample solutions were recorded within the same time interval and in the same manner as for the standard solutions. The concentrations of Np(IV) , (V), and (VI) in each sample solution were then calculated by the Beer-Lambert Equation using the molar absorptivities given in Figure 1. As can be noted in the figure, the molar absorptivities were dependent on the nitric acid concentration of the solution. Therefore, the calculations were made on the samples using the experimentally determined molar absorptivities found from the standards at corresponding nitric acid concentrations. Calculated percentages of Np(V) and (VI) present in the sample solution at the various nitric acid concentrations are given in Table I. No Np(IV) was detectable in any of the sample solutions.

TABLE I. Amount of Neptunium(V) and Neptunium(VI) Present in Nitric Acid Solutions.

Normality of Nitric Acid	Percent Neptunium(V)	Percent Neptunium(VI)
1	6.8	93.2
2	7.2	92.8
3	7.2	92.8
4	8.5	91.5
5	12.5	87.5
6	19.9	80.1
7	21.3	78.7
8	20.0	80.0
10	3.7	96.3

DISCUSSION

The acid concentration of solutions, in which Np is determined, presents a critical parameter in spectrophotometric methods. Previous studies of the effect of increasing HNO_3 concentration in Np solutions had been concerned chiefly with establishing limits of HNO_3 concentration for the absorption analytical methods. Further investigations were necessary to determine how the major absorption bands of Np(IV) , (V), and (VI) decrease in calculated molar absorptivity with an increase in HNO_3 concentration.

FIGURE 2. Absorption Spectra of Neptunium(IV) in 1, 5, and 10 Normal Nitric Acid.

All of the actinides show strong tendencies to associate with coordinating groups to form complex ions in solution.⁹ The formation of the Np-NO_3 (neptunium-nitrate) complexes can be followed on the spectra presented in Figures 2, 3, and 4 of the Np(IV) , (V) , and (VI) species in solutions of varying HNO_3 concentration. The Np(IV) -valence state would be expected to show the greatest degree of complex formation.¹⁰ This is indicated in the spectra of Figures 2 and 3. By comparing¹¹ Figures 2 and 3, it is apparent that the Np(V) is reduced by disproportionation to Np(IV) as

⁹ C. F. Metz and G. R. Waterbury. *Loc. cit.*

¹⁰ *Ibid.*

¹¹ It should be noted in Figures 2, 3, 4, and 5, that it was desired to plot three different spectra corresponding to three different acid-concentration conditions on a single figure for comparison purposes. In order to give greater clarity and to prevent spectral superimposition, the ordinate, as denoted by three different zero values, was shifted by 0.1 absorbance unit for each of the three spectra.

the HNO_3 concentration is increased. The Np(IV) then follows the same complexing pattern as the original Np(IV) solution, and no evidence is visible of any spectrum that would be indicative of a Np(V) -nitrate complex.

The spectrum of the Np(VI) standard, Figure 4, gives little indication of any absorption bands in the 10 N HNO_3 solution. When the Np concentration was increased to 4.3 g/l from 0.48 g/l, the absorption bands due to the Np(VI) -nitrate complex could be seen. In Figure 5, the band at 1.13μ can be noticed increasing with HNO_3 concentration. This band, the major absorption band of the Np(VI) -nitrate complex, reaches a maximum absorbance in the 13 N HNO_3 solution. At this HNO_3 concentration, less than 5 percent of the uncomplexed Np(VI) is calculated to be present.

FIGURE 3. Absorbance Spectra of Neptunium(V) in 1, 5, and 10 Normal Nitric Acid.

Spectral scans made on these solutions 24 hours later indicated a slow increase in Np(V) in all solutions.

The formation of a nitrate complex with Np(V) had not been observed. In solutions containing HNO_3 above 3 N in concentration, the Np(V) disproportionated and only the Np(IV)-nitrate complex was visible. An attempt was made to prepare a nitrate complex of the pentavalent neptunium (NpO_2^+) by addition of nitrate as calcium nitrate $[\text{Ca}(\text{NO}_3)_2]$ or aluminum nitrate $[\text{Al}(\text{NO}_3)_3]$. Solutions were made containing 0.52 grams per liter (g/l) Np in varying concentrations of the two salts and the spectra recorded. Results are shown in Table II. The effect of the same concentration of nitrate from HNO_3 is given for comparison.

The decrease in absorbance of the Np(V) band in the HNO_3 solution with increasing HNO_3 concentration is

TABLE II. Effect of Added Nitrate on Pentavalent Neptunium Spectra.

Concentration of Nitric Oxide	Absorbance of 980-Millimicrons, Pentavalent Neptunium Band		
	In Nitric Acid	In Calcium Nitrate	In Aluminum Nitrate
1.2 N	0.783	0.813	0.864
3.6 N	0.569	0.801	0.767
6.0 N	0.124	0.790	0.575

caused by the Np(V) disproportionation. A decrease was recorded also in the other two salt solutions, but the spectra did not reveal any absorption bands other than those of the Np(V) spectra. Evidence of a Np(V)-nitrate complex was therefore not observed in these solutions.

FIGURE 4. Absorption Spectra of Neptunium(VI) in 1, 5, and 10 Normal Nitric Acid.

FIGURE 5. Absorption Spectra of Neptunium (sample) in 1, 5, and 10 Normal Nitric Acid.