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SPECTROPHOTOMETRIC DETERMINATION OF MIXTURES OF NEPTUNIUM (IV) AND NEPTUNIUM (V) IN NITRIC ACID SOLUTIONS

by

E. K. Dukes and W. E. Shuler
Separations Chemistry Division

December 1960

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by

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December 1960

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ABSTRACT

The concentrations of Np(IV) and Np(V) ions in nitric acid solutions were determined quantitatively by a spectrophotometric method.

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SPECTROPHOTOMETRIC DETERMINATION OF MIXTURES OF NEPTUNIUM (IV) AND NEPTUNIUM (V) IN NITRIC ACID SOLUTIONS

INTRODUCTION

The absorption spectra of Np(III), (IV), (V), and (VI) ions in perchloric acid solutions have been reported.[1] The spectra of the (III), (IV), and (V) ions contain sharp absorption bands in the visible region, and the positions of the bands are sufficiently different to permit spectrophotometric analysis of mixtures of these oxidation states.

The spectra of Np(IV), (V), and (VI) ions in nitric acid solutions have also been reported[2,3]. Although the spectra are sufficiently different for spectrophotometric analysis, the analysis is complicated by the effect of nitrate complexing on the absorption spectrum of Np(IV).

The purpose of this study was to develop a quantitative spectrophotometric analysis for mixtures of Np(IV) and Np(V) in solutions of various nitric acid concentrations.

SUMMARY

The absorption spectra of Np(IV), Np(V), and Np(VI) were measured in 1M HNO_3 and a spectrophotometric method of analysis was devised for mixtures of Np(IV) and Np(V) in nitric acid solution. In the analysis the absorption of Np(IV) was measured at the sharp absorption band at about 715 mμ and the absorption of Np(V) was measured at 617 mμ.

A novel adaptation of a Beckman DU spectrophotometer permitted the neptunium solutions to be confined in a gloved box so that the instrument was not exposed to possible contamination by the alpha activity of Np^{237}.

DISCUSSION

EXPERIMENTAL PROCEDURE

PREPARATION OF NEPTUNIUM SOLUTIONS

A stock solution of Np^{237} was purified by solvent extraction and anion exchange. The neptunium was first oxidized to the (VI) state and extracted from 4M HNO_3 into 30% tri-n-butyl phosphate in n-dodecane. The organic phase was washed with 4M HNO_3, and the neptunium was stripped into 0.5M HNO_3 solution. This solution was made 8M in HNO_3 and ferrous sulfamate was added to reduce the neptunium to the (IV) state. The anionic nitrate complex of the Np(IV) was absorbed on a column of "Dowex" 21K anion exchange resin. The column was washed with 8M HNO_3, and the neptunium was eluted with 0.5M HNO_3. The ion exchange step was performed immediately before the neptunium sample

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was used in subsequent tests. Np(IV) was the predominant oxidation state in the ion exchange eluate immediately after elution, but oxidation to Np(V) occurred slowly on standing. Consequently, no reagent was needed to adjust to the (V) state. Ferrous sulfamate was used to reduce neptunium to the (IV) state; sodium bromate was used to oxidize neptunium to the (VI) state. Mixtures of Np(IV) and Np(V) were obtained by allowing an ion exchange eluate of Np(IV) to oxidize partially. The concentration of neptunium in the various solutions was determined by alpha counting.

MEASUREMENT OF ABSORPTION SPECTRA

The absorption spectra of pure Np(IV), (V), or (VI) were measured in a Beckman DU spectrophotometer that was modified in the manner described in the following section. A sample of the purified neptunium was adjusted to the desired valence state and diluted to the required concentration with nitric acid, and the absorbance was measured in a 1-cm cell. The absorption spectra of Np(IV), (V), and (VI) in 1M HNO_3 are shown in Figure 1. The molar extinction coefficients are in units of liters/(mole)(cm).

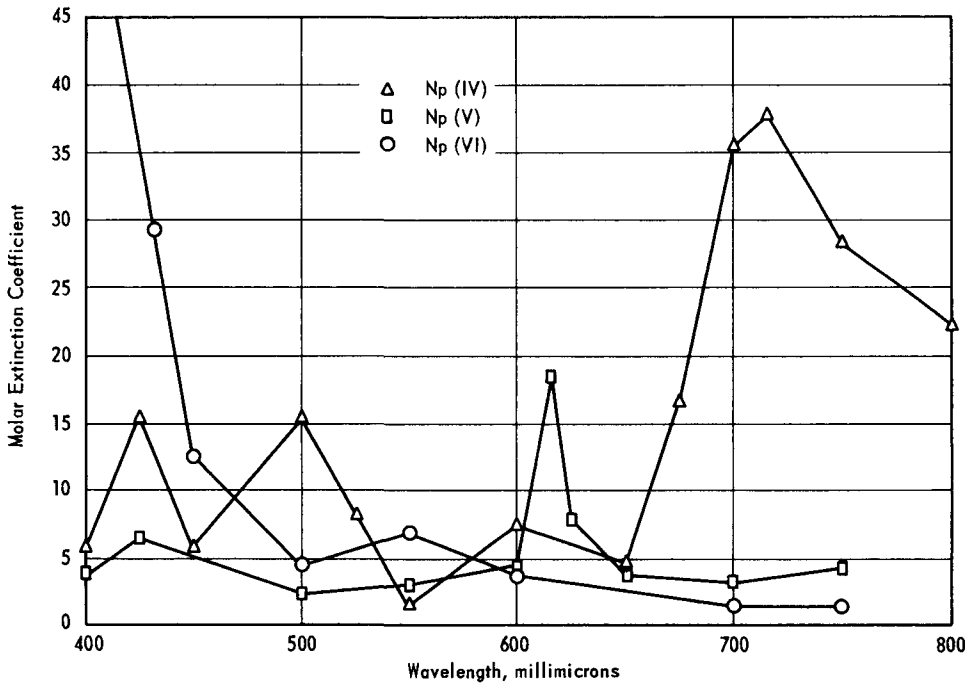

FIG. 1 ABSORPTION SPECTRA OF Np (IV), Np (V), AND Np (VI) IN 1M HNO_3

INSTRUMENTATION

A Beckman DU spectrophotometer was modified for use in a gloved box to avoid contamination of the instrument with neptunium. The monochromator was separated from the detector so that each unit formed one limb of a U-shaped optical path, as shown in Figure 2. Light was directed from the monochromator through a window in the gloved box, reflected from a mirror, passed through the sample, reflected from a second mirror, and finally passed through a second window in the gloved box onto the phototube in the detector housing. Since the radiation emerging from the monochromator was a divergent beam, it was necessary to place a lens (45 mm focal length) after the first mirror to form the image of the spectrophotometer slit at the sample position. A second lens (170 mm focal length) converged the beam on the phototube.

Ordinary glass lenses were used and the windows were made of "Plexiglas" plastic, 0.030 inch thick. Simple front-silvered mirrors were used. The entire mirror-and-lens assembly was mounted on a steel base and covered with a lighttight aluminum box.

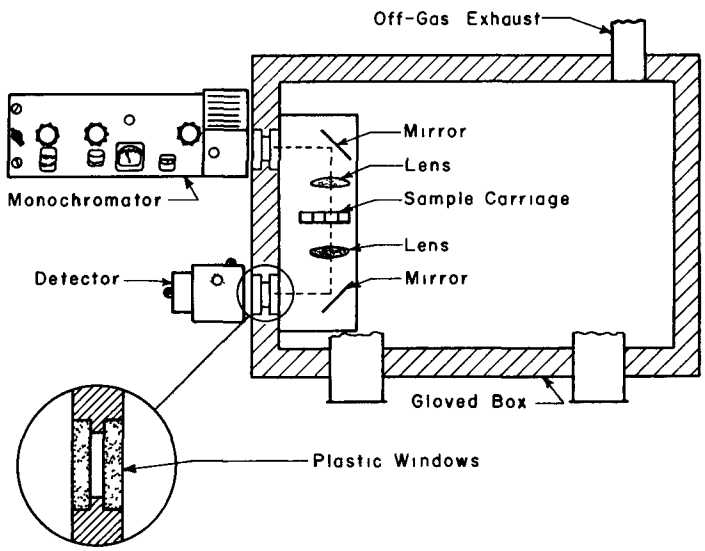

FIG. 2 MODIFICATION OF BECKMAN DU SPECTROPHOTOMETER FOR USE IN GLOVED BOX

RESULTS

The spectra in Figure 1 show sharp absorption bands at 715 mμ for Np(IV) and at 617 mμ for Np(V) in 1M HNO_3. Np(VI) exhibits only weak absorption in this region, with no pronounced absorption bands. The 617 and 715 mμ bands were used for the analysis of mixtures of Np(IV) and Np(V). The absorbance of a given mixture was measured at the two wavelengths, and the concentrations were determined by the simultaneous solution of the two equations:

$$A_{715} = E_{715}(IV)\cdot C(IV) + E_{715}(V)\cdot C(V)$$

$$A_{617} = E_{617}(IV)\cdot C(IV) + E_{617}(V)\cdot C(V)$$

The symbols A_{715} and A_{617} are the measured absorbances of the solution at 715 and 617 mμ, respectively. $E_{715}(IV)$ and $E_{715}(V)$ are the molar extinction coefficients of Np(IV) and Np(V) at 715 mμ. $E_{617}(IV)$ and $E_{617}(V)$ are the molar extinction coefficients of Np(IV) and Np(V) at 617 mμ. C(IV) and C(V) are the molar concentrations of Np(IV) and Np(V).

Ten mixtures of Np(IV) and Np(V) in 1M HNO_3 were analyzed by this method. The results are shown in the following table. No attempt was made to confirm the valence state analyses by an independent method, but the sum of the Np(IV) and Np(V) concentrations determined spectrophotometrically was compared with the total neptunium concentration determined by alpha counting. The average difference between the results of the two methods was 3%.

Spectrophotometric Analysis of Mixtures of Np(IV) and Np(V) in 1M HNO_3

Concentration of Np(IV), M	Concentration of Np(V), M	Total Np, M	
		Spectrophotometric	Alpha Counting
0.0131	0.0006	0.0137	0.0140
0.0122	0.0009	0.0131	0.0139
0.0120	0.0008	0.0128	0.0125
0.0112	0.0009	0.0121	0.0121
0.0049	0.0083	0.0132	0.0133
0.0034	0.0085	0.0119	0.0118
0.0019	0.0107	0.0126	0.0120
0.0005	0.0121	0.0126	0.0119
0.0002	0.0122	0.0124	0.0127
0.0001	0.0131	0.0132	0.0138

The spectrophotometric analysis of mixtures of Np(IV) and Np(V) may be applied in nitric acid solutions more concentrated than 1M, but the effect of nitrate complexing on the Np(IV) spectrum must be taken into account. At 6M HNO_3 the absorption band for Np(IV) is shifted from 715 to 700 mμ and the molar extinction coefficient is slightly diminished, as shown in Figure 3.

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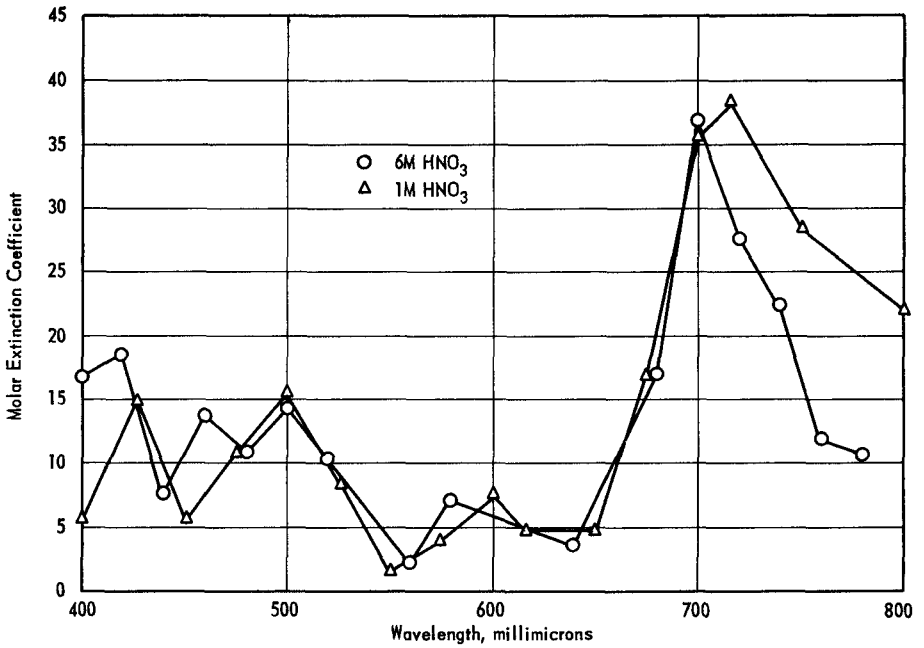

FIG. 3 EFFECT OF NITRATE CONCENTRATION ON THE ABSORPTION SPECTRUM OF Np (IV)

The Np(V) spectrum is essentially unchanged. For application at any HNO_3 concentration, the Np(IV) peak position must be determined, and the appropriate extinction coefficients must be measured.

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BIBLIOGRAPHY

1. Sjoblom, R. and J. C. Hindman. "Spectrophotometry of Neptunium in Perchloric Acid Solutions". J. Am. Chem. Soc. 73, 1744-51 (1951).

2. Hesford, E. and H. A. C. McKay. Chemical Studies Relating to the Recovery of Neptunium from the Windscale Plant. United Kingdom Atomic Energy Authority, Research Group. Atomic Energy Research Establishment, Harwell, Berks (England) AERE-C/R-1893, 20 pp. (February 1956)(Declassified June 1958).

3. McKay, H. A. C., J. S. Nairn, and M. B. Waldron. "The Chemistry and Metallurgy of Neptunium". Proc. U. N. Intern. Conf. Peaceful Uses Atomic Energy, 2nd, Geneva, 28, 299-306 (1958). P/304

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