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Abstract

Full Text

Chemistry

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On the Preparation of Trivalent Neptunium

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In works devoted to the chemistry of neptunium, comparatively little attention is given to the trivalent state of this element. This can be explained by the difficulty of obtaining and studying Np(III). In air Np(III) is rapidly oxidized, especially in the presence of fluorides or oxalates, and also in alkaline medium ([1]). Dilute solutions of Np(III) (0.005 M) in 1 M HCl have a pale violet color and in appearance resemble solutions of U(III) and Pu(III) ([2]). The absorption spectrum of Np(III) has been studied in perchloric ([3]) and hydrochloric ([4]) acid solutions, and the molar absorption coefficients at the maxima have been calculated, the principal ones of which occur at wavelengths of 402, 416, 462, 553, 602, 661, and 788 mμ.

Until now, electrochemical methods have been used to obtain Np(III) ([3], [4]), and considerable precautions were necessary in order to preserve neptunium in the trivalent state.

The aim of our work was to investigate the possibility of obtaining Np(III) by a chemical method, namely by the action of rongalite on neptunium solutions (sodium formaldehyde sulfoxylate, $NaHSO_2 \cdot CH_2O \cdot 2H_2O$). Identification of the valence states of neptunium in solutions was carried out by the spectrophotometric method, on an SF-4 instrument. In all measurements, as a reference, a solution was used that contained the same components as the measured one (with the exception of neptunium) and had undergone the same operations.

Fig. 1. Absorption curve of a neptunium solution (1 M HNO_3; $(NH_4)_2SO_4$ 10 g/l), reduced by rongalite in a nitrogen atmosphere.

Action of rongalite on nitric-acid solutions of neptunium. Addition of rongalite to a cuvette with a solution of neptunium(IV) in 1.3 M HNO_3 led to a change in color from yellow-green to intensely yellow. Measurement of the absorption spectrum revealed the formation of neptunium(III) in the solution.

Fig. 2. Absorption curve of a solution of Np(III) with an admixture of (IV) in 1 M HCl

Figure 2: Fig. 2. Absorption curve of a solution of Np(III) with an admixture of (IV) in 1 M HCl

The presence in the absorption spectrum of the reduced neptunium solution of maxima at wavelengths of 659, 784, and 850 mμ indicated the reduction of neptunium to the trivalent state. The greatest completeness of reduction was attained after 30–45 min.

In most experiments the rongalite concentration was 10 g/l, and that of neptunium 1–1.5 g/l. In order to protect the neptunium(III) solution from oxidation by atmospheric oxygen, experiments were carried out on the reduction of neptunium in a nitrogen atmosphere.

A certain amount of Np(IV) remains in the solution, as is evident from the presence of maxima at 728 and 973 mμ (Fig. 1). However, the stability of Np(III) increased appreciably: measurement of the spectrum after 24 hours revealed no oxidation in a closed cuvette. By passing air through, the neptunium was again converted to the tetravalent state. Taking the neptunium(IV) content in the oxidized solution as 100%, it was determined from the heights of the maxima at 728 and 973 mμ that reduction by rongalite proceeded to approximately 70%.

Fig. 2. Absorption curve of a solution of Np(III) with an admixture of (IV) in 1 M HCl

Action of rongalite on hydrochloric-acid solutions of neptunium. Addition of rongalite to a hydrochloric-acid solution of neptunium(IV) led to its reduction to the trivalent state. The greatest completeness of reduction was observed 30–60 min after addition of rongalite. However, whereas in nitric-acid solutions, after as little as 2 hours' standing in air, an increase in the Np(IV) maxima was observed, in the hydrochloric-acid solution after 4 hours only slight oxidation was observed. The hydrochloric-acid solution had a violet-blue coloration.

To estimate the completeness of reduction, as in the case of nitric-acid solutions, the content of neptunium(IV) in the oxidized solution was taken as 100%. A calibration curve was constructed expressing the dependence of the height of the 728 mμ maximum on the Np(IV) content. Using this curve, it was determined that reduction of neptunium to the trivalent state in hydrochloric-acid solutions containing no other reducing agents proceeds to 75–78%. In the presence of hydrazine ($N_2H_4 \cdot HCl$, 20 g/l) the completeness of reduction increases to 84–86%. Carrying out the process in a nitrogen atmosphere increased the completeness of reduction to 90–94%. After 24 hours' standing in a nitrogen atmosphere, no signs of oxidation were observed (Fig. 2).

Thus, in hydrochloric-acid solutions a more complete reduction to Np(III) occurs, and the latter is more stable here than in nitric-acid solutions.

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Note: Figure translations are in progress. See original paper for figures.