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NEPTUNIUM SEPARATIONS

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NEPTUNIUM SEPARATIONS

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INTRODUCTION

Neptunium is usually encountered as 2.14×10^6 -y ^{237}Np in acid solutions of uranium reactor fuel elements. Neptunium-237 is of relatively little use commercially except, possibly, for the production of pure sources of ^{238}Pu (by reactor neutron irradiation) and ^{233}U (the α -decay granddaughter of ^{237}Np). The amount of ^{237}Np in the environment is generally so small as to be unmeasurable as compared to ^{239}Pu , and no procedures were obtained by the author for separation of Np from environmental samples.

Neptunium-239 is a transient isotope in reactor fuel elements, due to its short half-life (2.35 d). It disappears completely shortly after the end of a neutron irradiation through decay to ^{239}Pu . Neptunium-239 is most frequently used as a tracer to study the chemistry of Np; it can be obtained from the neutron irradiation of ^{238}U or by milking a sample of ^{243}Am with which it is in equilibrium as the α -decay daughter.

I present two procedures for the separation of Np; the first involves separation of ^{239}Np from irradiated ^{238}U , and the second involves separation of ^{237}Np from a solution representing that from a dissolved fuel element.

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PROCEDURE 1

Chromatographic Separation of Neptunium Using
Quaternary Ammonium Nitrate Extractant

Source: V. K. Markov, A. N. Usolkin, and A. I. Ternovskii, Radiokhimiya 21, 862 (1979).

Sample Type: A 100 mg sample of mixed uranium oxides which has been irradiated with a neutron flux of $\sim 10^{12}$ n/cm² for one day to produce ²³⁹Np.

Procedure:

1. Prepare a 6 mm diam chromatographic column by mixing 7-8 mg of methyltri-octylammonium nitrate with ~ 600 mg of fluorocarbon powder (grain size of 150-250 μ m) and pouring the mixture into the column. Flush the column with 4 M HNO₃.
2. Dissolve the uranium oxide sample in 5 ml of 4 M HNO₃ with heating.
3. Add enough ferrous sulfamate to the cooled solution to make a concentration of 0.01 M.
4. Allow the solution to cool and pass it through the chromatographic column.
5. Wash the column with 8 ml of 2 M HNO₃.
6. Elute the ²³⁹Np from the column with 6 ml of a solution 0.03 M in ammonium oxalate and 0.2 M in HNO₃. Use a flow rate of about 1 ml/min.

Note: No radiochemical yield is given, but it is indicated that the extraction of Np from the uranium is virtually quantitative. Gamma-ray spectra of the ²³⁹Np product show no γ rays characteristic of fission-product contamination.

PROCEDURE II

A Spectrophotometric Method for the Determination of Neptunium in Process Solutions

Source: P. R. Vasudeva Rao and S. K. Patil, J. Radioanal. Chem. 42, 399 (1978).

Sample Type: 5 ml of a 1 M HNO_3 solution containing about 100 mg U, 0.25 mg Pu, and 0.50 mg Zr in addition to $\sim 1 \mu\text{g/ml}$ of ^{239}Np .

Procedure:

1. To the sample solution in a test tube add a known amount of ^{239}Np tracer solution (Note 1).
2. Adjust the solution to 0.1 M in each of ferrous sulfamate and hydroxylamine hydrochloride.
3. Add 5 ml of 0.5 M thenoyltrifluoroacetone (TTA) in benzene and shake for 10 min with a Vortex mixer to extract Np(IV) into the organic phase.
4. Pipet 4 ml of the TTA phase into another test tube containing 10 ml of a solution 1 M in HNO_3 , and $\sim 0.1 \text{ M}$ in Fe^{+2} and hydroxylamine hydrochloride.
5. Shake for 10 min to remove Pu(IV) extracted along with the Np(IV) .
6. Remove the aqueous phase and add 1 ml of 8 M HNO_3 to the organic phase. Shake for 10 min to extract the Np(IV) into the aqueous phase.
7. Separate the aqueous phase containing the Np(IV) and evaporate to dryness.
8. Redissolve the Np(IV) in 10 ml of a solution 0.1 M in HNO_3 and $\sim 0.1 \text{ M}$ in each of Fe^{+2} and hydroxylamine hydrochloride.
9. Add 5 ml of the TTA solution in benzene and reextract for 10 min.
10. Separate the organic phase, discard the aqueous phase and strip the Np(IV) into 5 or 10 ml of 5 M HNO_3 containing 5 mg/ml of sulfamic acid and 0.1 mg/ml Arsenazo III.
11. Measure the optical density of the solution at 665 nm with a Beckman DU, using 1 cm fused silica cells. Compare with the absorbance from a blank solution of 5 M HNO_3 containing 5 mg/ml sulfamic acid and 0.1 mg/ml Arsenazo III. Measure the chemical yield by comparing the γ activity of the ^{239}Np in the sample against that of a known solution of ^{239}Np (Note 2).

Note 1: ^{239}Np can be obtained by either irradiating ^{238}U in a reactor or by milking it from a sample of ^{243}Am (as the α -decay daughter).

Note 2: Beer's law for the Np(IV) -Arsenazo III complex holds at least up to $1.5 \mu\text{g Np(IV)}$ per ml; if H_3PO_4 is added to the absorbance solution to mask the Arsenazo III complex with Zr, a separate calibration curve for measuring the Np(IV) absorbance using H_3PO_4 must be obtained.