

ION EXCHANGE PROCEDURES

III. SEPARATION OF URANIUM, NEPTUNIUM AND PLUTONIUM^{*,**}FREDERICK NELSON, DONNA C. MICHELSON AND JAMES H. HOLLOWAY^{***}*Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn. (U.S.A.)*

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Numerous methods have been investigated in recent years for separating uranium and the trans-uranium elements. For a recent review of analytical methods see HOFFMAN². The present procedure, while based on existing methods^{3,4}, appears preferable because it is rapid, simple and permits quantitative separation of the elements. The method utilizes anion exchange in HCl for separating U, Np and Pu from "non-adsorbable" elements which include alkali metals, alkaline earths, rare earths, trivalent actinides and a number of other elements such as Al, Sc, Y, Ac, Th and Ni.

Adsorption of the uranides by anion exchangers from HCl solutions can occur in either the +4 or +6 oxidation states but not in the +3 or +5 states⁵. Adsorption and sequential elution thus can be achieved through control of the oxidation states. In this procedure, uranium is adsorbed in the +6 state while, with the mild oxidizing conditions used in the sample treatment, neptunium and plutonium are adsorbed presumably in the +4 state. Plutonium is selectively reduced to Pu(III) and eluted under conditions where Np(IV) and U(VI) remain adsorbed. The latter are then eluted in separate fractions with HCl-HF mixtures.

In a previous procedure¹, neptunium was adsorbed as Np(VI) from HCl-HF mixtures with chlorine as oxidizing agent. Adsorption of neptunium as Np(IV) from HCl solutions is often preferable because Np(VI) is difficult to maintain in either HCl or HCl-HF solutions and some leak-through may occur through reduction. While removal of neptunium as Np(IV) could be carried out with 4 M HCl, the present procedure employs HCl-HF mixtures because they give sharper bands and more rapid removal. In this respect Np(IV) is similar to U(IV), as expected⁶.

TYPICAL SEPARATION

A typical separation is illustrated in Fig. 1. A mixture of ²³⁷U, ²³⁸Np, ²³⁸-²³⁹Pu tracers and some non-adsorbable fission products in 9 M HCl-0.05 M HNO₃ was prepared. The solution was warmed to insure oxidation of the heavy elements and added to a 0.25 cm² × 2 cm column of Dowex 1-X10, -400 mesh, pretreated with 9 M HCl. The column was operated at 50° to improve exchange rates. After the sample had drained into the resin bed, elution was carried out with 5 column volumes (c.v.) of 9 M HCl

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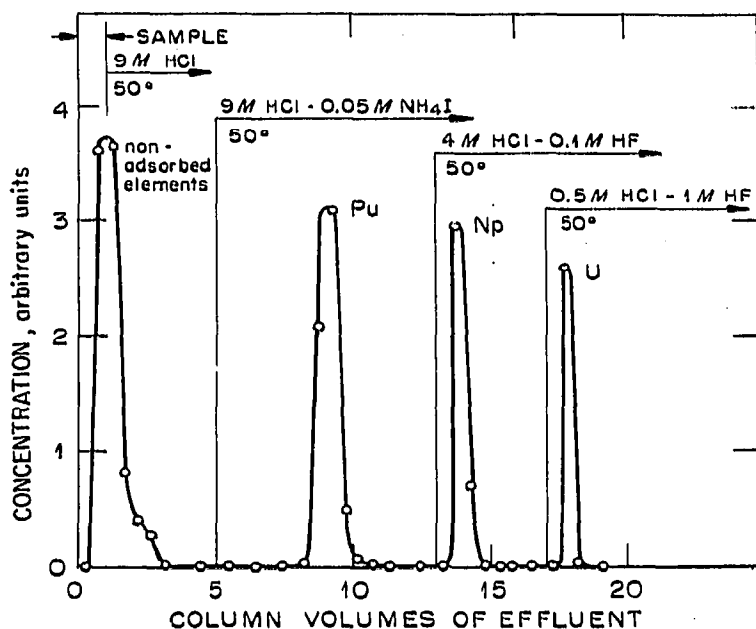


Fig. 1. Separation of Pu, Np and U (Dowex 1-X10, —400 mesh, $0.25 \text{ cm}^2 \times 3 \text{ cm}$ column).

which was sufficient to remove all the non-adsorbable elements; U, Np and Pu remained adsorbed. Plutonium was removed with $9 \text{ M HCl} - 0.05 \text{ M NH}_4\text{I}$. Breakthrough of plutonium was delayed until breakthrough of iodide occurred. Neptunium was removed with $4 \text{ M HCl} - 0.1 \text{ M HF}$ and uranium with $0.5 \text{ M HCl} - 1 \text{ M HF}$.

In the elution of plutonium, the HCl concentration should not exceed 10 M ; otherwise partial reduction of U(VI) by iodide can occur and the neptunium fraction can become contaminated with uranium. For the same reason, it is probably well to avoid use of excess iodide in the eluent.

PROCEDURE

(a) Materials and reagents

Resin. Dowex 1-X10 (—400 mesh), chloride form.

Apparatus. A section of plastic tubing 0.6 cm I.D. and 12 cm in length is used to prepare the column. The tubing is pulled out to a tip at one end and a porous Teflon plug inserted to retain the resin. Additional apparatus are plastic test tubes, Teflon evaporating dishes, and plastic transfer pipettes.

Column. Resin bed: $0.28 \text{ cm}^2 \times 3.0 \text{ cm}$; column volume 0.85 ml . Flow rate: *ca.* 0.3 cm/min . Temperature: 50° .

Effluent volumes (column volumes = c.v.):

Non-adsorbed fraction: 5 c.v. (4.2 ml) of solution II.

Pu fraction: 8 c.v. (6.8 ml) of solution III.

Np fraction: 4 c.v. (3.4 ml) of solution IV.

U fraction: 3 c.v. (2.5 ml) of solution V.

Solutions. (I): $9 \text{ M HCl} - 0.05 \text{ M HNO}_3$; (II): 9 M HCl ; (III): $9 \text{ M HCl} - 0.05 \text{ M NH}_4\text{I}$; (IV): $4 \text{ M HCl} - 0.1 \text{ M HF}$; (V): $0.5 \text{ M HCl} - 1 \text{ M HF}$.

(b) Sample preparation

The sample is dissolved by standard methods, evaporated to near dryness, and residue

is taken up in about 1 ml of 9 M HCl-0.05 M HNO₃. The solution is warmed, but not boiled, for 5 min.

(c) *Column operations*

Resin as a slurry in water is added to the plastic column until a resin bed about 3 cm in length (ca. 0.85 ml) is formed. The column is placed in a water jacket which is heated to 50°; it is then pretreated with at least 3 c.v. (2.5 ml) of 9 M HCl solution and the sample is added. Flow rate is controlled by air pressure to about 0.8 cm/min. After the sample has passed into the resin bed, 0.5 c.v. of 9 M HCl is added as wash, taking care not to disturb the resin at the top of the bed. When the wash solution has passed into the bed, an additional 3.5 c.v. (3 ml) of eluent are added and elution continued. The effluent is collected in a plastic test tube; it contains the non-adsorbed elements.

Plutonium is eluted by passing 8 c.v. (6.8 ml) of 9 M HCl-0.05 M NH₄I through the resin bed. The effluent is collected in a plastic tube. Neptunium is removed with 4 c.v. (3.4 ml) of 4 M HCl-0.1 M HF. Uranium is eluted with 0.5 M HCl-1 M HF. The column may be regenerated with 3 c.v. of 9 M HCl.

Column operation time for the separation of uranium, neptunium, plutonium and the non-adsorbed elements into individual fractions is about 80 min.

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SUMMARY

An anion exchange procedure is described for separating uranium, neptunium and plutonium from each other and from several non-adsorbed elements.

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