ION EXCHANGE PROCEDURES

II. SEPARATION OF ZIRCONIUM, NEPTUNIUM AND NIOBIUM*,**

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This procedure was devised for separation and individual isolation of trace amounts of neptunium and niobium from macro-amounts of zirconium. It makes use of the fact that Zr(IV) in HCl–HF media at high HCl concentrations is essentially non-adsorbable[2] by anion exchange resins under conditions where Np(VI) and Nb(V) are strongly adsorbed; these may then be sequentially eluted.

TYPICAL SEPARATION

Separation of milligram amounts of Zr(IV) and trace amounts of Np(VI) and Nb(V) is illustrated in Fig. 1. A 0.38 *M* $ZrOCl_2$ (*ca.* 34 mg Zr/ml) solution was prepared by dissolving $ZrOCl_2 \cdot 8\ H_2O$ in warm 6 *M* HCl–1 *M* HF. When dissolution was complete, tracer ^{95}Zr–^{95}Nb and ^{238}Np were added. Chlorine gas was bubbled through the solution for a few minutes to assure oxidation of neptunium to Np(VI).

A 0.67 $cm^2 \times 3$ cm resin column (bed volume 2 ml) was prepared with Dowex 1-X10, —400 mesh resin. The resin as a slurry in water was treated with chlorine gas before preparing the column to insure strongly oxidizing conditions in the bed. The column was pretreated with 5 ml of 6 *M* HCl–1 *M* HF–Cl_2 which was also used for elution after addition of the Zr–Np–Nb sample (1 ml). Flow rate was 0.8 cm/min. Effluent fractions (0.5 ml) were collected and counted. Zirconium was non-adsorbed and appeared in maximum concentration at less than 1 column volume (c.v.) of effluent while Np(VI) and Nb(V) remained essentially completely adsorbed. A small amount ($< 2\%$) of Np appeared in the Zr-fraction. The neptunium remaining on the column was selectively eluted with 0.5 *M* HCl–1 *M* HF–Cl_2 solution. Niobium was removed with 4 *M* HNO_3–1 *M* HCl–0.2 *M* HF.

DISCUSSION

This separation requires neptunium to be essentially completely oxidized to Np(VI). Since Np(V) is not adsorbed from HCl solutions[3], and Np(IV) is weakly adsorbed[4] from 6 *M* HCl–HF mixtures, the appearance of a small amount of neptunium in the zirconium fractions indicates that some reduction may occur even in the presence of

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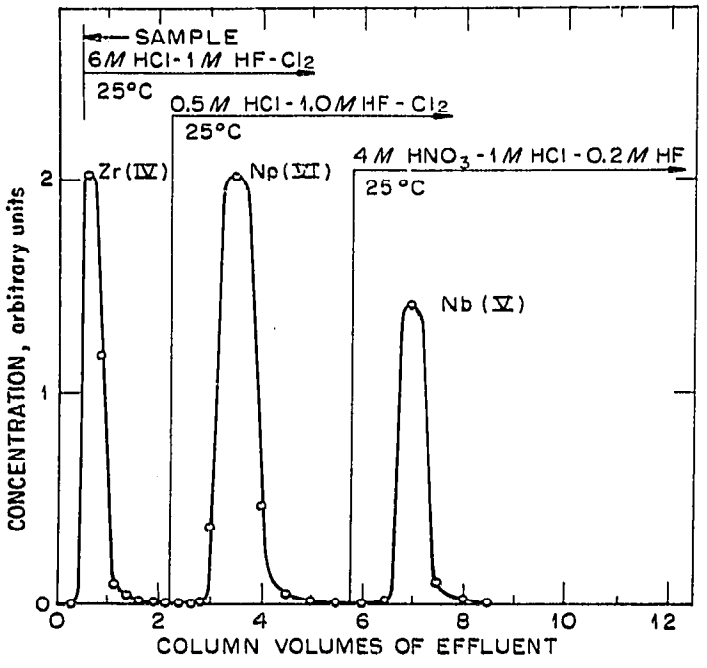

Fig. 1. Separation of milligram amounts of Zr(IV) and trace amounts of Np(VI) and Nb(V) (Dowex 1-X10, —400 mesh, 0.67 cm^2 × 3 cm column).

chlorine. Under the conditions described, however, neptunium leakthrough is relatively small, *i.e.*, less than 2%.

A fine mesh resin (—400) is used to permit separation with a shallow bed at reasonably rapid flow rates; with the resin used in this procedure, sharp elution bands are observed.

PROCEDURE

(*a*) *Materials and reagents*

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

Apparatus. A section of plastic tubing 0.9 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 used are plastic test tubes, Teflon evaporating dishes, and plastic transfer pipettes.

Column. Resin bed: 0.67 cm^2 × 3.0 cm. Flow rate: *ca.* 0.8 cm/min. Temperature: 25°. Effluent volumes (column volumes = c.v.):

Zr fraction: 3 c.v. (6 ml) of solution I.

Np fraction: 3 c.v. (6 ml) of solution II.

Nb fraction: 3 c.v. (6 ml) of solution III.

Solutions. (I): 6 *M* HCl–1 *M* HF–Cl_2; (II): 0.5 *M* HCl–1 *M* HF; (III): 4 *M* HNO_3–1 *M* HCl–0.2 *M* HF.

(*b*) *Sample preparation*

The sample containing milligram amounts of zirconium is dissolved by standard methods, evaporated to near dryness, and residue taken up in about 1 ml of 6 *M* HCl–1 *M* HF–Cl_2. If solids are present, the solution is warmed to hasten their dissolution. The sample is transferred to a plastic tube and a small stream of chlorine gas is bubbled through it for *ca.* 3 min.

(*c*) *Column operation*

Resin as a slurry in water is chlorinated about 3 min. with Cl_2 gas and then added to the plastic column until a resin bed about 3 cm in length (*ca.* 2.0 ml) is formed. The column is pretreated with at least 2 c.v. (4 ml) of 6 *M* HCl–1 *M* HF–Cl_2 solution and the sample 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 6 *M* HCl–1 *M* HF–Cl_2 are 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 c.v. (4 ml) of eluent are added and elution continued. The effluent is collected in a plastic test tube and contains > 99% of the Zr(IV) while Np(VI) and Nb(V) remained adsorbed.

Np(VI) is eluted by passing 3 c.v. (6 ml) of 0.5 *M* HCl–1 *M* HF through the resin bed. The effluent is collected in a plastic tube and contains > 98% of the Np. Nb(V) is removed with 3 c.v. (6 ml) of 4 *M* HNO_3–1 *M* HCl–0.2 *M* HF. The column may be regenerated by treating with 6 ml of 6 *M* HCl–1 *M* HF–Cl_2.

Column operation time for the separation of Zr(IV) and Np(VI) into individual fractions is about 20 min; an additional 10 min is required to remove Nb(V).

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SUMMARY

An anion exchange procedure for separating trace amounts of neptunium and niobium from each other and from macro-amounts of zirconium is described.

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