

## Separation and determination of zirconium in niobium using methylenebis(di-*n*-hexylphosphine oxide)\*

The determination of zirconium in the presence of large amounts of niobium poses a difficult analytical problem. Most methods for the determination of zirconium list niobium as a major interference; and, even in the best cases, the methods will tolerate only small amounts of niobium, usually no more than the amount of zirconium present. Thus, it is necessary to separate the zirconium from the niobium prior to analysis. The present paper describes the separation of small amounts of these elements by extraction chromatography using MHDPO, methylenebis(di-*n*-hexylphosphine oxide), as the stationary phase<sup>1,2</sup>.

### *Experimental*

*Apparatus and reagents.* The MHDPO was synthesized using the procedure of RICHARD *et al.*<sup>1</sup>. High-purity niobium metal was used to prepare the standard niobium solutions. Zirconium standards were prepared by fuming the desired amount of zirconium oxychloride with hydrofluoric acid to remove any chloride. The zirconium fluoride was taken up in 10 *M* hydrofluoric acid, transferred to a calibrated polyethylene bottle and diluted to volume with 10 *M* hydrofluoric acid. Reagent-grade chemicals were used throughout the study.

Schleicher and Schuell Blue Ribbon filter paper discs were used for the radial paper chromatographic studies. The papers were impregnated with the MHDPO by immersing them in a 0.2 *M* solution of MHDPO in carbon tetrachloride and then allowing them to air dry. The papers were spotted and developed as previously reported<sup>2</sup> except that polyethylene Petri dishes were used instead of glass. The zirconium and niobium bands were located on the paper by spraying with 8-hydroxyquinoline and ammonia.

The column used was prepared by drawing out the end of a section of 1-cm diameter polyethylene tubing. The column packing was prepared by slurring a solution of MHDPO in acetone with a fluorohalocarbon resin (Plaskon 3200 Molding Powder, Allied Chemical Corp., Morristown, N. J., U.S.A.) and then evaporating off the acetone. The column was packed with this dry material (bed height of 2.0 cm).

### *Results and discussion*

Initial studies on the feasibility of the separation of zirconium from niobium were performed using radial paper chromatography. Hydrofluoric acid was chosen as the mobile phase, because both niobium and zirconium are easily kept in solution in fluoride media. The zirconium moved directly with the acid front for all acid concentrations from 1 to 15 *M*. The  $R_f$  values for niobium were approximately 0.6 for dilute hydrofluoric acid and decreased to about 0.4 with 15 *M* hydrofluoric acid. These results indicate that the best separation of niobium from zirconium would occur at the higher acid concentrations. Papers spotted with 200  $\mu\text{g}$  niobium and 5 to 20  $\mu\text{g}$  zirconium were developed with 10 *M* hydrofluoric acid. They showed a very clear separation of zirconium from niobium.

Because the amount of material which can be handled by the paper technique is

\* This work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2115.

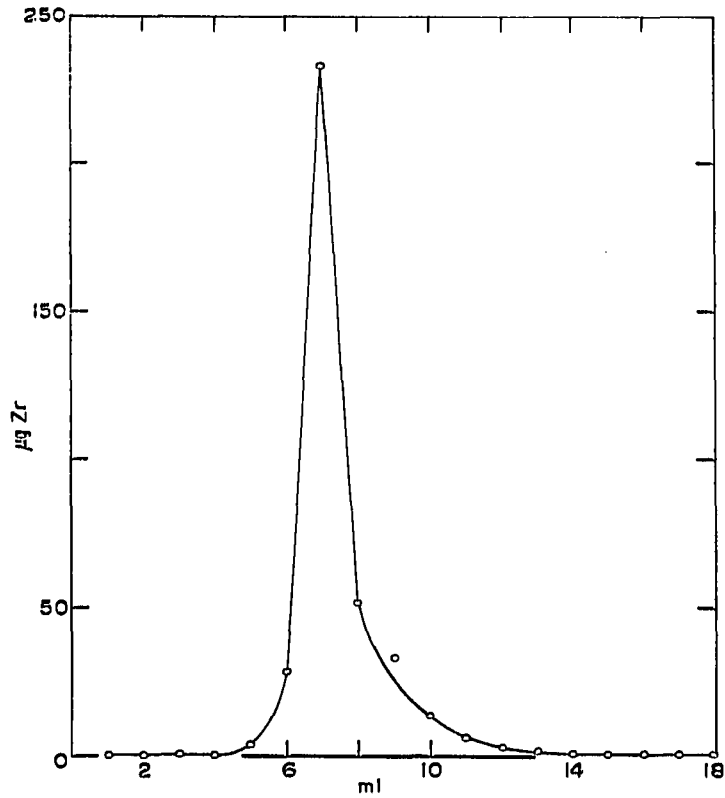


Fig. 1. Elution curve for zirconium with 10 *M* hydrofluoric acid.

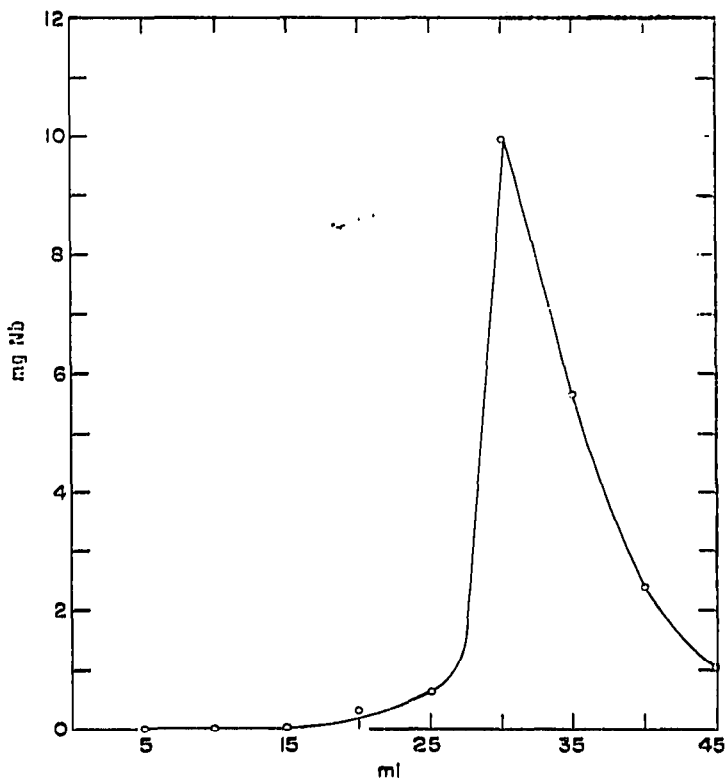


Fig. 2. Elution curve for niobium with 10 *M* hydrofluoric acid.

rather limited, it was decided to attempt the separations using a column technique. Elution curves were run for both zirconium and niobium using 10 *M* hydrofluoric acid as the mobile phase. The flow rate was adjusted to 0.25 ml/min. The elution curve for 387  $\mu\text{g}$  of zirconium is shown in Fig. 1. The zirconium was determined using the xylenol orange spectrophotometric technique<sup>3</sup>. The elution curve for 10 mg of niobium is shown in Fig. 2. The niobium was determined using the sulfuric acid–hydrogen peroxide spectrophotometric method<sup>4</sup>. A clean separation of niobium and zirconium seemed possible.

The following procedure for the analysis of zirconium–niobium alloys was adopted. The sample was dissolved in 10 *M* hydrofluoric acid with a few drops of 1:1 nitric acid to speed up the dissolution. The solution was taken to dryness in a platinum dish and the residue taken up in 10 *M* hydrofluoric acid and diluted to volume in a calibrated polyethylene bottle. An aliquot of the sample solution (taken with a polyethylene pipet) was placed on the column and eluted with 10 *M* hydrofluoric acid. The first 15 ml of eluent were collected for the zirconium analysis. Twenty milliliters of 2.5 *M* sulfuric acid were added to the zirconium fraction and the solution was evaporated to dryness in a platinum dish. The residue was taken up in 0.2 *M* sulfuric acid and analyzed spectrophotometrically with xylenol orange using the method reported by CHENG<sup>3</sup>. The column was then washed with 20 ml of a solution 1.25 *M* in hydrofluoric acid and 3.0 *M* in nitric acid to remove the niobium.

TABLE I  
Zr RESULTS FOR SYNTHETIC STANDARDS

$\mu\text{g Zr}$ <i>added</i>	<i>mg Nb</i> <i>added</i>	$\mu\text{g Zr}$ <i>found</i>	$\mu\text{g Zr}$ <i>added</i>	<i>mg Nb</i> <i>added</i>	$\mu\text{g Zr}$ <i>found</i>
198	0.0	200	198	8.0	200
198	0.0	197	198	8.0	198
198	0.0	198	198	8.0	201
387	0.0	386	387	4.0	390
387	0.0	389	387	4.0	387
387	0.0	390	387	4.0	392
198	4.0	196	387	8.0	388
198	4.0	200	387	8.0	385
198	4.0	195	387	8.0	391

TABLE II  
Zr RESULTS ON Zr–Nb ALLOYS

<i>Sample</i>	% Zr		
1	5.72	5.84	5.77
2	5.11	5.09	5.08
3	4.09	4.15	4.18
4	2.72	2.70	2.74
5	1.03	1.04	1.01
6	0.69	0.72	0.73
7	0.69	0.69	0.73
8	0.78	0.73	0.78

This mixed acid eluent was found to be more effective than hydrofluoric acid alone in removing the niobium. The column was then washed with 10 ml of 10 *M* hydrofluoric acid and was ready for re-use.

A series of known mixtures of zirconium and niobium were prepared and analyzed by the above procedure. The results are shown in Table I. The results obtained on several research samples of zirconium-niobium alloys by this method are shown in Table II. Replicate analyses show acceptable precision.

A few synthetic samples were analyzed for niobium recovery as well as for zirconium. For a series of samples in which 8.00 mg of niobium were taken, 7.89, 7.97, 8.02 and 7.95 mg were recovered. Thus, it appears that the method can be used for simultaneous analysis of both zirconium and niobium. Radial paper chromatographic studies on behavior of aluminum, hafnium and titanium in hydrofluoric acid media indicate that these elements could also be separated from niobium.

#### *Acknowledgement*

The authors wish to thank Mr. JOHN J. RICHARD for synthesizing the MHDPO used in these studies.

*Institute for Atomic Research and Department of  
Chemistry, Iowa State University, Ames, Iowa (U.S.A.)*

GEORGE J. KAMIN\*  
JEROME W. O'LAUGHLIN  
CHARLES V. BANKS

- 1 J. J. RICHARD, K. E. BURKE, J. W. O'LAUGHLIN AND C. V. BANKS, *J. Am. Chem. Soc.*, 83 (1961) 1722.
- 2 J. W. O'LAUGHLIN AND C. V. BANKS, *Anal. Chem.*, 36 (1964) 1222.
- 3 K. L. CHENG, *Talanta*, 2 (1959) 61.
- 4 G. TELEP AND D. F. BOLTZ, *Anal. Chem.*, 24 (1962) 163.

Received June 19th, 1967

---

\* Present address, Sylvania Electric Products, Inc.; Chemical and Metallurgical Division, Towanda, Pennsylvania.