

that the hydrazide analogs of the specific chymotrypsin amide or ester type substrates²⁻⁵ are not hydrolyzed by this enzyme. We therefore wish to point out that at least one of the acylated α -amino acid hydrazides possessing the structural characteristics required of ester or amide type specific chymotrypsin substrates,²⁻⁵ *i. e.*, nicotinyl-L-tyrosylhydrazide is hydrolyzed by this enzyme (Table I).

TABLE I
HYDROLYSIS OF NICOTINYL-L-TYROSYLHYDRAZIDE BY CHYMOTRYPSIN

| t , min. | Hydrolysis, % | $\frac{1}{t} \log \frac{s_0}{s}$ |
|------------|---------------|----------------------------------|
| 1.2 | 1.2 | 0.064 |
| 6.6 | 7.0 | .064 |
| 10.6 | 10.0 | .061 |
| 20.3 | 21.8 | .067 |
| 61.0 | 49.4 | .064 |
| 91.0 | 63.0 | .063 |

Nicotinyl-L-tyrosylhydrazide, m.p. 242-243° (cor.) (*Anal.* Calcd. for $C_{16}H_{16}O_3N_4$; C, 60.0; H, 5.4; N, 18.7. Found; C, 59.9; H, 5.3; N, 18.6) was prepared from nicotinyl-L-tyrosine ethyl ester, m.p. 147-149° (cor.) obtained by the acylation of L-tyrosine ethyl ester with nicotinyl azide.⁶ The enzymatic hydrolysis was conducted at 25° and pH 7.9 (0.02 *F* ethylenediamine-hydrochloric acid buffer) with an initial substrate concentration, s_0 of 5.0 micromoles per ml. reaction mixture and an initial enzyme concentration, E_0 , of 0.075 mg. protein nitrogen per ml. reaction mixture. A formol titration was used to determine the extent of hydrolysis.

(2) M. Bergmann and J. S. Fruton, *J. Biol. Chem.*, **118**, 405 (1937).

(3) J. S. Fruton and M. Bergmann, *ibid.*, **145**, 253 (1942).

(4) J. E. Snoke and H. Neurath, *Arch. Biochem.*, **21**, 351 (1949).

(5) S. Kaufman and H. Neurath, *ibid.*, **21**, 437 (1949).

(6) T. Curtius and E. Mohr, *Ber.*, **31**, 2493 (1898).

CONTRIBUTION NO. 1335 R. V. MACALLISTER
GATES AND CRELLIN LABORATORIES OF CHEMISTRY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA CARL NIEMANN

RECEIVED SEPTEMBER 29, 1949

SEPARATION OF COLUMBIUM AND TANTALUM WITH ANION EXCHANGE RESINS¹

Sir:

In a previous communication² an experiment was described indicating a partial separation of zirconium and hafnium on an anion exchange column in HCl-HF mixtures. While this separation was unusually difficult, the separation of the adjacent elements columbium and tantalum by the same method, under similar conditions, was very efficient.

The experiments were carried out with a 12.5-

(1) This document is based on work performed under Contract Number W-7405 eng 26 for the Atomic Energy Project at Oak Ridge National Laboratory.

(2) K. A. Kraus and G. E. Moore, *THIS JOURNAL*, **71**, 3268 (1949).

cm. column (0.0226 sq. cm. cross-section) of the anion exchange resin Dowex-1 using columbium⁹⁵ (β -emitter $T_{1/2} = 35$ days³) and tantalum¹⁸² (β -emitter $T_{1/2} = 117$ days³). The columbium was carrier-free fission product and the tantalum was prepared by a neutron bombardment of tantalum metal. In a typical experiment, the tracers were added to the column in a mixture of 9 *M* HCl and 0.05 *M* HF and elution carried out in the same medium at an average flow rate of *ca.* 0.3 ml./sq.cm./min.

The results are shown in Fig. 1 which represents a transcribed continuous record of the activity of the eluent. The bands were identified by standard radiochemical procedures.

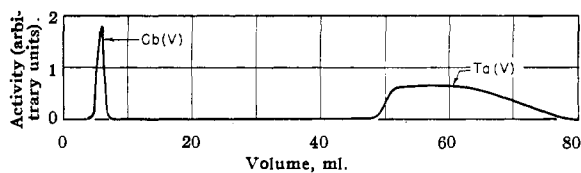


Fig. 1.—Separation of columbium (V) and tantalum (V) by anion exchange: dowex-1 column 12.5 cm. length 0.0226 sq. cm. cross-section, average flow rate; 0.3 ml./sq. cm./min.

Columbium eluted relatively rapidly in a sharp, well-shaped band and the tantalum very much more slowly in a somewhat diffuse band with a sharp front edge. The separation appears to be complete and could probably be achieved with better than 99% purity of the fractions using columns of considerably shorter length.

The experiments prove that both columbium and tantalum can form negatively charged complexes in this medium with probable negative charge minus two or greater. From the slower elution rate of the tantalum one can conclude that the average negative charge on this element is greater than that on columbium.

The very large difference in elution behavior of these two elements is somewhat surprising since both elements, in some complexes at least, show practically the same size. Thus Hoard⁴ found no significant difference in the lattice constants of the complex fluorides K_2CbF_7 and K_2TaF_7 . The rather large difference in the behavior of these elements on anion-exchangers may thus be due to comparatively large differences in their polarizability, causing considerable differences in the chloride complex constants, or to small differences in the value of each stability constant with a resulting large difference in the negatively charged series due to the fact that for these the product of a considerable number of such constants is involved.

OAK RIDGE NATIONAL LABORATORY KURT A. KRAUS
OAK RIDGE, TENNESSEE GEORGE E. MOORE

RECEIVED AUGUST 20, 1949

(3) Information from G. T. Seaborg and I. Perlman, "Table of Isotopes," *Rev. Mod. Phys.*, **20**, 585 (1946).

(4) J. L. Hoard, *THIS JOURNAL*, **61**, 1252 (1939).