A NEW SOLVENT EXTRACTION METHOD FOR THE SEPARATION OF NIOBIUM AND TANTALUM

Sir:

We wish to make a preliminary report of the separation of niobium and tantalum by a new solvent extraction technique. It has been found that niobium may be extracted essentially quantitatively from strong hydrochloric acid with a solution of methyldioctylamine in xylene. Under these conditions the extraction of tantalum appears to be negligible. The niobium may then be "stripped" from the organic phase with nitric acid, sulfuric acid or dilute hydrochloric acid.

Methyldioctylamine, a water-insoluble tertiary amine, is known[1] to form the corresponding amine acid salts which are also water-insoluble, in general, and preferentially extract into organic solvents. The work to date suggests that approximately 8 *M* hydrochloric acid concentration is satisfactory for the separation.

In a typical experiment an aqueous phase containing Nb^{95} tracer or Ta^{182} tracer was extracted for five minutes with an equal volume of a 5% solution of methyldioctylamine in xylene. Each phase was checked for Nb^{95} γ or Ta^{182} γ radioactivity by use of a scintillation counter. The results of the initial investigation of the effect of hydrochloric acid concentration on the extraction of niobium and tantalum are given in Tables I and II, respectively.

TABLE I

THE EFFECT OF HYDROCHLORIC ACID CONCENTRATION ON THE EXTRACTION OF Nb^{95} WITH METHYLDIOCTYLAMINE IN XYLENE

HCl, *M*	Nb^{95} Extracted, %
2	4.0
3	2.4
4	2.2
6	21.5
8	99.3
9.6	100.0
(control) 9.6 (no MDOA)	0.04

TABLE II

THE EFFECT OF HCl CONCENTRATION ON THE EXTRACTION OF Ta^{182} WITH METHYLDIOCTYLAMINE IN XYLENE

HCl, *M*	Ta^{182} Extracted, %
2.91	0.25
4.85	0.11
7.28	0.55
8.85	1.10
10.10	1.35
11.20	1.40

It has been found that Nb^{95} does not extract appreciably from nitric acid concentrations up to 10.6 *M* and from sulfuric acid concentrations up to 12 *M*. Ta^{182} does not extract from nitric acid concentrations up to 10.6 *M* nor from higher concentrations of sulfuric acid, but appears to extract appreciably from 2 *M* H_2SO_4. The extraction behavior of these elements in dilute sulfuric acid is being investigated.

(1) E. L. Smith and J. E. Page, *J. Soc. Chem. Ind.*, **67**, 48 (Feb., 1948).

Using the procedure given above, Nb^{95}–Ta^{182} tracer mixtures have been separated and nonradioactive Nb–Ta separations at one milligram/milliliter concentrations have been effected.

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RECEIVED FEBURARY 19, 1952

THE DIPOLE MOMENT OF DECABORANE

Sir:

In the course of a comprehensive investigation of decaborane,[1] $B_{10}H_{14}$, we have measured the dielectric constant of benzene solutions and have obtained a surprising value for its dipole moment which should be of considerable interest to those concerned with the structures and bonding of the boron hydrides.

Preliminary experiments showed that even short exposure to moist air led to variable results. Therefore the decaborane and benzene were purified with great care and stored under vacuum conditions. The solutions were prepared in a dry box and transferred to the dielectric cell without exposure to the air. The dielectric constants of solutions ranging in concentration from 0.0071345 to 0.018691 mole fractions of decaborane were measured at 25°, using a heterodyne-beat oscillator equipped with a precision condenser and operating at a frequency of 1.79 megacycles. The dielectric constant of benzene was taken to be 2.2773 at 25°. Subsequently the densities of the solutions were determined pycnometrically and values were calculated for the polarization of decaborane according to the method described by Smyth.[2] Graphical extrapolation to infinite dilution gives the value 297.0 for the total molar polarization of $B_{10}H_{14}$ in benzene solution. If the sum of the electronic and atomic polarizations is assumed to be 1.05 times the molar refraction this sum equals 43.9, and the dipole moment of $B_{10}H_{14}$ is then calculated to be 3.52 ± 0.02 Debye.

Mole fraction $B_{10}H_{14}$	Total molar Polarization of $B_{10}P_{14}$
0.0071345	295.5
.0073878	295.1
.0078698	294.8
.013943	293.3
.018691	291.2

This is an unexpectedly high value in the light of the Kasper, Lucht and Harker model[3] for the structure of decaborane and present theories of electronegativity and bonding. It appears, however, that high polarity may be characteristic of asymmetric boron hydrides having a number of hydrogen bridge bonds. This is supported by a recent microwave investigation of pentaborane, B_5H_5, by Pimentel and associates.[4] They report a dipole

(1) We wish to thank Dr. A. E. Newkirk of the Research Laboratory of the General Electric Company for providing the decaborane and for information concerning the characteristics of this compound.

(2) C. P. Smyth, "Dielectric Constant and Molecular Structure" (The Chemical Catalog Co.), Reinhold Publ. Corp., New York, N. Y., 1931.

(3) J. S. Kasper, C. M. Lucht and D. Harker, *Acta Cryst.*, **3**, 436 (1950).

(4) Professor G. C. Pimentel and associates describe this in a letter recently submitted to the *Journal of Chemical Physics*.

moment of 2.13 ± 0.04 debye for this compound which is believed to resemble decaborane by being asymmetric and having four hydrogen bridge bonds.[5]

We are continuing measurements on solutions of decaborane in other solvents.

(5) (a) K. Hedberg, M. E. Jones and V. Schomaker, THIS JOURNAL, **73**, 3538 (1951); (b) W. J. Dulmage and W. N. Lipscomb, *ibid.*, **73**, 3539 (1951).

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RECEIVED FEBRUARY 16, 1952

FRACTIONATION OF AN ACTH PREPARATION BY IONOGRAPHY

Sir:

The technique of ionography,[1,2,3,4] that is, electromigration on wet surfaces, was utilized to fractionate an ACTH preparation[5] obtained from pig pituitaries. This material was prepared by the acid acetone extraction method of Lyons[6] and further purified by treatment with 9% ammonium hydroxide solution and fractional acetone precipitation. The final material was freeze dried from aqueous solution. It was one half as active as Armour's LA la standard. The particular instrument employed was the Precision Ionograph.[7] The paper used was Eaton-Dikeman 613, 8 mm. in width. The experiments were conducted at 24–26° in a helium atmosphere.

The ionogram was dried on a glass plate by a stream of hot air. It was then passed through a saturated mercuric chloride solution of 95% ethyl alcohol containing 1 g. of brom phenol blue per 100 ml. of solution. The ionogram was again dried in a stream of hot air and then passed successively through several beakers containing saturated aqueous mercuric chloride solution until all the excess indicator was washed out of the paper strip. On re-drying the strip, the protein zone appeared as a dull green area which changed to a sharp deep blue color by passing the ionogram over concentrated ammonium hydroxide.

Using a veronal buffer of ionic strength 0.015 at *p*H 5.5, and applying a potential of 6 volts/cm. for three hours across the ends of the filter paper strips, the ACTH preparation separated into three fractions: a heavy-staining fraction "A" which moved to the negative pole, a light-staining fraction "B" which moved to the positive pole and a heavy-staining fraction "C" which did not move. As the *p*H of the buffer used to saturate the paper strips was increased to 6.0–6.6, the mobility of the heavy-staining fraction A was found to approach zero, indicating that its isoelectric point was in this region. This fraction contained 98% of the biological activity as determined by the adrenal ascorbic acid depletion test,[8] but only about 31% of the total input nitrogen. The isoelectric point of the light fraction B, which was found to have only 0.2% activity, but about 45% of the nitrogen was shown to be in the region of 4.2–4.8. The isoelectric point of fraction C, which contained 2% of the activity and 21% of the nitrogen, was shown to be in the region of 5.0–6.0. It would appear from these experiments, and others,[9] that the biological activity of ACTH is not uniformly distributed throughout the whole protein preparation.

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(1) H. J. McDonald, M. C. Urbin and M. B. Williamson, *Science*, **112**, 227 (1950).

(2) H. J. McDonald, M. C. Urbin and M. B. Williamson, THIS JOURNAL, **73**, 1893 (1951).

(3) H. J. McDonald, M. C. Urbin, E. P. Marbach and M. B. Williamson, *Federation Proc.*, **10**, 218 (1951).

(4) H. J. McDonald, M. C. Urbin and M. B. Williamson, *J. Colloid Sci.*, **6**, 236 (1951).

(5) The ACTH preparation (control X1-134-3) was supplied by G. D. Searle and Co. We are indebted to Dr. F. J. Saunders of G. D. Searle and Co. for the determinations of biological activity.

(6) W. R. Lyons, *Proc. Soc. Exptl. Biol. Med.*, **35**, 645 (1937).

(7) Manufactured by Precision Scientific Co., Chicago 47, Ill.

(8) M. Sayers, G. Sayers and L. A. Woodbury, *Endocrinology*, **42**, 379 (1948).

(9) G. P. Hess, J. I. Harris, F. H. Carpenter and C. H. Li, THIS JOURNAL, **73**, 5918 (1951).

(10) Reuben Myron Strong Research Fellow.