O_8 which under similar conditions yields mixtures of UCl_4, UCl_5 and UCl_6.[10]

We have, however, succeeded in preparing a well defined oxygenated Np(V) compound. A solution prepared by dissolving 10 mg. of Np(V) hydroxide in 0.1 cc.[8] of 1 *M* HCl was added to 3 cc. of a 10% solution of oxalic acid in anhydrous *t*-butyl alcohol. A pale green precipitate was obtained which after centrifugation was washed 3 times with 3-cc. portions of anhydrous ethyl ether. The final washed and dried precipitate had a distinct but complex X-ray diffraction pattern. The absorption spectrum of 1 mg. of the material in water solution was characteristic of Np(V).[7] A slight shift, from 983 to 990 mμ was observed in the chief absorption peak and may be attributed to complexing of the NpO_2^+ ion by oxalate. The remainder of the product, approximately 10 mg., was analyzed for neptunium spectrophotometrically and by α-count, for oxalate by means of permanganate titration, and for carbon, hydrogen and water by combustion. *Anal.* Calcd. for $NpO_2C_2O_4H \cdot 2H_2O$: Np, 60.15; $C_2O_4^{--}$, 22.33; C, 6.09; H_2O and H, 13.70. Found: 60.80, 60.50 (α-count), 60.11 (spectrophotometric); $C_2O_4^{--}$, 22.82; C, 3.75, 3.37; H_2O and H, 11.29, 11.51.

Studies of the Np(V) oxalate complex in aqueous solution are under way.

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[10] A. Miller and L. B. Dean, Collected Paper, National Nuclear Energy Series, Vol. 6 (to be published).

CHEMISTRY DIVISION
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Method for Freeing Zirconium of Common Impurities and for Preparing Zirconium Sulfate and Oxide

BY W. STANLEY CLABAUGH AND RALEIGH GILCHRIST

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The complex nature of zirconium salts and the incomplete knowledge of their chemistry have made it a matter of considerable difficulty to purify zirconium compounds.

In the course of a project on the separation of hafnium from zirconium, observations were made which should prove useful in manipulating certain reactions whereby zirconium can be freed of its common impurities.

Many of the salts of zirconium, including methods for their preparation, are described by Meyer and Hauser.[1] The authors give a method for preparing anhydrous $Zr(SO_4)_2$ and its tetrahydrate, by treating the zirconium oxide with sulfuric acid. Included also is a discussion of some of the possible basic sulfates of zirconium.

According to Falinski,[2] who investigated the system ZrO_2–SO_3–H_2O as a function of the concentration of SO_3, when $ZrOCl_2 \cdot 8H_2O$ is added to a sulfuric acid solution containing less than 64% of sulfur trioxide, $Zr(SO_4)_2 \cdot 4H_2O$ is precipitated. With a solution containing from 64 to 72% of SO_3, one obtains well-crystallized $Zr(SO_4)_2 \cdot H_2SO_4 \cdot 2H_2O$, and with an acidity corresponding to 72 to 79% of SO_3, finely crystalline $Zr(SO_4)_2 \cdot H_2SO_4 \cdot H_2O$. With concentrations of SO_3, greater than 79%, it is stated that probably $Zr(SO_4)_2 \cdot H_2SO_4$ crystallizes.

Preparation of Zirconium Sulfate.—It was found in this Laboratory that when concentrated sulfuric acid is poured into a fairly concentrated aqueous solution of zirconium sulfate or chloride, a dense white crystalline precipitate of $Zr(SO_4)_2 \cdot 4H_2O$ is obtained. The optimum proportion appears to be 1 volume of concentrated sulfuric acid to 2 volumes of concentrated zirconium solution. The zirconium sulfate produced in this manner can be readily caught on a sintered glass filter of medium or coarse porosity. Since approximately 1 g. of the salt so produced will dissolve in 1 ml. of water, the zirconium sulfate can be redissolved in water and reprecipitated by adding sulfuric acid

It was further found that the presence of hydrochloric acid was essential for the removal of iron. For instance, zirconium sulfate which was recrystallized 5 times in the absence of hydrochloric acid retained nearly all of its original iron. On the other hand, when recrystallized in the presence of approximately 10% hydrochloric acid, the iron content was reduced by a factor of more than 1000.

The most effective solution tried for washing the precipitate consisted of 75 volumes of water, 40 volumes of concentrated sulfuric acid and 5 volumes of concentrated hydrochloric acid. After several washings with this mixed acid, three washings with acetone are recommended. It should be pointed out that alcohol should *not* be used for this final washing, because, in some way, it causes interference in subsequent recrystallizations, probably through complex-formation.

With a starting material consisting of 1135 g. of a commercial zirconium chloride, corresponding to 1731 g. of $Zr(SO_4)_2 \cdot 4H_2O$, which contained about 0.3% of iron and 2.7% of hafnium, 1212 g. of zirconium sulfate (70% of original) of very high purity was obtained. Spectrochemical analysis of the original zirconium tetrachloride showed that, in addition to the hafnium and iron, it contained calcium, copper and manganese in the range of 1 to 10 p.p.m. of each; silver, aluminum, barium and titanium in the range of 10 to 100 p.p.m. of each; and magnesium and silicon in the range of 100 to 1000 p.p.m. of each. The rapidity of elimination of iron, the volumes of solutions used, as well as the yields of salt in the six crystallizations, may be seen in Table I.

TABLE I

ELIMINATION OF IRON BY REPEATED RECRYSTALLIZATION OF $Zr(SO_4)_2 \cdot 4H_2O$

$Zr(SO_4)_2 \cdot 4H_2O$ taken, g.	Vol. of Zr soln.,[c] ml.	H_2SO_4 added, ml.	$Zr(SO_4)_2 \cdot 4H_2O$ obtained, g.	Yield, %	Fe found in 1 ml. of filtrate, mg.
1731[a]	2100	1000	1640	94	20
...	..	..	..	..	....
1597[b]	2200	1000	1569	98	0.2
1569	2400	1100	1495	95	.02
1495	2200	1000	1451	97	.01
1451	2000	1000	1385	96	.005
1385	1950	950	1212	87	.002

[a] Calculated from 1135 g. of $ZrCl_4$ taken. [b] Amount of soluble $Zr(SO_4)_2 \cdot 4H_2O$ obtained from original precipitate. [c] Includes 250 ml. of concentrated hydrochloric acid.

Chemical analysis of the final product showed that it contained less than 0.1 part per million of iron and also less than 0.1 p.p.m. of copper. Spectrochemical analysis showed that the silver content was less than 1 p.p.m. and that calcium, magnesium, sodium and silicon were each less than 10 p.p.m. No other elements, except hafnium, were detected spectrochemically. The salt did contain approximately 0.01% of chloride ion. This latter impurity can be removed by merely recrystallizing the salt in the absence of hydrochloric acid. It should be emphasized that the refining process above described does not appreciably alter the original hafnium content.

Not every type of zirconium salt is suitable for purification by the foregoing method. The types best suited were found to be the salt formed by dissolving zirconium tetrachloride in water, without resorting to heat, and that formed by dissolving in dilute hydrochloric acid the peroxidized oxide, that is, the product formed by treating a solution or slurry of zirconium salts with sodium hydroxide and hydrogen peroxide.

Composition and Ignition Behavior of the Zirconium Sulfate Obtained.—The theoretical % values in the compound $Zr(SO_4)_2 \cdot 4H_2O$ are: ZrO_2, 34.67; SO_3, 45.05; H_2O, 20.28.

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[1] R. J. Meyer and O. Hauser, "Die Analyse der seltenen Erden und der Erdsäuren," Verlag von Ferdinand Enke, Stuttgart, Germany. 1912.

[2] Marie Falinski, *Ann. chim.*, **16**, 237 (1941).

Spectrochemical analysis of this material showed the hafnium–zirconium ratio to be 0.027 (Hf/Zr = 2.7). The theoretical % values in a compound of this composition are: oxides, 35.09; SO_3, 44.76; H_2O, 20.15.

Determination of the oxides by precipitation with ammonium hydroxide gave 35.0%. Determination of SO_3 by precipitation with barium chloride gave 44.5%. Determination of the water by difference gave 20.5%.

It was observed that samples of the $Zr(SO_4)_2 \cdot 4H_2O$ lost only 0.05% in weight when dried for 18 hours at 105°. The same samples when heated at 400° for 18 hours lost an average of 21.4% which was assumed to be mostly water. Further heating of these same samples at 600° for 18 hours caused them to lose SO_3 to the extent of 41%. The remaining SO_3 was evolved extremely slowly and probably not completely because at the end of 186 hours of heating at 600 to 650° the loss for SO_3 rose to a total of 43.1%. In the last 18 hours of heating at 650° the loss in weight amounted to only 0.15%. If the material remaining after ignition at 650° is oxides, a value of 35.5% oxides in the original salt is indicated.

Examination of the final ignited product, by X-ray diffraction showed it to be ZrO_2, monoclinic form. The zirconium oxide so produced was found to be readily soluble in strong sulfuric acid.

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Effect of Temperature and Aggregation on the Absorption Spectrum of the Amylose–Iodine Complex[1]

BY JOSEPH F. FOSTER AND EUGENE F. PASCHALL

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A relationship between the wave length of maximum absorption of the iodine complex and the molecular weight of the amylose has been indicated by Baldwin, *et al.*[2] Higginbotham[3] has recently shown that the maxima reported by Baldwin are obtained only under conditions of limited iodine binding and that at higher iodine levels there is a shift of approximately 30 mμ in the direction of longer wave lengths. He attributed this shift to the forcing of additional iodine into the amylose helices.

It is the purpose of this note to report some preliminary results which suggest that this shift in absorption spectrum may be related, instead, to the state of aggregation of the complex. The figure summarizes data on the wave length of maximum absorption of two amylose preparations in the presence of excess iodine as a function of temperature. In this experiment the complex was formed at room temperature, then the solution raised to successively higher temperatures. The solution was permitted to equilibrate for approximately 15 minutes at each temperature prior to measuring the absorption spectrum. It will be noted that both amylose preparations give initial absorption maxima which agree approximately with those found by Higginbotham in the presence of excess iodine. At 40° the values agree rather well with those reported by Baldwin, and by Higginbotham in the presence of limited amounts of iodine. Above 40° there is little if any further shift. Furthermore the shift is largely irreversible since the wave length shifts back only partially on re-cooling to room temperature. Solutions held at temperatures of 70° in the presence of excess iodine for many hours showed little if any further shift, which tends to rule out any possibility of explaining the results on the basis of oxidative degradation at temperatures as low as 40°. Solutions of amylose held at 80° for long periods of time and cooled to 25° prior to addition of iodine gave the high values of λ_{max}.

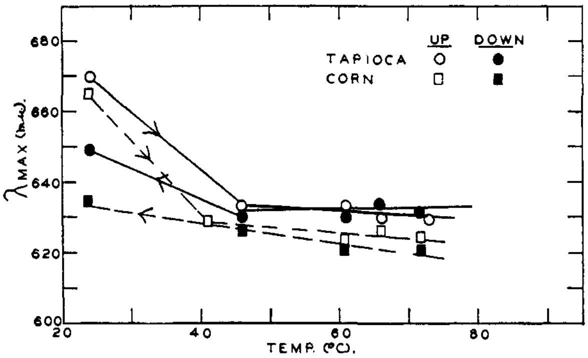

Fig. 1.

Other experiments led us to speculate on the possibility that the long wave lengths were a result of the presence of a special type of aggregate which we have shown to exist in amylose solutions even after dissolving in *N* KOH.[4] Therefore corn amylose was permitted to age in *N* KOH for two weeks, a treatment which has been found to result in an appreciable, though not complete, dissociation of these "native" aggregates.[4]

The λ_{max} shifted from 655 mμ, after 15 minutes and 3 hours standing, to 625 mμ after two weeks. Regeneration of the amylose by ethanol precipitation following this treatment did not affect the spectrum.

Another observation which suggests difference in the state of aggregation as the underlying cause of the spectral shift concerns the stability of the dispersions of the complex. Those showing the high λ_{max}. values invariably settled out of solution within three or four days. On the other hand, the heated complexes did not precipitate even after several weeks.

Within the framework of the theory of the amylose–iodine complex suggested by Rundle, Foster and Baldwin[5] these results suggest the possibility that in the form of the "native" aggregates there is an interaction between adjacent amylose helices which enhances the dipolar field.

We are indebted to Drs. Dexter French and R. E. Rundle for helpful discussions of these observations.

Experimental

The amylose samples were prepared by Dr. T. J. Schoch by pentasol crystallization followed by subfractionation with

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(1) Journal paper Number J-2043 of the Iowa Agricultural Experiment Station, Project 817. Supported in part by a grant from the Corn Industries Research Foundation. Taken from a thesis presented by Eugene F. Paschall in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Iowa State College, 1951.

(2) R. R. Baldwin, R. S. Bear and R. E. Rundle, THIS JOURNAL, **66**, 111 (1944).

(3) R. S. Higginbotham, *J. Textile Inst.*, **40**, T783 (1949).

(4) E. F. Paschall and J. F. Foster, *J. Polymer. Sci.*, in press.

(5) R. E. Rundle, J. F. Foster and R. R. Baldwin, THIS JOURNAL, **66**, 2116 (1944).