malachite green oxalate in the acidified ethanol. The absorption of the dye solutions at 6200 Å. followed Beer's law within the error of the determinations for solutions in which the dye concentration was in the range of 0.1 to 10 $\times$ 10^{-6} M. The molecular extinction coefficient, ϵ, at 6200 Å. for the dye in the acidified ethanol solutions (0.02 ml. of 0.3 M hydrochloric acid to 3.80 ml. of the leucocyanide in absolute ethanol solution) is 9.49 $\times$ 10^4 (an average value), where $\log_{10} (I_0/I) = \epsilon cl$. The time of the exposure was regulated so that the final dye concentration in most experiments was about 1 $\times$ 10^{-6} M. Exposure times of about 3 and 100 minutes were required for runs at light intensities providing 1 $\times$ 10^{13} and 3 $\times$ 10^{11} quanta/sec., respectively. Stirring was accomplished during photolysis by bubbling through the solution nitrogen gas saturated with ethanol. All of the experiments were carried out at room temperature (20–25°). The results are summarized in Table I.

Method II.—A ratio of quantum yields of uranyl oxalate and malachite green leucocyanide photolyses at 3130 Å. was determined at room temperature. An optical train providing pure, high intensity 3130 Å. radiation[8] followed the light source described in Method I. A collimated beam of light about 35 mm. in diameter and of constant intensity (±1%) was incident on the cell face. The photolysis of both solutions was effected in a quartz cell with 4.0-cm. path length. The cell contained 55 ml. of solution which was stirred magnetically during exposure. Concentrations of both solutions were such that essentially complete absorption of the light occurred. The uranyl oxalate solution (0.005 M in uranyl nitrate and 0.025 M in oxalic acid) was photolysed at full intensity. Filters with measured transmissions were placed in the light path to lower the intensity used in the leucocyanide photolyses, since the previous results indicated that absorption of light by product dye may be serious at high light intensities because of inadequate mixing. The concentration of leucocyanide solutions was 6.0 $\times$ 10^{-4} M. To 55.0 ml. of the alcoholic solution 0.29 ml. of 0.3 M hydrochloric acid was added before photolysis. Final dye concentration was about 1 $\times$ 10^{-6} M in each experiment. The data are presented in Table II.

TABLE II

COMPARISON OF QUANTUM YIELDS OF URANYL OXALATE AND MALACHITE GREEN LEUCOCYANIDE ACTINOMETERS AT 3130 Å. AND ROOM TEMPERATURE

Number of run	(1) Filter % *trans.*	(2) Dye mol. formed/sec. $\times$ 10^{-15}	(3) Calcd. dye mol. formed/sec. $\times$ 10^{-15} for full intensity	(4) ($H_2C_2O_4$ mol. decompd./sec.[a])/(dye mol. formed/sec.)
1	38.6	1.21	3.14	0.72
2	16.2	0.584	3.60	.63
3	8.81	.338	3.84	.59
4	3.32	.137	4.12	.55
5	1.99	.0820	4.12	.55

[a] Photolysis of uranyl oxalate solution at full intensity gave an average value of 2.27 $\times$ 10^{15} molecules of oxalic acid decomposed/sec.

The exposure times necessary in these experiments were about 10 hr. for the uranyl oxalate actinometer (10% oxalate decomposition) and from 19 to 371 sec. for the runs 1 and 5, respectively, in Table II. The data of column (2) of Table II are the measured rates of formation of dye in light decreased from full intensity by the filter of transmission given in column (1). The data of column (3) are calculated rates of dye formation for full intensity, (100) (rate in column (2))/(transmission in column (1)). Data of column (4) are the ratios of molecules of oxalic acid decomposed/sec. at full intensity, 2.27 $\times$ 10^{15}, to the calculated number of molecules of dye formed at full intensity, data of column (3). Absorption by dye product in the leucocyanide photolyses at low light intensities is unimportant with the stirring rate used; the data of these experiments, runs 4 and 5 of Table II, indicate a ratio of the quantum yield of the uranyl oxalate actinometer to that of the leucocyanide photolysis to be 0.55. The quantum yield of oxalate decomposition is 0.56 at 3130 Å.[1]; hence the quantum yield of malachite green leucocyanide photolysis at wave length 3130 Å. is estimated to be 1.02.

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[8] R. Hunt and W. J. Davis, THIS JOURNAL, **69**, 1415 (1947).

Some Observations on Neptunium(V) Compounds[1]

BY G. GIBSON,[2] D. M. GRUEN AND J. J. KATZ

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Although neptunium has a stable +5 oxidation state in solution,[3] the only Np(V) compounds which have hitherto been reported are Np(V) hydroxide[4] and mixtures of Np(V) oxychlorides of varying composition[5] obtained by rapid evaporation of HCl solutions.

The recent preparation of the oxide Np_3O_8[6] suggested a convenient starting material for the synthesis of Np(V) compounds, and it was of interest to attempt to determine the oxidation state of the neptunium in this compound. In one experiment 1 mg. of Np_3O_8 was dissolved in 5 cm.³ of 1 M $HClO_4$. Spectrophotometric examination of this solution with a Beckman Model D Spectrophotometer showed that the absorption was due only to Np(V) and Np(VI) ions. Approximately 1% of Np(IV) could have been detected by this means. This experiment does not rule out the existence of Np(IV) in Np_3O_8, however, since under the conditions of the dissolution Np(IV) would rapidly react with Np(VI) to form Np(V).[7] (Dissolution of U_3O_8 results in a mixture of U(IV) and U(VI) but here again the oxidation states in solution give no clue as to the situation in the solid since U(V) disproportionates into U(IV) and U(VI).)

Thermodynamic calculations for $NpCl_5$ give an estimated value of −246 ± 2 kg./mole for the heat of formation and a Cl_2 decomposition pressure of less than 10^{-3} atm. at 500°K.[8] Various attempts were made to prepare $NpCl_5$ from 2- to 4-mg. amounts of Np_3O_8: (a) Refluxing with 0.5 cm.³ of redistilled hexachloropropene at atmospheric pressure for 4 hours resulted in no reaction. (b) Bomb tube experiments with either hexachloropropene or carbon tetrachloride between 120–250° and 3–6 atm. also failed to yield a reaction. (c) Vapor phase chlorination with carbon tetrachloride carried out by passing CCl_4 vapors over the sample contained in a platinum boat in a hot tube furnace gave a reaction which resulted only in the formation of $NpCl_4$. A previous attempt to prepare $NpCl_5$ by reaction of $NpCl_4$ with Cl_2 at 500° was unsuccessful.[9] Np_3O_8 is thus quite different from U_3-

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[1] Reported in part at the Spring, 1950, Meeting of the American Chemical Society.

[2] On leave from Illinois Institute of Technology, Chicago, Ill.

[3] L. B. Magnusson, J. C. Hindman and T. J. La Chapelle, National Nuclear Energy Series, Vol. 14B, p. 1059, 1949.

[4] *Ibid.*, p. 1097.

[5] T. J. La Chapelle, UCRL-336, May, 1949.

[6] J. J. Katz and D. M. Gruen, THIS JOURNAL, **71**, 2106 (1949).

[7] R. Sjoblom and J. C. Hindman, *ibid.*, **73**, 1744 (1951).

[8] L. Brewer, L. Bromley, P. W. Gilles and N. L. Lofgren, MDDC-1417 (1947), corrected (1948).

[9] S. Fried and N. R. Davidson, National Nuclear Energy Series, Vol. 14B, p. 1072, 1949.

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).

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

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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).