substantial agreement with those computed from the velocity measurements, and similar to those of corresponding equilibria among the cobalt ammines. They are all, however, markedly displaced away from the aquo, as compared with the corresponding cobalt ammines.

5. The values for the concentrations found in the bromo bromide equilibrium, and these are our most trustworthy data of this kind, have been shown to agree reasonably well with the requirements of an empirical equation similar to that found for the cobalt ammines.

6. The conclusion has, therefore, been drawn that, while the exchange of the central cobalt atom for an iridium atom in the ammines studied has produced a general shift in the velocity and equilibria constants, it has produced no relative displacements.

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A METHOD FOR THE QUANTITATIVE SEPARATION OF BERYLLIUM AND URANIUM

BY PAUL H. M.-P. BRINTON AND REUBEN B. ELLESTAD

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The separation of beryllium from uranium is not often required in analyses, as the 2 elements seldom occur together. In a few minerals,[1] however, both elements occur, and in the course of an investigation by one of us it became necessary to find an accurate method for the determination of beryllium and uranium in mixtures of the two. Search through the literature showed that the problem had received but little attention.

In the exhaustive paper of Kern[2] on the separation of uranium from a great number of elements no mention is made of beryllium; nor is this element considered in Brearley's book.[3] Schoeller and Powell[4] describe a method for the separation of uranium from iron, titanium, cobalt, nickel, manganese, zinc, beryllium and the alkaline earth elements, by pouring the boiling solution containing these elements into hot sodium carbonate solution, boiling, diluting, and again boiling. However satisfactory this method may be for the separation of uranium from the other elements, we found it inaccurate for the separation from beryllium, as the precipitation of beryllium was incomplete, and the basic carbonate was contaminated by uranium. Approximate results may sometimes be obtained by this compensation of errors, but the method cannot be regarded as reliable.

Wunder and Wenger[5] proposed the precipitation of uranium as $UO_4.2H_2O$ by hydrogen peroxide as a method of separating uranium from beryllium. With pure solutions and using hydrogen peroxide prepared with elaborate precautions to eliminate impurities,

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[1] Duparc, Sabot and Wunder, *Bull. soc. franç. mineral.*, **36**, 5 (1913).

[2] Kern, THIS JOURNAL, **23**, 685 (1901).

[3] Brearley, "The Analytical Chemistry of Uranium," Longmans, **1903**.

[4] Schoeller and Powell, "The Analysis of the Minerals and Ores of the Rarer Elements," Griffin and Co., **1919**, p. 185.

[5] Wunder and Wenger, *Z. anal. Chem.*, **53**, 371 (1914).

accurate results may perhaps be obtained, but the formation of soluble peruranates in the presence of alkali and alkaline earth salts renders the method of little value for practical purposes. Mazzucchelli[6] has shown that many compounds interfere with the completeness of this precipitation. Schwarz[7] also criticizes the hydrogen peroxide precipitation as entirely unsuited to the determination of uranium.

Hydroxylamine has been used in the separation of uranium from some elements by Jannasch,[8] and the precipitation of beryllium hydroxide with ammonia in presence of hydroxylamine hydrochloride offered hope of a satisfactory separation from uranium, but we found it impossible to prevent the retention of considerable amounts of uranium by the bulky, slimy beryllium hydroxide precipitate, which was washed with great difficulty.

The precipitate of basic beryllium carbonate obtained by boiling the ammonium carbonate solution of beryllium and uranium filtered easily and was easily washed, but a little uranium was precipitated with the beryllium, and the retention of uranium became very appreciable when the boiling of the carbonate solution was continued sufficiently long to give a nearly quantitative precipitation of beryllium.

A satisfactory method has now been developed by using both ammonium carbonate and hydroxylamine hydrochloride, the last traces of beryllium being removed from the filtrate by precipitation with ammonium hydroxide in presence of hydroxylamine hydrochloride. From this small hydroxide precipitate the uranium can be completely washed.

Before uranium can be precipitated from the filtrate it is necessary to destroy the hydroxylamine hydrochloride. Jannasch accomplishes this in his methods by evaporation and ignition, but we have found it fully as accurate and much more rapid to remove the hydroxylamine by direct oxidation in the solution. Hydrogen peroxide proved a satisfactory oxidizing agent, but it was later replaced by potassium bromate on account of the more rapid action of the latter, which has the further advantage of doing away with the long boiling necessary to expel the excess of hydrogen peroxide. Unless this expulsion is complete the precipitation of ammonium uranate will be hindered by the formation of soluble peruranates.

Experimental Part

A standard solution of beryllium was prepared from the purest beryllium hydroxide of commerce. The freshly reprecipitated hydroxide was dissolved in a strong solution of sodium bicarbonate, diluted, and precipitated by steam. The basic carbonate so obtained was freed from occluded sodium salts by solution in hydrochloric acid and precipitation by redistilled ammonia. The hydroxide thus obtained was dissolved in a slight excess of hydrochloric acid, and this solution was standardized by precipitation with ammonium hydroxide and ignition to oxide. The details given by Bleyer and Boshart[9] were followed in all precipitations of beryllium hydroxide.

For the preparation of the standard uranium solution, "chemically pure" uranyl nitrate was dissolved in water, and the slight trace of iron found to be present was re-

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[6] Mazzucchelli, *Atti accad. Lincei,* [5] **15,** II, 429, 494 (1906).

[7] Schwarz, *Helvetica Chim. Acta,* **3,** 330 (1920).

[8] Jannasch, "Praktischer Leitfaden der Gewichtsanalyse," Veit and Co., Leipzig, **1904,** pp. 161–2.

[9] Bleyer and Boshart, *Z. anal. Chem.,* **51,** 748 (1912).

moved by precipitation with ammonium carbonate. From this solution ammonium uranate was precipitated after acidification and removal of carbon dioxide by boiling the solution. From this precipitate a solution of uranyl chloride was prepared, the bulk of the ammonium chloride being separated by its slight solubility in absolute alcohol. The uranyl solution was standardized by precipitation with ammonium hydroxide in presence of ammonium chloride, followed by gentle ignition in an open porcelain crucible, and weighing as U_3O_8.

In the first five analyses tabulated below, the hydroxylamine was oxidized by hydrogen peroxide; in the last four by potassium bromate.

The Proposed Method

To the hydrochloric acid solution of the beryllium and uranium about 5 g. of ammonium chloride (unless sufficient ammonium salt is already present) and 5 g. of hydroxylamine hydrochloride are added. A concentrated solution of ammonium carbonate is now added until the precipitate which at first forms has entirely redissolved. The solution is heated to boiling, and the boiling is continued for from $^1/_2$ to 1 minute after the appearance of the heavy white precipitate of basic carbonate. (Excessively long boiling here is to be avoided.) The precipitate is filtered without delay and thoroughly washed with cold water. This basic carbonate precipitate is free from uranium. It is set aside to be ignited with the small amount of beryllium hydroxide which is to be separated from the filtrate.

The filtrate from the basic carbonate is acidified with hydrochloric acid and boiled to remove the carbon dioxide. After the addition of 1 g. more of hydroxylamine, ammonia is added in slight excess to the cold solution, and the small precipitate of beryllium hydroxide is filtered and washed with 2% ammonium nitrate solution to which have been added a few crystals of hydroxylamine hydrochloride and enough ammonia to insure alkalinity. If this precipitate has any tinge of yellow it should be dissolved in hydrochloric acid and reprecipitated by ammonia in the presence of 1 g. of hydroxylamine hydrochloride. The combined beryllium precipitates are ignited with their papers in a platinum crucible, finally over the blast, and weighed as BeO.

For the determination of uranium the combined filtrate is slightly acidified with hydrochloric acid, and the hydroxylamine is oxidized by one of the following methods.

1. An excess of hydrogen peroxide (75–100 cc. of 3% solution) is added and the solution is boiled until the evolution of oxygen ceases, and the solution has been con-

TABLE I

ANALYTICAL DATA

BeO taken	BeO found	U_3O_8 taken	U_3O_8
0.1101	0.1104	0.3070	0.3066
0.1037	0.1038	0.1869	0.1866
0.1037	0.1038	0.1869	0.1867
0.1037	0.1039	0.1869	0.1865
0.2074	0.2070	0.1869	0.1865
0.1037	0.1034	0.3738	....
0.1037	0.1037	0.3738	....
0.2074	0.2076	0.3738	....
0.1037	0.1037	0.1869	....
0.1037	0.1034	0.1869	....
0.1037	0.1038	0.1869	0.1874
0.1037	0.1036	0.1869	0.1861
0.1037	0.1035	0.1869	0.1875
0.1037	0.1040	0.1869	0.1862

centrated to about $^1/_3$ its volume. Any precipitate formed is dissolved by the addition of more hydrochloric acid.

2. Solid sodium or potassium bromate is added to the cold solution in small portions with stirring (under a watch glass to prevent loss by spattering) until the liquid assumes an intense color of bromine.

The solution obtained in 1 or 2 is heated nearly to boiling, and a slight excess of ammonium hydroxide is added gradually with constant stirring. After settling, the ammonium uranate is filtered, and washed with 2% ammonium nitrate solution which contains a little ammonia but, of course, no hydroxylamine hydrochloride. The precipitate is ignited at dull red heat in an uncovered porcelain crucible to constant weight and weighed as U_3O_8.

The figures in the preceding table attest the accuracy of the method developed.

Summary

The scanty literature dealing with the separation of beryllium from uranium has been critically reviewed, and a method for this separation has been developed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE REACTION BETWEEN SILVER PERCHLORATE AND IODINE. CHLORINE TETRA-OXIDE

BY M. GOMBERG

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Silver perchlorate is unique in that it is soluble in a variety of organic solvents[1] and may, therefore, undergo reactions which would not be feasible under ordinary conditions, such as in the presence of water. The reaction indicated in the title to this paper is one of this nature, and the investigation was undertaken in order to ascertain whether the compound radical $(ClO_4)_x$ could be prepared.

$$2AgClO_4 + I_2 = 2AgI + 2(ClO_4) \longrightarrow (ClO_4)_x \qquad (1)$$

Such a reaction would be analogous to that which Söderbäck recently employed with such eminent success in obtaining free thiocyanogen[2] from metal thiocyanates; it is also, in principle, a variation of the general method used in preparing triarylmethyl radicals, and in other syntheses.

$$R_3C.Cl + Ag = R_3C + AgCl \qquad (2)$$

Would the prospective new oxide of chlorine prove more stable, or less so, than are the 3 known oxides of chlorine, namely, the Cl_2O of Balard, the ClO_2 of Davy, and the Cl_2O_7 of Michael and Conn?[3] Would it remain monomolecular and as a free radical, isomeric with the ClO_4' anion, or

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[1] (a) Gomberg, *Ber.*, **40,** 1867 (1907); (b) *Ann.* **370,** 160 (1909). (c) Hill, THIS JOURNAL, **43,** 254 (1921).

[2] Söderbäck, *Ann.*, **419,** 219 (1919).

[3] (a) Michael and Conn, *Am. Chem. J.*, **23,** 444 (1900); (b) Meyer and Kessler, *Ber.*, **54,** 566 (1921).