VOL. XXIII. [OCTOBER, 1901.] No. 10.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 31.]

THE QUANTITATIVE SEPARATION AND DETERMINATION OF URANIUM.

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Received August 1, 1901.

THE work described in this article was undertaken with the object of finding out the most accurate and satisfactory method for the technical estimation of uranium.

The usual quantitative methods for the estimation of uranium were first repeated, then new methods for its separation and estimation were tried on solutions containing known amounts of pure salts, and the best conditions for both separation and determination were carefully worked out.

The research was drawn to a close by making a number of assays of uraninite, in which the results obtained from the work on pure salt solutions were applied. These assays tested the methods on the most important ore of uranium, and thus collected the data in the form of analytical methods.

HISTORICAL INTRODUCTION.

Uranium was discovered by M. H. Klaproth, who separated what he thought to be a new element from pitchblende—also known as uraninite—the principal ore of uranium. This was in

1789, and what he obtained was not the element, but its lower oxide, UO_2. He named the element uranium in remembrance of the planet Uranus, which Herschel discovered in 1781.

From 1789 to 1795 much work was done on the investigation of uranium, but nothing new was discovered till 1840, when E. Péligot succeeded in isolating metallic uranium in powder form by heating uranous chloride (UCl_4) with metallic sodium.[1] He made a great number of experiments, the results of which proved that what was previously thought to be the element uranium was its lower oxide (UO_2), which plays the part of a base, a true inorganic radical. This discovery seems to have been an impetus to the further study of this element, as we find records in the different journals, of the years that follow, of several of the eminent chemists of the day investigating uranium and trying to find new methods for its estimation.

Clemens Zimmerman was the next chemist of note to investigate uranium. He studied methods for isolating the metal, and methods for its estimation and separation from other elements, and prepared many of its salts, studying their chemical and physical properties.[2] This work covered a number of years, from 1877 to 1884. So 1877 marks the second revival of interest in the element uranium. The first revival was in 1840, when Péligot isolated metallic uranium. The third revival is the present time, brought on by the great industrial demand for uranium ores.

In 1854 the only use to which uranium was put was for making a very fine black for porcelain painting,[3] and from 1850 to 1866 it was much used in photography. At present its uses are for the preparation of acetate and nitrate salts (which are used as chemical reagents), for the manufacture of a certain highly prized canary-yellow colored glass, for the preparation of a pigment used for porcelain painting, and lastly for making a steel which has properties superior to nickel steel.[4]

PART I.—SEPARATION OF URANIUM.

SEPARATION OF URANIUM FROM MEMBERS OF THE FIFTH AND SIXTH GROUPS.

The only point to be determined for the well-known separation

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[1] *Ann. Chem.* (Liebig), **41**, 141 (1842).

[2] *Ibid.*, Vols. **119**, **204**, **213** and **214**.

[3] Whitney's "Mineral Wealth of the United States."

[4] *Moniteur Industrial*, **27**, 44 (1900).

by hydrogen sulphide was the exact acidity of the solution. This was done by mixing standardized solutions of lead, copper, and uranium in different proportions, and precipitating the lead and copper by hydrogen sulphide, under varying conditions of acidity and temperature. The experiments were all conducted quantitatively. These showed that a perfect separation was effected when 1 cc. of concentrated nitric acid (sp. gr. 1.42) was present to every 50 cc. of solution, and the solution saturated with hydrogen sulphide in the cold.

With hydrochloric acid, 1 cc. of concentrated acid (sp. gr. 1.20) to 50 cc. of solution gave excellent results. This amount must not be exceeded, as when 2.5 per cent. of concentrated acid was present the precipitation of the lead was incomplete. Less acid must be present if the precipitation is done from a hot solution, but this is not recommended.

As 5 cc. of concentrated acid in a bulk of 250 cc. solution gave a perfect separation of uranium from the metals of the fifth group, whose sulphides are the most soluble—lead and cadmium—and also from copper, these conditions must also be suitable for the other members of this group. Lead requires the least amount of free acid to retain it in solution ; then follow in order of succession, cadmium, mercury, bismuth, copper, and silver.[1]

SEPARATION OF VANADIUM FROM URANIUM.

Vanadium is one of the common associates of uranium, and especially so in the minerals which occur in Colorado. Carnotite, the most common of these minerals, has of late reached commercial importance.

The separation of vanadium from uranium presents very little difficulty unless phosphoric acid is present, in which case the separation is troublesome. Friedel and Cumenge[2] separated vanadium from uranium by evaporating the solution to dryness with nitric acid. The uranium was then extracted from the dry mass with a warm dilute solution of ammonium nitrate. For this separation, no phosphoric acid should be present as it renders the uranium oxide, with which it is combined, insoluble in the dilute ammonium nitrate solution.

The method for the separation of vanadium from iron by means

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[1] Fresenius' "Quantitative Chemical Analysis," p. 456, 1900.

[2] *Am. J. Sci.*, **10**, 135 (1900).

of mercuric oxide and mercurous nitrate[1] has been used with success by A. C. Langmuir,[2] for the separation of vanadium from uranium in the analysis of carnotite. The finely divided mineral was dissolved in the smallest possible amount of nitric acid, and the silica filtered off. The solution was diluted to about 500 cc. and the vanadium precipitated by means of mercurous nitrate as follows: The nitric acid solution was nearly neutralized with pure yellow mercuric oxide, and the vanadium then precipitated by the addition of a strong solution of mercurous nitrate. The solution was brought to boiling, after which it was filtered. (If chromium, tungsten, or molybdenum are present they go down as mercurous salts with the mercurous vanadate.) The precipitate was washed with a warm dilute solution of mercurous nitrate, after which it was dried, ignited, and weighed as V_2O_5. The excess of mercury in the filtrate was removed by means of hydrogen sulphide gas. After expelling the hydrogen sulphide from the filtrate by slow boiling, the uranium was determined by the ordinary method.

O. P. Fritchie's Method[3] is said to be particularly adapted to the mineral carnotite. The finely divided mineral was decomposed at boiling temperature with 10 cc. nitric acid, taken up with 10 cc. water, neutralized with a saturated solution of sodium carbonate, added 5 cc. in excess, and 20 cc. of a 20 per cent. sodium hydroxide solution; it was boiled slowly for half an hour, and the precipitate allowed to settle. The vanadium, uranium, and iron were all precipitated by the sodium carbonate, but on adding a moderate excess and a large excess of sodium hydroxide, the vanadium was dissolved while the uranium and iron remained insoluble. Uranium is easily precipitated by sodium carbonate and sodium hydroxide in the presence of an iron salt. The precipitate was washed with a solution of sodium hydroxide. The uranium and iron were then separated by the ordinary method, and each determined volumetrically by means of standard permanganate, after reducing their sulphate solutions at boiling temperature with metallic aluminum.

SEPARATION OF URANIUM FROM MEMBERS OF THE THIRD AND FOURTH GROUPS, PARTICULARLY IRON.

The methods ordinarily used for separating uranium from the

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[1] Blair's "Chemical Analysis of Iron," 3rd edition, p. 200.

[2] Paper read before N. Y. Section of American Chemical Society, at March meeting.

[3] *Eng. Min. J.*, Nov. 10, 1900; *Chem. News*, **82**, 258 (1900).

other members of the fourth group and those of the third group depends on the solubility of uranium hydroxide and sulphide in an excess of a strong solution of an alkali carbonate. The hydroxides and sulphides of the other members of these two groups are, with the exception of iron and nickel, insoluble in alkali carbonate solutions. The hydroxides of these two metals are only slightly soluble in strong alkali carbonate solutions ; in cold dilute solutions they are almost insoluble.

The element which gives the most trouble in effecting a separation from uranium is iron. A great number of methods have been proposed, of which the best known are Pisani's ammonium carbonate[1] and Patera's sodium carbonate[2] methods, neither of which are very satisfactory. Rose used ammonium carbonate followed by ammonium sulphide,[3] thus precipitating the iron. This latter method is far from satisfactory, especially if the uranium is small in amount. Rheineck's basic acetate method[4] has been used with success when the uranium was present in considerable quantity.

Ether Separation.—The use of ether to effect a separation of iron from uranium was suggested by A. C. Langmuir in a recent article[5] on the analysis of nickel ores. He found that iron could be separated from copper, manganese, aluminum, cobalt, nickel, and zinc, by taking advantage of the solubility of ferric chloride in ether free from alcohol. The chlorides of the other metals are not taken up by the ether but remain in the aqueous hydrochloric acid solution. When iron is in the ferrous condition, Rothe[6] found that it was not taken into solution by the ether, but remained with the other metals in the aqueous solution. So it is necessary to oxidize the iron before attempting to make the separation.

EXPERIMENTAL.

The separation of iron from uranium by means of ether was tried, and, as the result, a clean and rather rapid separation has been worked out. This separation depends on the complete extraction of ferric chloride (in an aqueous hydrochloric acid solu-

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[1] *Compt. rend.*, **52**, 106.

[2] *Ztschr. anal. Chem.*, **5**, 228 (1866).

[3] *Ibid.*, 1, 410 (1862).

[4] *Chem. News*, **24**, 233 (1871).

[5] This Journal, **22**, 102 (1900).

[6] *Chem. News*, **66**, 182.

tion) by ether which is free from alcohol, and the retention of uranyl chloride in the aqueous hydrochloric acid solution.

Before undertaking the separation of iron from uranium by means of ether, two solutions containing uranium alone were treated three times with ether, as described in the following experiments, in order to test the solubility of uranyl chloride in ether. These experiments showed uranyl chloride to be entirely insoluble in ethyl ether which is free from alcohol.

The experiments which follow were made with solutions containing both uranium and iron. Measured amounts of a standard uranium nitrate solution and of a standard ferric chloride solution were placed in a small beaker and the solution twice evaporated to dryness with 10 cc. hydrochloric acid (sp. gr. 1.20). The dry mass was taken up with about 10 cc. dilute hydrochloric acid (sp. gr. 1.10) and heated till all salts were dissolved, but not long enough to lose any of the acid by volatilization. After the solution had cooled, it was poured into a 250 cc. separatory funnel and the beaker rinsed out with dilute hydrochloric acid (sp. gr. 1.10). The rinsings were added to the separatory funnel till the volume of the solution had reached 50 cc. Fifty cc. of ether, free from alcohol and previously shaken up with hydrochloric acid (sp. gr. 1.10), were added and agitated for about ten minutes, occasionally relieving the pressure in the funnel. After thoroughly shaking together, the two solutions were allowed to separate and the lower aqueous hydrochloric acid solution of uranyl chloride, containing some iron, was drawn off catching it in another separatory funnel. The ether solution of ferric chloride was washed twice with 10 cc. dilute hydrochloric acid (sp. gr. 1.10) and the washings, after allowing to separate, were run into the funnel containing the uranium.

On determining the amount of iron extracted from the hydrochloric acid solution by the ether, it was found that all the iron was not separated from the uranium by one extraction, about 10.5 per cent. of the amount taken remaining in the aqueous solution with the uranium.

On finding that all of the iron was not separated from the uranium by one "ether extraction," two extractions were made on a solution containing 0.1155 gram uranium and 0.0901 gram of iron. The first extraction was made in the same manner as outlined above, and the second as follows: The solution in the lower separatory funnel was again shaken for about seven minutes with 50 cc. ether. After thoroughly shaking together, the two solutions were allowed to separate, and the lower aqueous hydrochloric acid layer run into a second funnel. The ether solution was twice washed with 10 cc. hydrochloric acid (sp. gr. 1.10), and the washings caught in the second funnel. The ether solution was run into a beaker which contained the ether from the first extraction. After distilling off the ether, the iron was determined by titration with 0.01 normal potassium permanganate solution. About 3.5 per cent. of the iron taken remained in the aqueous solution with the uranium.

The next five separations of iron from uranium were made by using hydrochloric acid of about 1.10 specific gravity (1 part acid (sp. gr. 1.20) and 1 part distilled water). In all cases three "ether extractions" were made, whereby practically complete separations of iron from uranium were obtained. The solutions contained from 0.0901 to 0.1802 gram iron and from 0.0962 to 0.2310 gram uranium. The amount of metal in their respective solutions was determined volumetrically, and did not vary more than 0.3 per cent. of the theoretical amounts taken.

The next five experiments were made by varying the strength of the hydrochloric acid used. The procedure was the same as above, making three extractions with ether. For the first three solutions, hydrochloric acid of about 1.133 specific gravity (2 parts acid (sp. gr. 1.20) and 1 part distilled water) was used ; and for the last two solutions hydrochloric acid of about 1.066 specific gravity (1 part acid (sp. gr. 1.20), and 2 parts distilled water). The separation in both cases, of iron from uranium, was incomplete. When hydrochloric acid of 1.133 specific gravity was used, the amount of iron remaining with the uranium, after three "ether extractions," was about 6 per cent. of the amount taken. With hydrochloric acid of 1.066 specific gravity, the amount of iron which remained with the uranium after three "ether extractions," was about 25 per cent. of the amount taken.

The most complete separations of iron from uranium by means of ether are evidently obtained by using hydrochloric acid of 1.10 specific gravity. This is the same strength as was found by Speller[1] to be the best for the separation of iron from copper, manganese, aluminum, chromium, cobalt, and nickel.

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[1] *Chem. News*, **83**, 124 (1901).

When rather concentrated hydrochloric acid (sp. gr. 1.133) was used for the solution of the chlorides of iron and uranium, it was noticed that on diluting the aqueous solution, after agitating with ether, quite an amount of ether separated. This seems to explain the reason why iron is not readily separated from uranium by means of ether when strong hydrochloric acid is used to bring their chlorides into solution, the iron being retained by the large quantity of ether which remains with the acid solution.

The results obtained are shown in the following table:

SEPARATION OF IRON FROM URANIUM BY EXTRACTION WITH ETHER.

Experiment No.	Specific gravity of HCl used.	Volume of solution at first extraction. cc.	Number of ether extractions made.	Ether used for			Theoretical am't of uranium taken.	Amount of uranium determined in aqueous HCl solution.	Theoretical am't of iron taken.	Amount of iron determined in ethereal extract.
				First extraction. cc.	Second extraction. cc.	Third extraction. cc.				
1	1.10	40	3	50	40	40	0.09625	0.09588	......	......
2	1.133	40	3	50	40	40	0.09625	0.09643	......	......
3	1.10	50	1	50	..	..	0.11550	0.13171	0.09010	0.08415
4	1.10	50	1	50	..	..	0.11550	0.14700	0.09010	0.07700
5	1.10	50	2	50	50	..	0.11550	0.12466	0.09010	0.08690
6	1.10	40	3	50	50	50	0.09625	0.09643	0.09010	0.08993
7	1.10	25	3	75	50	35	0.11550	0.11525	0.09010	0.09020
8	1.10	25	3	75	50	35	0.09625	0.09643	0.18021	0.18029
9	1.10	25	3	75	50	35	0.19250	0.19228	0.09010	0.08993
10	1.10	25	3	75	50	35	0.23099	0.23069	0.09010	0.09037
11	1.133	40	3	50	50	50	0.09625	0.10584	0.09010	0.08663
12	1.133	25	3	75	50	35	0.11550	0.12068	0.09010	0.08580
13	1.133	25	3	75	50	35	0.19250	0.20815	0.09010	0.08250
14	1.066	25	3	75	50	35	0.09625	0.20933	0.18022	0.12705
15	1.066	25	3	75	50	35	0.23099	0.27224	0.09010	0.07150

SEPARATION OF URANIUM FROM COBALT, NICKEL, AND ZINC.

Wolcott Gibbs separated uranium from cobalt, nickel, and zinc by means of hydrogen sulphide. He states that this method is much simpler than those ordinarily used, and also gave excellent results.[1] To the neutral or nearly neutral solution of the chlorides of uranium, cobalt, nickel, and zinc, add sodium acetate in excess and a few drops of acetic acid. The solution is boiled, and a rapid current of hydrogen sulphide passed through the boiling solution for half an hour. Every trace of the cobalt, nickel, and zinc is precipitated as sulphides while the whole of the uranium, and

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[1] Silliman's *Am. J. Sci. and Art*, [2], **39**, 62 (1865).

any manganese, if present, remains in the boiling solution. The precipitate is thrown on a ribbed filter and quickly washed with cold hydrogen sulphide water. The precipitate is easily washed, and though the sulphides of cobalt and nickel formed in this manner are more easily oxidized than when precipitated by sodium sulphide from a boiling solution, they will be found to present no difficulty as regards oxidation upon the filter. If manganese is in the filtrate it may be determined by boiling with hydrochloric acid and precipitating it in the usual manner with sodium carbonate. The uranium in the filtrate is determined by the ordinary method.

Rose separated uranium from cobalt, nickel, and zinc by means of barium carbonate.[1] The precipitation of the uranium is complete from uranic solutions which contain a small amount of free acid, either hydrochloric or nitric acid. Barium carbonate, which is diffused in water, is added in excess and the solution allowed to stand twenty-four hours. The presence of ammonium chloride is necessary in order to keep the cobalt, nickel, and zinc in solution. The uranium is separated from the excess of barium carbonate by dissolving the precipitate in hydrochloric acid, and adding dilute sulphuric acid. The uranium in the filtrate is precipitated with ammonia, and weighed as oxide. C. Rammelsberg[2] employed this method to separate uranium from cobalt and nickel and obtained excellent results; but when manganese and zinc are present it cannot be advantageously employed.

SEPARATION OF URANIUM FROM THE ALKALI AND THE ALKALINE EARTH METALS.

If a solution containing uranium, alkalies, and alkaline earths is precipitated with ammonia, a portion of the alkalies and alkaline earths is carried down by the ammonium uranate,[3] thus preventing a complete separation.

Hillebrand[4] found that it is possible to completely separate uranium from the alkalies and alkaline earths by several precipitations with ammonia. In order to verify this statement, solutions containing a measured amount of standard uranium nitrate solution and sodium and potassium salts were precipitated by

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[1] Rose's "Chimie Analytique—Analyse Quantitative," p. 248, (1862.)

[2] *Chem. Centrbl.* (1884), p. 806.

[3] Fresenius' "Quantitative Chemical Analysis," 6th edition, p. 533.

[4] *Am. J. Sci.*, 10, 136 (1900).

means of a slight excess of ammonia, and the solutions brought to boiling. The precipitates were washed with a warm 2 per cent. solution of ammonium chloride, after which they were dissolved from the filters with warm hydrochloric acid (sp. gr. 1.10) and caught in beakers. The precipitation of the uranium by ammonia, in the presence of ammonium chloride and from hot solutions, was repeated twice, and it was found that after three precipitations the ammonium uranate was free from alkalies.

Magnesium may be separated from uranium by means of ammonium sulphide in the presence of ammonium chloride[1] and also by ammonia in the presence of an excess of ammonium chloride. The latter method is the one ordinarily used.[2] To the solution containing uranium and magnesium, add ammonium chloride and boil. When the solution becomes clear, add a slight excess of ammonia to the hot solution and continue boiling for a few minutes. Filter while hot and wash the precipitate with hot water containing ammonium chloride. Dry, ignite, and weigh the uranium as oxide.

The separation of uranium from barium, strontium, and calcium is usually done by means of sulphuric acid in the presence of alcohol.[3] The metals should be in solution as chlorides, having present the smallest possible amount of free hydrochloric acid. To the moderately dilute solution, add sulphuric acid, then alcohol, which precipitates the barium, strontium, and calcium, in the form of sulphates. The uranium in the filtrate is precipitated with ammonia and weighed as oxide.

The separation of uranium from barium, strontium, and calcium, may be brought about by precipitating the uranium with freshly prepared ammonium sulphide (free from carbon dioxide).[4]

In 1885, G. Alibigoff studied the action of mercuric oxide on uranium solutions and found a means of separating uranium from the alkalies and alkaline earths.[5] He showed that neither ammonium sulphide, nor ammonium carbonate followed by ammonium oxalate, can be successfully employed for separating uranium from calcium. The latter method is, however, preferable to the first. He states that a com-

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[1] *Ztschr. anal. Chem.*, **4**, 384 (1865).

[2] Fremy's "Encyclopédie Chimique, p. 86, (1884).

[3] *Ibid*, p. 86, (1884).

[4] Fresenius' "Quantitative Chemical Analysis," p. 534.

[5] *Ann. Chem.* (Liebig), **233**, 147 (1886).

plete separation of uranium from calcium, strontium, magnesium and the alkalies can be effected by the use of mercuric oxide ; it does not, however, afford a separation of uranium from barium. The precipitation is made by adding a slight excess of freshly prepared mercuric oxide (in the form of an emulsion) to the boiling solution which contains ammonium chloride or nitrate. The boiling is continued for a few minutes longer and then rapidly cooled by placing the vessel into cold water. Wash the precipitate by decantation with a cold dilute solution of ammonium chloride. It is placed along with the filter in a platinum crucible, cautiously heated at first, after which the temperature is gradually raised and finally ignited over a blast-lamp. The residue consists of pure U_3O_8. The separation of uranium from the alkali metals by this method does not give any undue trouble, but when calcium and strontium are present they are rather hard to rid from the uranium precipitate. This difficulty is overcome by boiling several times, during washing by decantation, with a solution of ammonium chloride and each time rapidly cooling the solution before pouring off the supernatant liquid. The calcium and strontium in the filtrate are determined by the ordinary methods after the removal of the mercury by hydrogen sulphide.

SEPARATION OF URANIUM FROM THE ALKALI AND ALKALINE EARTH METALS BY ELECTROLYSIS OF ACETATE SOLUTION.

Uranium is a very difficult metal to separate from the alkalies and alkaline earths by gravimetric methods ; but by electrolyzing an acetate solution of these elements a perfect separation can be effected[1]. It can be readily separated from sodium, potassium, rubidium, cesium, magnesium, calcium, strontium, and barium. This method was used by E. F. Smith for separating uranium from the alkalies, the alkaline earths, and the rare earths in the analysis of certain rare minerals.

A very peculiar property of uranium is that it is not deposited as metal on the cathode, but as the hydrated protosesquioxide. Molybdenum is the only other metal known which, like uranium, is deposited as oxide on the cathode.

EXPERIMENTAL.

This research was made in order to fully confirm the reliability of the electrolytic method for the estimation of uranium and its

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[1] *Am. Chem. J.*, **1**, 329 (1879) ; this Journal, **20**, 279 (1898).

separation from the alkalies, and also to find the conditions which are best suited for rather dilute solutions.

The cathodes for the first six experiments, when a current of $N.D_{140} = 0.6$ to 0.7 ampere was employed, were two platinum dishes of about 250 cc. capacity. For experiments Nos. 7 to 10, the cathode was a platinum dish of about 150 cc. capacity.

The anodes were made of heavy platinum wire. One was made of 30 cm. of No. 12 gauge platinum wire wound into a flat spiral of 4 cm. diameter. The other anode was made of 37 cm. of No. 14 gauge platinum wire wound into a flat spiral of 4 cm. diameter. The results obtained by the use of either anode were the same.

Storage cells were the source of current.

For the electrolysis, a measured amount of standard uranium nitrate solution was run into a cleaned and weighed platinum dish. A known amount of sodium acetate and of acetic acid was added, and the solution diluted to a definite volume. After heating to about 60° C., the current was started and the electrolyzation continued till the solution was clear and colorless, and no uranium was indicated when about 2 cc. of the electrolyte was removed and tested with potassium ferrocyanide in the presence of hydrochloric acid. As soon as all the uranium was precipitated, the current was interrupted and the electrolyte was emptied into a beaker. The black deposit was several times washed with warm distilled water. The electrolyte and washings were then poured through a fluted filter, so as to prevent the loss of any particles of the deposit which are apt to be removed during washing. The filter was washed with warm water, dried over a Bunsen flame, ignited, and added to the dish. The dish was ignited at "redness" for about fifteen minutes, after which it was allowed to cool in a desiccator. The dish was weighed and the final weight taken when it had remained on the balance pan for about five minutes, thus allowing its weight to become constant.

The deposit consisted principally of black hydrated protosesquioxide of uranium ($U_3O_4.3H_2O$), which on ignition changed to U_3O_8.

At the beginning of the electrolysis the deposit formed as yellow uranic hydroxide, but as the deposition continued it changed to the black hydrated protosesquioxide.

The results obtained[1] are :

Experiment No.	Grams of sodium acetate.	Amount of glacial acetic acid. cc.	Dilution. cc.	Current. Current. $N.D_{140}$ = ampere.	Current. Volts.	Temperature. °C.	Time in hours.	Theoretical am't of U_3O_8 taken.	Weight of deposited U_3O_8.
1	2	0.7 Drops.	200	0.55	5	68–70	8	0.1098	0.1095
2	2	12 cc.	200	0.60	5	70	7	0.1098	0.1097
3	2	0.5	200	0.60–0.65	8–6	68–75	5	0.1098	0.1100
4	2	0.5	200	0.65	8–7.3	65–67	5½	0.1318	0.1319
5	2	0.5	200	0.65	7.5–6	68–70	5	0.1318	0.1318
6	2	0.5	200	0.60–0.65	8–5.5	69–71	5½	0.1318	0.1320

These results were obtained by electrolyzing a solution of 200 cc. volume with a current of $N.D_{140} = 0.55$ to 0.65 ampere.

The results obtained, when a solution of 125 cc. was electrolyzed with a current of $N.D_{100} = 0.70$ to 1.50 ampere, are as follows :

Experiment No.	Grams of sodium acetate.	Amount of 50 per cent. acetic acid. cc.	Dilution. cc.	Current. $N.D_{100}$ = amperes.	Temperature. °C.	Time in hours.	Theoretical am't of U_3O_8 taken.	Weight of deposited U_3O_8.
7	1.0	2	125	0.70–0.85	80–85	6	0.1361	0.1363
8	2.0	2	125	0.70–0.93	70–80	6½	0.1814	0.1816
9	2.0	2	125	0.95–1.50	70–75	7½	0.2268	0.2270
10	0.3	1	125	0.90–1.30	73–80	8	0.2268	0.2260

According to the above results, the best conditions for the electrolytic precipitation of uranium from a rather dilute acetate solution are as follows : To the solution containing about 0.10 gram of U_3O_8 add from 1 to 2 grams of sodium acetate (if alkalies are present, no sodium acetate is needed) and from 1 to 2 cc. of 50 per cent. acetic acid, or if glacial acetic acid is used only half the quantity is needed. Dilute to from 125 to 200 cc., heat to about 65° C. and electrolyze with a current of $N.D_{140} = 0.60$ to 0.70 ampere and 6 to 8 volts. The uranium is completely precipitated in from five to seven hours.

With solutions containing about 0.15 gram of U_3O_8 more current

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[1] This part of the work, including experiments 1–6, was done under the direction of Prof. E. F. Smith at the University of Pennsylvania, during April, 1900.

is necessary, and the best conditions are: Add from 1 to 2 grams of sodium acetate, and from 1 to 2 cc. of 50 per cent. acetic acid, dilute the solution to 125 cc. and electrolyze with a current of $N.D_{100}$ = from 0.70 to 1.0 ampere. The temperature of the solution should be about 65° to 70° C. After the current is started no heat need be applied outwardly as the current itself keeps the solution heated. The time required for the complete precipitation of about 0.15 gram of U_3O_8 is from six and one-half to seven and one-half hours.

When solutions containing more than 0.15 gram of U_3O_8 were electrolyzed, some difficulty was experienced in precipitating all within eight hours by a current not exceeding $N.D_{100}$ = 1 ampere. With a current greater than this the deposits were very spongy and peeled from the dish; so the amount of U_3O_8 in solution should not exceed 0.15 gram.

The electrolytic precipitation of uranium has been used a number of times for the estimation of uranium and for separating it from the alkalies and alkaline earths. The results obtained were concordant with those obtained by precipitating it gravimetrically.

The simplicity of the electrolytic method for the determination of uranium, and the short time required, are in favor of this method.

SEPARATION OF URANIUM FROM PHOSPHORIC ACID.

Review of Methods.

Reynoso's Method.[1]—The uranium compound should be in solution as nitrate, having a small amount of free nitric acid present. Dilute to about 150 cc., add a strip of pure metallic tin, and boil. The phosphoric acid unites directly with the tin, to form oxyphosphate of tin, which is insoluble. The precipitate is filtered off and thoroughly washed. The filtrate is made alkaline with ammonia, and the precipitate which forms is treated with acetic acid. If it does not entirely dissolve, nitric acid is added and the precipitation by pure metallic tin repeated.[2] Heat the solution to boiling, filter off the oxyphosphate of tin, and wash with warm water. The precipitate rarely contains any uranium. The tin in the filtrate is removed by

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[1] *Ann. Chem.* (Liebig), **81**, 368 (1852).

[2] Fremy's "Encyclopédie Chimique," p. 86, (1884).

means of hydrogen sulphide. The filtrate from the tin sulphide is boiled till all hydrogen sulphide is expelled, after which the uranium is determined by any of the ordinary methods.

W. Hintz[1] had occasion to investigate this method and stated that a complete separation of phosphoric acid from uranium is effected by means of metallic tin.

Knopp and Arendt Method.[2]—The separation of uranium from phosphoric acid may be effected by fusing the ignited mass of uranium and phosphoric acid with a mixture of potassium cyanide and potassium carbonate, and treating the fused mass with warm water to dissolve out the phosphoric acid as soluble alkaline phosphate. The uranium is left as protoxide, which is reignited and weighed, or else dissolved in acid and precipitated by ammonia. The phosphoric acid in the filtrate is precipitated with magnesia mixture and weighed as magnesium pyrophosphate. Hintz[3] used sodium carbonate in place of potassium carbonate, and obtained very satisfactory results.

E. Reichardt's Method[4] is based on the direct precipitation of phosphoric acid, from an acetate solution as uranyl-ammonium phosphate, provided the uranium is in excess. The precipitate is filtered off, washed, dissolved in a solution of sodium carbonate, and the solution added to a solution of magnesia mixture, which precipitates the phosphoric acid as magnesium ammonium phosphate. If iron is present it is first precipitated from a nitric acid solution by adding an excess of sodium carbonate and boiling.[5] The phosphoric acid in the filtrate is precipitated as magnesium ammonium phosphate, and the uranium determined by the ordinary method, after expelling all the carbon dioxide.

Fresenius and Hintz Method.[6]—This method provides a means of separating arsenic and phosphoric acid from copper, uranium, and iron. Have the solution feebly acid with hydrochloric acid, add an excess of potassium ferrocyanide, then saturate with sodium chloride. The ferrocyanides of copper, uranium, and iron are washed by decantation, and subsequently decomposed by a warm solution of caustic potash, changing them to hydroxides.

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[1] *Ann. Chem.* (Liebig), **151**, 216 (1869).

[2] *Chem. Centrbl.*, **773**, (1856).

[3] *Ann. Chem.* (Liebig), **151**, 216 (1869).

[4] *Ztschr. anal. Chem.*, **8**, 116 (1869); *Bull. Soc. Chim.*, **20**, 347 (1873).

[5] *Ztschr. anal. Chem.*, **8**, 116 (1869).

[6] *Ibid.*, **34**, 437; *Chem. News*, **72**, 206 (1895).

Filter and wash with a dilute solution of ammonium chloride till no ferrocyanide is recognized in the washings. The mixed hydroxides are treated with dilute hydrochloric acid. If any residue remains it is decomposed by a warm solution of caustic potash, going through with the same treatment as before. The solution by hydrochloric acid is free from arsenic and phosphoric acid. The copper, iron, and uranium are separated by ordinary methods.

Friedel and Cumenge[1] separated phosphoric acid from uranium by dissolving the substance in nitric acid, and precipitating the phosphoric acid with ammonium molybdate.

This method was used[2] for estimating the amount of phosphoric acid in precipitates of uranous phosphate, which were formed by electrolysis. The sample was dissolved in 30 cc. nitric acid (sp. gr. 1.42) and 3 cc. hydrochloric acid (sp. gr. 1.20). When iron was present, the sample was dissolved in a mixture of 20 cc. hydrochloric acid (sp. gr. 1.20) and 10 cc. nitric acid (sp. gr. 1.42). The solution was diluted to about 100 cc., and nearly neutralized with ammonia. A few drops of nitric acid were added to clear the solution, making it slightly acid, then to the hot solution (not above 65° C.) 50 cc. of molybdate solution[3] for every decigram of phosphorus pentoxide present. After digesting at 65° C. for an hour and a half, the yellow precipitate was filtered, and washed with cold water. The filtrate was tested for phosphoric acid by adding more molybdate solution and reheating at 65° C. The yellow precipitate of ammonium phosphomolybdate was dissolved from the filter with ammonia and hot water, and washed into a beaker to a bulk not exceeding 100 cc. It was nearly neutralized with hydrochloric acid, cooled, and magnesia mixture added, drop by drop from a burette, stirring all the while. After about twenty minutes, 30 cc. ammonia (sp. gr. 0.96) were added and the solution allowed to stand in the cold for three hours. The precipitate of magnesium ammonium phosphate was filtered and washed with dilute ammonia (2.5 cc. ammonia and 100 cc. water) till free from chlorides. The precipitate was dried, ignited, and weighed as magnesium pyrophosphate.

The uranium in the filtrate, from the ammonium phospho-

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[1] *Am. J. Sci.*, 10, 135 (1900).

[2] At the University of Pennsylvania in 1900.

[3] Prepared according to the formulas given in the "Official Methods of the U. S. Agricultural Chemists.

molybdate, was determined by three precipitations with ammonia, and weighed as U_3O_8.

PART II.—THE DETERMINATION OF URANIUM.

DETERMINATION OF URANIUM AS OXIDE.

The precipitant which Péligot used in 1840 for the estimation of uranium was ammonia, the principal reagent used for that purpose at the present time. The yellow precipitate which forms when ammonia is added to a uranyl solution is hydrated ammonium uranate[1] ($(NH_4)_2U_2O_7.xH_2O$, or $(NH_4)_2O.2UO_3.xH_2O$), which is soluble in alkali carbonate solutions, and slightly soluble in pure water; but in water containing ammonia, ammonium nitrate, or ammonium chloride it is insoluble.[2] The presence of tartaric acid, oxalic acid, or non-volatile organic substances prevents the precipitation of ammonium uranate.[3]

If the solution contains any alkalies or alkaline earths, a portion of these will be precipitated along with the uranium.[4]

Berthier's Method.[5]—The reagent next in importance to ammonia, for the estimation of uranium, is ammonium sulphide, which was first used (in 1840) by Berthier. A complete precipitation of uranium by ammonium sulphide is obtained, provided the solution is previously nearly neutralized by ammonia, and no carbonates are present. The precipitate which forms is usually black in color, sometimes changing to reddish brown.[6] When a large excess of the precipitant is added and it is allowed to stand, the liquid sometimes assumes a brown color.[7] This color, says Zimmerman,[8] is due to the solubility of uranyl sulphide in ammonium carbonate contained in the ammonium sulphide. When the ammonium sulphide contains a considerable amount of thiosulphate the red sulphide described by Remele[9] is formed; but when thiosulphate is absent only the dark precipitate results. Thiosulphate in the reagent is due to the oxidation of ammonium sulphide by atmospheric oxygen.

In 1865, A. Remele studied the method for the estimation of

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[1] *Chemiker Kalender*, p. 270, (1899).

[2] Comey's "Dictionary of Chemical Solubilities."

[3] Fresenius' "Qualitative Chemical Analysis," 219.

[4] *Ibid.*, 6th edition, p. 533.

[5] *Ann. Chem.* (Liebig), **46**, 184.

[6] Pogg. *Ann.*, 116, 352.

[7] *Ibid.*, **124**, 120.

[8] *Ann. Chem.* (Liebig), **204**, 224 (1880).

[9] Pogg. *Ann.*, **116**, 352.

uranium by the use of ammonium sulphide and found the best results were obtained by the following procedure:[1] The ammonium sulphide should be fresh and kept well corked, as it absorbs carbon dioxide when exposed to the atmosphere. To the nearly neutral ammoniacal solution, add an excess of yellow ammonium sulphide and keep the solution near boiling for an hour, in order to convert the $(UO_2)S$, which is first formed, into a mixture of UO_2 and sulphur. This precipitate is rapidly dissolved by alkali carbonates and by tartaric acid. It is slightly soluble in pure water, is soluble in dilute, but insoluble in absolute, alcohol. It is readily soluble in acids, even acetic acid.[2] The presence of ammonium chloride or ammonium nitrate assists the precipitation of $(UO_2)S$, as it is less soluble in these solutions. The precipitate, containing all the uranium, is filtered off and washed with cold or hot water containing a small amount of ammonium sulphide and ammonium chloride or nitrate. Wash first by decantation and finally on the filter. The precipitate during washing passes to yellow uranic hydroxide. It is dried, then roasted to remove all the sulphur and finally converted into U_3O_8 by ignition in the air, or into UO_2 by ignition in a current of hydrogen and allowing to cool in same.

A complete separation of uranium from the alkalies and alkaline earths is obtained by means of ammonium sulphide.[3]

C. Winkler made a comparison of this method with Péligot's ammonium method[4] and states that the precipitation of uranium by pure ammonium sulphide is trustworthy.[5]

EXPERIMENTAL.

Precipitation of Uranium by Ammonia.—For each determination a measured amount of standard uranium nitrate solution was run into a beaker and enough distilled water added to bring the volume to from 150 to 200 cc. The solutions were brought to boiling and a few drops of nitric acid added, and the uranium precipitated by adding an excess of ammonia to the hot solution. The precipitates which formed were a bright lemon-yellow color and settled rapidly. The precipitates were allowed to settle, and washed several times by decantation and twice on the filter with

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[1] *Ztschr. anal. Chem.*, 4, 379.

[2] Comey's "Dictionary of Chemical Solubilities," 1896.

[3] *Ztschr. anal. Chem.*, 1, 411.

[4] Fresenius' "Quantitative Chemical Analysis," p. 281.

[5] *Chem. News*, 43, 153 (1881).

warm dilute ammonium chloride solution (2 grams salt to 100 cc. water), after which they were dried in a hot oven, and ignited and weighed as oxides.

The following table gives the conditions observed :

THE THEORETICAL AMOUNT OF URANIUM TAKEN WAS 0.1925 GRAM.

Experiment No.	Approximate dilution. cc.	Salts present.	Crucible in which ignited.	Weighed as:	Weight of U_3O_8.	Uranium equivalent of U_3O_8.	Ignited in hydrogen for: Hours.	Weight of UO_2.	Uranium equivalent of UO_2.
1	200	NH_4Cl	Platinum	U_3O_8	0.2242	0.19130	..	....	......
2	200	NH_4Cl	Platinum	U_3O_8	0.2268	0.19252	..	....	......
3	150	NH_4Cl	Platinum	U_3O_8	0.2269	0.19260	..	....	......
4	150	NH_4Cl	Platinum	U_3O_8	0.2266	0.19235	..	....	......
5	175	NH_4Cl	Platinum	U_3O_8	0.2268	0.19252	2	0.2191	0.19329
6	175	NH_4Cl $CHCl_3$	Platinum	U_3O_8 UO_2	0.2267	0.19243	¾	0.2179	0.19223
7	175	NH_4Cl $CHCl_3$	Porcelain	U_3O_8	0.2269	0.19260	2½	0.2207	0.19479
8	150	NH_4Cl	Platinum	U_3O_8	0.2268	0.19252	1	0.2211	0.19505
9	150	NH_4Cl	Platinum	U_3O_8	0.2270	0.19268	¾	0.2221	0.19593
10	150	NH_4Cl Alcohol	Porcelain	U_3O_8	0.2280	0.19353	..	....	......
11	175	NH_4Cl Alcohol	Porcelain	U_3O_8	0.2270	0.19268	..	....	......
12	175	NH_4Cl	Platinum	UO_2	....	......	½	0.2180	0.19232
13	150	NH_4Cl	Porcelain	....	....	......	1	0.2240	0.19761

U_3O_8 multiplied by 0.84884 gives the uranium equivalent ; UO_2 multiplied by 0.88218 gives the same. These are the factors obtained by taking the atomic weight of uranium as 239.6 and that of oxygen as 16.[1]

For all the above precipitations the solutions, of from 150 to 200 cc. volume, were made decidedly acid with from 0.5 to 1 cc. nitric acid (sp. gr. 1.42), brought to boiling and ammonia added in excess. Some of the solutions were boiled for about fifteen minutes after the precipitation by ammonia, while others were filtered directly without boiling. The boiling caused the lemon-yellow colored voluminous amorphous precipitate to change to a more crystalline form, less voluminous and of a slightly darker color. The precipitates which were boiled were much easier to filter and wash, and were less liable to pass through, which usually happened when boiling was omitted.

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[1] This Journal, **23**, 94 (1901).

The presence of chloroform or alcohol (as recommended by some chemists) did not assist the precipitation, but the presence of ammonium chloride or ammonium nitrate was essential. Five to ten grams were added previous to the addition of ammonia.

Some of the precipitates were ignited separate from the paper, and others without separating from the paper. The results obtained, whether the precipitates were ignited separately or not, were identical, showing that it is unnecessary to ignite the precipitate and the filter-paper separately, as is recommended by the German chemists.

When the uranium was weighed as U_3O_8, the precipitates together with the filter-paper were placed in a crucible and slowly ignited till the paper had completely burned; then the ignition was continued for about fifteen minutes in a blast-flame, and allowed to cool slowly in a gradually decreasing Bunsen flame. During ignition the crucibles were placed in a slanting position in order to allow of free circulation of air in the crucible, thus obtaining complete oxidation. The results were the same whether porcelain or platinum crucibles were used.

In all directions given in text-books and journals for weighing uranium as oxide, it is recommended that the dry precipitate of ammonium uranate be strongly ignited over a blast-lamp to U_3O_8, and allowed to slowly cool in a gradually decreasing flame and finally in a desiccator. It is then weighed, and as a means of ascertaining its purity for the purpose of control, it is reignited in a current of pure hydrogen and reduced to its lower oxide, UO_2. This was tried, but only in one case was it possible to completely reduce U_3O_8 to UO_2, even when the ignition in hydrogen was continued for two hours. This time (experiment No. 6) the reduction was brought about by using a platinum crucible and igniting strongly in a current of pure hydrogen over the hottest blast-lamp that could be obtained. When a porcelain crucible was used in which the ignition was made, the reduction did not proceed so far as when a platinum crucible was used. The reason for this is the fact stated by Roberts-Austen[1] as follows: "Saint Claire Deville and Troost discovered that hydrogen and hydrocarbons pass through platinum at a red heat." The further reduction of U_3O_8, when a platinum crucible is used, would seem to indicate that hydrocarbons of the flame play as important a

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[1] Roberts-Austen's "Introduction to Metallurgy," p. 54, (1898).

part in the reduction as the hydrogen. It was impossible to obtain a single complete reduction of the precipitate to UO_2 when a porcelain crucible was used, even when the precipitate was not previously ignited. When a platinum crucible was used, and the precipitate not previously ignited in the air, the complete reduction to UO_2 occurred within half an hour by igniting it in a current of pure hydrogen over a blast-lamp, and allowing it to cool in an atmosphere of hydrogen over a gradually decreasing flame. The U_3O_8 is a velvety black colored mass, and the UO_2 a dull brown colored mass.

For the above reductions ordinary porcelain and platinum Rose crucibles were used. The hydrogen was purified by Schobig's method,[1] by first passing it through a strong solution of potassium permanganate to remove the hydrides of arsenic, antimony, phosphorus, and carbon ; then through a strong solution of caustic soda to remove hydrogen sulphide ; and finally through sulphuric acid (sp. gr. 1.84) to remove moisture.

DETERMINATION OF URANIUM AS PHOSPHATE.

Review of Method.

The precipitation of uranium by an alkali phosphate has rarely been employed as a means of estimating uranium, because the precipitate which forms is gelatinous and difficult to wash free from alkali. This trouble has been overcome by adapting the method to volumetric means, which is the reverse of the volumetric estimation of phosphoric acid by a standard uranium solution. The uranium in solution as acetate is titrated by means of a standard solution of sodium-hydrogen-ammonium phosphate ($NaHNH_4PO_4$), which is added till a drop of the precipitated solution brought in contact with a drop of freshly prepared solution of potassium ferrocyanide does not give a brown coloration.[2]

The quantitative estimation of uranium by means of an alkali phosphate was first suggested by Leconte[3] and later worked out by Pisani ;[4] but owing to the difficulty of filtering and washing the greenish yellow, slimy precipitate of UO_2HPO_4, this method has not come into use.

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[1] *J. prakt. Chem.*, (2), **14**, 289-299.

[2] Mohr's "Lehrbuch der Chemisch-analytischen Titrirmethode," p. 521. Dammer's "Handbuch der anorg. Chemie," **3**, 686 (1893).

[3] Liebig and Kopp: *Jahresbericht*, p. 642, (1853).

[4] *Chem. News*, **3**, 211 (1862).

EXPERIMENTAL.

Were it not for the difficulty of washing the uranium phosphate, which is formed by disodium hydrogen phosphate, this method would afford a decided advantage over precipitating it with ammonia and weighing it as oxide (U_3O_8) because any error would be greatly diminished by weighing as $(UO_2)_2P_2O_7$. U_3O_8 multiplied by 0.84884 gives the uranium equivalent, while $(UO_2)_2P_2O_7$ multiplied by 0.66815 gives the same; so by weighing the uranium as pyrophosphate the error or loss is decreased.

This method was studied, and the best conditions for weighing uranium as uranyl pyrophosphate were worked out, the results of which are tabulated below.

PRECIPITATION OF URANIUM BY DISODIUM HYDROGEN PHOSPHATE.

Experiment No.	Approximate dilution. cc.	Salts added.	Temperature of solution after precipitation.	Crucible in which ignited.	Time of ignition. Minutes.	Weight of $(UO_2)_2P_2O_7$	Uranium equivalent.	Theoretical am't of uranium taken.
1	150	NH_4NO_3 $NN_4C_2H_3O_2$	Cold, then heated to b.p.	Platinum	15	0.2875	0.1921	0.1925
2	150	NH_4Cl $NH_4C_2H_3O_2$	"	"	10	0.2884	0.1927	0.1925
3	150	NH_4NO_3 $NH_4C_2H_3O_2$	"	Porcelain	10	0.2878	0.1923	0.1925
4	150	NH_4NO_3 $NH_4C_2H_3O_2$	b.p. for 1 hour after precipit.	Platinum	10	0.2851	0.1905	0.1925
5	150	Chloroform $NH_4C_2H_3O_2$	"	"	10	0.2848	0.1903	0.1925
6	150	NH_4NO_3 $NH_4C_2H_3O_2$	"	Porcelain	15	0.2875	0.1921	0.1925
7	150	Chloroform $NH_4C_2H_3O_2$	"	"	20	0.2870	0.1918	0.1925

These determinations were made by measuring 50 cc. of standard uranium nitrate solution into a beaker, diluting to 150 cc. and adding nitric acid (sp. gr. 1.42), varying the amount from 0.5 cc. to 1.5 cc. The solutions were brought to boiling and ammonia (sp. gr. 0.90) added to neutral reaction and a measured amount in excess—from 1 cc. to 10 cc. The yellow precipitate of ammonium uranate was dissolved by adding 50 per cent. acetic acid till the precipitate disappeared, and then an excess varying from 1 cc. to 5 cc. To the solution—which contained besides uranium acetate, an excess of acetic acid, ammonium nitrate, and ammonium acetate—an excess of a saturated solution of disodium hydrogen phosphate was added. The precipitate which formed was greenish white in color and voluminous. The solution was brought to boiling, then allowed to cool, and filtered. In experiments Nos. 4 to 7 the solutions were kept for one hour on water-baths at the temperature of boiling water, after which they were allowed to cool, then filtered. This treatment assisted the settling of the precipitate, but did not change its gelatinous character.

The washing of the precipitates was done by four decantations and twice on the filter with a hot dilute solution of ammonium chloride (2.5 grams of salt to 100 cc. of water). The washing was not so easy as the ammonium uranate precipitates, even when as much as 5 grams of ammonium chloride were added to the solution previous to its precipitation. Neither the addition of chloroform nor of ammonium chloride had any effect on the appearance of the precipitate, as there were already sufficient ammonium salts present, formed by the neutralization of nitric acid by ammonia and of ammonia by acetic acid.

The precipitates, after washing, were dried at a temperature of from 100° C. to 115° C., separated from the filter-paper, which was first ignited in the crucible, then the precipitate added and the ignition continued for from ten to twenty minutes at "redness" over a Bunsen burner. The residue in most cases was green in color, due to the partial reduction of uranyl pyrophosphate. Whenever the temperature of ignition was above "redness" a reduction always occurred, especially when a platinum crucible was used. When a porcelain crucible was used the ignition could be done at "redness," but above this temperature (as over a blast-lamp) reduction always resulted.

The reduced uranyl pyrophosphate was not weighed as such, but was moistened with a few drops of nitric acid (sp. gr. 1.42), dried over a low flame, and reignited at "low redness" over a Bunsen burner. The mass after such treatment was always of a lemon-yellow color. The weight of the yellow uranyl pyrophosphate remained constant, no matter how long it was ignited at a temperature not exceeding "low redness," but above this temperature it always lost weight and assumed a green color. Whenever this occurs it may be reoxidized by treating it with nitric acid and reigniting at "low redness."

This green residue of pyrophosphate most probably has the composition $U_2O_3.P_2O_7$, which is indicated by the weights of several which varied from 0.2820 to 0.2827 gram. 0.2820 multiplied by 0.6833 gives 0.1929 gram uranium, the theoretical amount of uranium being 0.1925 gram.

One of the residues which was more intensely ignited than the others, with the cover on the platinum crucible, was of a reddish brown color. Its weight was 0.2800 gram, showing that the reduction had gone further than $U_2O_3.P_2O_7$.

The composition of the lemon-yellow colored uranyl pyrophosphate is $(UO_2)_2P_2O_7$.

PRECIPITATION OF URANIUM BY AMMONIUM DIHYDROGEN PHOSPHATE.

As the precipitates formed by disodium hydrogen phosphate were slimy and difficult to wash, it was suggested that possibly this difficulty could be overcome by means of an ammonium phosphate. The precipitant used was ammonium dihydrogen phosphate. The mode of procedure was the same as when disodium hydrogen phosphate was used.

To a solution containing 0.1925 gram of uranium were added from 0.1 cc. to 1.5 cc. nitric acid (sp. gr. 1.42) and sufficient water to make 150 cc. volume. The solution was brought to boiling, ammonia (sp. gr. 0.90) was added to neutral reaction and from 1 cc. to 10 cc. in excess. The ammonium uranate which formed was taken into solution by the addition of 50 per cent. acetic acid and from 1 cc. to 5 cc. in excess. The solutions, then acid with acetic acid, were brought to boiling and the uranium precipitated by an excess of a saturated solution of ammonium dihydrogen phosphate. The best precipitations, that is, those which were most crystalline and easiest to handle, were formed when about one and a half as much precipitant was added as was necessary for the precipitation. The solutions were boiled for half an hour, and the precipitate allowed to settle before filtering. The precipitates were washed three times by decantation and three times on the filter with a hot dilute solution of ammonium chloride (2 grams salt to 100 cc. water). The addition of ammonium chloride or of chloroform to the solution was found unnecessary, as enough ammonium salts were already present. The precipitates which formed were pulverulent and crystalline, and were as readily filtered and washed as the precipitates of ammonium uranate.

The precipitates were dried, separated from the filter-paper, and the paper ignited in a porcelain crucible, after which the precipitate was added and the ignition continued at "redness" for about five minutes. The crucible was allowed to cool and the residue moistened with a few drops of nitric acid (sp. gr. 1.42). The mass was dried over a low flame, then reignited for from ten to twenty-five minutes at "low redness" over a Bunsen burner. The mass after this treatment was, in all cases, a lemon-yellow color. The crucibles were allowed to cool in a desiccator, and weighed.

The results obtained are as follows :

PRECIPITATION OF URANIUM BY AMMONIUM DIHYDROGEN PHOSPHATE.

Experiment No.	Approximate dilution. cc.	Salts added.	Temperature of solution after precipitation.	Crucible in which ignited.	Time of ignition. Minutes.	Weight of $(UO_2)_2P_2O_7$.	Uranium equivalent.	Theoretical amount of uranium taken.
8	150	NH_4NO_3 $NH_4C_2H_3O_2$	b.p., boiled for 1 hour.	Porcelain	10	0.2879	0.1924	0.1925
9	150	"	b.p., boiled for 10 min.	"	15	0.2880	0.1924	0.1925
10	200	"	b.p., boiled for $\frac{3}{4}$ hour.	"	20	0.2881	0.1925	0.1925
11	200	"	"	"	20	0.2879	0.1924	0.1925
12	150	NH_4Cl NH_4NO_3 $NH_4C_2H_3O_2$	"	"	25	0.2881	0.1925	0.1925
13	150	NH_4NO_3 $NH_4C_2H_3O_2$	"	"	25	0.2883	0.1926	0.1925
14	200	"	"	"	15	0.2879	0.1924	0.1925
15	150	NH_4Cl $NH_4C_2H_3O_2$	"	"	15	0.2878	0.1923	0.1925
16	150	"	"	"	15	0.2882	0.1926	0.1925

The filtrates were evaporated and tested for uranium with potassium ferrocyanide. No uranium was indicated.

In several cases when the ignition was done at a temperature above "redness," the precipitate would invariably assume a green color, especially where the residue was in contact with the crucible. Whenever this occurred, the mass was again moistened with nitric acid (sp. gr. 1.42), dried over a low flame, and reignited at "low redness." By this treatment the mass was oxidized to $(UO_2)_2P_2O_7$.

Several precipitates, after having been weighed as uranyl pyrophosphate, were reignited over a blast-lamp for about fifteen minutes. The residue, in all cases, after such treatment was entirely green, but when moistened with nitric acid (sp. gr. 1.42) and reignited at "low redness," always changed back to lemon-yellow uranyl pyrophosphate, and their weight was the same as the original weight.

Solution No. 15 was allowed to stand for six days before filtering. The appearance of the precipitate was the same as those which were filtered directly.

The weighing of uranium as uranyl ammonium phosphate ($UO_2.NH_4.PO_4$) was undertaken, but without success. The filtering through Gooch crucibles was tried, but owing to the fineness of the precipitate this could not be done. After trying to filter six solutions in this manner, the idea of weighing uranium as uranyl ammonium phosphate was abandoned as impracticable.

THE VOLUMETRIC ESTIMATION OF URANIUM.

Belohoubeck,[1] in 1866, estimated uranium by reducing the solution in a flask with metallic zinc and sulphuric acid. For small amounts of uranium, he states that the reduction is complete in about fifteen minutes, while for larger quantities the time required is much longer. The solutions, after reduction, were diluted and titrated by a standard potassium permanganate solution, the standard of which was made on ferrous ammonium sulphate.

Uranium differs from iron, as regards reduction, in that it is not reduced by hydrogen sulphide. When mercuric salts are present the uranium is, however, reduced by this reagent.[2]

The permanganate used for titrating uranium solutions is standardized by iron, two atoms of iron corresponding to one of uranium.

The reaction[3] which occurs during the titration of sulphate solutions of uranium is:

$$5U(SO_4)_2 + 2KMnO_4 + 2H_2SO_4 + 2H_2O = 5(UO_2)SO_4 + 2MnSO_4 + 2KHSO_4 + 3H_2SO_4.$$

The reaction which occurs during the titration of ferrous solution is:

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[1] *Ztschr. anal. Chem.*, **6**, 120 (1867); Sutton's "Volumetric Analysis," p. 375, (1900).

[2] Dammer's "Handbuch der anorg. Chemie," Vol. III, p. 686 (1893).

[3] Mohr's "Lehrbuch der chem.-analyt. Titrirmethoden," p. 267.

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O.$$

$5U(SO_4)_2$ is equivalent to $10FeSO_4$, or $1U = 2Fe$.

The reduction of uranium by zinc and sulphuric acid corresponds to the change of UO_3 to UO_2.[1]

EXPERIMENTAL.

The fact that iron is so easily and, at the same time, accurately determined by means of potassium permanganate, and that uranium solutions can be reduced, and then oxidized by potassium permanganate, suggested that possibly, with a few modifications, the Belohoubeck method could be adapted to the technical assay of uranium ores.

In order to demonstrate the best means of reducing uranium solutions, several different reducing agents were employed, the results of which are given below :

The first series of experiments was made by reducing the uranyl solution by means of zinc and sulphuric acid at boiling temperature, then by means of zinc and hydrochloric acid.

The second series was made by reducing the uranyl solution by means of strips of metallic aluminum, first in dilute sulphuric acid solutions, then in dilute hydrochloric acid solutions.

The third series was made by reducing the uranyl solutions by means of metallic magnesium, first in dilute sulphuric acid, then in dilute hydrochloric acid solutions.

The fourth series was made by passing the uranyl solutions through a long Jones' reductor.

The fifth series was made by reducing the uranyl solution by means of a strong solution of stannous chloride and destroying the excess of stannous chloride by adding sufficient mercuric chloride, as in the Zimmerman-Reinhart method, so largely used for the estimation of iron.

The standard solution of potassium permanganate was made by dissolving 18.96 grams of the salt in distilled water and diluting it to 6 liters, thus making a 0.01 normal solution. The standard was obtained by titrating ferrous sulphate solutions, containing a known quantity of iron.

1 cc. $KMnO_4 = 0.00548$ gram iron.

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[1] Watts' "Chemical Dictionary," 4, 820.

The uranium standard was calculated from the iron standard by the proportion :

$$239.6 : 2\,(55.9) = x : 0.00548\,; \quad x = 0.01176.$$

Two equivalents of iron correspond to one equivalent of uranium, or the iron standard multiplied by 2.1425 gives the uranium standard. In order to get the uranium standard in terms of U_3O_8, multiply the iron standard by 2.5243.

The standard of the permanganate solution was verified by taking a measured amount of standard uranium nitrate solution, and reducing it with about 50 grams of pure zinc and sulphuric acid (30 cc. sulphuric acid (sp. gr. 1.84) in 150 cc. of solution). The solution was diluted to 500 cc. and titrated. The results obtained agreed to the fifth decimal place with those of the iron titration.

TITRATION OF URANIUM SOLUTIONS WITH POTASSIUM PERMANGANATE.

Zimmerman[1] recommends, when uranous solutions are titrated with standard potassium permanganate solution, that the permanganate be added in excess and the excess then titrated back with a standard solution of ferrous sulphate. He stated that by this procedure the oxidation of the uranous solution by air is prevented. In the following titrations—about sixty in number, and also a number of others made later—the recommendation of Zimmerman was not observed, but the uranous solution was titrated in the same manner as a ferrous solution. The oxidation of the uranous solutions was prevented by placing about 1 gram of dry sodium carbonate in the large Erlenmeyer flask in which the titrations were made. The mouth of the flask was closed by a 2½ inch funnel, and the solution which was reduced in a small Erlenmeyer flask was emptied into it. The solutions, which were quite acid, on coming in contact with the dry sodium carbonate, liberated carbon dioxide which filled the "titration flask" and prevented the oxidation of the uranous solutions.

The reductions, whether made by metallic zinc, aluminum, or magnesium, were made in a small 250 cc. Erlenmeyer flask, the mouth of which was closed by a small funnel. The uranyl solutions were poured into the flask, acidified, the metal added, and the reduction carried on at boiling temperature. After the reduc-

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[1] *Ann. Chem.* (Liebig), **213**, 300 (1882).

tion had occurred, the funnel and sides of the flask were washed down with distilled water and the hot solution rapidly emptied into the " titration flask " which contained about 1 gram of dry sodium carbonate. The flask in which the reduction was made was rinsed out four times with cold distilled water, the rinsings poured into the " titration flask," and the solution diluted to from 500 to 600 cc. The titrations were made at once, adding the permanganate solution till pink "end-point," which was very delicate, when sulphate solutions were titrated.

The determinations were made as follows: A measured amount of standard uranium nitrate solution was measured into a small beaker, and from 10 to 15 cc. of sulphuric acid (sp. gr. 1.84), added. The solution was evaporated to dense white fumes, allowed to cool, then poured into an Erlenmeyer flask, which contained a small amount of water. The solution was diluted to a definite volume (100 to 200 cc.) and more sulphuric acid added.

The best and most rapid reductions occurred when the amount of free sulphuric acid (sp. gr. 1.84) present was within the limits, 1 part acid to 4 parts solution, and 1 part acid to 5 parts solution. When the concentration is more than 1 to 4, the metal, especially zinc, is coated with a rather insoluble sulphate which retards the generation of hydrogen.

Comparing the time required for the complete reduction of uranyl solutions with that required for the reduction of iron solutions, it was found to be about twice as long, when equivalent amounts of uranium and iron salts were reduced.

When zinc was the metal used for generating the hydrogen, about 50 grams of pure metal (15 lumps) were used.

When the solutions were reduced by means of aluminum, fifteen strips of the metal were used, size 8 mm. wide by 15 mm. long, and 0.5 mm. thick.

The reductions by means of metallic magnesium were made by using eight pieces of a bar 8 mm. in diameter and 15 mm. long.

The reductions, whether made by means of metallic zinc, aluminum, or magnesium, were in all cases the same. The only difference noticed was the rapidity of solution of the metals ; aluminum dissolved more rapidly than zinc, and magnesium more rapidly than aluminum. The reduction, whether carried on at boiling temperature for one hour, or for as long as five hours, did not go further than $U(SO_4)_2$. The time required for the reduction of about 0.1 gram of uranium by zinc is about one hour, for about 0.2 gram not less than one and a half hours. The uranyl sulphate solution, at first yellow in color, changes to light green and finally to green with bluish tinge, having the appearance of a dilute solution of nickel chloride, which color it retains even though the reduction be continued for as long as four hours.

The results, which were obtained by titrating uranous sulphate solutions, are all that can be desired, as they agree within analytical limits with those obtained by the standard gravimetric method, which is to precipitate the uranium with ammonia, and weigh it as U_3O_8.

The reduction of hydrochloric acid solutions was also tried. For this purpose, a measured amount of standard uranium nitrate solution was twice evaporated to dryness with 10 cc. hydrochloric acid (sp. gr. 1.20). The dry mass of uranyl chloride was taken up with 15 cc. hydrochloric acid (sp. gr. 1.20), and water added, after which the solution was poured into a small Erlenmeyer flask and diluted to from 100 to 200 cc. More hydrochloric acid was added, and the solutions reduced at boiling temperature in the same manner as the sulphate solutions. The reductions were made first by the use of metallic zinc, then by metallic aluminum, and lastly by metallic magnesium. In all cases when the reduction was carried on for from two to four hours, it approached (and in several cases reached) the subchloride (U_2Cl_6 or UCl_3). With solutions of about 100 cc. volume and rather strongly acid (1 part hydrochloric acid (sp. gr. 1.20) to 4 parts solution), at boiling temperature the reduction to UCl_3 was complete within about two hours. By longer treatment the reduction went no further. The color of the hydrochloric acid solution of uranium, at first yellow, changed to green, to bluish green, to olive-green, and finally to reddish-brown —resembling the color of old port wine. The solutions, previous to titration, were cooled by running water, diluted to about 600 cc., and titrated in the same manner as the uranous sulphate solutions.

The "end-point" was not so delicate as when sulphate solutions were titrated. As no "preventative solution" was added, a small amount of chlorine was evolved after the solutions were allowed to remain standing for a few minutes. The interference of the "end-point" by chlorine was prevented by having a very small amount of free hydrochloric acid present, not over 3 per cent. of the total solution.

The results obtained are as follows:

REDUCTION OF URANYL SOLUTIONS BY METALLIC ZINC.

Experiment No.	Dilution at reduction. cc.	Time of reduction. Hours.	Dilution at the time of titration. cc.	Amount of free acid present. cc.	Amount of $KMnO_4$ required. cc.	Uranium equivalent.	Theoretical amount of uranium taken.
1	100	2¾	600	15 H_2SO_4	13.10	0.15406	0.15400
2	200	3	600	20 "	13.15	0.15464	0.15400
3	125	1¼	500	20 "	8.20	0.09643	0.09625
4	135	1¼	500	25 "	8.20	0.09643	0.09625
5	130	1	600	20 "	16.40	0.19286	0.19250
6	130	1	600	20 "	16.35	0.19228	0.19250
7	125	1¼	500	20 "	19.60	0.23050	0.23100
8	125	1½	500	25 "	19.65	0.23108	0.23100
9	100	2½	600	30 HCl	21.10	....	0.15400
10	200	2¾	600	25 "	19.80	....	0.15400

REDUCTION OF URANYL SOLUTIONS BY METALLIC ALUMINUM.

Experiment No.	Dilution at reduction. cc.	Time of reduction. Hours.	Dilution at the time of titration. cc.	Amount of free acid present. cc.	Amount of $KMnO_4$ required. cc.	Uranium equivalent.	Theoretical amount of uranium taken.
11	110	½	600	15 H_2SO_4	13.15	0.15464	0.1540
12	150	1½	600	20 "	13.05	0.15350	0.1540
13	150	2½	600	20 "	13.10	0.15406	0.1540
14	100	2¾	500	15 "	13.05	0.15350	0.1540
15	100	3	500	15 "	13.10	0.15406	0.1540
16	200	4	600	25 "	13.15	0.15464	0.1540
17	120	1½	600	30 "	13.15	0.15464	0.1540
18	200	2½	600	40 "	13.10	0.15406	0.1540
19	200	2½	600	50 "	13.15	0.15464	0.1540
20	75	1½	700	20 HCl	20.10	....	0.1540
21	75	1½	700	20 "	18.85	....	0.1540
22	200	3	700	20 "	17.40	....	0.1540
23	200	3	700	20 "	19.60	....	0.1540

REDUCTION OF URANYL SOLUTIONS BY METALLIC MAGNESIUM.

Experiment No.	Dilution at reduction. cc.	Time of reduction. Hours.	Dilution at the time of titration. cc.	Amount of free acid present. cc.	Amount of $KMnO_4$ required. cc.	Uranium equivalent.	Theoretical amount of uranium taken.
24	125	1	600	20 H_2SO_4	13.10	0.15406	0.1540
25	125	1	600	29 "	13.05	0.15347	0.1540
26	125	2¼	700	20 HC6	16.90	....	0.1540
27	125	2¼	700	20 "	17.60	....	0.1540

The reduction of uranyl solutions to the uranous state can also be made by passing the solution through a Jones reductor. The reductor used was much longer than those ordinarily employed for the reduction of iron solutions. It was made of a 50 cc. burette, in the lower part of which was placed an inch layer of broken glass and on top of this was poured an 18 inch column of 20 mesh amalgamated zinc. The amalgamation was done by washing the zinc with a warm dilute solution of mercurous nitrate, then thoroughly washing it with warm distilled water.

The determinations were made by taking a measured amount of standard uranium nitrate solution and evaporating it to dense white fumes with 10 cc. sulphuric acid (sp. gr. 1.84). The solution was allowed to cool, then diluted to from 100 to 150 cc. and more sulphuric acid added. The warm solution was poured through the reductor, and caught in a large Erlenmeyer flask which contained about 1 gram of dry sodium carbonate, and the mouth of which was closed by a small funnel. After all the solution had been emptied into the reductor, it was followed by about 250 cc. distilled water. The solution was then diluted to 500 cc., and titrated with 0.01 normal potassium permanganate solution to faint red end-reaction.

The time required for 100 cc. of uranyl solution and 250 cc. of water to pass through the reductor was about ten minutes; for 150 cc. uranyl solution and 250 cc. of water to pass through it required about twenty minutes.

Sutton[1] states that while washing the reductor free from iron solutions, the wash-water should be kept above the zinc level, so as not to allow of any air-spaces between the successive additions of water, in which case hydrogen peroxide is formed, thus causing high results. This caution was observed in the reductions.

The most satisfactory results were obtained when the ratio of free sulphuric acid (sp. gr. 1.84) to total solution was not less than 1 to 6, nor more than 1 to 5. When the solutions contained more acid than the ratio of 1 to 5, the zinc sulphate which formed did not go into solution, and prevented the ready passage of the solution through the reductor. When the acid was present in amounts less than the ratio of 1 to 7, the reduction of the solution was incomplete, due to too slow action of the acid on the zinc. The reduction was complete in all cases when the ratio of

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[1] Sutton's "Volumetric Analysis," under "Iron."

free sulphuric acid (sp. gr. 1.84) to total solution was within the limits of 1 to 6 and 1 to 5. Even when the solutions were twice run through the reductor no further reduction occurred than when run through once.

The results obtained are shown in the table.

REDUCTION OF URANYL SOLUTIONS BY PASSING THROUGH REDUCTOR.

Experiment No.	Dilution at reduction. cc.	Time of reduction. Minutes.	Dilution at the time of titration. cc.	Amount of free acid present. cc.	Amount of $KMnO_4$ required. cc.	Uranium equivalent.	Theoretical amount of uranium taken.
28	100	9	600	20 H_2SO_4	8.20	0.09643	0.09625
29	100	9	600	15 "	8.20	0.09643	0.09625
30	110	10	500	10 "	13.15	0.15464	0.1540
31	110	10	500	10 "	13.05	0.15347	0.1540
32	115	11	500	15 "	13.10	0.15406	0.1540
33	115	11	500	15 "	13.10	0.15406	0.1540
34	120	12	500	20 "	13.10	0.15406	0.1540
35	120	12	600	20 "	13.10	0.15406	0.1540
36	100	10	500	20 "	16.40	0.19286	0.1925
37	100	10	600	20 "	16.35	0.19228	0.1925
38	125	12	600	25 "	26.20	0.30810	0.3080
39	130	14	600	30 "	26.20	0.30810	0.3080
40	150	18	600	35 "	26.20	0.30810	0.3080
41	110	15	600	15 "	16.40	0.19286	0.1925
42	115	18	600	20 "	16.40	0.19286	0.1925
43	135	20	600	25 "	26.20	0.30810	0.3080

Solutions Nos. 41, 42, and 43 were twice passed through the reductor.

REDUCTION OF URANYL SOLUTIONS BY STANNOUS CHLORIDE.

These reductions were made in the same manner as iron by the Zimmerman-Reinhardt method. In some of the reductions the stannous chloride was allowed to act much longer than is ordinarily done for iron; but with the majority the procedure was the same as for iron reductions.

The color of the uranyl chloride solutions was yellow, but on continued boiling with stannous chloride it changed to green, and on still further boiling to reddish brown. When the solutions were boiled with stannous chloride, a small amount of dry sodium carbonate was added to the flask, the mouth closed by a small funnel, and the boiling continued.

When the reductions were allowed to continue for a minute or so, as for the reduction of ferric solutions, a very slight reduction occurred, but when the reduction was continued for from fifteen minutes to half an hour, the reduction approached and in several cases proceeded to the subchloride (UCl_3), the same as when a hydrochloric acid solution of uranium is reduced by either zinc, aluminum, or magnesium.

The uselessness of stannous chloride for the reduction of uranium solutions is shown by the following table:

REDUCTION OF URANYL SOLUTIONS BY STANNOUS CHLORIDE.

Experiment No.	Dilution at reduction. cc.	Time of reduction. Minutes.	Dilution at the time of titration. cc.	Amount of free acid present. cc.	Amount of $KMnO_4$ used. cc.	Uranium equivalent.	Theoretical amount of uranium taken.
44 45 46	20	½	600	15	0.6-0.7	0.00823	0.1925
47 48 49	75	½	500	20	0.8-1.5	0.01764	0.1925
50 51	75	½	500	20	0.4-0.6	0.00706	0.1925
52	35	1	550	35	0.8	0.00941	0.1925
53	50	1	550	45	2.0	0.02352	0.1925
54	35	5	600	35	16.0	0.18816	0.1925
55	50	5	600	45	18.5	0.21756	0.1925
56	75	10	600	10	4.0	0.04704	0.1925
57	75	10	600	10	8.5	0.09996	0.1925
58	35	10	600	25	11.0	0.12936	0.1925
59	30	10	600	15	15.5	0.18228	0.1925
60	30	15	600	15	20.9	0.24578	0.1925

PART III.—ESTIMATION OF URANIUM IN PITCHBLENDE.

In order to apply the preceding separations and determinations, to an actual technical assay of pitchblende, samples of the ore were analyzed by two entirely different methods: the Patera method with modifications, and the "ether extraction" method. In both cases the uranium was determined in several different ways. These assays gave an actual comparison of results, and at the same time tested the separations and estimations of uranium which were worked out on pure solutions.

The assays were first made by Patera's method as follows:

Eight samples of the finely divided ore (about 1.3 grams) were weighed into small beakers, and decomposed by adding 5 cc. water and 10 cc. nitric acid (sp. gr. 1.42). Complete solution was brought about by heating almost to boiling in covered beakers on a hot asbestos plate till the residues were almost white in color, then the watch-glasses were removed and the solutions slowly evaporated to a pasty mass. After cooling, the masses were taken up with 50 cc. water and 3 cc. nitric acid (sp. gr. 1.42), and the solution brought to boiling. The silica was filtered off and washed with boiling water and rejected. The filtrates were diluted to 200 cc. volume and hydrogen sulphide gas passed through the cold solutions for one hour. The precipitates of sulphides of lead, copper, etc., were filtered, washed with hydrogen sulphide water, and rejected. The filtrates from the sulphides were at first slowly heated, and finally boiled in order to expel hydrogen sulphide gas and to oxidize the iron. Evaporation was continued till the bulk of the solutions was about 125 cc., then the separated sulphur was filtered off and washed. The solutions were brought to boiling and 150 cc. of a saturated solution of sodium carbonate added, boiling was continued for twenty minutes, after which the precipitates (principally ferric hydroxide) were filtered off and washed three times by decantation and four times on the filter with hot water. The filtrates containing the uranium were evaporated to half volume (about 150 cc.), slowly neutralized with hydrochloric acid (sp. gr. 1.20) and about 3 cc. in excess, then boiled for half an hour till all carbon dioxide was expelled. The uranium was precipitated from the hot solutions by means of a slight excess of sodium hydroxide (free from carbonate), and boiling for about ten minutes, keeping the beakers covered with watch-glasses. The orange-yellow precipitates of sodium uranate were allowed to settle, the supernatant liquids poured through filters, and the precipitates twice washed by decantation and three times on the filters with hot water.

Precipitates Nos. 1 and 2, were dried in a hot oven, separated from the filters and ignited in platinum crucibles after which the ash of the papers was added to the crucibles and ignition continued at "redness" for five minutes. The residues on cooling were treated several times with hot water, after each treatment pouring the water through a small filter. The filters were dried, ignited, added to the crucibles, and reignited at "redness" for ten minutes. After cooling in a desiccator, they were weighed. According to Patera, the residue consists of $NaO.2(U_2O_3)$, 100 parts of which contain 88.3 parts of U_3O_8.

Precipitates Nos. 3, 4, 5, 6, and 7 were dissolved from the filters by warm dilute hydrochloric acid (sp. gr. 1.13), and caught in small beakers. The solutions were evaporated twice to dryness on a warm asbestos plate, the second time with 10 cc. hydrochloric acid (sp. gr. 1.20). The dry residues were taken up with 3 cc. hydrochloric acid, diluted to 100 cc., and brought to boiling. The silica, dissolved from the beakers by the strong alkali solution, was filtered off, and washed with boiling water.

Solutions Nos. 3 and 4 were brought to boiling, 5 cc. hydrochloric acid (sp. gr. 1.20) added, and ammonia (sp. gr. 0.90) in excess. The solutions were boiled for fifteen minutes, thus changing the voluminous amorphous precipitate of yellow ammonium uranate into a more crystalline form, darker in color, which was readily and rapidly washed. The precipitates were allowed to settle, the supernatant liquids poured through filters, and the precipitates washed three times by decantation and twice on the filter with a hot dilute solution of ammonium chloride (2 grams of salt to 100 cc. water). The precipitates were dried, placed in platinum crucibles together with filter-paper, and slowly ignited till the paper was completely destroyed, then ignited in a blast-flame for ten minutes, after which they were slowly cooled in a gradually decreasing Bunsen flame. During ignition the crucibles were placed in a slanting position in order to allow of free circulation of air in the crucible, thus obtaining complete oxidation to U_3O_8. They were allowed to cool in a desiccator, and weighed.

Solution No. 5 was diluted to 150 cc., brought to boiling, and 5 cc. hydrochloric acid (sp. gr. 1.20) added. The solution was neutralized with ammonia (sp. gr. 0.90) and 5 cc. added in excess. Acetic acid was slowly added to the hot solution, stirring all the while, till the yellow precipitate disappeared. The uranium was then precipitated by means of ammonium dihydrogen phosphate, adding about twice as much as was necessary for complete precipitation. The solution was boiled for fifteen minutes, allowed to cool, then filtered, and the precipitate washed four times on the filter with a hot 2 per cent. solution of ammonium chloride. The precipitate was dried, separated from the filter-paper which was first ignited in a porcelain crucible, after which the precipitate was added and ignited at low redness for ten minutes over a Bunsen flame. The crucible was allowed to cool, the residue moistened with a few drops of nitric acid (sp. gr. 1.42), dried on a hot plate, and reignited at low redness for ten minutes. The lemon-yellow colored precipitate of uranyl pyrophosphate ($(UO_2)_2P_2O_7$) was weighed, and the U_3O_8 equivalent obtained by multiplying the weight by 0.66815.

Solutions Nos. 6 and 7 were evaporated to about 30 cc. volume allowed to cool, 30 cc. sulphuric acid (sp. gr. 1.84) added, and evaporation continued to dense white fumes. The solutions were poured into 250 cc. Erlenmeyer flasks, diluted to 150 cc., and reduced at boiling temperature by about 50 grams of pure granulated zinc. The reductions were continued for one and a half hours till the solutions were a clear green color. The solutions were then poured into a large Erlenmeyer flask, which contained about one gram of dry sodium carbonate, diluted to 500 cc. and titrated by 0.01 normal potassium permanganate solution.

Precipitate No. 8, of sodium uranate, was dissolved from the filter with warm dilute nitric acid (1 part acid (sp. gr. 1.42) and 2 parts water) and caught in a small beaker. The solution was evaporated to dryness twice, the second time with 10 cc. nitric acid (sp. gr. 1.42). The dry mass was taken up with 5 cc. of 50 per cent. acetic acid, diluted to 50 cc., and the solution boiled till all salts were dissolved. The silica, which was dissolved from the beaker by the strong sodium carbonate solution, was filtered off and washed with hot water. The solution was diluted to exactly 100 cc. in a graduated flask, 50 cc. were measured into a large clean platinum dish and the uranium determined by electrolysis as follows: Added 0.5 gram sodium acetate, diluted to 125 cc. and electrolyzed at a temperature of 65° to 75° C., with a current of $N.D._{100} = 0.8$ to 1.0 ampere. The uranium was completely precipitated, as hydrated protosesquioxide, within eight hours. The electrolyte was emptied into a beaker, and the black deposit washed with warm water. The electrolyte and the washings were poured through a fluted filter-paper, the paper several times rinsed with hot water, dried, and ignited on the cover of a platinum crucible, and the ash added to the dish. The dish was then dried, ignited over a blast-lamp for ten minutes, and allowed to cool in a gradually decreasing Bunsen flame. It was placed in a desiccator and, after thoroughly cooling, was weighed. The ignited deposit consisted of U_3O_8.

The results obtained by this series of assays are as follows :

Experiment No.	Amount of ore taken. Grams.	Weighed as :	Weight. Gram.	Calculated to U_3O_8 equivalent.	Per cent. of U_3O_8.	Average per cent.
1	1.2863	$NaO(U_2O_3)_2$	0.3064	0.27055	21.03	20.76
2	1.3278	$NaO(U_2O_3)_2$	0.3071	0.27117	20.49	
3	1.2882	U_3O_8	0.2616	0.26160	20.31	20.46
4	1.2880	U_3O_8	0.2653	0.26530	20.60	
5	1.2840	$(UO_2)_2P_2O_7$	0.3297	0.25940	20.20	20.20
6	1.4004	Titrated	....	0.29090	20.77	20.63
7	1.2164	Titrated	....	0.24940	20.50	
8	0.6416	U_3O_8	0.1306	0.13060	20.36	20.36

Estimation of Uranium in Pitchblende by the Ether Extraction Method.—The ether extraction method differs from the Patera method in that the uranium is not separated from the fourth group members by means of sodium carbonate, but by ether and by ammonium carbonate. The iron was separated from uranium and the other metals by shaking the hydrochloric acid solution with ether, free from alcohol. The uranium was then separated from the other associated metals (aluminum, manganese, zinc, and nickel) by means of ammonium carbonate.

The procedure was as follows: Seven samples (about 1.3 grams) of the finely divided pitchblende were decomposed with boiling dilute nitric acid (1 part acid (sp. gr. 1.42) and 1 part water) till the residues which remained were almost white in color. The solutions were then evaporated to a pasty mass, taken up with 15 cc. hydrochloric acid (sp. gr. 1.20), and evaporated to dryness twice, the second time with 10 cc. hydrochloric acid (sp. gr. 1.20). The salts were taken up with 5 cc. hydrochloric acid (sp. gr. 1.20), diluted to 150 cc., brought to boiling, and the silica filtered off and washed. The filtrates were diluted to 250 cc. and the lead, copper, etc., precipitated as sulphides by passing hydrogen sulphide gas through the cold solutions for about an hour. The filtrates from the sulphides were evaporated slowly to about 150 cc., and boiled for a few minutes in order to expel all hydrogen sulphide. The separated sulphur was filtered off and washed. The solutions were brought to boiling, 5 cc. nitric acid (sp. gr. 1.42) added, and boiling continued till the iron was completely oxidized, after which ammonia (sp. gr. 0.90) was added in excess and boiling continued for fifteen minutes. The precipitates of impure ferric hydroxide, ammonium uranate, etc., were filtered off and washed with a warm 2 per cent. solution of ammonium chloride. The wet precipitates were dissolved from the filters with warm dilute hydrochloric acid (sp. gr. 1.10) and caught in small beakers. The solutions were twice evaporated to dryness, the second time with 10 cc. hydrochloric acid (sp. gr. 1.20). The dry salts were taken up with 15 cc. hydrochloric acid (sp. gr. 1.10), the beakers covered with watch-glasses, and the solutions heated till all salts had dissolved but not long enough to lose any of the acid by evaporation. After cooling, the solutions were emptied into 250 cc. separatory funnels, and the beakers rinsed out four times with 5 cc. hydrochloric acid (sp. gr. 1.10). Fifty cc. of pure ether, which had previously been shaken up with hydrochloric acid (sp. gr. 1.10), were added to each funnel, and thoroughly shaken for about seven minutes with the aqueous hydrochloric acid solutions, occasionally relieving the pressure, due to evaporation of ether. After agitation, the funnels were allowed to stand for a few minutes till the two solutions separated, then the lower aqueous layers were run into other separatory funnels. The ether layers, containing most of the iron, were twice shaken up with 5 cc. hydrochloric acid (sp. gr. 1.10) and the washings added to the main solutions containing the uranium. The second extractions were made with 50 cc. ether, and the third with 30 cc. ether. In both cases the ether solutions were twice washed with 5 cc. hydrochloric acid (sp. gr. 1.10). The aqueous hydrochloric acid solutions, now free from iron, contained a small amount of ether, which was allowed to evaporate spontaneously by exposure. They were then evaporated to about half volume (40 cc.), diluted to 100 cc., nearly neutralized with ammonia, and 100 cc. of a saturated solution of ammonium carbonate added, which precipitated all the metals except uranium. The solutions were slowly boiled for five minutes, filtered, and the precipitates washed with hot water. The filtrates were evaporated to half volume in order to get rid of most of the carbon dioxide. Yellow precipitates of ammonium uranate separated during boiling, and were dissolved by acidifying the solutions with hydrochloric acid. The solutions were again boiled for about half an hour longer, and the uranium determined in four different ways as outlined below.

Solutions Nos. 9 and 10 were precipitated with ammonia in the same manner as solutions Nos. 3 and 4 and the uranium weighed as U_3O_8.

Solutions Nos. 11 and 12 were precipitated by an excess of ammonium dihydrogen phosphate the same as solution No. 5, and the uranium weighed as $(UO_2)_2P_2O_7$.

Solutions Nos. 13 and 14 were evaporated with sulphuric acid, reduced by metallic zinc and titrated by potassium permanganate as described under Nos. 6 and 7.

In solution No. 15, the filtrate from the ammonium carbonate precipitation was evaporated to dryness with nitric acid, and the uranium determined electrolytically as already described under No. 8.

The results obtained by the ether extraction method are as follows:

Experiment No.	Amount of ore taken. Grams.	Weighed as:	Weight. Gram.	Calculated to U_3O_8 equivalent.	Per cent. of U_3O_8.	Average per cent.
9	1.2405	U_3O_8	0.2565	0.2565	20.67	20.61
10	1.2409	U_3O_8	0.2550	0.2550	20.55	
11	1.2390	$(UO_2)_2P_2O_7$	0.3233	0.2545	20.54	20.66
12	1.2991	$(UO_2)_2P_2O_7$	0.3431	0.2701	20.79	
13	1.2892	Titration	....	0.2672	20.80	20.71
14	1.2828	Titration	....	0.2646	20.63	
15	0.6207	U_3O_8	0.1283	0.1283	20.67	20.67

A comparison of these results with those obtained by the Patera separation shows greater uniformity here. The close agreement is proof not only of the superiority of the ether extraction, method, but also of the accuracy of the methods of determination of uranium already described.

SUMMARY OF RESULTS.

The conclusions drawn from this investigation on the separation and determination of uranium, briefly stated, are as follows:

1. In order to separate uranium (and the other members of

group 4) from the metals of groups 5 and 6, the solution should contain not over one part of concentrated acid (either hydrochloric or nitric acid) in fifty parts of solution.

2. The separation of uranium from the metals of groups 3 and 4 is best accomplished by means of either a saturated solution of sodium carbonate, or else by ether followed by a saturated solution of ammonium carbonate. The latter method is preferable when the introduction of fixed alkalies and silica is undesirable.

3. The ether extraction method for the separation of uranium from iron depends on the fact that ferric chloride is extracted from an aqueous hydrochloric acid solution, whereas the uranyl chloride is retained in the aqueous solution. For this separation it is necessary that the hydrochloric acid used for the solution be of 1.10 specific gravity and that three ether extractions be made. The ether used should be free from alcohol, and also previously shaken up with hydrochloric acid (sp. gr. 1.10).

4. The separation of uranium from iron by means of sodium carbonate is complete, provided a large excess of a saturated solution of sodium carbonate be used, and the solution boiled for at least fifteen minutes after the precipitation. The boiling is necessary in order to get all the uranium into solution. By such treatment, no uranium remains with the iron, which is completely precipitated as ferric hydroxide in a form readily filtered and washed.

5. The separation of uranium from the alkalies and alkaline earths by means of electrolysis is complete, easily accomplished and gives accurate results.

6. The separation of uranium from the alkalies and alkaline earths is accomplished by precipitating the uranium three times from a hot solution with ammonia in the presence of ammonium chloride.

7. The separation of uranium from the alkalies and alkaline earths by means of an excess of ammonium phosphate in the presence of ammonium acetate is complete. The precipitations should be made from a hot solution and the boiling continued for at least fifteen minutes.

8. The yellow slimy amorphous precipitate of an ammonium uranate, formed by precipitating uranium with ammonia in the presence of an ammonium salt, is converted into a darker crystalline form by boiling it for about twenty minutes, and then allowing it to settle in the cold.

9. The separation of the filter-paper from the precipitate of ammonium uranate for the purpose of igniting to UO_2 or U_3O_4 is unnecessary.

10. The complete oxidation of uranium to U_3O_8 is accomplished by igniting ammonium uranate, in either a platinum or porcelain crucible, over a blast-lamp. This is done by having the crucible in a slanting position and igniting intensely over a blast-lamp for about ten minutes, after which the crucible is allowed to cool in a slowly decreasing Bunsen flame.

11. The reduction of U_3O_8 to UO_2, as recommended by Rose for the purpose of control, was found unreliable.

12. The estimation of uranium as phosphate is easily and accurately done when the precipitant used is ammonium phosphate, in the presence of ammonium acetate. The precipitate of $UO_2NH_4PO_4$ on boiling becomes crystalline, and is easily filtered and washed. The ignited precipitate previous to weighing should be moistened with nitric acid (sp. gr. 1.42), dried and reignited at low redness in a porcelain crucible. Above this temperature, and especially so in platinum, a reduction of the $(UO_2)_2P_2O_7$ always occurs. Whenever this happens it may be reoxidized to $(UO_2)_2P_2O_7$ by moistening the greenish mass with nitric acid (sp. gr. 1.42) and reigniting at low redness. The ignitions should be done in porcelain.

13. The most rapid determination of uranium is accomplished by reducing a sulphate solution by means of pure metallic zinc and titrating it with standard potassium permanganate solution in an atmosphere of carbon dioxide. The reductions, whether made by means of metallic zinc, aluminum, magnesium, or in a long Jones reductor, were in all cases complete, and the results obtained were concordant with those obtained gravimetrically.

14. When hydrochloric acid solutions of uranium are reduced by means of metallic zinc, aluminum or magnesium, the reduction goes lower than UCl_4. It approached and in several cases reached the subchloride UCl_3. When stannous chloride is used the results are utterly unreliable; so no reduction of uranium in an hydrochloric acid solution can be used for the estimation of uranium.

This work was suggested by Dr. Edmund H. Miller, and carried out under his direction.

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COLUMBIA UNIVERSITY, May, 1901.