

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

The Volumetric Determination of Uranium with Potassium Dichromate as Reagent and the Application of the Method to the Indirect Titration of Minute Quantities of Sodium

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Lundell and Knowles¹ and more recently N. H. Furman and J. C. Schoonover² have shown conclusively that reduction of hexavalent uranium in either hot or cold solutions leads to the formation of U^{IV} with some U^{III}, and that the latter can be oxidized easily to the quadrivalent state by treating the cold reduced solution with a stream of air for one to five minutes. It was also found that the U^{IV} solution is quite stable in contact with air at room temperature at the proper acidity. The results of the above authors have substantially been confirmed in the present investigation. Instead of using permanganate or ceric sulfate as reagents in the quantitative oxidation of U^{IV} to U^{VI}, the application of potassium dichromate is recommended in this paper. The latter reagent can be kept indefinitely without change in titer, and the end-point easily can be detected with diphenylamine-sulfonate, diphenylamine or diphenylbenzidine as indicator, if some ferric iron is added to the U^{IV} solution.

Materials Used

Uranyl Acetate UO₂(CH₃COO)₂·2H₂O, c. p.—Approximately 0.1 *N* solution was prepared by dissolving 21.2125 g. of the salt in conductivity water and diluting to one liter. The solution was standardized by precipitation of uranium as ammonium uranate and weighing as U₃O₈: 25-cc. portions of the solution yielded 0.3536, 0.3519, 0.3529, 0.3529, g. U₃O₈, resp.; average 0.3528 g., corresponding to a normality of the uranium acetate solution of 0.1005 *N*.

Potassium Dichromate, c. p.—Purified by three crystallizations and dried at 200° to constant weight. An exactly 0.1 *N* solution was prepared by dissolving 4.9012 g. in one liter.

Ferric Chloride, c. p. (free of ferrous iron).—A 2% solution of this product in water was used.

Sodium Chloride, c. p.—Purified by recrystallization from concentrated hydrochloric acid and dried at 600–700° in an electric furnace. A solution containing 0.8 mg. of sodium per cc. was prepared; gravimetric determinations of the chloride as silver chloride agreed within 0.1% with the calculated concentration.

Uranyl Zinc Acetate Reagent.—This reagent was prepared according to the directions of H. H. Barber and I. M. Kolthoff.³ It was saturated with the triple salt at 20° and filtered before use.

Diphenylamine Sulfonate.—0.2% solution of the barium salt in water.

Diphenylamine.—0.5% solution in concentrated sulfuric acid.

Zinc amalgam, c. p. zinc, iron free, containing 2–3% of mercury.

(1) Lundell and Knowles, *THIS JOURNAL*, **47**, 2637 (1925).

(2) Furman and Schoonover, *ibid.*, **53**, 2561 (1931); the reader is referred to this paper for a review of the literature regarding the uranium titration.

(3) Barber and Kolthoff, *THIS JOURNAL*, **50**, 1625 (1928).

Determination of Uranyl.—It was found that the direct titration of U^{IV} with dichromate, using either diphenylamine or diphenylamine sulfonate as indicator, is not feasible because of the extreme slowness of color development at the end-point. Experiments showed that uranyl inhibits the speed of oxidation of these indicators. The difficulty, however, can be overcome easily by the addition of an adequate amount of ferric iron



Since ferrous iron is a powerful catalyst in the oxidation of the above indicators to the colored forms, a sharp end-point is obtained in the titration in the presence of an excess of ferric iron. The diphenylamine sulfonate gave a more pronounced color change than diphenylamine or diphenylbenzidine; the former therefore has been generally used in this work.

Procedure.—The method employed for the reduction of the uranium was essentially that of Lundell and Knowles.¹

The reductor used for the experiments with the 0.1 *N* solutions contained a 21-cm. column of pure 20-mesh amalgamated zinc (2–3% Hg).

A second small size reductor was used with the 0.01 *N* uranium solutions. This second reductor contained a 14-cm. column of amalgamated zinc and was 12 mm. in diameter. The volume of the zinc column was one-sixth that of the large reductor.

The procedure for the reduction was as follows. The solution to be reduced was diluted to 100 cc., acidified with 5 cc. concd. sulfuric acid, and cooled to room temperature; 50 cc. of 5% sulfuric acid was then passed through the reductor and discarded. The solution to be reduced was then passed through at the rate of about 50 cc. per minute using gentle suction. The last traces of uranium were washed out of the reductor with three 30-cc. portions of 5% sulfuric acid followed by three 35-cc. portions of distilled water. The reduced solutions possessed the characteristic olive-green color of a mixture of tervalent and quadrivalent uranium.

Washed air was then bubbled rapidly through the solutions for five to ten minutes to oxidize all U^{III} to U^{IV} . During the aeration the color changed from olive-green to the characteristic light green of U^{IV} .

The reduced solutions were then titrated according to the following procedure: 25 cc. of 2% ferric chloride (0.12 *N*), 15 cc. of 85% phosphoric acid and 10 to 12 drops of 0.2% barium diphenylamine sulfonate were added and the addition of the standard 0.1 *N* dichromate was begun. The dichromate should be added slowly with constant mixing of the solution and finally dropwise as the equivalence point is approached. The titration is complete when one drop of the dichromate produces a strong violet color which is stable for at least one and one-half minutes. The color change is very sharp. Table I shows that the procedure yields good and reproducible results.

In Table II are given the results obtained in the titration of extremely dilute uranium solutions with 0.01 *N* dichromate. Here the small Jones reductor was employed since the volume of the solution to be reduced was only 25 cc. Correspondingly small volumes of wash acid and wash water were also used, seven washings with 5-cc. portions of 5% sulfuric acid followed by three washings with 5 cc. of water). The solution to be titrated had a volume of approximately 100 cc.; 5 drops of 0.2% diphenylamine sulfonate were added after the aeration. The indicator correction was

TABLE I

25 cc. of 2% (0.12 *N*) ferric chloride, 15 cc. of 85% phosphoric acid, and 10 to 12 drops of 0.2% barium diphenylamine sulfonate. Total volume of solution titrated approximately 300 cc.

0.1005 <i>N</i> UO ₂ (CH ₃ COO) ₂ taken, cc.	0.1 <i>N</i> K ₂ Cr ₂ O ₇ used, cc.	0.1 <i>N</i> K ₂ Cr ₂ O ₇ calcd., cc.	Error, %
25.00	25.16	25.12	+0.15
25.00	25.13	25.12	.0
25.00	25.13	25.12	.0
25.00	25.12	25.12	.0
25.00	25.14	25.12	+ .1
25.00 ^a	25.15	25.12	+ .1
25.00 ^a	25.14	25.12	+ .1
10.00	10.05	10.05	.0
10.00	10.09	10.05	+ .4
5.00	5.08	5.03	+1.0
5.00	5.06	5.03	+0.6
5.00	5.06	5.03	+ .6

^a Seven drops of 0.5% diphenylamine used as indicator.

determined empirically by working with mixtures of the same composition as the solution to be titrated at the equivalence point. In agreement with the data of L. A. Sarver and Kolthoff⁴ the correction was found to be 0.15 cc. of 0.01 *N* dichromate per 0.24 cc. of 0.2% indicator (to be subtracted from the amount of dichromate used in the titration). The data reported in Table II have been corrected for the indicator error. The results show that as little as 6 mg. of uranium in 100 cc. of solution can be determined with an accuracy of 0.5 to 1%.

TABLE II

5 cc. of 2% (0.12 *N*) ferric chloride. 5 cc. 85% phosphoric acid and 5 drops 0.2% barium diphenylamine sulfonate. Total volume of solution titrated about 100 cc.

0.01005 <i>N</i> UO ₂ (CH ₃ COO) ₂ taken, cc.	0.01 <i>N</i> K ₂ Cr ₂ O ₇ used, cc.	0.01 <i>N</i> K ₂ Cr ₂ O ₇ calcd., cc.	Error, %
25.00	25.06	25.12	-0.25
25.00	25.10	25.12	- .1
25.00	25.07	25.12	- .20
25.00	25.11	25.12	.0
25.00	25.08	25.12	- .15
25.00	25.11	25.12	.0
10.00	10.07	10.05	+ .2
10.00	10.03	10.05	- .2
10.00	10.05	10.05	.0
5.00	5.06	5.03	+ .6
5.00	5.08	5.03	+1.0
5.00	5.06	5.03	+0.6

Notes.—1. Although Lundell and Knowles¹ have shown that a solution of quadrivalent uranium in 5% sulfuric acid is quite air stable, it was thought necessary to test this point with very dilute solutions. Experiments were made with 100-cc. portions of 0.001 *N* U^{IV} in 5% sulfuric acid, through which air was bubbled for various lengths of

(4) Sarver and Kolthoff, *THIS JOURNAL*, **53**, 2906 (1931).

time. It appeared that the solutions were stable for at least half an hour; after passing air through for one hour 1% of the U^{IV} was oxidized to the hexavalent state.

2. It is recommended to add an amount of ferric iron to the U^{IV} solution in excess of the amount of uranium present. With a deficiency of iron a good end-point is obtained; the results, however, have a tendency to be slightly low.

Application of the Uranium Titration to the Indirect Determination of Sodium

In the precipitation of sodium as sodium uranyl zinc acetate the directions of Barber and Kolthoff³ were closely followed. Precipitations were made at 20° by immersing the mixture in a water-bath maintained at 20°, and shaking every five minutes. The wash alcohol saturated with the triple salt was removed by two washings with ether. Experiments made with 25 cc. of 0.01 *N* uranyl solution showed that in the presence of 0.5 cc. of alcohol a positive error of 2% and of 1 cc. of alcohol of 4% occurred. The precipitate was collected on a sintered glass crucible (Schott 1 G-4), and after washing dissolved in 5% sulfuric acid and treated as described in the first part of this paper. In experiments in which more than 1 mg. of sodium was present, the precipitate was weighed before dissolving it. In cases where less than 0.5 mg. of sodium was present a special filtration apparatus was used. This was an immersion filter which consisted of a 6-mm. Pyrex tube having a disk of fritted Pyrex glass fused into its lower flared end. The upper end of the tube was attached by a rubber connection and a glass tube to a suction flask.

The method of using the apparatus is as follows. The "filter-stick" is immersed in the solution containing the precipitated triple salt and the suction is turned on, which causes the liquid to be drawn up through the filtering disk and into the suction flask. By proper manipulation the whole of the solution may be removed from the precipitation flask, leaving the precipitated triple salt on the under side of the filter disk; 1-2 cc. of the reagent is then added to the precipitation flask and drawn off, followed by five or six 1-2-cc. portions of 95% alcohol (saturated with the triple salt) and finally by two small portions of ether. During the entire washing process the suction should be left on with the bottom of the "filter-stick" resting on the bottom of the flask. In this manner a very rapid and thorough washing of the precipitate is effected.

The filter-stick is then disconnected from the apparatus at the rubber connection, being kept in the precipitation flask meanwhile. The dry precipitate is then dissolved in 5% sulfuric acid by directing a stream of the dilute acid from a wash bottle down the inside of the filter-stick and forcing the liquid out through the filter disk into the flask by means of pressure from the mouth. The process is repeated three or four times with 2-cc. portions of the acid in order to remove the last traces of the salt from the filter disk. The solution in the flask is then diluted to 20-25 cc. with 5% sulfuric acid and is ready for reduction and titration.

If the filter disk is coarse, so as to permit small crystals to pass through, it is necessary to augment its effectiveness with a small disk of filter paper as follows. A disk of filter paper is cut so as to be slightly larger than the filter disk and is wetted with a drop of water. It is then pressed against the face of the filter disk with the suction turned on. In this manner the paper is held securely in place on immersion in the liquid to be filtered, and loss of precipitate through the filter disk is prevented.

This method of filtration and washing is very rapid. A total time of twenty-six minutes was required to filter, wash and dissolve six precipitates, an average time of slightly more than four minutes for each sample.

Discussion

The volumetric determination of uranium in sodium uranyl magnesium acetate, prepared according to the direction of E. C. Caley and C. W.

TABLE III
GRAVIMETRIC AND VOLUMETRIC DETERMINATION OF SODIUM
1 cc. 0.1 N dichromate corresponds to 0.383 mg. of Na

Sodium taken, mg.	Weight triple salt, g.	0.1 N $K_2Cr_2O_7$ used, cc.	Sodium found, mg.		Error, %	
			Grav.	Vol.	Grav.	Vol.
8.000	0.5339	20.82	7.98	7.98	-0.25	-0.25
8.000	.5327	20.81	7.96	7.97	-.5	-.4
4.000	.2687	10.56	4.02	4.05	+.5	+1.2
4.000	.2688	10.55	4.02	4.05	+.5	+1.2
1.600	.1107	4.32	1.65	1.65	+3.0	+3.0
1.600	.1091	4.32	1.63	1.65	+1.8	+3.0
1.600	.1099	4.30	1.64	1.64	+2.4	+2.4
1.600 ^a	.1099	4.30	1.64	1.64	+2.4	+2.4
1.600 ^a	.1093	4.31	1.64	1.64	+2.4	+2.4

^a 25 mg. of potassium chloride added to 1 cc. of sodium solution.

TABLE IV
DETERMINATION OF 0.8 TO 0.08 MG. OF SODIUM

Sodium taken, mg.	0.01 N $K_2Cr_2O_7$ cc.	Sodium found, mg.	Error, %	Sodium taken, mg.	0.01 N $K_2Cr_2O_7$ cc.	Sodium found, mg.	Error, %
.800	20.91	.801	+ .1	.080	2.09	.080	0.0
.800	20.69	.792	-1.0	.080	2.11	.081	+1.2
.800	20.80	.796	-0.5	.080	2.05	.079	-1.2
.400	10.35	.396	-1.0	.080	2.25	.086	+7.5
.400	10.37	.397	-0.7	.080	2.06	.079	-1.2
.400	10.35	.396	-1.0	.16 ^a	4.05	.155	-3.2
.160	4.05	.155	-3.2	.16 ^a	4.15	.159	-0.7
.160	4.05	.155	-3.2	.08 ^a	1.95	.075	-6.2
.160	4.05	.155	-3.2	.08 ^a	2.20	.084	+5.2

^a Ten mg. of potassium chloride added to 1 cc. of the sodium solution.

Foulk,⁵ has been studied by N. H. Furman, E. R. Caley and J. C. Schoonover.⁶ Their procedure gives accurate results with relatively large amounts of sodium, but fails in the determination of minute quantities of this element. In a special study of the latter problem, Caley⁷ states: "When it is considered that this is not intended as a micro method, it will be seen that the results obtained down to and including 0.20 mg. quantities of sodium are, in general, satisfactory." However, results reported in Table I of Caley's paper reveal that relative errors of -10 to +35% occur in the determination of quantities of sodium of about 0.2 mg. Even with his modified reagent, which Caley does not recommend for general use, deviations of 10% or more were found with small amounts of sodium. Now it should be realized that the volumetric determination of sodium is of practical importance only when we are dealing with minute quantities of

(5) Caley and Foulk, *THIS JOURNAL*, **51**, 1664 (1929).

(6) Furman, Caley and Schoonover, *ibid.*, **54**, 1344 (1932); see also Kahane, *Bull. soc. chim.*, [4] **47**, 382 (1930).

(7) Caley, *THIS JOURNAL*, **54**, 432 (1932).

sodium, yielding precipitates of too small a weight to allow accurate weighing on an ordinary analytical balance. If the weight of the precipitate is more than about 50 mg., it can be weighed without any further manipulation in the air dry state. Comparison of the results obtained by Caley with those reported in Table IV shows definitely that the sodium uranyl zinc acetate reagent is far superior to the corresponding sodium uranyl magnesium reagent in the determination of small amounts of sodium.

In addition it may be stated that the presence of 10 mg. of potassium chloride in 1 cc. of the sodium solution has no influence upon the results, as may be inferred from some of the figures in Table IV. One per cent. of sodium in potassium chloride can be determined with a relative accuracy of a few per cent. if 10 mg. of potassium chloride is dissolved in 1 cc. of water and treated with 10 cc. of the reagent according to the standard procedure. If the amount of sodium present is larger than 1 mg. the presence of 25 mg. of potassium chloride is without any influence; however, if traces of sodium of the order of 0.1 mg. have to be determined, irregular and high results are found in the presence of 25 mg. or more of potassium chloride.

Summary

1. Quadrivalent uranium can be titrated with great precision using potassium dichromate as a reagent and diphenylamine sulfonate (or similar substances) as indicator. Following the directions for the reduction given by Lundell and Knowles, a simple procedure has been given by which very small quantities of uranyl can be determined.

2. The method has been applied to the indirect sodium determination, this cation being precipitated in the form of sodium uranyl zinc acetate. This method is especially advantageous in the estimation of minute quantities of sodium and yields highly satisfactory results.

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