[Contribution from the Chemical Laboratory, Connecticut Agricultural College.]

THE ESTIMATION OF URANIUM AND PHOSPHORUS.

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It has been shown by Newton[1] that ferric iron in sulfate solution can be quickly and accurately estimated by reducing with titanous sulfate, oxidizing the excess of titanous salt with bismuth trioxide, filtering off the excess of bismuth trioxide and reduced bismuth, and titrating the resulting clear solution with a 0.1 *N* solution of potassium permanganate. As it was afterwards discovered that uranyl salts in sulfate solution were apparently reduced by titanous sulfate to the uranous condition, the present investigation was undertaken for the purpose of applying the above method to the estimation of uranium and to the estimation of phosphorus after the latter had been precipitated as ammonium-uranyl phosphate.

For this work a solution of titanous sulfate of convenient strength was prepared as follows: To 100 cc. of sulfuric acid were added little by little and with continual stirring 25 g. portions of the best hydrous c. p. titanium oxide, the whole being kept constantly heated to the fuming point of the acid. The resulting pasty mass was allowed to come to room temperature and cautiously transferred to a beaker containing about 200 cc. of cold water. After standing a short time the somewhat cloudy solution of titanic sulfate was filtered, reduced to the titanous condition by means of zinc, and then filtered directly into about two liters of recently boiled distilled water contained in a reservoir to which a Squibb's automatic buret and a hydrogen generator were immediately attached. By this means the easily oxidized titanous sulfate was kept under a constant pressure of hydrogen and measured amounts of the solution were drawn as wanted. As it was convenient to know the strength of the titanous sulfate solution it was titrated directly against a 0.1 *N* solution of potassium permanganate.

An approximately 0.1 *N* solution of uranyl sulfate was obtained by treating an equivalent amount of uranyl acetate of tested purity with sulfuric acid, filtering and diluting to the required volume. This solution was standardized in the gravimetric way by precipitating the uranium by ammonia, washing with dilute ammonium nitrate solution, igniting and weighing as U_3O_8.

A phosphate solution was obtained by dissolving about 6.359 g. of microcosmic salt in a liter of water, the solution being afterwards standardized by use of the magnesium pyrophosphate method as outlined by B. Schmitz.[2]

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[1] *Am. J. Sci.*, **25**, 343 (1908).

[2] F. P. Treadwell's "Analytische Chemie," 1911.

The potassium permanganate solution of approximately 0.1 *N* value was exactly standardized by titrating against carefully weighed portions of purified sodium oxalate previously dissolved in a convenient volume of water, acidulated with 1:1 sulfuric acid and heated to 80°. This method is the one recommended by the Bureau of Standards when using sodium oxalate as a standard in volumetric analysis and is exactly described in their Circular, Number 40. The sodium oxalate here used was kindly furnished by the above-mentioned Bureau.

A bismuth trioxide must be taken which shows no appreciable reducing action toward potassium permanganate. A number of 2 g. lots of the sample used, when dissolved in sulfuric acid, cooled, and diluted, were permanently colored by the first drop of 0.1 *N* solution of potassium permanganate.

The Estimation of Uranium.

In preliminary experiments it was found that bismuth trioxide had no appreciable oxidizing action on uranous salts. Table I contains results obtained by titrating with permanganate the uranous solution left after reducing with zinc a measured amount of uranyl sulfate, cooling, adding a gram of bismuth trioxide, and filtering.

TABLE I.—DATA SHOWING LACK OF OXIDIZING EFFECT OF BISMUTH TRIOXIDE ON URANYL SULFATE.

$KMnO_4$ used. cc.	UO_2 present. g.	UO_2 found, g.	Error. g.
8.01	0.1083	0.1088	0.0005+
7.91	0.1083	0.1074	0.0009—
7.97	0.1083	0.1082	0.0001—
7.98	0.1083	0.1084	0.0001+
7.93	0.0183	0.1077	0.0006—
8.00	0.1083	0.1086	0.0003+
7.95	0.1083	0.1080	0.0003—

In Table II are recorded results obtained when titanous sulfate was used as the reducing agent. For these experiments measured amounts of uranyl sulfate were run into an Erlenyemer flask of 150 cc. capacity and followed by a slight excess of titanous sulfate solution. Enough concentrated sulfuric acid was then added to make the solution approximately 16% acid by volume. (It was found that uranyl salts are more easily reduced and when reduced much more stable in an acid solution of this concentration than in one that is weaker.) The flask and contents were then cooled under the tap, a small amount of bismuth trioxide was added (enough in each case to oxidize the excess of titanous sulfate) and the flask then left to stand a minute or two with occasional shaking. By the use of the filter pump and a platinum cone well padded with asbestos the solution was quickly filtered free from bismuth trioxide and reduced bismuth, the asbestos pad carefully washed three or four times with a 16% sulfuric acid solution and the combined filtrates titrated with standard potassium permanganate. As the titanous sulfate solution contained a small amount of iron, a slight correction had to be made in the permanganate reading. This correction was easily and accurately made by a method of estimating iron in the presence of titanium as worked out by Gooch and Newton.[1]

TABLE II.—DATA ON TITRATION OF URANIUM AFTER REDUCTION BY TITANOUS SULFATE IN PRESENCE OF BISMUTH TRIOXIDE.

$KMnO_4$ used, cc.	UO_2 present, g.	UO_2 found, g.	Error, g.
4.03	0.0541	0.0545	0.0004+
4.06	0.0541	0.0549	0.0008+
8.06	0.1083	0.1092	0.0009+
8.03	0.1083	0.1088	0.0005+
7.96	0.1083	0.1079	0.0004—
12.03	0.1624	0.1631	0.0007+
12.00	0.1624	0.1626	0.0002+
12.00	0.1624	0.1626	0.0002+
12.00	0.1624	0.1626	0.0002+
16.03	0.2166	0.2173	0.0007+
16.00	0.2166	0.2169	0.0003+
16.03	0.2166	0.2173	0.0007+
16.03	0.2166	0.2173	0.0007+

As 1 cc. of 0.1 *N* permanganate corresponds to 0.01350 + g. of uranium dioxide and one drop or one-thirtieth of a cc. corresponds to 0.00045 + g. of uranium dioxide, it appears that any appreciable error in the process is probably due to the reading of the end point.

The Estimation of Phosphorus.

It has long been known that under proper conditions an alkali phosphate is completely precipitated by adding to it an excess of uranyl nitrate. In using the above reaction for the estimation of phosphorus when a separation of the ammonium-uranyl phosphate is involved, the process of filtration has always been the principle difficulty. In fact, E. F. Kern[2] made the statement that owing to its extreme fineness, ammonium-uranyl phosphate could not be filtered successfully through a Gooch crucible. Pulman[3] in his paper on "The Estimation of Uranium and Uranyl Phosphate" which involved the filtering of the finely divided ammonium-uranyl phosphate, after giving Kern's statement, wrote of his own experience as follows:

> "It was found that the precipitate went through two ashless filter papers (Schleicher and Schüll, No. 589), and also that an asbestos felt of ordinary tightness in a Gooch crucible would not entirely retain the precipitate. By shaking up the flask containing the asbestos, however, allowing it to settle a minute and then pouring off the particles still in suspension, a very finely divided asbestos was obtained, which when poured

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[1] *Am. J. Sci.*, **23**, 365 (1907).

[2] THIS JOURNAL, **23**, 710 (1901).

[3] *Am. J. Sci.*, **16**, 229 (1903).

upon the felt made in the ordinary way, was found to give a pad of such tightness that the filtrate obtained from the ammonium-uranyl phosphate was perfectly clear."

And in conclusion he writes:

> "The only objection to the process is that the filtering and washing of the precipitate are apt to be slow, especially when large amounts of the material are being treated."

When using the Gooch crucible our experience was similar to that of Pulman, two to three hours being sometimes needed to complete the filtering process when larger amounts of microcosmic salt were taken for analysis. It was thought that a perforated platinum cone lined with an asbestos felt would allow of faster filtering and still retain the finely divided ammonium-uranyl phosphate. A few experiments with a 2.5 in. cone sufficed to show that not only did the liquid filter much faster, but also that it was not necessary to use an extremely fine asbestos, because the ordinary asbestos as usually prepared for the Gooch crucible (when put on with some care) answered the purpose quite as well. With the help of this filtering cone, experiments were carried on in the effort to adapt the previously described method for the estimation of phosphorus.

The process as finally adapted is as follows: a measured amount of standard microcosmic salt solution was drawn into a 250 cc. beaker and a mixture of 10 g. of ammonium acetate, freshly prepared by neutralizing concentrated ammonium hydroxide with 50% acetic acid, and 5 cc. of glacial acetic acid was added. The volume was then made up to 150 cc. and the solution heated nearly to the boiling point. An excess of uranium nitrate was then slowly added with constant stirring, after which the beaker and contents were kept heated nearly to the boiling point for half an hour. After cooling to room temperature the resulting ammonium-

TABLE III.—INDIRECT DETERMINATION OF PHOSPHORUS IN AMMONIUM-URANYL PHOSPHATE.

$KMnO_4$ used, cc.	UO_3 equiv. to P_2O_5 present, g.	UO_3 found. g.	P_2O_5 present, g.	P_2O_5 equiv. to UO_3 found, g.	Error on P_2O_5, g.
3.3	0.0477	0.0470	0.01183	0.0116	0.0002—
3.35	0.0477	0.0479	0.01183	0.0118	0.0000
3.35	0.0477	0.0477	0.01183	0.0118	0.0000
3.33	0.0477	0.0474	0.01183	0.0117	0.0000
3.3	0.0477	0.0470	0.01183	0.0116	0.0002—
6.7	0.0954	0.0959	0.02367	0.0237	0.0001+
6.65	0.0954	0.0952	0.02367	0.0236	0.0000
6.63	0.0954	0.0949	0.02367	0.0235	0.0001—
6.63	0.0954	0.0949	0.02367	0.0235	0.0001—
9.96	0.1431	0.1428	0.03550	0.0354	0.0000
9.95	0.1431	0.1427	0.03550	0.0353	0.0001—
9.95	0.1431	0.1427	0.03550	0.0353	0.0001—
13.26	0.1909	0.1903	0.04734	0.0472	0.0001—
13.33	0.1909	0.1913	0.04734	0.0474	0.0001+
13.3	0.1909	0.1909	0.04734	0.0473	0.0000

uranyl phosphate ($UO_2NH_4PO_4$) was filtered on an asbestos felt contained in the platinum cone which had been previously moistened with a 2% solution of ammonium acetate. After carefully washing the precipitate with the 2% ammonium acetate solution the cone and contents were transferred to a funnel of convenient size and the precipitate was dissolved and washed into a 150 cc. Erlenmeyer flask with the use of a 16% solution of sulfuric acid. This solution was then treated in turn with titanous sulfate and bismuth trioxide and titrated with potassium permanganate exactly as described in the process for the estimation of uranium. The results obtained are given in Table III.

STORRS, CONN.

EXPERIMENTS ON THE DISTILLATION OF LIQUID AIR IN A MAGNETIC FIELD.[1]

BY R. S. MCBRIDE.

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In a letter to the Bureau of Standards dated February 8, 1912, Mr. A. Cressy Morrison of New York City, suggested that the magnetic properties of liquid oxygen were such as perhaps to make possible an improvement in the separation of oxygen and nitrogen by distillation of liquid air in a strong magnetic field and requested the Bureau to investigate this point. No extended search of the literature was made, but it was believed that this possibility had not been previously tested. Although there was no evident theoretical ground for the belief that the separation might be improved by this method, the possibilities seemed sufficient to justify the Bureau in making the preliminary tests which are described below.

It was found necessary to use small Dewar tubes so that the evolution of the gas would be sufficiently slow and uniform to make possible accurate sampling at different stages of the distillation. For each comparison the tubes, which were about 2.8 cm. inside diameter and 20 cm. long, were first filled with a sample of the liquid air to chill them, then emptied, filled with equal quantities (25 to 50 cc.) of the liquid and one was placed in position between the poles of a powerful electromagnet and the other entirely outside the magnetic field.

Samples of the gases coming off from the tubes were collected over water at known intervals and analyzed. By comparison of the results obtained from the two simultaneous distillations, the influence of the magnetic field was determinable. Since the speed of evaporation could not be made exactly the same in the two distillations which were to be compared, the quantity of gas evolved during the intervals between collection of samples was measured roughly and the comparison between dis-

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[1] Published with the permission of the Director, Bureau of Standards, Washington.