Volumetric determination of uranium using titanous sulfate as reductant before oxidimetric titration

By James S. Wahlberg, Dwight L. Skinner, and Lewis F. Rader, Jr.

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TEPCO, RPS, Washington, (including master)	2
	70

CONTENTS

ILLUSTRATIONS

TABLES

VOLUMETRIC DETERMINATION OF URANIUM USING TITANOUS SULFATE AS REDUCTANT BEFORE OXIDIMETRIC TITRATION

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ABSTRACT

A new method for determining uranium in samples containing 0.05 percent or more U_3O_8, using titanous sulfate as reducing agent, is much shorter, faster, and has fewer interferences than conventional methods using reductor columns.

The sample is dissolved with sulfuric, nitric, perchloric, and hydrofluoric acids. Elements that would otherwise form insoluble fluorides are kept in solution by complexing the fluoride ion with boric acid. A precipitation is made with cupferron to remove interfering elements. The solution is filtered to remove the precipitated cupferrates instead of extracting them with chloroform as is usually done. Filtration is preferred to extraction because any niobium that may be in solution forms an insoluble cupferrate that may be removed by filtering but is very difficult to extract with chloroform.

Excess cupferron is destroyed by oxidizing with nitric and perchloric acids, and evaporating to dense fumes of sulfuric acid. The uranium is reduced to U(IV) by the addition of titanous sulfate, with cupric sulfate used as an indicator of the completeness of the reduction. Metallic copper is formed when all the uranium is reduced. The reduced copper is then reoxidized by the addition of mercuric perchlorate, an excess of ferric

sulfate added, and the solution titrated immediately with standard ceric sulfate with ferroin as an indicator.

Precision of the method compares favorably with methods in common use, both for uranium ores and for most types of uranium-rich materials.

INTRODUCTION

Methods in common use for the determination of uranium require the reduction of the uranium to U(IV) and subsequent titration to U(VI) with a standard oxidant. This reduction has usually been done by passing the solution through a reductor column filled with metal (6, 12). The method here described has significant advantages over methods using reductor columns both in speed and in freedom from interferences.

Reductor columns for reducing uranium have four disadvantages: 1. Solutions must be reduced by passage through the column one at a time. This individual treatment of each solution adds to the time needed in making a series of determinations. 2. Metal columns become "poisoned" by ions contained in the solutions, particularly nickel (3) and cobalt, and their reducing power is thus lost. 3. Amalgamated zinc in the reductor columns partially reduces uranium to U(III), making it necessary to oxidize the uranium to U(IV) by aeration before titrating. 4. If air enters the column, peroxides form and these give variable results.

Metal columns which reduce uranium only to the quadrivalent state are an amalgamated cadmium column (2) and a lead metal column (1, 15). Liquid bismuth amalgam will reduce uranium to the quadrivalent state in 6 to 10N sulfuric or hydrochloric acid (18).

The method here described using titanous sulfate as a reducing agent eliminates the use of any reductor column or liquid amalgam for reducing the

uranium ion. Titanous solutions are strong reducing agents but because of their instability in air they are not in common use. Titanous solutions have been used chiefly in reductimetric titrations of easily reduced ions (5, 8, 9, 10, 13, 19). Rodden and associates (13) refer to the use of titanous sulfate as a reductant in the oxidimetric titration of uranium, excess titanous ion being removed by the use of bismuth oxide. The bismuth metal formed and the excess bismuth oxide must be removed by filtering before titrating the solution.

Titanous sulfate is not used as a titrant in the method here described, but merely as a reductant prior to the oxidimetric titration of the reduced uranium. For this reason the titanous solution does not have to be kept at a standard strength. It is used in excess and the excess destroyed. The instability of the titanous solution is overcome by storing it in a closed container with zinc amalgam as a stabilizer.

The reduction of uranium just to U(IV) is thus accomplished by simple addition of reagents to the test solution and involves no difficult manipulative step. The new method not only offers a simple and rapid means of reduction but also eliminates the need for removal of the hydrogen sulfide group, which is required when using a metal column reductor.

The method has been applied successfully to the general sandstone-type uranium ores both oxidized and reduced, and both high and low in vanadium. Also tested successfully were varieties of uranium ores high in iron, copper, nickel and cobalt, selenium, low-rank high-ash coals, and petroliferous material. No difficulty with the method was experienced in the analysis of uranium-rich samples containing relatively large amounts of thorium, rare earths, niobium and titanium such as might be expected in uranium ores associated with euxenite or brannerite. The method of sample solution described

below obviously needs to be more elaborate for such refractory materials as monazite or zircon.

CHEMICAL PRINCIPLES

A slight excess of titanous sulfate is used in this procedure to reduce uranium to the quadrivalent state. Cupric ion in the solution serves to indicate an excess of the titanous reagent by being reduced to red copper metal. An excess of mercuric perchlorate is then added to oxidize the copper metal to cupric ion, Cu^{++}, an equivalent amount of mercurous ion, Hg^{+}, being formed in the solution. A trace of ferric iron, too small to cause error in the final titration, catalyzes these reactions. The mercurous ion formed is not oxidized by the ceric sulfate titrant except at boiling temperature (17). Because air oxidation of the quadrivalent uranium is catalyzed by the cupric ion in the solution (13) the titration of the solution is done immediately by adding an excess of ferric sulfate and titrating with standard ceric sulfate in the presence of ferroin indicator.

The possibility of interference by ions not removed by cupferron, perhaps by catalyzing the oxidation of the mercurous ion by the titrant or through other side reactions, was thoroughly studied. These ions were found to have no effect either on the blank titrations or with known quantities of uranium. As further evidence of the validity of the method, a large number of comparisons have been made with results obtained by the reductor column method to be sure that side reactions did not invalidate the results.

Selenium, if present in large amounts, causes difficulty because it is reduced to red selenium metal that masks the end-point of the titration. With moderate amounts of selenium the end-point was not masked seriously, and correct titres for uranium were obtained.

In preparing the sample solution, if boric acid is not added, low results are obtained in samples high in rare earths and thorium due to the precipitation of their insoluble fluorides and coprecipitation of uranium. The boric acid forms complexes with the fluoride ion and keeps these elements in solution.

Metals precipitated by cupferron are removed by filtration, rather than by extraction, because any niobium that may be in solution forms an insoluble cupferrate that is difficult to extract. This filtration is a rapid semiautomatic step using equipment herein described. Sufficient niobium occurs in many of the uranium ores from various locations in the western United States to make its removal necessary.

EXPERIMENTAL DATA

Reagents and apparatus

All reagents used are of analytical grade.

1. Two percent potassium permanganate solution.
2. Cupferron.
3. Ferric sulfate solution, about 0.3M: 170 grams of $Fe_2(SO_4)_3 \cdot 9H_2O$ and 50 ml sulfuric acid (conc.) per liter.
4. Orthophenanthroline ferrous complex stock solution (ferroin), (0.025M): Dissolve 1.5 grams of 1-10 orthophenanthroline monohydrate in 20 ml of water containing 0.7 gram of $FeSO_4 \cdot 7H_2O$ and dilute to 100 ml.
5. Ferroin indicator solution, (0.001M): 10 ml of the 0.025M solution (above) diluted to 250 ml.
6. Cupric sulfate solution: 35 grams of $CuSO_4 \cdot 5H_2O$ and 5 ml of 0.3M ferric sulfate solution per liter.

7. Titanous sulfate solution: Mix 20 grams of reagent grade titanium dioxide with 45 grams of ammonium sulfate. Add 125 ml of concentrated sulfuric acid. Heat carefully over a Meker burner, in a well-ventilated hood, until all foaming stops. Heat to boiling and swirl the boiling liquid vigorously over the full flame of the burner until all or most of the titanium dioxide dissolves. (A clear or slightly cloudy yellow solution results). Cool. Add carefully, with swirling, enough cold distilled water to dilute to approximately 500 ml. Decant or filter immediately, before hydrolysis takes place, into a flask containing zinc amalgam prepared by adding 8 g of zinc to 6 ml of mercury and 5 ml of 5 percent sulfuric acid. Swirl the solution occasionally, cover loosely until the evolution of gas stops, and then stopper the flask tightly. The solution has a deep-purple color.

8. Mercuric perchlorate solution, about 1M: This solution may be prepared as follows: Dissolve 334 grams of $Hg(NO_3)_2 \cdot 1/2H_2O$ in approximately 1 liter of water. Precipitate the mercury as hydrated oxide with sodium hydroxide. Filter and wash the precipitate well with water. Transfer the precipitate to a 1-liter beaker and add 185 ml of perchloric acid to dissolve the mercuric oxide. Transfer to a 1-liter volumetric flask and dilute to volume.

9. Standard uranium solution, 1.000 mg U/ml: Dissolve 1.1804 grams 99.9 percent U_3O_8 (Black oxide MS-ST) in 50 ml of concentrated nitric acid in a 300-ml Erlenmeyer flask. Add 50 ml of (1+1) sulfuric acid and evaporate to dense fumes of sulfuric acid. Cool and transfer to a 1-liter volumetric flask and dilute to volume.

If the pure U_3O_8 is not available, prepare a solution from the appropriate weight of reagent grade uranyl nitrate or other suitable

salt, by adding 50 ml of (1+1) sulfuric acid and evaporating to dense fumes, cooling, and diluting to 1 liter. Standardize by precipitating the uranium from replicate aliquots with ammonia and weighing as U_3O_8 after ignition to 1000° C. (4, 7, 11, 18).

10. Ceric sulfate solution: 0.01N: Dissolve 21.2 grams of $Ce(HSO_4)_4$ in 220 ml of 1+1 sulfuric acid. Dilute to 4 liters. One ml = 1.3 mg U (approximately). Standardize by titrating with the ceric sulfate solution a number of 50-ml aliquots of the standard uranium solution, each in 175 ml of five percent sulfuric acid, in accordance with steps 6, 7, and 8 of the procedure immediately following. Establish the blank titration by titrating the acid solution without addition of uranium. Calculate the uranium equivalence of the ceric sulfate solution.

An independent check of the titre of the ceric sulfate solution may be made with N.B.S. arsenious oxide by the Gleu procedure (14). The titre obtained by this method should check that obtained by standard uranium solution.

11. Bulb, for precipitation and filtration of the cupferrates: A 500-ml leveling bulb with the connection for rubber tubing cut off, and the hole made to fit a no. 0 rubber stopper. The top of the bulb is also fitted with a rubber stopper. Use of this bulb is described under procedure. A 300-ml Erlenmeyer flask may be substituted for the bulb if the flask is fitted with a rubber stopper drilled in the center to fit a no. 0 rubber stopper which may be removed for the filtration.

12. Filter stand: A stand for holding the bulb described in 9 at the proper distance above the filter paper in a funnel, as shown in Figure 1.

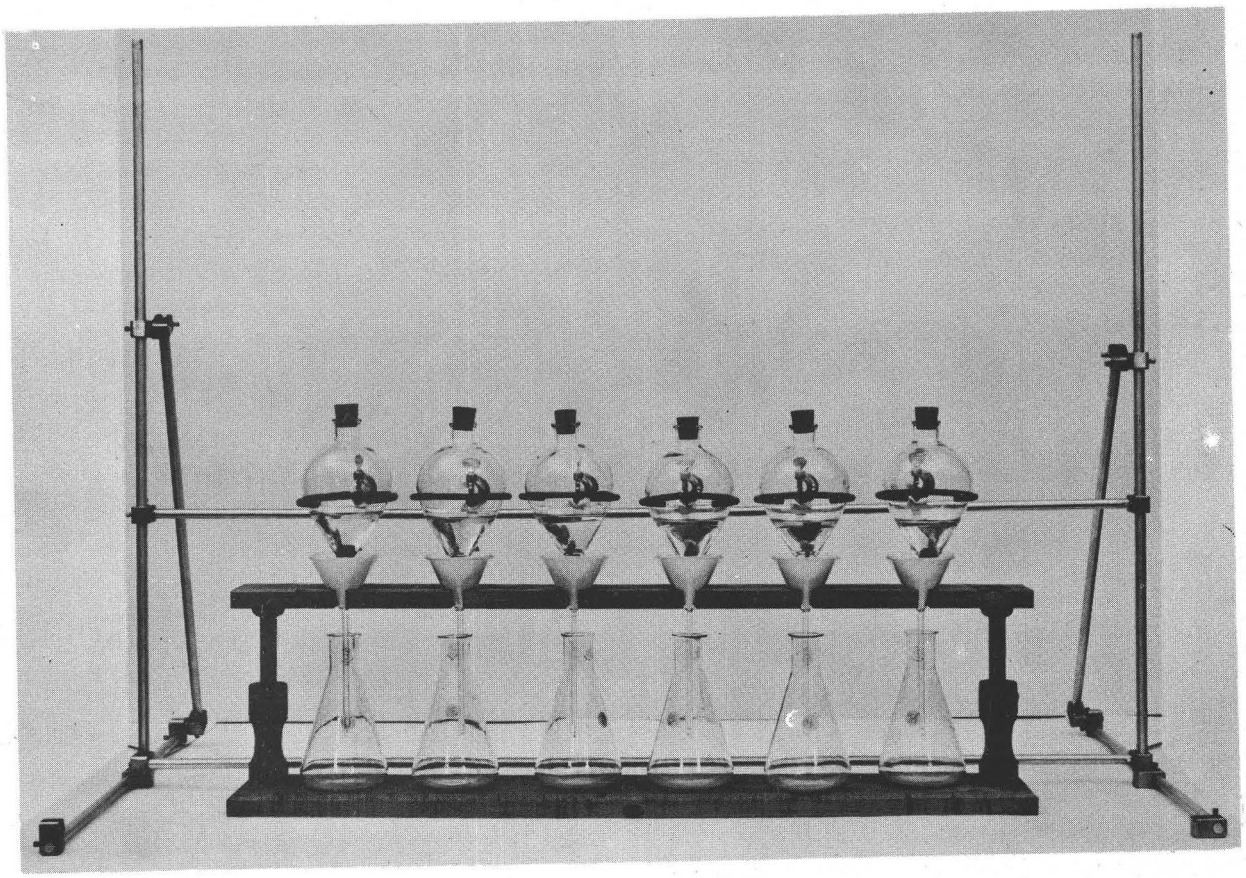

Figure 1.--Apparatus for semiautomatic filtration to remove insoluble cupferrates.

Procedure

1. Accurately weigh and transfer to a 300-ml Erlenmeyer flask an appropriate weight of the sample, indicated by the figure for equivalent uranium (eU) which may be obtained by radiometric technique. For 0.050 to 0.3 percent U, use a 4-g sample; for 0.3 to 3 percent U, use 2 g; for 3 to 6 percent U, use 1 g; for 6 to 10 percent U, use 0.5 g; and above 10 percent use a 0.25-g sample.

2. Add 20 ml of (1+1) sulfuric acid, 10 ml of concentrated nitric acid, and 2 to 3 ml of perchloric acid. Heat to boiling and then add 3 to 4 ml of hydrofluoric acid (48 percent). Digest on the hot plate until action on the sample is complete (about 1/2 hour). For precautions in the use of perchloric acid, see Smith (16).

3. Evaporate to dense fumes of sulfuric acid to remove organic matter, perchloric and nitric acids. Add more nitric and perchloric acids if necessary to insure complete destruction of organic matter, and again evaporate to dense fumes. Organic matter is evidenced by the solution remaining brown after reaching dense fumes of sulfuric acid.

4. Remove the metals precipitated by cupferron as follows: After cooling the solution add 80 ml of water and 50 to 100 mg of boric acid, and heat to boiling to dissolve soluble salts. Oxidize while hot with 2 percent potassium permanganate solution to a permanent pink. Cool in an ice bath to below 4° C. Transfer to a 500-ml leveling bulb (see 9 under Reagents and Apparatus), rinsing the flask well with water cooled in an ice bath. Add about 4 g of cupferron to the solution in the leveling bulb and shake thoroughly. If the supernatant liquid is still brown, add more cupferron, again shake the solution, and continue with small additions of cupferron

until the supernatant liquid is clear. Filter the solution into a 500-ml Erlenmeyer flask through a 15-cm fast filter paper by suspending the leveling bulb above the funnel through a ring in the filter stand (fig. 1), previously adjusted so that the bottom opening of the leveling bulb is well below the top of the filter paper to prevent overflow. To suspend the leveling bulb turn it upside down, remove the smaller stopper now above, place a finger over the hole, invert the bulb and slide it through the slot in the ring, lower it into the ring and remove the finger. Rinse the finger and stopper, catching the rinsings in the filter paper. The top stopper remains in place. The solution flows from the bulb onto the filter only as fast as air enters the bulb from below, the level of liquid in the funnel thus being automatically kept below the edge of the filter paper. Add a few drops of a 6 percent cupferron solution to the filtrate to test the completeness of the precipitation (shown by a white precipitate). If a brown precipitate appears, add an excess of cupferron and again filter. Wash the interior of the leveling bulb with cold 2 percent sulfuric acid saturated with cupferron, catching the washings on the paper, and wash the precipitate on the paper eight times with small portions of the same wash solution.

5. To the filtrate add 15 ml of concentrated nitric acid and 2 to 3 ml of perchloric acid. Evaporate the solution to dense fumes of sulfuric acid. (If the solution is yellow or brown, indicating the presence of organic matter, evaporate to dryness, cool, and add 15 ml of (1+1) sulfuric acid.) After cooling cautiously add 60 ml of water, heat to boiling, and digest on the steam bath to dissolve all soluble salts. Cool. Filter if there is any precipitate (usually the precipitate is calcium sulfate or manganese dioxide). Transfer the solution to a 400-ml beaker, rinsing the Erlenmeyer flask with water and dilute to 175 ml total volume.

6. Add 1 ml of the cupric sulfate solution, place the beaker on a white surface, and then add the titanous sulfate solution slowly, with vigorous stirring, until a slight excess is shown by the appearance of a red precipitate of metallic copper. Allow the solution to stand for fifteen minutes to permit the reaction to reach equilibrium. Add rapidly, with vigorous stirring, 2 ml of the mercuric perchlorate solution.

Note: If the mercuric perchlorate solution is not added rapidly enough, some metallic mercury forms which gives slightly high results for uranium (equivalent to about 0.2 mg of U). If metallic mercury forms, its effect on the titration can be eliminated by covering it with a small quantity of chloroform or carbon tetrachloride.

7. As soon as the metallic copper disappears, add 2 ml of the ferric sulfate solution and 2 ml of the ferroin indicator solution. Titrate immediately with standard ceric sulfate solution.

8. Run a reagent blank on 175 ml of 5 percent sulfuric acid following the procedure in steps 6 and 7.

9. From the volume of ceric sulfate solution used, after subtracting the blank, calculate the weight of uranium in the sample taken and the percentage of uranium in the ore.

Results of the method

Table 1 shows that consistently good results can be obtained with the method. In these experiments six samples, representative of the types of material usually analyzed for uranium in the laboratory but containing essentially no uranium, were selected. Solutions of these were prepared according to the procedure through step 3, and known quantities of uranium (0.0200, 0.0300, and 0.0400 g) were added as standard solutions.

Table 1.--Determination of known quantities of uranium.

Sample	U added (g)	U found (g)	Error, mg U
A	0.0200	0.0199	-0.1
	0.0300	0.0295	-0.5
	0.0400	0.0395	-0.5
B	0.0200	0.0199	-0.1
	0.0300	0.0297	-0.3
	0.0400	0.0393	-0.7
C	0.0200	0.0202	+0.2
	0.0300	0.0297	-0.3
	0.0400	0.0399	-0.1
D	0.0200	0.0202	+0.2
	0.0300	0.0299	-0.1
	0.0400	0.0399	-0.1
E	0.0200	0.0200	none
	0.0300	0.0299	-0.1
	0.0400	0.0398	-0.2
F	0.0200	0.0199	-0.1
	0.0300	0.0297	-0.3
	0.0400	0.0395	-0.5

In table 2 results with the new method are compared with those obtained with the usual method, in which interfering elements are separated with hydrogen sulfide and with cupferron, the solution passed through an amalgamated zinc column (10 percent Hg), and the uranium oxidized by aeration to the quadrivalent state before titrating. The standard deviation between the two methods for the samples shown in table 2 is 0.014 percent.

The precision of the method may be somewhat greater than this, as replicate determinations on 11 ore settlement pulps in the range of 0.20 to 0.40 percent U_3O_8 show a standard deviation of 0.0034 percent.

Table 2.--Comparison of results by the titanous sulfate method with those obtained by use of an amalgamated zinc column.

Sample no.	Uranium percent		
	Titanous sulfate method (col. A)	Amalgamated zinc method (col. B)	Difference (col. A - col. B)
1	0.34	0.32	+0.02
2	0.51	0.53	-0.02
3	0.61	0.61	none
4	0.81	0.81	none
5	0.82	0.83	-0.01
6	0.93	0.93	none
7	0.95	1.01	-0.06
8	0.98	0.98	none
9	1.11	1.12	-0.01
10	1.44	1.43	+0.01
11	3.02	3.02	none
12	3.80	3.79	+0.01

Two samples high in rare earths and niobium, which failed to give consistent results with the chloroform extraction of the cupferrates, did give consistent results when the insoluble cupferrates were filtered, as in the new method (0.38 and 0.38 percent; 1.05 and 1.07 percent, respectively).

STUDY OF POSSIBLE INTERFERENCES

The elements of the hydrogen sulfide group not removed by cupferron do not interfere, unless present in extremely large amounts, and are not usually removed.

Tests were made to study the effect of large quantities of these and other ions not removed by cupferron both on the blank and on the titration of known amounts of uranium (table 3). The elements were added in quantities equivalent to 2.5 percent of each ion in a 2-g sample. The ions were added to the test solution as salts, 20 ml of (1+1) sulfuric acid was added, and then the solution was evaporated to fumes of sulfuric acid, cooled, diluted, and filtered if necessary. The solutions were then taken through steps 6, 7, 8, and 9 of the procedure.

The results in table 3 show that selenium, when present in abnormally large amounts, is the only serious interference. Samples known to be high in selenium must be given special treatment because the selenium is reduced to the metal by titanous sulfate and the red color of the selenium metal masks the end-point of the ferroin indicator. The selenium may be removed at the time of sample solution by boiling the sample with a mixture of sulfuric acid, hydrobromic acid, and bromine before the addition of the nitric and perchloric acids.

Tests made on samples containing large amounts of mercury show that a small amount of metallic mercury is produced. (See also note, step 6 of Procedure.) This may be overcome by adding a small amount of chloroform or carbon tetrachloride to the beaker to cover the surface of the metal to prevent its consuming the titrant solution.

Large amounts of nickel and cobalt do not interfere.

Table 3.--Noninterference from ions not removed by cupferron.

Ion taken (wt. 0.05 g)	U taken (g)	U found (g)
Ag	0.0220	0.0216 1/
Ag	0	0
Hg^{++}	0.0220	0.0219
Hg^{++}	0	0
Sb^{+3}	0.0220	0.0219
Sb^{+3}	0	0
As^{+3}	0.0220	0.0219
As^{+3}	0	0
Cr^{+3}	0.0220	0.0220
Cr^{+3}	0	0
Cd	0.0220	0.0219
Cd	0	0
Pb	0.0220	0.0217
Pb	0	0
Co	0.0220	0.0219
Co	0	0
Ni	0.0220	0.0219
Ni	0	0
In	0	0
Ge	0	0
Te^{+}	0	0
Tl^{+4}	0	0
Se^{o}	0.0220	Red color 2/ Not titrated
Se^{o}	0	Red color 2/ Not titrated

1/ Silver is reduced to metal by the titanous sulfate forming a cloud before all of the uranium is reduced. This masks the precipitation of copper metal used as an indicator of the reduction and may cause slightly low results due to incomplete reduction. This cloud disappears upon the addition of mercuric perchlorate.

2/ Titration not possible because of the red color of the selenium metal. When only 0.005 g of Se was taken, correct titrations for U were obtained.

All of the halogens cause serious interference because of their complexing action with Cu^{+} ion which prevents reduction to metallic copper. They are, however, removed in the procedure for preparing the sample solution.

A large concentration of nitrate may interfere by preventing the precipitation of metallic copper or by being reduced and consuming the titrant. However, 5 ml of concentrated nitric acid added to a standard uranium solution caused no error in the titre for uranium. Residual nitrates which may be left in the solution would, therefore, cause no serious error.

CONCLUSIONS

The results obtained with the method and the lack of interference of elements that may be left in the solution show that this simple and rapid procedure is a reliable one for determining uranium in ores. It offers advantages in simplicity of operation and freedom from interference over the usual method using a column of metal for reducing the uranium.

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