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Analytical Report

on

TITRIMETRIC DETERMINATION OF URANIUM WITH POTASSIUM DICHROMATE

Submitted

on

Classification changed to Unclassified/Declassified
Authorized by Charles E. Teeter Jr (12755)
Changed by Hugh Kinser Date 6-7-12

March 8, 1946

under

Contract No. W-7405 eng-74

by

Purdue Research Foundation

and

Department of Chemistry, Purdue University

by

M. M. Kruder, W. S. Barnhart, H. Hunt, E. S. Gantz, and M. G. Mellon

Photostat Price \$ 1.80

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Research at Purdue University

by

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March 8, 1946

TITRIMETRIC DETERMINATION OF URANIUM WITH POTASSIUM DICHROMATE

Abstract

A rapid titrimetric procedure for the determination of uranium is discussed. Using this method, the samples are first fumed with sulfuric acid in the presence of 30% hydrogen peroxide to remove organic material and nitrates. After fuming, the samples are reduced with hot liquid zinc amalgam to the uranium²⁺ (III) state. Air is used to oxidize uranium (III) to uranium (IV). Ferric alum is added and the sample titrated with 0.1 N potassium dichromate solution with barium diphenylamine sulfonate as the indicator.

Moderate amounts of chromium, copper, nickel, and chlorine do not interfere. Organic matter, nitrates, iron, and copper in large quantities give high results. Nitrates must be fumed out and organic matter destroyed with 30% hydrogen peroxide. Corrections are made for iron. A precision of about 1 part in 1000 is obtained under routine conditions. If 75 mg or more of copper per 500 mg of uranium are present, some purification step prior to the reduction of the uranium is necessary.

TITRIMETRIC DETERMINATION OF URANIUM

For the determination of uranium in samples coming from the pilot plant and from products of the research group, a simple yet rapid titrimetric method was needed. The titration of uranium from oxidation state IV to VI by a standard potassium dichromate solution, in the presence of ferric alum and phosphoric acid offered the most promise. The uranium in the presence of acetate, was reduced with 3% zinc amalgam. Erratic results were often obtained when sulfate solutions were used. However, when the solution was heated to the boiling point, the reduction of uranium by means of zinc amalgam along with c p mossy zinc proved to be satisfactory. Since part of the uranium was reduced to the tervalent state the solution had to be air oxidized to convert uranium (III) to uranium (IV) before titration. A correction for iron is necessary with this method. Small amounts of copper, nickel, and chromium cause no interference.

Reagents

1. H_2SO_4 , 1:1 c p (approx. 9 M)
2. $\text{K}_2\text{Cr}_2\text{O}_7$, 0.1 N soln., 0.1 M in H_2SO_4 , standardized with MS-ST U_3O_8
3. H_3PO_4 , c p, sp gr 1.7
4. $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, c p 0.1 N soln., 48.5 g of salt per liter containing 10 ml of 1:1 H_2SO_4 .

5. Barium diphenylamine sulfonate (indicator), 0.2 g of salt per 100 ml of soln.
6. Liquid zinc amalgam, 10 lb of pure mercury is washed with 1 N H_2SO_4 and added to 30 g of 30 mesh c p zinc which previously had been washed several times with 1 N H_2SO_4 . One hundred milliliters of 1 N H_2SO_4 is added and the mixture digested on the steam block for 6-8 hours. The cooled mixture is transferred to a separatory funnel. The liquid portion of the amalgam is allowed to drain slowly into 1 N H_2SO_4 . The solid amalgam left in the funnel is saved for the next preparation.
7. Mossy zinc, c p
8. H_2O_2 , 30% c p

Apparatus

1. Leeds and Northrup potentiometer assembly with galvanometer (R=100) and a standard Weston cell.
2. The weights and burets used must be calibrated.
3. Mercurous sulphate and Pt electrodes.

Procedure

Weigh samples containing 450-550 mg of uranium. Transfer quantitatively to 400-ml beakers. Add 20 ml of 9 M sulfuric acid and 5 ml of 30% hydrogen peroxide. Evaporate on an electric hot plate, set at "low heat" overnight or until sample has fumed for at least two hours. Cool, wash

down beaker and watch glass with distilled water. Add 5 ml of 30% hydrogen peroxide, evaporate and fume for one hour. (If any organic material is still present, a third fuming will be necessary.) Cool, add 20 ml of zinc amalgam and 3-4 g of mossy zinc. Adjust the acidity to 15% with 9 M sulfuric acid. Place the beaker on an electric hot plate on "medium heat", and heat until the uranium is reduced, as evidenced by the appearance of the deep red hue of uranium (III). The reduction will require 15-25 minutes. Cool to 20°C in an ice bath. Decant the solution through a separatory funnel into a 600 ml beaker. Wash the amalgam 3-4 times with distilled water adding the washings to the bulk of the solution. Pass air, filtered through glass wool and distilled water, through the solution slowly with stirring. Determine the completion of oxidation of uranium (III) to uranium (IV) by means of a potentiometer. (The potential change for the oxidation of uranium (III) to uranium (IV) is 0.5-0.8 v. Add 30 ml of 9 M sulfuric acid, 15 ml of 0.1 N ferric alum, 5 ml of concentrated phosphoric acid, and 5 drops of barium diphenylamine sulfonate. Titrate with 0.1 N potassium dichromate to a pale reddish-purple hue as viewed in the light from a 60 watt frosted tungsten-filament light bulb.

The results of the titration will represent the uranium and any other constituents that might be present which are reduced by the zinc amalgam and are not reoxidized when air is bubbled through the solution. A correction can easily be made for iron based on its colorimetric determination.

For highly precise work a reagent blank should be determined. Also the usual buret and temperature corrections should be made.

Notes

1. Moderate amounts of chromium, copper, nickel, and chloride do not interfere. In samples analyzed in this laboratory the following amounts have been found to be present: 10-12 mg, Cu^{+2} , 0.3-0.4 mg Cr^{+3} , and 0.1-0.2 mg Ni^{+2} per 500 mg of uranium.
2. Organic matter, nitrate, iron, and large amounts of copper cause high results. The fuming procedure will destroy organic matter and remove nitrate from the samples. Iron should be determined separately and a correction made. Large amounts of copper, of the order of 75 mg or more, will cause high results with this method unless removed prior to the reduction of the uranium.
3. In the reduction procedure as described the uranium is usually reduced in 15-25 minutes. Should reduction not begin within 20 minutes, the acidity may be too low or the amount of mossy zinc insufficient.

Data showing the precision of the titrimetric determination are summarized in Table 1. The endpoint of the air oxidation of uranium (III) to uranium (IV) was determined potentiometrically for samples P-60 - P-63, inclusive.

For the other samples aeration for ten minutes was assumed to be adequate for the oxidation of uranium (III) to uranium (IV). Each result represents the average of 3-10 titrations.

SUMMARY

A rapid titrimetric procedure is described for the determination of uranium in the presence of moderate amounts of chromium, copper, nickel, chlorine, and iron. After correcting for iron, a precision of about one part in 1000 was obtained under routine conditions.

Table 1

Sample No.	Uranium, Determined, g	Mean Deviation, g	Sample No.	Uranium Determined g	Mean Deviation g
P-5	538.6	0.3	P-43	490.2	0.0
P-7	438.0	0.2	P-44	500.3	0.0
P-8	257.7	0.1	P-45	501.4	0.4
P-13	492.0	0.5	P-46	535.4	0.3
P-14	487.4	1.7	P-48	505.5	0.9
P-15	431.2	1.3	P-49	497.4	0.9
P-17	507.4	0.9	P-50	544.7	1.4
P-18	429.9	0.8	P-51	549.0	0.3
P-19	396.4	0.5	P-52	995.5	0.4
P-21	235.9	0.2	P-53	890.7	0.8
P-23	423.8	0.2	P-54	911.6	0.4
P-28	422.5	0.5	P-55	943.9	0.5
P-32	382.5	1.8	P-56	758.3	0.3
P-35	366.6	0.1	P-57	719.4	0.5
P-37	366.8	0.6	P-60	887.7	1.0
P-38	495.5	0.3	P-61	1037	2.2
P-40	495.4	0.4	P-62	1103	1.3
P-41	475.5	0.5	P-63	1073	1.1

Average deviation = 1.15/1000

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