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A PRECISE POTENTIOMETRIC TITRATION METHOD
FOR THE DETERMINATION OF URANIUM

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ABSTRACT

A precise potentiometric method for the determination of uranium in essentially pure uranium oxides is described. Ten gram samples of oxides are reduced in a Jones reductor and titrated potentiometrically to U^{+4} , using platinum and tungsten electrodes. A weighed amount of solid Bureau of Standards potassium dichromate is then used to oxidize at least 99 percent of the uranous ion, and the oxidation is completed by titration with 0.01 N potassium dichromate using calomel and platinum electrodes. This method, which is based on a primary chemical standard, has a precision of $\pm 0.015\%$ on a single determination at the 95 percent confidence interval.

Since nontechnical and nonessential prefatory material has been deleted, the first page of the report is page 5.

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A PRECISE POTENTIOMETRIC TITRATION METHOD
FOR THE DETERMINATION OF URANIUM

An accurate and precise method of uranium analysis for essentially pure uranium oxides has been developed. This method, which is based on Bureau of Standards potassium dichromate as a primary standard, was necessary to solve several problems at the K-25 Laboratories.

First, the laboratory was assigned the project of furnishing isotopic standards for commission-wide use. These standards were to be prepared by mixing uranous-uranic oxides of known isotopic concentrations. Since it had been determined that the uranium concentration of uranous-uranic oxide is dependent upon the compound from which it is prepared and also upon the conditions of ignition, it was necessary to determine the uranium content of these oxides very precisely and accurately to calculate the amount of each oxide to be mixed. Second, a discrepancy existed between the analytical results on pure uranyl fluoride solutions at the K-25 and Y-12 plants, and a precise referee method was necessary to help resolve this discrepancy. Third, it was desirable to accurately evaluate the amount of uranium present in laboratory control samples to better determine the quality of the work in the uranium analysis laboratory.

Previous work on a high precision method of uranium analysis is summarized by Rodden (1). Simon, Asbury, and Flanders (2) have also reported a precise method which employed refined weighing and titration techniques.

The general principle of most previous methods consisted of dissolving samples weighing 0.25 to 3 g. in sulfuric acid and reducing the solution to U^{+3} and U^{+4} in a suitable reductor. The solution was then aerated to U^{+4} and titrated to U^{+6} with a standard oxidizing agent. Since considerable effort had been expended in attempting to improve the precision of uranium analyses by this general procedure, it was decided in this investigation to maintain a similar approach, but to deviate from the usual procedure in several important respects. First, a ten gram sample of oxide was used instead of a 0.25 to 3 g. sample. Second, a titration was substituted for an aeration because it was found that aeration oxidizes a small amount of the U^{+4} to U^{+6} . Finally, a quantity of solid, dried, Bureau of Standards potassium dichromate calculated to oxidize at least 99 percent of the U^{+4} to U^{+6} was added to the U^{+4} solution. The oxidation was then completed by titrating the remaining U^{+4} with 0.01N potassium dichromate. This procedure was equivalent to titrating the entire sample with a 0.01N primary standard.

EXPERIMENTAL

Selection of Electrodes

Since it was desirable to titrate the samples potentiometrically, combinations of gold, platinum, tungsten, and calomel electrodes were investigated. At the U^{+4} end point, the sharpest breaks were obtained with the

platinum and tungsten electrodes, while the calomel and platinum electrodes were more satisfactory to determine the U^{+6} end point. By using these electrodes a break of 200 to 300 millivolts was observed upon the addition of 0.1 milliliter of 0.01N potassium dichromate.

Procedure*

The method consists of dissolving a ten gram sample of oxide in perchloric acid, and reducing the uranium by passing it through a Jones reductor. The solution, which after reduction contains uranium in the trivalent and tetravalent states only, is kept under nitrogen and titrated potentiometrically to the U^{+4} end point, using tungsten and platinum electrodes. Two solutions of potassium dichromate are used in this titration; a 0.1N solution is added until nearly all of the U^{+3} is oxidized and the titration is then completed with a 0.01N solution. After the U^{+4} end point has been reached, a quantity of solid Bureau of Standards potassium dichromate calculated to oxidize approximately 99 percent of the U^{+4} to U^{+6} is added. The oxidation is completed by titrating to the U^{+6} end point with a 0.01N solution of potassium dichromate, using the platinum and calomel electrodes.

RESULTS

A sample of approximately 100 grams of essentially pure UO_2F_2 was pyrohydrolyzed and ignited for 200 hours. The resulting oxide was blended to insure homogeneity, and the uranium concentrations of seven ten gram samples of the oxide were determined. The results are shown in Table 1.

TABLE 1

URANIUM CONTENT OF OXIDE IGNITED FROM URANYL FLUORIDE

<u>Sample Number</u>	<u>Uranium, Percent</u>
1	84.814
2	84.816
3	84.824
4	84.815
5	84.820
6	84.818
7	84.828
Average	84.819 $\pm$ 0.005
Theoretical	84.802
Precision of single determination	$\pm$ 0.013 ($\pm$ 0.015% of the value)

The precision is expressed as the 95% confidence limit.

* A detailed description of this method is given in the appendix.

The method was then used to determine the uranium content of uranous-uranic oxides prepared from various uranium compounds. Several ten gram samples of essentially pure uranium metal, uranyl nitrate hexahydrate, uranyl fluoride, and uranium trioxide were ignited in air for three hours at 800°C and the resulting oxides were analyzed. The results as listed in Table 2 show that the uranium contents of the various oxides were significantly different.

TABLE 2

URANIUM CONTENTS OF OXIDES IGNITED FROM VARIOUS MATERIALS

<u>Oxide Prepared From</u>	<u>Detn's</u>	<u>Uranium, Percent</u>
Uranium Metal	4	84.719 $\pm$ 0.024
Uranyl Nitrate Hexahydrate	3	84.659 $\pm$ 0.018
Uranyl Fluoride	6	84.807 $\pm$ 0.013
Uranium Trioxide	7	84.806 $\pm$ 0.008

In Table 2 the precisions are poorer than those listed in Table 1, since equilibrium in oxide composition is not reached in three hours of ignition time.

DISCUSSION

The principle advantages of this method of uranium analysis are: (1) it is based on a Bureau of Standards primary standard, (2) the aeration and indicator blanks are eliminated because a potentiometric titration is employed, and (3) the use of a large sample and the addition of a weighed amount of potassium dichromate have the effect of titrating ten grams of oxide with a 0.01N solution.

One disadvantage of the method is that a larger amount of sample is required, but this is offset by the fact that fewer samples are necessary to obtain a given precision. The method also requires a sample free of metallic impurities, but it could be used in conjunction with a purification procedure, and in this respect is not different from other methods of uranium analysis.

In the development of the method, other conditions and standard oxidants were used before the present method was adopted. It was found that potassium permanganate gave a sharper break at the U⁺⁴ end point, but that the presence of the decomposition products interfered with the U⁺⁶ end point. Ceric ammonium sulfate and ceric sulfate were satisfactory oxidants, but they had nothing to recommend them over potassium dichromate, and did not have the advantage of being primary standards. The dichromate titrations were also performed at elevated temperatures, however this did not improve the precision.

The method outlined has been used to solve the problems for which it was developed. The uranium concentrations of the oxides used to prepare commission-wide isotopic standards have been determined, the

discrepancy in the chemical analysis of uranium between K-25 and Y-12 has been resolved, and the quality control program of the uranium analysis laboratory is now based on this method.

SUMMARY

A precise potentiometric titration method for the determination of uranium has been developed. The precision of the method is ± 0.015 percent of the value on a single determination at the 95 percent confidence interval, which is better than that of any other published method. Since it is also based on Bureau of Standards potassium dichromate as a primary standard, it is to be recommended for all applications where the highest precision and accuracy are required.

BIBLIOGRAPHY

- (1) Rodden, C. J., Analytical Chemistry of the Manhattan Project, National Nuclear Energy Series, McGraw-Hill, 1950, Vol. VIII-1, P. 51-77.
- (2) Simon, W., Asbury, I., and Flanders, V. E., A Precise Volumetric Method for the Determination of Uranium in Uranium Oxides, Carbide and Carbon Chemicals Company, K-25 Plant, August 27, 1948, (K-245).

APPENDIX

A PRECISE POTENTIOMETRIC TITRATION METHOD
FOR THE DETERMINATION OF URANIUMMethod

A 10 gram sample of a pure uranium oxide is dissolved in perchloric acid and reduced to the trivalent and tetravalent valence states by means of a Jones reductor. The solution is titrated to the U^{+4} end point with potassium dichromate. Solid dichromate is then added to oxidize at least 99 percent of the uranium to U^{+6} . The oxidation of the remaining U^{+4} is then completed by titration with 0.01N potassium dichromate.

Apparatus

1. Vacuum tube voltmeter - Should be equipped with both a 0-1 volt and a 0-200 millivolt scale.
2. Jones reductor - A reductor having a 15 millimeter diameter and a 300 millimeter effective length was used. This reductor was filled with amalgamated 20 mesh zinc.
3. Magnetic Stirrer - The stirrer magnet should be covered with inert plastic.
4. Beakers - Tall form, one liter.
5. Tungsten electrode
6. Platinum electrode
7. Calomel electrode
8. Burettes - Two 50 milliliter Normax burettes

Reagents

1. Potassium dichromate - U.S. Bureau of Standards.
2. Perchloric acid - 70-72% reagent grade.
3. Potassium dichromate solutions - Standard 0.1N and 0.01N solutions, prepared from Bureau of Standards dichromate.
4. Sulfuric acid solutions - 2N solution prepared from iron-free sulfuric acid

Procedure

1. Weigh approximately 10 g. of sample to ± 0.0001 g. and transfer to a one liter tall form beaker.
2. Calculate the amount of solid potassium dichromate necessary to oxidize approximately 99 percent of the U^{+4} to U^{+6} , and weigh this quantity to ± 0.0001 g.
3. Add 30 ml. of concentrated perchloric acid to the sample and heat until it is in solution.
4. Dilute the sample to approximately 150 ml. and draw it through the Jones reductor at a rate of about 25 ml. per minute.
5. Wash the reductor 3 times with 25 ml. portions of 2N sulfuric acid and 3 times with 25 ml. portions of water. Allow each wash to drain to the top of the zinc column before the next wash is added.
6. Transfer the solution to the titration apparatus, keeping a flow of nitrogen over the solution.
7. Titrate to a 200 millivolt reading on the voltmeter with 0.1N potassium dichromate solution using the platinum and tungsten electrodes. The solution should be stirred with the magnetic stirrer during all titrations.
8. Titrate to 0 millivolts with 0.01N potassium dichromate.
9. Add the previously weighed solid dichromate to the solution immediately and allow it to stir for ten minutes.
10. Using the platinum and calomel electrodes, titrate to the U^{+6} end point with 0.01N potassium dichromate solution.

NOTES

1. The platinum and tungsten electrodes are cleaned before each titration. The platinum is cleaned by anodic treatment in a sulfuric acid solution, and the tungsten is given anodic treatment in a sodium hydroxide solution.
2. Vacuo corrections are applied to all weights.
3. The potassium dichromate is dried for one hour at 110°C .