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POTENTIOMETRIC TITRATION OF MILLIGRAM QUANTITIES OF
URANIUM IN THE PRESENCE OF IRON

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EXPERIMENTAL

Reagents

Standard Ceric Sulfate Solution
Chromous Sulfate Solution
1,10-Phenanthroline Solution

Apparatus

Titration Vessel
Titrator
Electrodes
Reference Electrode
Indicator Electrode

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For The Atomic Energy Commission
William A. Johnson
Chief, Declassification Branch

Procedure

Results

DISCUSSION

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POTENTIOMETRIC TITRATION OF MILLIGRAM QUANTITIES OF URANIUM
IN THE PRESENCE OF IRON

by Richard B. Hahn and Myron T. Kelley

Milligram quantities of uranium can be determined by semimicro titration of uranium(IV) with ceric sulfate, potassium dichromate or potassium permanganate⁽¹⁾. The reduction of uranium(VI) with a slight excess of chromous sulfate followed by a potentiometric titration of the uranium(IV) with standard ceric sulfate in an atmosphere of carbon dioxide has been employed successfully in this laboratory. This method cannot be used in the presence of iron at room temperatures, however, since the iron is reduced to Fe(II) and titrated along with the uranium. At a higher temperature (about 60° C) the iron does not interfere, but the difficulty of working with small volumes at elevated temperatures makes such a procedure impractical.

This interference can be overcome at room temperatures by complexing the Fe(II) with 1,10-phenanthroline. The oxidation potential of the Fe(II)-Fe(III) system is thus changed, and the iron no longer interferes with the titration of the uranium(IV).

EXPERIMENTAL

A description follows of the reagents, apparatus and procedure used.

Reagents: Standard Ceric Sulfate Solution, approximately 0.1 N. Slowly add 30 ml concentrated H₂SO₄ to 500 ml water with constant stirring. To this add 63 g Ce(SO₄)₂·2(NH₄)₂SO₄·2H₂O, stir to dissolve, cool, filter if turbid and dilute to 1 liter. Standardize against arsenious oxide. Ammonium hexanitrate cerate cannot be used for the preparation of this reagent because of nitrate interference.

Chromous Sulfate Solution, approximately 10%. Prepare a 10% solution of potassium chromic sulfate and pour it through a glass reactor filled

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with amalgamated zinc. Store the resulting chromous sulfate under a carbon dioxide atmosphere.

1,10-Phenanthroline Solution, approximately 0.25 g/ml. Suspend 2.5 g of 1,10-phenanthroline in 10 ml of water. Add 6 M sulfuric acid dropwise with stirring until the reagent is completely dissolved.

Apparatus: Titration Vessel. A flat-bottomed tube, 15 cm tall and 2 cm in diameter, fitted with a sidearm positioned so as to admit carbon dioxide gas above the solution.

Titration. A Precision-Dow Recordomatic Titrator modified for semimicro titrations by replacing the 50-ml syringe buret with a 0.5-ml syringe buret.

Electrodes. (a) Reference Electrode. A straight platinum wire (20 gauge, 7 in. length) sealed into the buret containing the standard ceric sulfate solution. (b) Indicator Electrode. A straight gold wire (12 gauge) which dips into the solution being titrated to a depth of approximately 5 mm. A gold indicator electrode was preferred to platinum because platinum appeared to catalyze the Cr(II)-Cr(III) oxidation by H^+ ion. For best results the gold electrode should be cleaned after each titration by dipping into a chromic acid cleaning mixture and rinsing thoroughly with distilled water.

Procedure: The nitrate-free solution is placed in the titration vessel, 50 λ of concentrated (36 M) sulfuric acid added, and the volume adjusted to about 2 to 4 ml. A stream of carbon dioxide gas is maintained over the sample, and the solution stirred magnetically, during the entire titration, using a 3/8 inch glass-covered nickel wire stirrer. Chromous sulfate is added slowly from a 50 λ micro pipet until the potential indicates complete reduction of the U(VI) to U(IV). The ceric sulfate feed is

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then turned on, and the titration continued until the Cr(II)-Cr(III) oxidation is complete. At this point 12.5 mg of 1,10-phenanthroline (50 λ of the above solution) is added for each 0.1 mg of iron present.

The 1,10-phenanthroline must not be added prior to the oxidation of the Cr(II) since it also forms a stable complex with this ion. The titration is continued until a second break in potential (the U(IV)-U(VI) break) is obtained. The instrument is standardized by determining the distance of chart travel in inches equivalent to the milligrams of uranium in a standard uranyl sulfate solution, i.e., the distance between the Cr(II)-Cr(III) break and the U(IV)-U(VI) break is measured. The quantity of uranium represented by one inch of chart is calculated and is used as a factor to calculate the amount of uranium in an unknown sample. For example: a standard sample containing 2.00 mg of U gave 7.10 inches of chart travel between the breaks which is equivalent to $\frac{2.00}{7.10} = 0.282$ mg U per inch of chart travel. An unknown gave 8.45 inches of chart travel between breaks and therefore contained $8.45 \times 0.282 = 2.38$ mg uranium. A sample titration curve is shown in Figure 1.

Results: The above procedure was used to determine milligram quantities of uranium in the presence of various amounts of iron impurity. The results are given in Table I.

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TABLE I

DETERMINATION OF URANIUM IN PRESENCE OF IRON

Sample	Fe Added (mg)	1,10-Phenanthroline Added (mg)	U (mg)		d
			Taken	Found	
1	0.125	25	2.53	2.51	0.05
2	0.250	25	2.53	2.54	0.02
3	0.370	25	2.53	2.56	0.00
4	0.500	25	2.53	2.62	0.06
5	0.250	63	2.53	2.53	0.03
6	1.00	63	2.53	2.61	0.05
7	1.00	125	2.53	2.56	0.00

$$\text{Mean} = 2.56 \pm d = 0.21$$

Average deviation of single measurement = $\frac{0.21}{7} = 0.030$ percent absolute.

$$= \frac{0.030}{2.56} \times 100 = 1.17\%$$

8	1.00	125	1.76	1.79	
9	1.00	125	0.51	0.51	

DISCUSSION

A precision and accuracy of about 1% can be obtained with samples containing only uranium and iron as metallic constituents.

Other nonreducible cations (uranium, nickel, etc.) do not interfere although their presence may cause a slight decrease in the accuracy of the method.

The method does not work successfully for the analysis of samples containing much more than one milligram of iron, even if a correspondingly larger amount of 1,10-phenanthroline is added.

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