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Ammonium Thioglycolate as a Colorimetric Analytical Reagent for Uranium (VI) in the Presence of Various Anions.

W. H. Davenport, Jr., and P. F. Thomason

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Abstract

Hexavalent uranium forms a yellow-orange soluble complex with ammonium thioglycolate in a basic solution. The color intensity remains constant over a wide pH range and is independent of the exact reagent concentration. The complex is fairly stable and unaffected by many of the common anions. A number of cations interfere either by reacting with the reagent or by precipitating in ammoniacal solutions. Some of these interferences may be eliminated by the use of excess reagent or complexing agents. The method is best suited to the determination of uranium in the concentration range 0.100 - 1.600 mg. in 25 ml. Solutions containing uranium in this range obey Beer's Law.

Introduction

Currah and Beamish (1) reported the satisfactory determination of uranium in the presence of relatively large amounts of certain cations, using ammonium thiocyanate. Other reagents (2) of varying sensitivity such as potassium ferrocyanide and sodium salicylate have been proposed. All of these methods, however, are affected by many of the common anions.

In an investigation of conditions affecting the determination of iron with ammonium mercaptoacetate (thioglycolate), Swank and Mellon (3) reported that uranyl ions formed a strong orange complex with the reagent. Anions had little effect on the iron thioglycolate color. This suggested the possibility that the reagent might be used for the colorimetric determination of uranium in the presence of various anions.

Experimental

Solutions and Methods

Ammonium Thioglycolate Ten milliliters of thioglycolic acid,

obtained from Eastman Kodak Company, were diluted with about 50 ml. of water, neutralized with 1:1 ammonium hydroxide and made up to a final volume of 100 ml. This concentration of ammonium thioglycolate was used throughout the investigation.

Standard Uranium Solution A solution of uranium, 10.6 mg/ml., was prepared from C. P. uranyl nitrate hexahydrate. The solution was standardized by evaporating aliquots to dryness and igniting to the oxide, U_3O_8, at 850° C. An aliquot of the standard solution was diluted to give a solution 0.106 mg/ml.

Ammonium Hydroxide A 1:1 solution was prepared from C. P. reagent.

Foreign Ion Solution Reagent grade salts were taken for the preparation of all foreign ion solutions. The potassium salts of the nitrate, chlorate, chromate, and bichromate ions were used and the remaining anion solutions were prepared from their ammonium salts. The cation solutions were prepared from chloride salts with the exception of lead nitrate.

Redistilled water was used for all solutions. The complexes were developed in a 25 ml. volume by adding 2 ml. of ammonium thioglycolate and 2 ml. of 1:1 ammonium hydroxide in excess of neutrality. Solutions were read vs. a reagent blank in a Beckman spectrophotometer using 1 cm. cells.

The Uranium Thioglycolate Complex

The uranium thioglycolate complex must be developed in a basic medium. Critical adjustment of pH is not necessary. In this investigation the concentration of ammonium hydroxide added gave a pH of about 10, but no change in color intensity resulted by varying the pH over the range 7.6 to 10.7.

The concentration of ammonium thioglycolate is not critical within limits. From 1 to 4 ml. of the neutralized 10 per cent reagent may be added without affecting the color. The color intensity increases slightly as excess reagent is added.

The color is stable for at least 30 minutes in direct light. A decrease

of about 4 per cent in color intensity results on standing 2 hours.

The yellow-orange complex does not show a sharp absorption maximum, fairly strong absorption taking place over the range 330-400 mμ. (Figure 1).

A plot of extinction vs. concentration for 0.100 - 1.600 mg. of uranium gave a straight line curve, indicating that the color obeys Beer's Law (Figure 2).

Effect of Anions

As much as 500 mg. of chloride, chlorate, nitrate or sulfate ion may be present without affecting the color intensity of 0.530 mg. of uranium. Smaller concentrations of fluoride, tartrate, acetate, citrate or oxalate are also without affect on the color. Carbonate and phosphate ions must be absent. As little as 1 mg. of either ion causes an appreciable decrease in color intensity. The effect of a number of anions on the color developed with 0.530 mg. of uranium is indicated in Table I. An allowance was made of ±2.5% error for the method. In the case of tartrate ion, 500 mg. may be tolerated if 4 ml. of ammonium thioglycolate are used. More than 8 ml. of reagent are required to restore the color when 500 mg. of fluoride ion are present.

Effect of Cations

Cation interference presents a more serious problem. Iron, copper, nickel lead, and cobalt contribute to the color intensity. Aluminum, thorium, chromium titanium, zirconium and magnesium precipitate in ammoniacal solution. Cadmium when present to the extent of 50 mg., causes a 4% decrease in the color intensity of 0.530 mg. of uranium. Many of the interferences may be eliminated partially or completely. Aluminum, thorium, titanium and zirconium may be kept in solution by adding tartaric acid in the ratio 3 ml. of 10% reagent per 50 mg. of cation. The latter three may also fade the color if present in sufficient concentration. Excess reagent restores the color. The precipitation of magnesium may be prevented

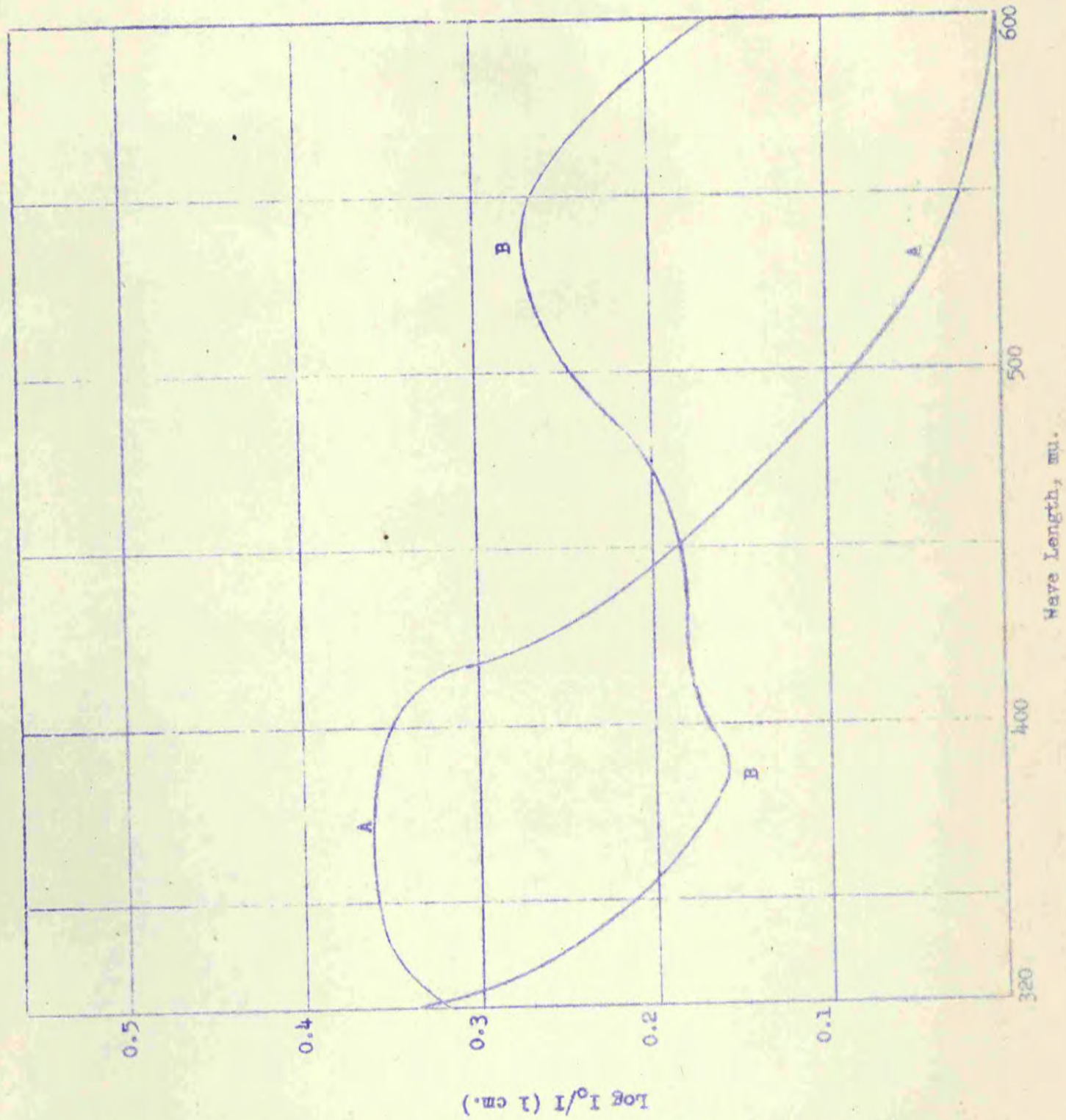

Figure 1. Spectral Absorption of Uranium Thioglycolate and Iron Thioglycolate

A. 1.060 mg. U B. 0.100 mg. Fe

Complexes were developed by adding 2 ml. of a neutralized ten percent solution of thioglycolic acid, adjusting to a pH of ca. 10.1 with ammonium hydroxide (1:1) and diluting to 25 ml.

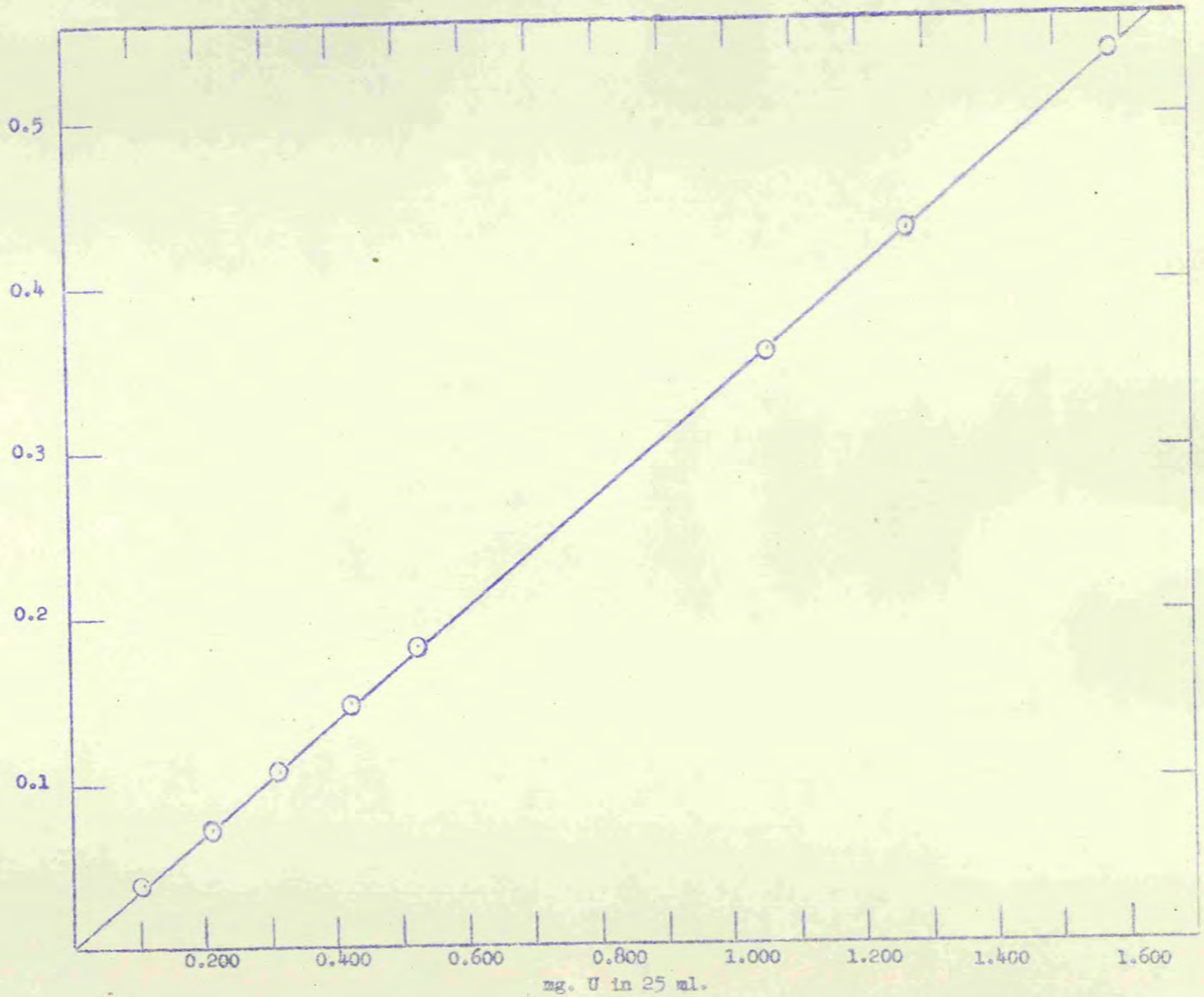

Figure 2.

Calibration Curve for Uranium (VI) Using Ammonium Thioglycolate

Table I

Effect of Anions on the Uranium Thioglycolate Complex

(0.530 mg. of Uranium in 25 ml. of Solution)

Solution	Anion Added	Anion Conc. in 25 ml.	Change in Color Intensity	Approximate Limiting Concentration
1	Chloride	500 mg.	±0%	>500 mg.
2	Nitrate	500 mg.	±0%	>500 mg.
3	Sulfate	500 mg.	±0%	>500 mg.
4	Fluoride	300 mg.	-9%	200 mg.
5	Tartrate	500 mg.	-14%	200 mg.*
6	Nitrite	500 mg.	Intense Yellow	--
7	Acetate	500 mg.	+4%	400 mg.
8	Citrate	200 mg.	Fades rapidly	20 mg.
9	Carbonate	10 mg.	-30%	< 1 mg.
10	Orthophosphate	1 mg.	Destroys color	--
11	Chlorate	500 mg.	±0%	>500 mg.
12	Molybdate	500 mg.	Intense orange	--
13	Oxalate	100 mg.	-7%	50 mg.
14	Chromate	100 mg.	Intense green	--
15	Bichromate	100 mg.	Intense green	--

*No change in color intensity in presence of 500 mg. of tartrate ion when 4 ml. of ammonium thioglycolate are used.

Table II

Effect of Cations on the Uranium Thioglycolate Complex

(0.530 mg. of Uranium in 25 ml. of Solution)

Solution	Cation Added	Cation conc. in 25 ml.	Change in Color Intensity
1	[a] Al^{+++}	100 mg.	±0%
2	[ab] Th^{+4}	50 mg.	±0%
3	[ac] Zr^{+4}	5 mg.	±0%
4	Fe^{++} or Fe^{+++}	0.025 mg.	+24%
5	Cu^{++}	1 mg.	+6%
6	[ac] Ti^{+++}	5 mg.	±0%
7	Ba^{++}	200 mg.	±0%
8	Ca^{++}	200 mg.	±0%
9	[d] Mg^{++}	200 mg.	±0%
10	Ni^{++}	1 mg.	+200%
11	Pb^{++}	1 mg.	+13%
12	Co^{++}	1 mg.	Intense red
13	[b] Cd^{++}	50 mg.	±0%
14	[e] Mn^{++}	50 mg.	±0%
15	[f] Cr^{+++}	10 mg.	Precipitate

a. Complex with 3 ml. of 10% tartaric acid per 50 mg.

b. Add 8 ml. of 10% ammonium thioglycolate.

c. Add 4 ml. of 10% ammonium thioglycolate.

d. Add excess ammonium chloride.

e. Allow to stand 10 minutes.

f. Precipitate forms in ammoniacal solution. Chromium is not complexed by 10 ml. of 10% tartaric acid.

by adding ammonium chloride in excess. Manganese forms a green complex which fades on standing. The effect of various cations is shown in Table II.

Interference of Iron

At 380 mμ an iron solution absorbs approximately five times as strongly as a solution of uranium of equal concentration. Since iron is a frequent contaminant in many materials, a method whereby it might either be removed or tolerated would be desirable. One technique which might be employed is to make use of the mixed colors formed when ammonium thioglycolate is added. The iron thioglycolate complex absorbs fairly strongly at 380 mμ and also at 600 mμ. (Figure 1). The uranium complex also absorbs at 380 mμ but not at 600 mμ. The concentration of iron present in a solution may thus be estimated by a spectrophotometric measurement at 600 mμ. The optical density of this concentration of iron at 380 mμ may be calculated from a calibration curve and subtracted from the total density of the iron-uranium solution at 380 mμ. Values for uranium obtained by this method proved to be quite accurate. Some typical results appear in Table III.

Table III

Estimation of Uranium in Uranium-Iron Solutions Using Mixed Color Method

Mg U Present	Mg Fe Added	Mg U Found	% Error
0.530	0.025	0.540	+1.9
0.424	0.050	0.420	-0.9
0.318	0.100	0.315	-0.9
1.060	0.100	1.080	+1.9
1.060	0.025	1.060	±0
0.530	0.050	0.530	±0

Discussion

The pH range for optimum color development may extend beyond 7.6 - 10.7, the limits investigated. Adjustment of the solution to this range is easily made and considerable latitude is permitted in the addition of ammonium hydroxide before an appreciable change in pH occurs.

Fading of the color will occur if too large an excess of tartaric acid is used to prevent cation precipitation. Satisfactory results are obtained if the tartaric acid added is equal to three or four times the weight of the cation as its oxide. This is in agreement with Hillebrand and Lundell (4).

The mixed color method for solutions containing iron, is not recommended where the ratio of iron to uranium is greater than one part iron per five parts uranium. With larger concentration of iron, the compensation for interference becomes greater than 50% of the total value.

Summary

Ammonium thioglycolate may be used for the accurate estimation of small amounts of uranium in the presence of a relatively large number of anions. The method is not specific for cation solutions but if necessary, certain of the cation interferences may be eliminated.

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