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COLORIMETRIC DETERMINATION OF URANIUM(IV)

by

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ABSTRACT

A colorimetric method was developed for the determination of uranium(IV) in the presence of uranium(VI), nitric acid, hydroxylamine sulfate, and hydrazine. A coefficient of variation of 2.4% (n = 25) was obtained.

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COLORIMETRIC DETERIMINATION OF URANIUM(IV)

INTRODUCTION

The substitution of uranium(IV) nitrate in place of ferrous sulfamate as a reductant for plutonium(VI) in the Purex process would reduce the amount of solid waste and lower the rate of corrosion in the waste evaporators[1]. Stable solutions of uranium(IV) in nitric acid were needed for small-scale tests of the feasibility of this substitution. Evaluation of processes for the production of a stable uranium(IV) solution in nitric acid requires the determination of uranium(IV) in the presence of uranium(VI), nitric acid, hydroxylamine sulfate, and hydrazine.

A search of the literature failed to produce a practical method for the analysis of uranium(IV) in the presence of these constituents. Methods that involve the determination of uranium(IV) by determining uranium(VI) before and after oxidation of uranium(IV) are not accurate for solutions containing low ratios of uranium(IV) to uranium(VI). Methods that are based on the titration of uranium(IV) to uranium(VI) are unsuitable because of the interference from hydroxylamine sulfate. The gravimetric separation of uranium(IV) followed by a colorimetric determination is too time-consuming for routine use.

A direct colorimetric method for the determination of the uranium(IV) ion offers the advantage of rapid analysis and involves no reaction that might change the oxidation state of uranium. The direct colorimetric determination of uranium(IV) in phosphoric acid solutions in the presence of uranium(VI) was described by Andrews, et al.[2], Menis[3], and Rodden[4]. On the basis of these works, development of a colorimetric method for the determination of uranium(IV) in the presence of uranium(VI), nitric acid, hydroxylamine sulfate, and hydrazine was undertaken.

SUMMARY

A colorimetric method was developed for the determination of uranium(IV) in the presence of uranium(VI), nitric acid, hydroxylamine sulfate, and hydrazine. The method is applicable to sample aliquots that contain 3-30 mg. of uranium(IV). The absorbance of the uranium(IV) ion was measured directly in a hydrochloric acid medium in a spectrophotometer. A coefficient of variation of 2.4% (n = 25) was obtained.

DISCUSSION

This study was made in a hydrochloric acid medium to take advantage of the high molar absorptivity of uranium(IV) and the ease of preparation of pure and stable solutions of uranium(IV) as standards in

this acid. Rodden[4] showed that the molar absorptivity of uranium(IV) was higher in hydrochloric acid than in phosphoric acid. Sulfuric and nitric acids not only decrease the absorptivity but also are poor solvents for the preparation of pure solutions of uranium(IV).

WAVELENGTH SELECTION

The absorbance of uranium(IV) and uranium(VI) in separate and combined solutions was measured to determine the proper wavelength for measuring uranium(IV) in hydrochloric acid. A 1 molar solution of hydrochloric acid was used. A plot of molar absorptivity vs. wavelength is shown in Figure 1. Measurements were made in 1-cm cells with a Beckman Model B Spectrophotometer. Uranium (IV) has absorption peaks at 430, 500, 555, and 665 mμ. Uranium(VI) has an absorption peak at 410 mμ. A 665-mμ setting was chosen for continued study because of the high molar absorptivity and the absence of uranium(VI) interference at this wavelength.

ABSORPTION SPECTRA

Absorption spectra were obtained to determine the effect of hydrochloric and nitric acids, hydroxylamine sulfate, and hydrazine concentrations on the 665-mμ absorption peak of uranium(IV). None of these constituents shifted the absorption peak of uranium(IV). However, nitric acid and hydroxylamine sulfate did decrease the molar absorptivity as shown in Figure 2.

The decrease in the molar absorptivity of uranium(IV) in the presence of nitric acid and hydroxylamine sulfate is probably due to the formation of uranium(IV) complexes with nitrate and sulfate. Uranium(IV) standards that were spiked with nitric acid and sulfuric acid showed a decrease in the molar absorptivity. Identical standards spiked with nitric acid and sulfuric acid were analyzed volumetrically for uranium(IV). There was no decrease in the uranium(IV) content. Thus, the decrease in the molar absorptivity is due to the presence of the nitrate and sulfate ions and is not due to a change in oxidation state of uranium by nitric acid or hydroxylamine sulfate.

EFFECT OF HYDROCHLORIC ACID

The influence of concentration of hydrochloric acid on the absorbance of uranium(IV) was measured over an acid concentration range from 0.02 to 6 molar (Table I). Absorbance increased with increasing hydrochloric acid concentration until an acidity of 1.2 molar was reached. Over the concentration range of 1.2 to 6 molar, the absorbance was constant. A hydrochloric acid concentration of 2 molar was selected as optimum for further studies.

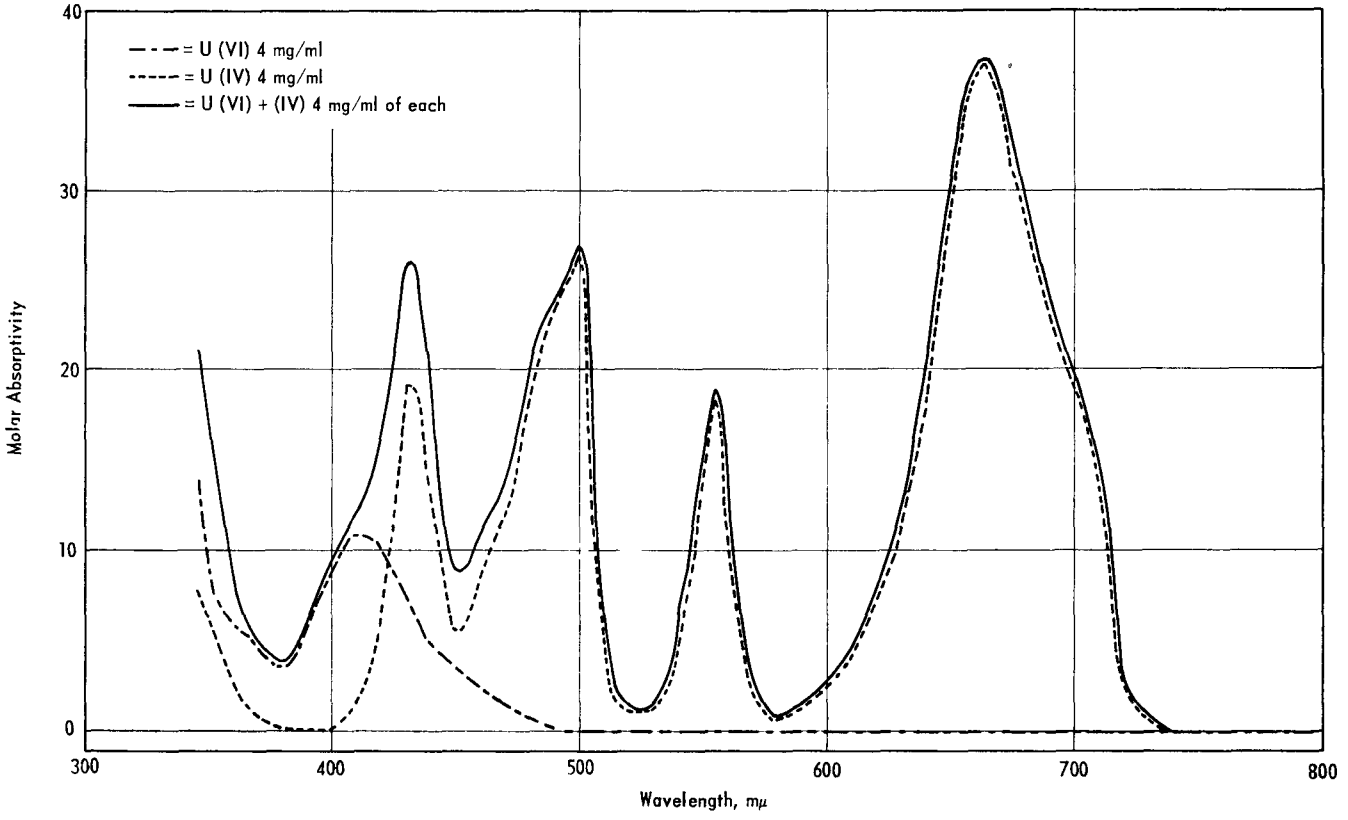

FIG. 1 ABSORPTION SPECTRA OF URANIUM (IV) AND URANIUM (VI)

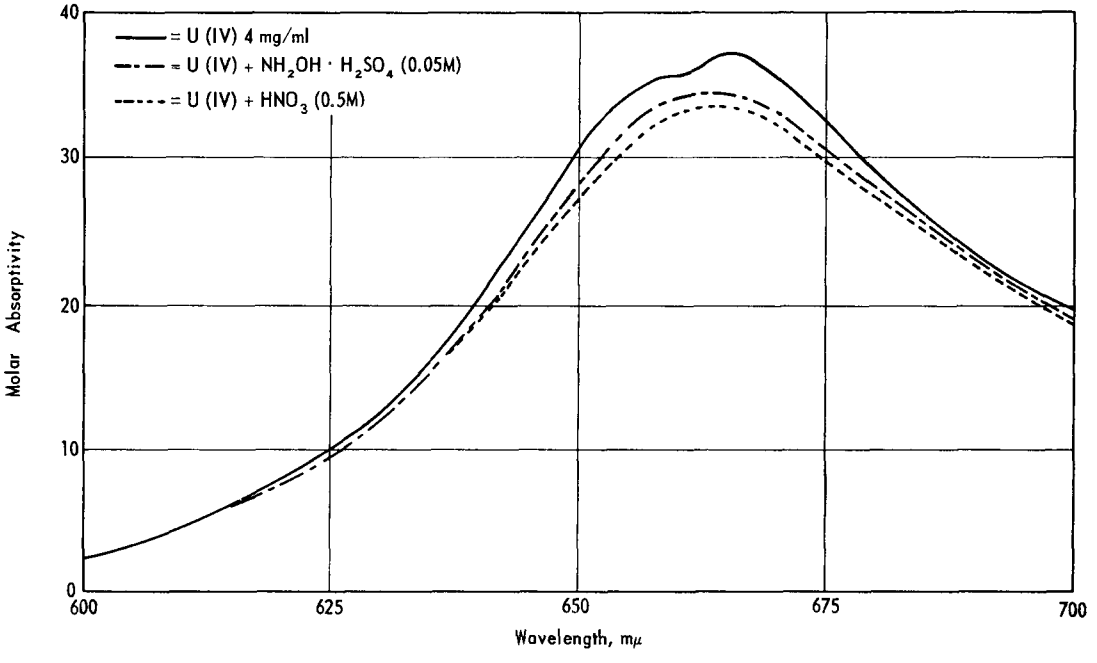

FIG. 2 EFFECT OF NITRATE AND SULFATE ON MOLAR ABSORPTIVITY OF URANIUM (IV)

INTERFERENCES

Standard solutions of uranium(IV) in 2 molar hydrochloric acid were spiked with uranium(VI), nitric acid, hydroxylamine sulfate, and hydrazine to determine permissible levels of these interferences (Table I). The concentration of spikes were chosen to encompass the expected level of interferences in the samples (nitric acid, 0.05 molar; hydroxylamine sulfate, 0.005 molar; hydrazine, 0.02 molar; a maximum uranium(VI) to uranium(IV) ratio of 5). The hydrazine and uranium(VI) to uranium(IV) ratio had no significant effect on the absorbance of uranium(IV). However, increasing concentrations of nitric acid and hydroxylamine sulfate significantly decreased the absorbance of uranium(IV) (0.20 molar nitric acid and 0.025 molar hydroxylamine sulfate each introduced a systematic error of -4%). In the analysis of samples, this error is eliminated by adjusting the concentration of nitric acid to 0.10 ±0.10 molar and hydroxylamine sulfate to 0.01 ±0.01 molar; these samples are compared to standards that have been adjusted to a nitric acid concentration of 0.1 ±0.001 molar and hydroxylamine sulfate concentration of 0.01 ±0.0001 molar.

TABLE I

Effect of Interferences on Absorbance of U(IV)

HCl, M	Absorbance	HNO_3, M	Absorbance	$NH_2OH \cdot H_2SO_4$, M	Absorbance	N_2H_4, M	Absorbance	U(VI) to U(IV) Ratio	Absorbance
0.02	0.265	0.00	0.295	0.00	0.295	0.00	0.295	1.00	0.296
0.14	0.281	0.05	0.293	0.005	0.292	0.02	0.295	3.00	0.295
0.38	0.289	0.10	0.291	0.015	0.287	0.10	0.299	5.00	0.291
0.62	0.292	0.20	0.282	0.025	0.283				
1.2	0.294	0.30	0.273						
3.6	0.295	1.5	0.205						
6.0	0.295								

PRECISION

A coefficient of variation of 0.8% was obtained from the analyses of 10 standards in which the uranium ranged from 3 to 30 mg and the nitric acid and hydroxylamine sulfate were constant. A coefficient of variation of 2.4% was obtained from the analyses of 25 standards in which the uranium(IV) was held constant and the nitric acid was varied from 0 to 0.2 molar and the hydroxylamine sulfate was varied from 0 to 0.02 molar.

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APPENDIX - PROCEDURE FOR ANALYSIS OF SAMPLES

Each day that samples are analyzed, standardize the uranium(IV) standard by direct titration with ceric ammonium sulfate (in a 24-hour period, the uranium(IV) concentration decreases approximately 1%).

A. PREPARATION OF STANDARD URANIUM(IV) - 30 mg/ml

Dissolve approximately 40 g of uranium metal in 200 ml of 20% hydrochloric acid with heating. After dissolution is complete, centrifuge to remove uranium dioxide particles. Filter the centrifugate through "Millipore"* filter paper (0.45-μ pore size) and dilute the filtrate to 1 liter. (Approximately 99% of total uranium is uranium(IV).)

B. ANALYSIS OF SAMPLES

1. Into a 10-ml volumetric flask, pipet 4 ml of 6M HCl.

2. Pipet into the flask a sample aliquot containing 3-30 mg of uranium(IV). The sample aliquot should contain less than 1.0 millimoles of HNO_3 and less than 0.10 millimoles of $NH_2OH \cdot H_2SO_4$.

3. Add sufficient 1.0M HNO_3 to adjust the HNO_3 concentration to 0.1M (0-0.2M).

4. Add sufficient 0.10M $NH_2OH \cdot H_2SO_4$ to adjust the $NH_2OH \cdot H_2SO_4$ concentration to 0.01 ±0.01M.

5. Dilute the sample in the flask to the mark with distilled water. Mix thoroughly and measure the absorbance in a Beckman Model B Spectrophotometer at a wavelength of 665 mμ. (A red sensitive phototube and a sensitivity setting of 1 should be used.) Samples are measured against a distilled water reference.

C. DETERMINATION OF STANDARD FACTOR

1. Into each of four 10-ml volumetric flasks, pipet 4 ml of 6M HCl.

2. Pipet into the flasks duplicate 300- and 700-μl aliquots of a 30-mg/ml uranium(IV) standard.

3. Add 1 ml of 1.0M HNO_3 and 1 ml of 0.1M $NH_2OH \cdot H_2SO_4$.

4. Same as B5.

*Produced by Millipore Filter Corporation

D. CALCULATIONS

$$\frac{\text{mg U(IV)}}{\text{ml}} = \frac{(\text{absorbance})(\text{standard factor})}{\text{ml of sample aliquot}}$$

$$\text{standard factor} = \frac{\left(\frac{\text{mg U(IV) of standard}}{\text{ml}}\right)\left(\text{ml of standard}\right)}{\text{absorbance of standard}}$$

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