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THE SPECTROPHOTOMETRIC DETERMINATION OF URANIUM BY MEANS OF THE AZIDE ION

By H. I. Feinstein

Trace Elements Investigations Report 544

UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

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IN REPLY REFER TO:

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DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY
WASHINGTON 25, D. C.

AEC-360/6

January 12, 1956

Mr. Robert D. Nininger, Assistant Director
Division of Raw Materials
U. S. Atomic Energy Commission
Washington 25, D. C.

Dear Bob:

Transmitted herewith are three copies of TEI-544, "The spectrophotometric determination of uranium by means of the azide ion," by H. I. Feinstein, August 1955.

On December 20, 1955, Mr. Hosted approved our plan to publish this report in Analytica Chimica Acta.

Sincerely yours,

John H. Eric

for W. H. Bradley
Chief Geologist

Chemistry

This document consists of 11 pages.
Series A.

UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

THE SPECTROPHOTOMETRIC DETERMINATION OF URANIUM BY MEANS OF THE AZIDE ION*

By

H. I. Feinstein

August 1955

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This preliminary report is distributed without editorial and technical review for conformity with official standards and nomenclature. It is not for public inspection or quotation.

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*This report concerns work done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

USGS - TEI-544

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THE SPECTROPHOTOMETRIC DETERMINATION OF URANIUM BY MEANS OF THE AZIDE ION

By H. I. Feinstein

ABSTRACT

A method has been devised for the spectrophotometric determination of uranium by means of the azide ion. The method possesses several advantages over the various thiocyanate procedures. It has a slightly higher sensitivity, an aqueous medium is used, and the reaction product is more stable.

Within the concentration limits tested, Beer's law is obeyed.

INTRODUCTION

Univalent anions derived from halogenoids or pseudohalogens possess striking similarities both to the halogens and to themselves (Moeller, 1952). Two such halogenoid anions are the thiocyanate ion and the azide ion, both of which have the same electronic structure (Pauling, 1950). Not only are

$$[:\ddot{S}::C::\ddot{N}:]^- \qquad [:\ddot{N}::N::\ddot{N}:]^-$$

their electronic structures similar but their chemical behavior with such ions as ferric, lead, silver, and thallous are closely parallel. As it is well known that thiocyanate produces a yellow color with uranium (VI), it was hoped that azide might react in a similar fashion and that the color produced might be utilized for the quantitative determination of uranium. Tests showed that a yellow is produced the intensity of which is proportional to the concentration of uranium.

The absorbancy of a solution containing 1 mg uranium per 25 ml under comparable conditions of wavelength (375 mμ) is 0.750 for the uranium-azide system, 0.620 for the uranium-thiocyanate system in 3:2 acetone:water (Crouthamel and Johnson, 1952), and 0.840 for uranium-thiocyanate in ethyl acetate-acetone-water (DeSesa and Nietzel, 1954). The molar absorbancy index, a_M, $(\frac{\text{absorbancy}}{\text{cell length x concentration}}$, where cell length in these systems is in centimeters and concentration is in moles per liter) is 4450, 3690, and 5000, respectively. At 360 mμ, however, the molar absorbancy index of the uranium-azide system is 5300. Hence, the uranium-azide reaction is more sensitive than the uranium-thiocyanate reaction in acetone water but not quite as sensitive as the uranium-thiocyanate reaction in ethyl acetate acetone water at 375 mμ. Furthermore, an aqueous solution of the azide reagent is used which is considerably more stable than the acetone solution of thiocyanate usually employed. Another advantage of the azide method is the greater stability of the colored product.

Because of the interest in uranium analysis at this time, this report is being issued to encourage further investigations with this reagent.

EXPERIMENTAL DATA

Spectrum of uranyl azide complex

The absorption spectrum of the uranyl azide system was determined on a solution (25 ml total volume) containing 1 mg uranium, 5 ml of 7 percent HNO_3, and 20 ml of 3 molar sodium azide, with water as reference, using a Beckman recording spectrophotometer. There is an increase in absorbancy as the wavelength decreases from 530 mμ (fig. 1). For further work a wavelength of 360 mμ was chosen because this gives good sensitivity.

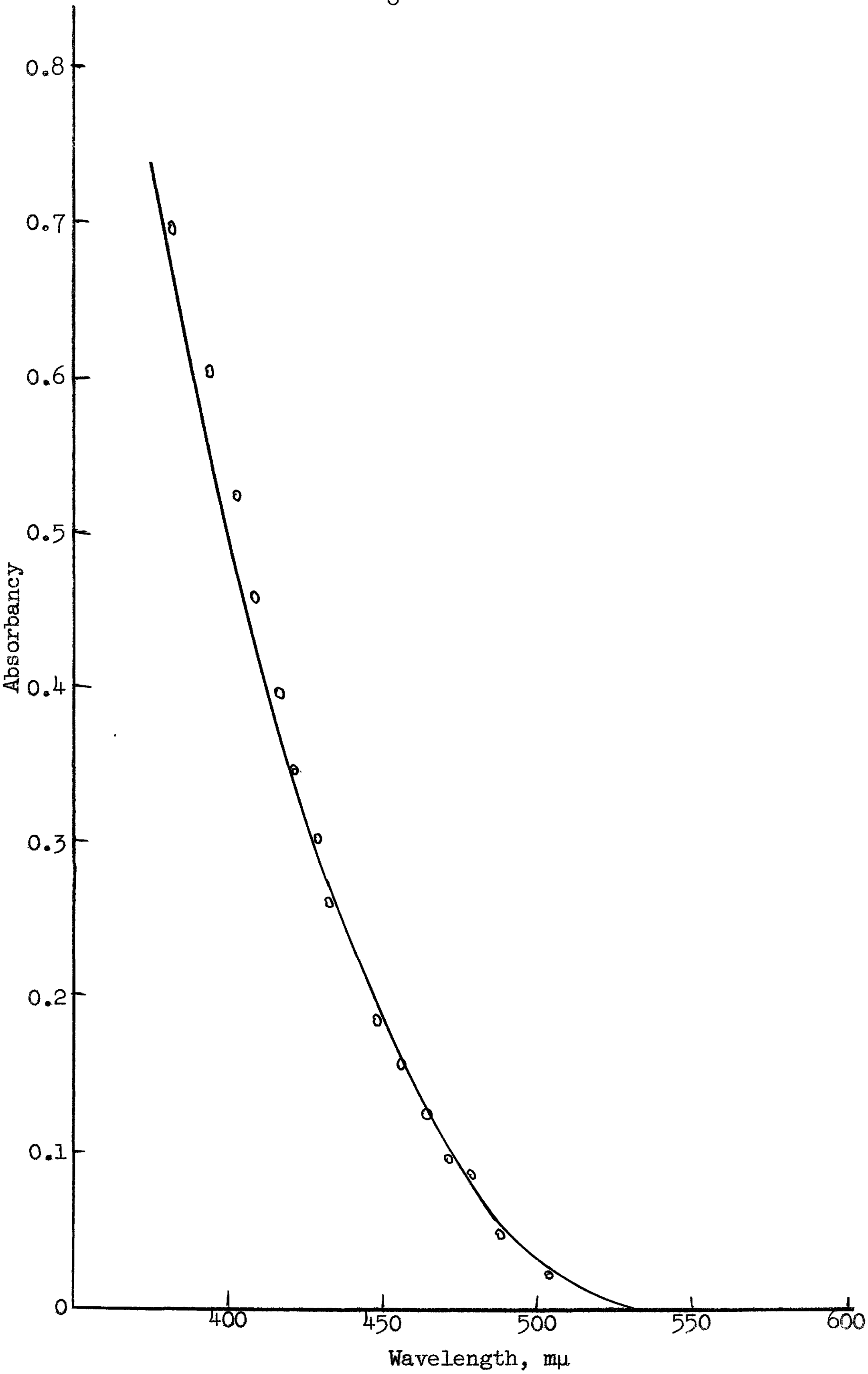

Figure 1.--Spectrum of uranyl azide.

Concentration of azide

The absorbancy of a solution (25 ml total volume) containing 0, 0.1, and 1 mg uranium and 5 ml of 7 percent HNO_3 varies with azide concentration (table 1).

Table 1.--Absorbancy as a function of azide concentration. Each solution contains 5 ml of 7 percent HNO_3 per 25 ml. γ = 360 mμ, slit width = 0.10 mm, 1 cm silica cells, reference water.

U (mg)	3 molar NaN_3 (ml)	Absorbancy
0	5	0.017
0	10	0.020
0	15	0.020
0	20	0.032
0.1	5	0.091
0.1	10	0.098
0.1	15	0.103
0.1	20	0.111
1.0	5	0.748
1.0	10	0.852
1.0	15	0.880
1.0	20	0.895

Nitric acid concentration

Only one acid, nitric acid, has so far been tried. With 0, 0.1, and 1 mg uranium, increasing the acid concentration in a solution containing 20 ml of 3 molar NaN_3 is accompanied by increasing absorbancy at lower acidity and bleaching at higher acidity (table 2).

Table 2.--Absorbancy as a function of acid concentration. Each solution contains 20 ml of 3 molar sodium azide per 25 ml of solution. γ = 360 mμ, slit width = 0.10 mm, 1 cm silica cells, reference water.

U (mg)	Equivalent of 7 percent HNO_3 (ml)	Absorbancy
0	0	0.033
0	5	0.032
0.1	1	0.093
0.1	5	0.111
0.1	15	0.122
0.1	30	0.112
0.1	60	0.047
1.0	1	0.835
1.0	5	0.895
1.0	15	0.915
1.0	30	0.895
1.0	60	0.046

Stability of the color

The yellow color produced when 1 mg U in 5 ml of 7 percent HNO_3 was treated with 20 ml of 3 molar sodium azide was found to be stable for at least 20 hours.

Working curve

For the working curve (fig. 2), a standard stock solution of uranium containing 1 mg uranium per ml in 7 percent nitric acid (7+93) was prepared from 99.96 percent U_3O_8 (MS-ST). Each solution measured contained the required amount of uranium, 5 ml of 7 percent HNO_3 (7+93) and 20 ml of 3 molar sodium azide all in a volume of 25 ml. The sodium azide was added last. Absorbancies were measured in 1-cm silica cells (corex will do), with a Beckman DU spectrophotometer, at a wavelength of 360 mμ and slit width of 0.10 mm corresponding to an effective band width of 0.7 mμ.

Interfering elements

A systematic study of interfering elements has not as yet been made. However, under the conditions described, many hydroxides and azides would be expected to precipitate. Hence the application of the azide reaction to practical uranium analysis would require the absence of most of the other metals with the exception of the alkalis and the alkaline earths.

Procedure

Beckman DU spectrophotometer (or equivalent), with 1-cm silica or corex cells, can be used.

Nitric acid (7 percent). 70 ml of the concentrated acid are added to 930 ml of water.

Sodium azide (3 molar). 195 g of the best available sodium azide are dissolved in water at room temperature, filtered, and diluted to 1 liter in a volumetric flask.

The uranium-containing solution, free of interfering elements, preferably containing about 1 mg uranium in nitric acid solution, is evaporated to

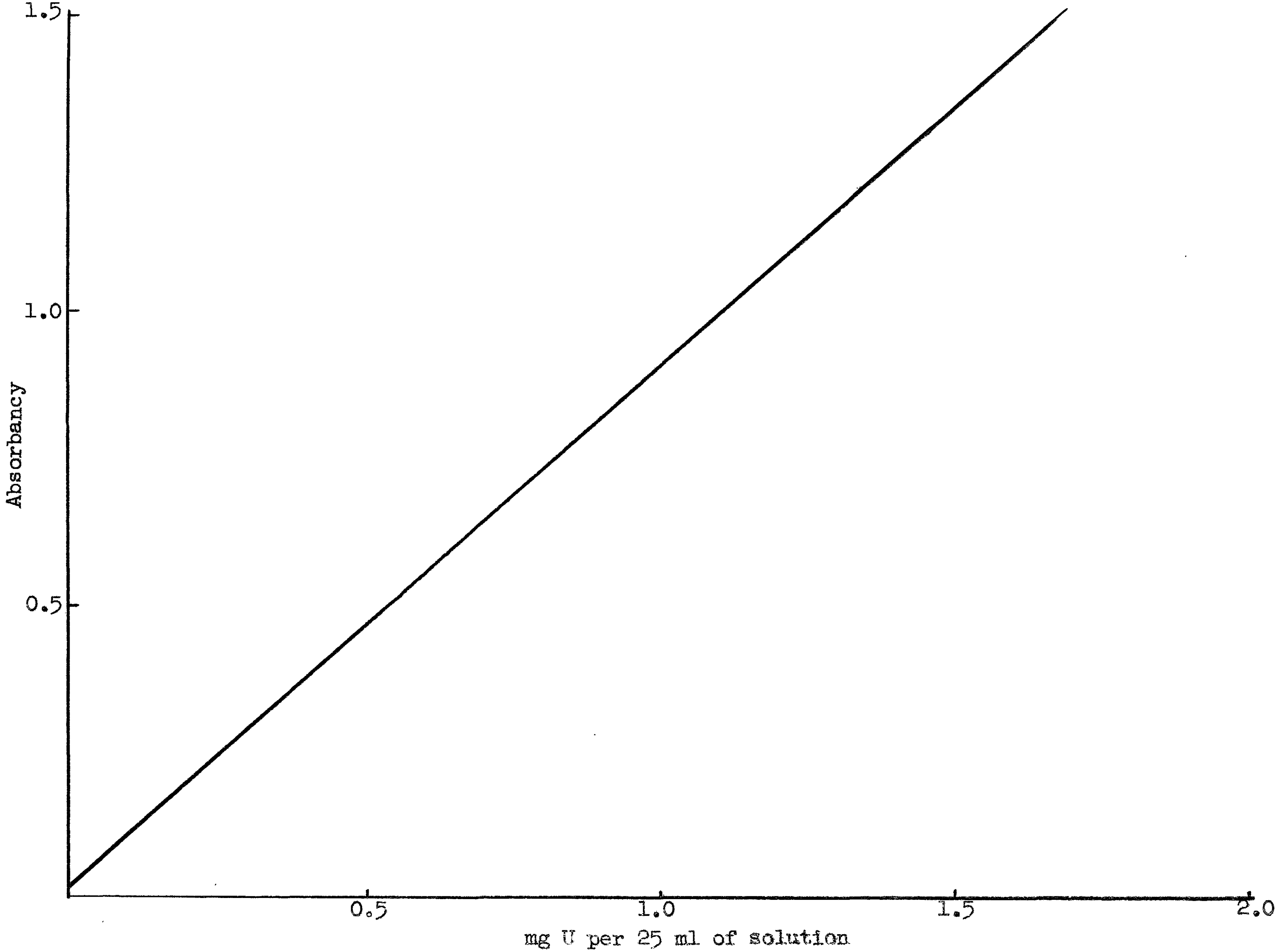

Figure 2.--Working curve.

dryness in a beaker. The residue is dissolved in 5 ml of 7 percent nitric acid solution and transferred to a dry 25-ml volumetric flask. The beaker is rinsed with several small portions of the 3 molar sodium azide and transferred to the volumetric flask using only the sodium azide reagent for diluting to volume. Absorbancy is measured in the Beckman spectrophotometer at a wavelength of 360 mμ in a 1-cm cell using water as reference. Alternatively, a curve could be constructed using the reagents as reference and the procedure varied accordingly.

Hydrazoic acid and the metal azides are explosive and toxic and should be handled with care.

This investigation is part of a program being conducted by the Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

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