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THE DETERMINATION OF URANIUM IN ORES: SEPARATION BY ETHYL ACETATE EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION BY THE THIOCYANATE METHOD IN ACETONE-WATER MEDIUM

By
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This report is preliminary and has not been edited or reviewed for conformity with U. S. Geological Survey standards and nomenclature.

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GEOLOGICAL SURVEY

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Separation by ethyl acetate extraction and spectrophotometric determination by the thiocyanate method in acetone-water medium*

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

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THE DETERMINATION OF URANIUM IN ORES:

Separation by ethyl acetate extraction and spectrophotometric determination by the thiocyanate method in acetone-water medium

By H. I. Feinstein

ABSTRACT

The thiocyanate method is applied to the determination of uranium in ores after separation by ethyl acetate extraction. Reasonable control of acidity and thiocyanate concentration eliminates the erratic results that are sometimes obtained by thiocyanate methods. The use of the extraction procedure permits the determination of uranium in vanadium-bearing ores, minerals, and rocks. An accuracy of $\pm$ 2 percent of the accepted value can be readily achieved.

INTRODUCTION

The need has existed for a method for uranium determination in minerals, ores, and rocks that would serve in the range between the fluorimetric and volumetric procedures. The method should be simple, rapid, precise, and relatively free from interference by those elements such as vanadium that are often associated with uranium. Such a method has been developed, based on the yellow color produced between thiocyanate and uranium (VI). Reasonable control of acidity and thiocyanate concentration and the use of an aqueous solution of the thiocyanate reagent has eliminated the erratic results often obtained by thiocyanate methods. By combining this with an extraction procedure, the method has been made applicable to vanadium-bearing minerals and ores.

The thiocyanate method has been studied by Currah and Beamish (1947), Nelson and Hume (1945), and Gerhold and Hecht (1951). Various modifications of this method have been made with a view to increasing the sensitivity and color stability and minimizing interferences. These modifications involve the use of acetone-water (Crouthamel and Johnson, 1952), dibutoxytetraglycol (Silverman and Moudy, 1953), ether and alcohol (Gerhold and Hecht, 1951), and ethyl acetate-acetone-water (DeSesa and Nietzel, 1954).

The method developed in this report makes use of the thiocyanate reaction in a 3:2 acetone-water medium for the determination, following an ethyl acetate separation (Grimaldi and Levine, 1954) from vanadium and other possible interferences.

The factors that may cause erratic results in the final determination were critically studied and eliminated. These include inexact control of thiocyanate and acid concentrations which leads to nonreproducible absorbancies especially in the presence of acetone. Use of an acetone solution of ammonium thiocyanate as reagent has been replaced by an aqueous solution which is much more stable and can be kept for at least 6 months.

The efficiency of the extraction process was extended to 100 mg uranium and the effect of extractable metals upon the analysis of uranium was determined.

PRELIMINARY EXPERIMENTS

Concentration of nitric acid and thiocyanate

Various concentrations of ammonium thiocyanate and nitric acid were mixed in a 3:2 acetone-water medium both in the absence of uranium and in the presence of 0.5 mg and 2.0 mg uranium per 25 ml. The absorbances of these

solutions were measured both immediately and after one hour at 375 mμ wavelength and 0.13 mm slit width (1.1 mμ effective band width) at room temperature using 1-cm cells with water as reference. Mixtures of maximum relative stability were considered to be those which did not increase in absorbance more than corresponded to approximately 0.01 mg U per hour. In figure 1 are curves representing nitric acid and thiocyanate concentrations below which are the areas of maximum relative stability for 0, 0.5, and 2.0 mg uranium. These areas were different in the three cases in figure 1. Concentrations of 1 molar ammonium thiocyanate and 0.25 molar nitric acid were chosen for subsequent measurements. Although this combination is not quite in the region of maximum relative stability for 2 mg uranium, if measurements are made within 15 minutes after development of the color, the error introduced is negligible. Nitric acid was used in this work because, in the procedure for the analysis of minerals, nitric acid was the medium from which uranium was extracted (Grimaldi and Levine, 1954), although other acids could be present (DeSesa and Nietzel, 1954). Nitric acid 0.25 molar was low enough so that it would not decompose the thiocyanate significantly in the time interval used in the procedure and high enough to prevent hydrolytic separation of uranium.

Optical density varies with acid concentration (Rodden, 1950) as well as with thiocyanate concentration (table 1).

Ethyl acetate extraction of uranium

The method employed for the separation of uranium has been described by Grimaldi and Levine (1954). They found that 10 ml of ethyl acetate will quantitatively extract up to 5 mg uranium. In this investigation, various quantities of uranium up to 100 mg were extracted with 10 ml ethyl acetate

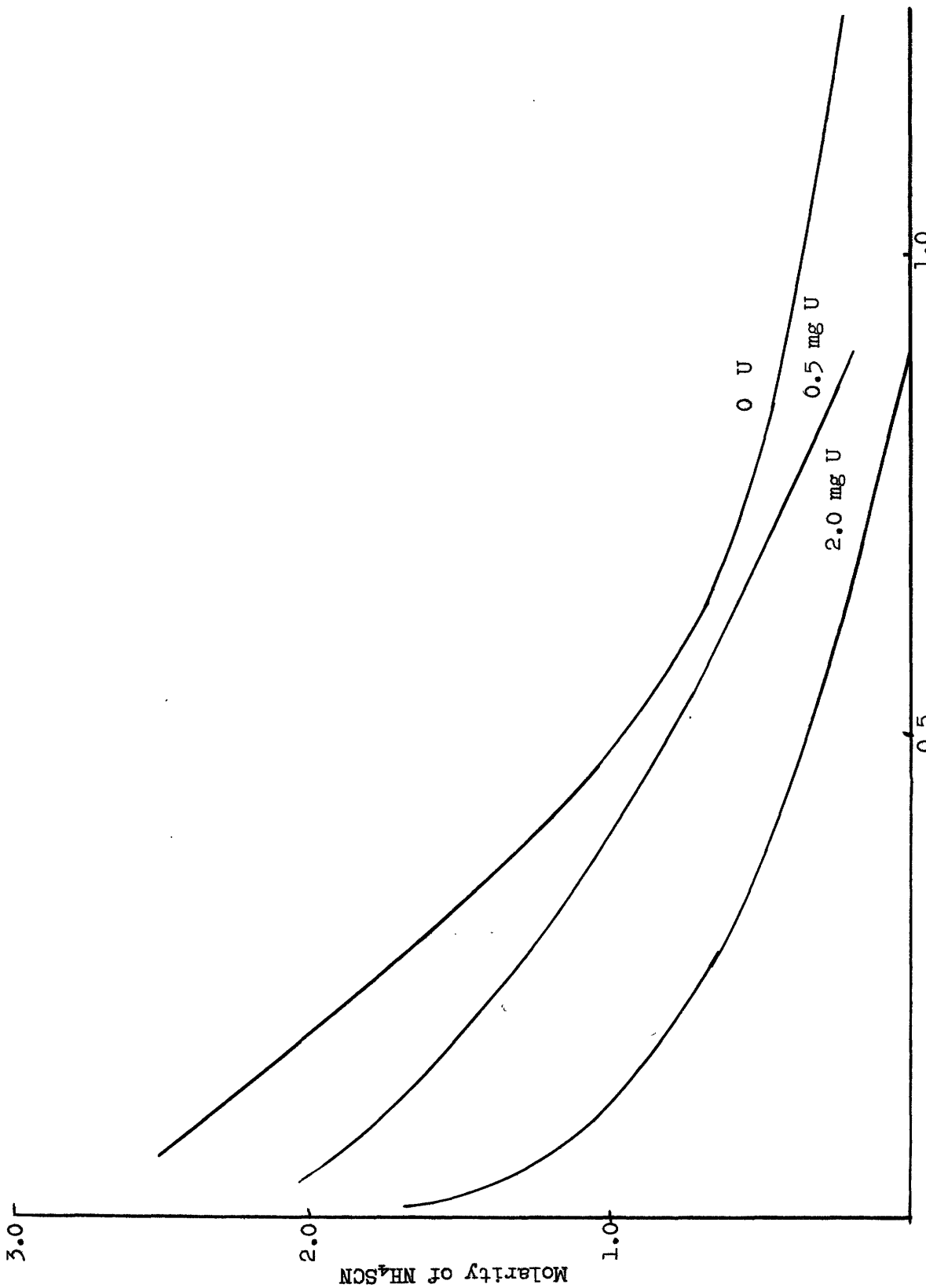

Figure 1.--Areas of maximum relative stability of reaction product.

Table 1.--Optical density as a function of ammonium thiocyanate concentration at two levels of uranium in 3:2 acetone-water medium. γ = 375 mμ, slit width = 0.13 mm, 1-cm cell, reference water.

mg U/25 ml	HNO_3 molarity	NH_4SCN molarity	Optical density
0.5	0.25	1.0	0.308
0.5	0.25	1.5	0.334
0.5	0.25	2.0	0.362
2.0	0.25	0.5	1.047
2.0	0.25	1.0	1.183
2.0	0.25	1.5	1.278

from 5 ml of nitric acid solution (7+93) to which had been added 9.5 g aluminum nitrate enneahydrate. The uranium was then stripped into water and determined by thiocyanate as in the regular procedure (table 2).

Table 2.--Efficiency of ethyl acetate extraction.

U taken (mg)	U found (mg)	Percent recovery
1.00	1.00	100
1.00	1.00	100
1.00	0.982	98.2
5.00	4.98	99.6
5.00	5.00	100
5.00	4.92	98.4
5.00	4.90	98.0
5.00	4.95	99.0
25.0	25.3	101
40.0	39.8	99.4
100.0	99.9	99.9

Interference studies

Vanadium, cerium (IV), thorium, and zirconium are partly extracted with ethyl acetate (Grimaldi and Levine, 1954). The extent of the interference of these elements and of molybdenum was determined by taking 5 mg of each and determining their equivalent in terms of uranium before and after extraction. The results are given in table 3.

PROCEDURE FOR THE ANALYSIS OF URANIUM ORES AND MINERALS

Apparatus:

Beckman DU (or equivalent) spectrophotometer with 1-cm silica cell or less preferably corex cells.

Reagents and solutions:

Nitric acid (1+1). One volume of concentrated acid is added to an equal volume of water.

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

Aluminum nitrate 9-hydrate. Reagent grade.

Aluminum nitrate-nitric acid solution. Dissolve 475 g of the enneahydrate in 250 ml of 7 percent nitric acid. Filter.

Ammonium thiocyanate, 8.33 molar. Dissolve 158.5 g reagent-grade ammonium thiocyanate (A.C.S. grade) with slight warming in nearly enough distilled water to make 250 ml, cool, dilute to 250 ml in a volumetric flask, and filter through a dry filter paper.

Stannous chloride solution. Dissolve 10 g $SnCl_2 \cdot 2H_2O$ in 10 ml concentrated hydrochloric acid with slight warming, and dilute with 90 ml of water. Filter if necessary. Add several pieces of mossy tin to keep reduced.

Table 3.--Interference of V, Ce(IV), Th, Zr, and Mo.

Element	Amount taken (mg)	Equivalent in mg U	
		Before extraction	After extraction
V	5	0.2	0
Ce 1/	5	0	--
Th	5	< 0.01	--
Zr	5	0.02	0.02
Mo	5	> 5	0.06

1/ Ce(IV) is reduced by $SnCl_2$ to Ce(III) which has no effect on thiocyanate.

Acetone, reagent grade or redistilled.

Standard uranium solutions were prepared by dissolving the required amount of 99.96 percent U_3O_8 in enough 1+1 nitric acid to make a solution of the desired uranium concentration in 7 percent nitric acid.

Outline of procedure

Ignition to destroy organic matter.

Decomposition.

Solution in 7 percent nitric acid.

Extraction with ethyl acetate.

Stripping with water.

Determination.

Detailed procedure

A sample weight is taken such that the final determination is made on a solution containing 1 mg of uranium per 25 ml. The sample is first ignited at a temperature not less than 600° C to destroy organic matter.

The method of decomposition will vary with the nature of the ore or mineral. Carnotite ores were decomposed with nitric and hydrofluoric acids. Care must be taken on adding acid due to the possibility of effervescence. Any manganese or cerium (IV) may be reduced with a little hydrogen peroxide. After decomposition, the solution is evaporated to dryness on the steam bath and then dissolved in (1+1) nitric acid. The evaporation to dryness and solution in nitric acid is repeated twice. Occasionally some undecomposed quartz will remain but this can be neglected. If the residue is dark, it may be necessary to filter, ignite, and fuse with a little sodium carbonate, the fusion allowed to cool, and then dissolved in nitric acid (1+1). This is added to the acid-decomposable portion and evaporated to dryness.

The residue is treated with 7 ml (1+1) nitric acid, about 15 ml of water added, and solution effected by warming. The solution is transferred to a 50-ml volumetric flask and diluted to the mark with water at room temperature.

A suitable aliquot of the prepared solution is added to $Al(NO_3)_3 \cdot 9H_2O$ in a 30-ml beaker: 9.5 g of this salt is used for a 5-ml aliquot of the solution. The solution before addition of the salt should contain 7 percent HNO_3 by volume. A 5- or 10-ml aliquot is generally taken. If less than 5 ml is taken, 7 percent HNO_3 should be added to bring it to that volume. The salt is dissolved by warming, the solution cooled, and then transferred to a 60-ml separatory funnel. The beaker is rinsed twice with 5-ml portions of ethyl acetate (10-ml portions if a 10-ml aliquot and 19 g of $Al(NO_3)_3 \cdot 9H_2O$

were taken). The rinsings are added to the separatory funnel. The funnel is stoppered using a rubber stopper that had been previously soaked in ethyl acetate for several hours, and shaken for one minute. The layers are allowed to separate, and the aqueous layer discarded. The ethyl acetate layer is washed twice with 5-ml portions of aluminum nitrate-nitric acid solution (10 ml of wash for the 10-ml aliquot). The combined washings are extracted with 5 ml of ethyl acetate (8 ml if a 10-ml aliquot was used), and the acetate layer combined with the previous one. The aqueous layer is discarded.

The ethyl acetate layer is stripped with two 10-ml portions of water and these are collected in a 30-ml beaker. If the amount of uranium extracted is 1 mg or less, the solution is evaporated to dryness; if more, it is diluted to a definite volume and an aliquot evaporated. The residue is dissolved in 5 ml of 7 percent nitric acid and transferred to a 25-ml volumetric flask. The reagents are pipetted separately into the beaker and transferred, in turn, to the volumetric flask, mixing after each reagent is added in the following order: 1 ml of stannous chloride solution, 15 ml of acetone, 3 ml of 8.33 molar ammonium thiocyanate, and finally water to the mark.

The absorbancy is measured against distilled water as a reference solution with a Beckman DU spectrophotometer using 1-cm silica cells, at a wavelength of 375 mμ and slit width of 0.13 mm. If the final concentration is between 1.5 mg and 11 mg U per 25 ml, a wavelength of 420 mμ can be used. Advantage is taken of the lower sensitivity but wider range at the longer wavelength. Readings should be made at a definite time after development of the color, for instance 15 minutes. A standard working curve obtained by following the above procedure with known amounts of U is reproduced in figure 2. Results on a group of samples are given in tables 4 and 5.

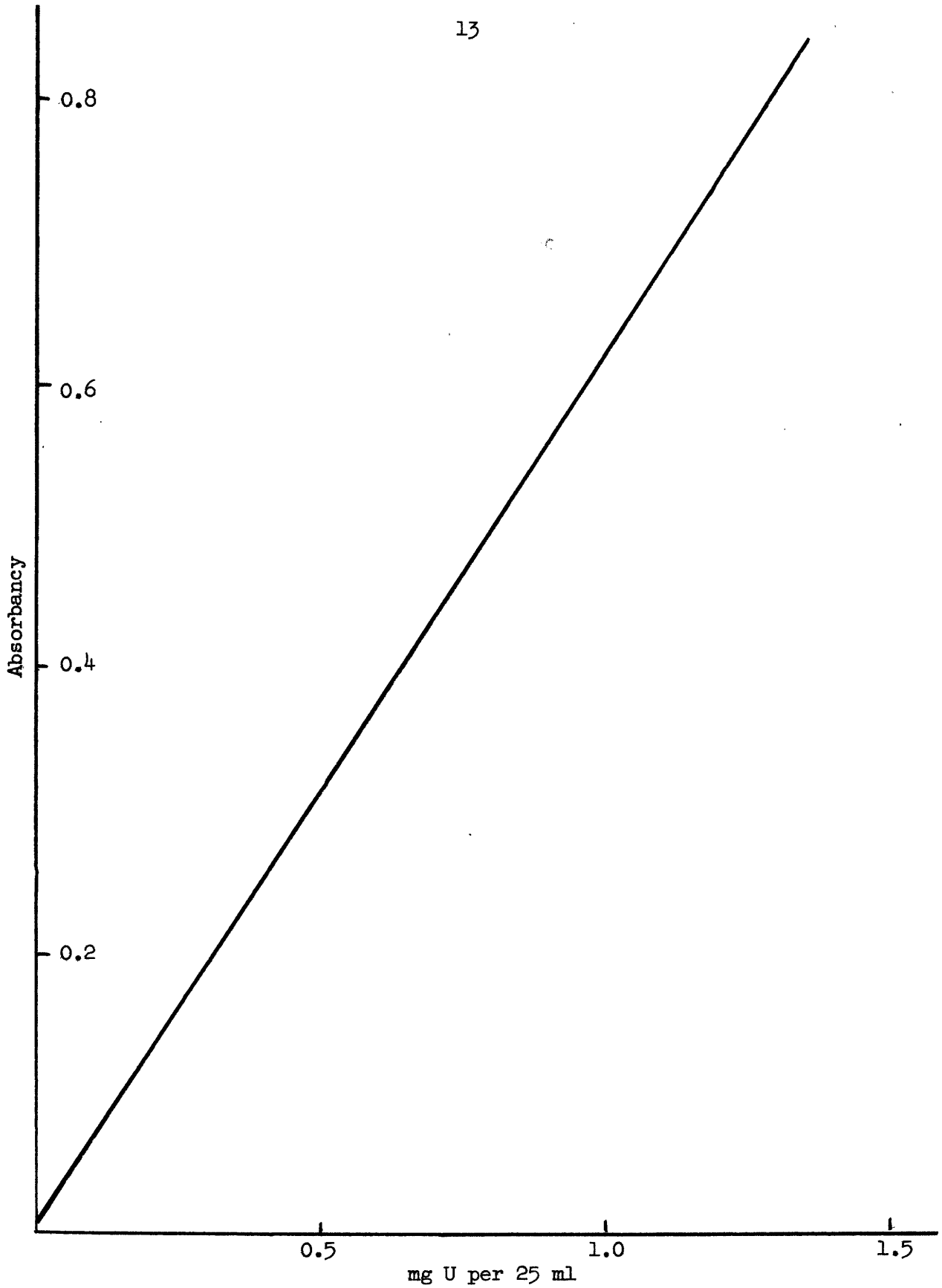

Figure 2.--Working curve

Note. If the concentration of uranium in the water strippings is high, the combined strippings may be brought up to 25-ml volume and a 5-ml aliquot taken for colorimetric analysis. To this aliquot is added 0.5 ml (1+1) HNO_3 before adding the stannous chloride solution.

Table 4.--Analysis of standard carnotite ores.

Sample no.	U_3O_8, percent	
	Present	Thiocyanate method
1	0.18	0.18_2, 0.182
2	0.11	0.11_5, 0.117
3 (contains 0.52 percent V_2O_5)	0.109	0.10_8, 0.106
4 (contains 1.25 percent V_2O_5)	0.399	0.40_0, 0.397
5 (contains 3.73 percent V_2O_5, 0.20 percent Cu)	0.754	0.76_1, 0.755
6 (contains 0.04 percent V_2O_5, 1.99 percent Cu)	0.528	0.51_9, 0.524
7 (contains 0.19 percent V_2O_5)	0.346	0.34_3, 0.348

Table 5.--Analyses of miscellaneous uranium-bearing ores and minerals.

Sample	U_3O_8, percent Volumetric method	Thiocyanate method
Carnotite	8.75 1/	8.84
	8.79 1/	8.93
	8.94 2/	
	8.99 2/	
Carnotite	3.38 1/	3.34
	3.34 1/	3.37
	3.41 2/	3.40
	3.44 2/	3.41
Carnotite	0.64 1/	0.63
	0.64 1/	0.63
	0.65 2/	
	0.65 2/	
Carnotite-bearing sandstone	1.95	2.09, 2.07
Carnotite-bearing sandstone	1.75	1.71, 1.72, 1.70, 1.72
Mineralized sandstone (weathered) (contains 2.96 percent V_2O_5)	1.57	1.66, 1.63
Mineralized sandstone (unweathered) (contains 7.39 percent V_2O_5)	1.62	1.50, 1.53
Ore	8.07	7.86, 7.92

1/ Analyses by H. Levine.
2/ Analyses by F. Cuttitta.

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