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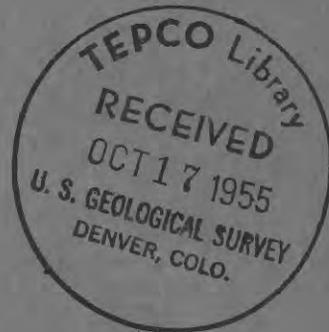
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no. 543

THE SPECTROPHOTOMETRIC  
DETERMINATION OF VANADIUM AS  
THIOCYANATE IN ACETONE-WATER MEDIUM

By H. I. Feinstein

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Trace Elements Investigations Report 543

UNITED STATES DEPARTMENT OF THE INTERIOR  
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October 11, 1955

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

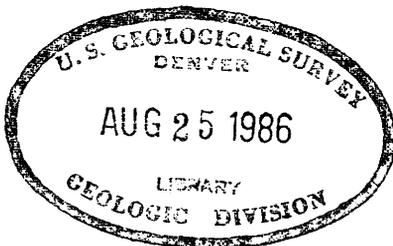
Dear Bob:

Transmitted herewith are three copies of TEI-543, "The spectro-  
photometric determination of vanadium as thiocyanate in acetone-water  
medium," by H. I. Feinstein, September 1955.

We are asking Mr. Hosted to approve our plan to submit this  
report for publication in *Analytica Chimica Acta*.

Sincerely yours,

*John H. Eric*  
for W. H. Bradley  
Chief Geologist



*WMB*  
JAN 23 2001

Chemistry

This document consists of 11 pages.  
Series A.

UNITED STATES DEPARTMENT OF THE INTERIOR  
GEOLOGICAL SURVEY

THE SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM  
AS THIOCYANATE IN ACETONE-WATER MEDIUM\*

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H. I. Feinstein

September 1955

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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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	82

## CONTENTS

	Page
Abstract .....	4
Introduction .....	4
Experimental data .....	5
Reducing agent .....	5
Thiocyanate and sulfuric acid concentrations .....	5
Acetone .....	5
Absorption spectrum of V(IV) thiocyanate .....	7
Interfering elements .....	7
Procedure .....	7
Literature cited .....	10

## ILLUSTRATIONS

	Page
Figure 1. Area of usefulness of $\text{NH}_4\text{SCN} - \text{H}_2\text{SO}_4$ in 3:2 acetone-water mixture .....	6
2. Spectrum of vanadium (IV) thiocyanate .....	8
3. Working curve .....	9

THE SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM  
AS THIOCYANATE IN ACETONE-WATER MEDIUM

By H. I. Feinstein

ABSTRACT

A method devised for the spectrophotometric determination of vanadium in acetone-water medium is based on the reaction between vanadium (IV) and thiocyanate. Within the concentration limits tested, Beers law is obeyed.

Although not as sensitive as the peroxide method, the vanadium (IV)-thiocyanate reaction product shows greater absorbancy than the blue vanadyl ion. In the absence of interfering elements, the method may be used in place of the volumetric procedure for the determination of macro quantities of vanadium.

INTRODUCTION

While studying the method for the spectrophotometric determination of uranium by thiocyanate in acetone-water medium (Crouthamel and Johnson, 1952), it was observed that under approximately similar conditions vanadium gave a blue color. The absorption of the vanadium thiocyanate blue in acetone-water is greater than that of the blue vanadyl ion (Santini et al., 1952), and experiments were performed to test its applicability to the determination of vanadium.

Absorption spectra of V(III and IV) thiocyanate in aqueous solution were reported by Furman and Garner (1951), and Crouthamel, Johnson, and Hjelte (1955) reported absorption spectra of V(III) thiocyanate in acetone-water solution.

This work was done as part of a program conducted by the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

#### EXPERIMENTAL DATA

Reducing agent.--Stannous chloride could not be used because, under even the most favorable conditions, it caused the solution to turn cloudy. Hydroxylamine hydrochloride, although satisfactory in this respect was sluggish in its action, but it finally gave the maximum absorbancy under the experimental conditions for the quantities of vanadium determined. Sulfurous acid reacted rapidly and appeared to increase the stability of the final color.

Thiocyanate and sulfuric acid concentrations.--It was observed early that for certain combinations of thiocyanate and sulfuric acid concentrations in a 3:2 acetone-water mixture, separation of two phases occurred, with or without the simultaneous separation of a white solid. Accordingly, a study was made of the range of useful concentrations of ammonium thiocyanate sulfuric acid in 3:2 acetone-water medium. In the region below the curve in figure 1, the various combinations of ammonium thiocyanate and sulfuric acid gave a homogeneous solution. For studying the absorbancy of the system, a solution 1 molar in ammonium thiocyanate and 0.14 normal in sulfuric acid was used.

Acetone.--Both acetone and thiocyanate have to be used in order to obtain an increased sensitivity. Acetone has been used previously for such a purpose in the determination of uranium (Crouthamel and Johnson, 1952), cobalt (Sandell, 1950, p. 285), and iron (Woods and Mellon, 1941). In the absence of thiocyanate, acetone does not increase the absorbancy of the blue vanadyl ion formed by sulfurous acid reduction (Santini et al., 1952).

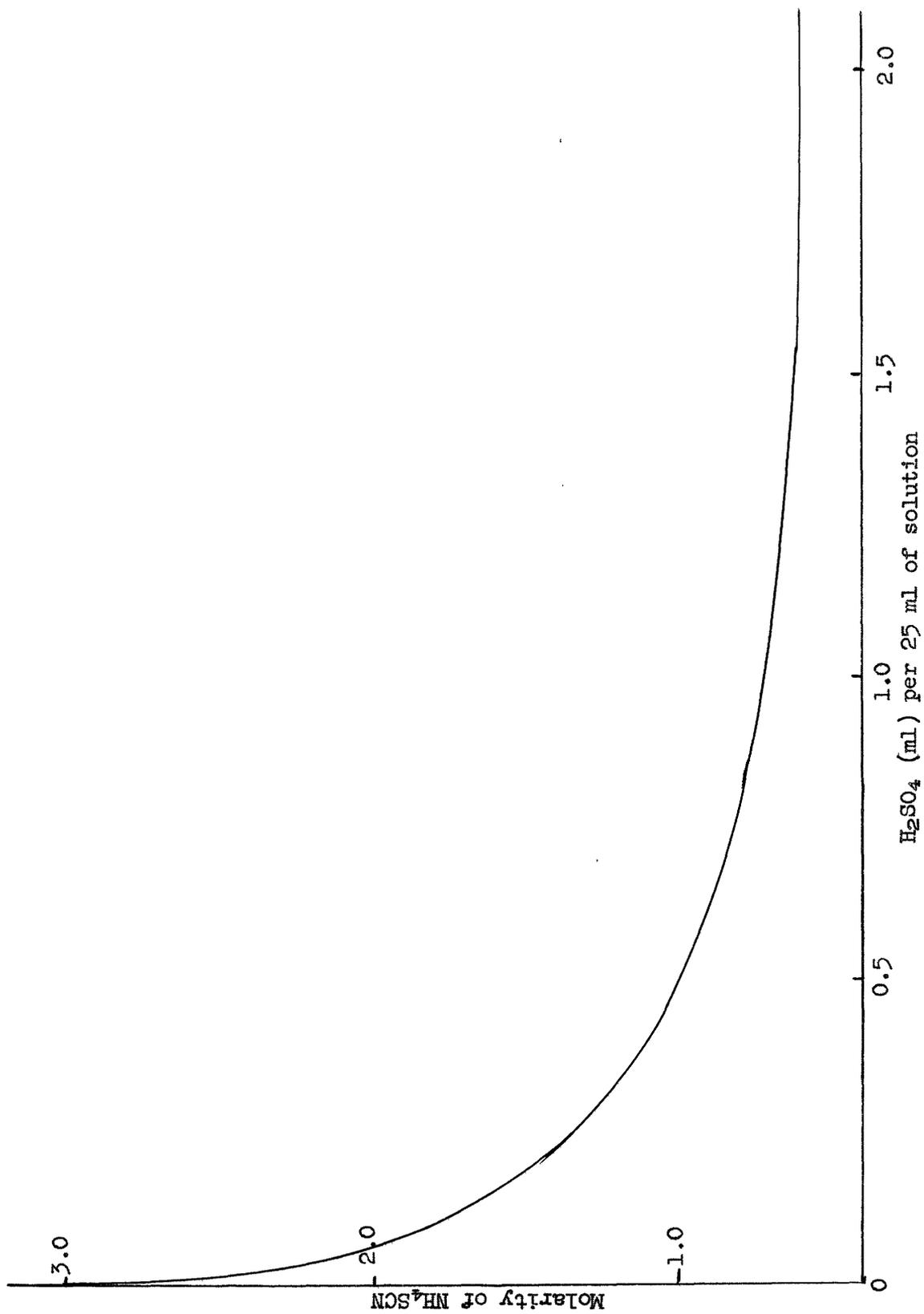


Figure 1.---Area of usefulness of  $\text{NH}_4\text{SCN}-\text{H}_2\text{SO}_4$  in 3:2 acetone-water mixture.

Absorption spectrum of V(IV) thiocyanate.--The absorbancy of the blue compound produced by vanadium, sulfurous acid, and thiocyanate in 3:2 acetone-water was measured with a Beckman DU spectrophotometer using 1-cm cells. The absorption spectrum, figure 2, shows a maximum absorbancy at 750 m $\mu$ .

Conformance to Beers law at 750 m $\mu$  is shown in figure 3. The sensitivity of this system is not as great as that of the peroxide system (Sandell, 1950, p. 609), but is 4 to 5 times as great as the vanadyl blue system (Santini et al., 1952).

Interfering elements.--No attempt was made to study this reaction in the presence of other elements; however, vanadium is often separated from many interfering elements as the cupferride (Hillebrand et al., 1953) and converted to a sulfuric acid solution. Macro quantities of vanadium are then determined volumetrically. The method here developed is suggested in place of the volumetric procedure.

It should be emphasized that before this procedure is applied to other than pure vanadium solutions, the effect of other elements present should first be determined, and if they are found to interfere, the necessary separations should be made.

#### PROCEDURE

##### Apparatus:

Beckman DU (or equivalent) spectrophotometer.

1-cm corex cells.

##### Reagents and solutions:

Sulfurous acid, not less than 6 percent, analyzed reagent.

Acetone, reagent grade or redistilled.

Ammonium thiocyanate, 8.33 molar solution.

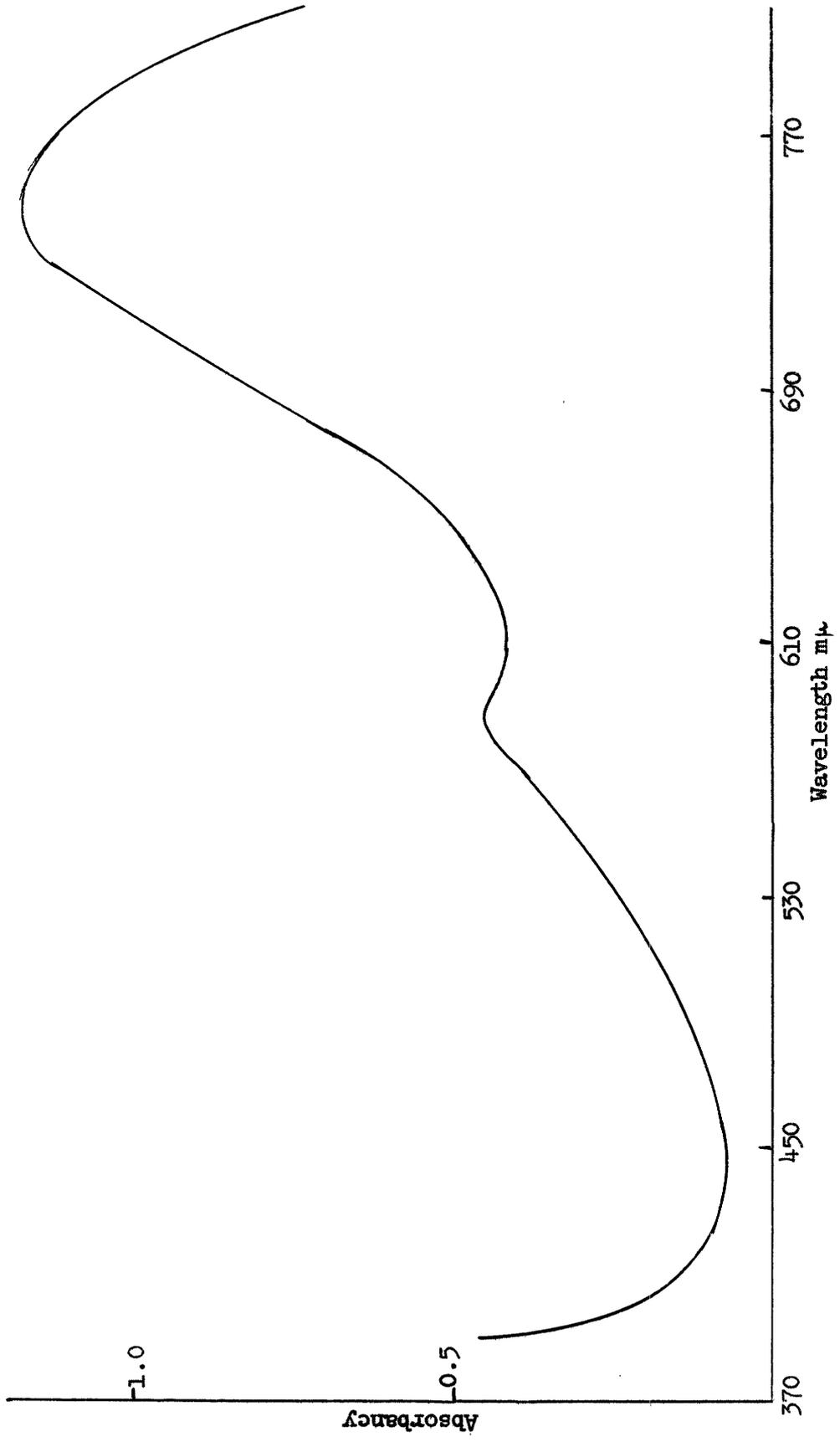


Figure 2.--Spectrum of vanadium (IV) thiocyanate.

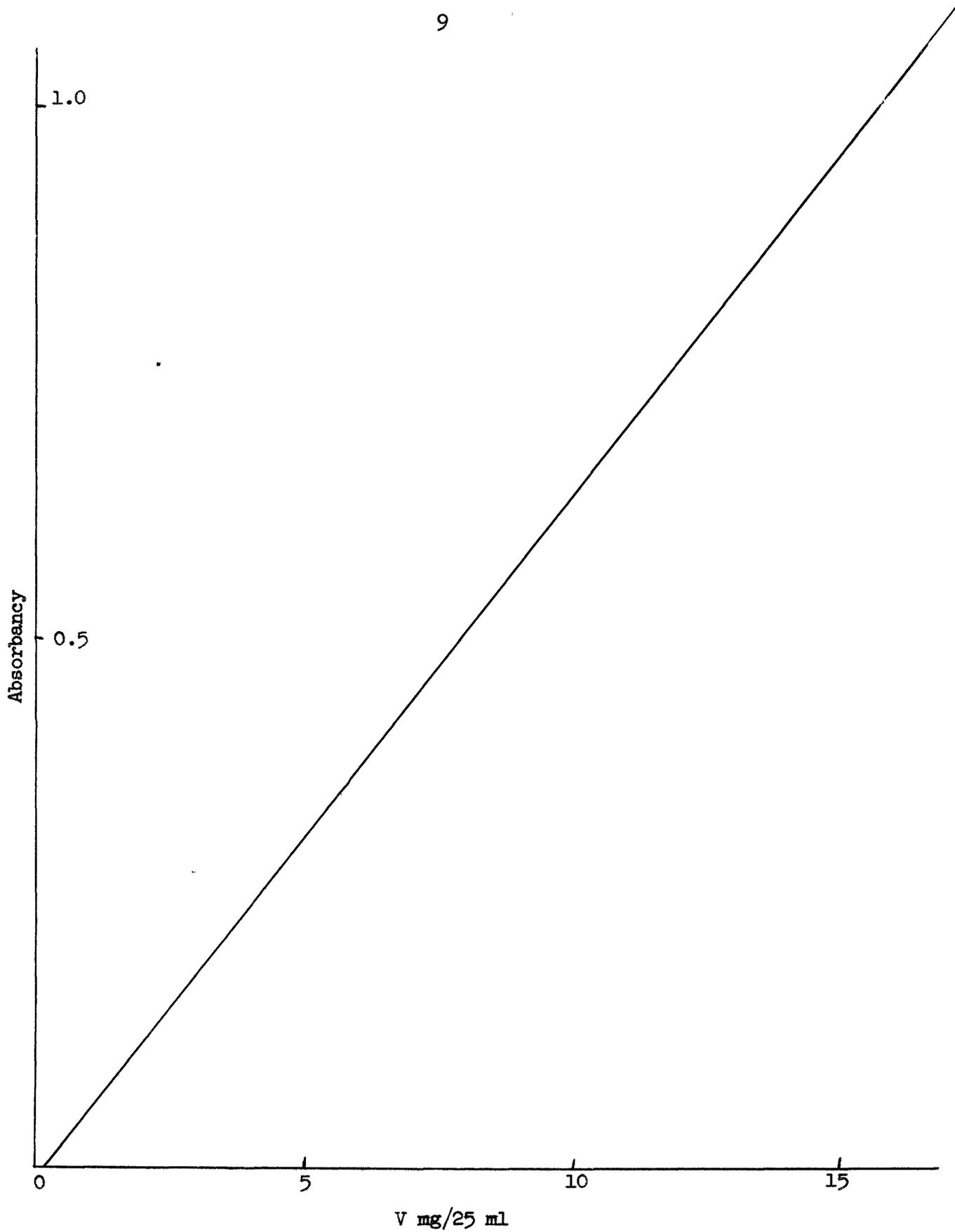


Figure 3.--Working curve.

Dissolve 158.5 grams of ammonium thiocyanate, A.C.S. grade, in distilled water with slight warming, cool, dilute to 250 ml in a volumetric flask and filter through a dry filter.

Standard vanadium solutions were prepared from a stock solution of potassium vanadate (1 ml  $\equiv$  0.033 gram  $V_2O_5$ ) that had been analyzed volumetrically.

Detailed procedure:

A 5-ml aliquot of the prepared vanadium solution free of interferences, containing between 5 and 15 milligrams of vanadium and 0.1 ml free sulfuric acid, is transferred to a 25-ml volumetric flask. The reagents are pipetted into the flask in the following order, mixing after each addition: 1 ml of sulfurous acid solution, 15 ml 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 (or equivalent) spectrophotometer using 1-cm cells at a wavelength of 750 m $\mu$ . The concentration of vanadium can be read from a curve prepared in the same manner from standard vanadium solutions (figure 3). The color developed under these conditions is stable for at least 48 hours.

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