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Chemistry Division

Section C-V

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D. N. Hume, Section Chief

THE SPECTROPHOTOMETRIC DETERMINATION OF MICROGRAM AMOUNTS OF URANIUM BY MEANS OF AMMONIUM THIOCYANATE

Problem Assignment No. CX7-2

By

C. M. Nelson and D. N. Hume

November 1, 1945

Received: 11/9/45 Issued: 11/9/45

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Abstract

An ammonium thiocyanate procedure for the colorimetric determination of uranium has been thoroughly examined with respect to errors inherent in the analytical method and possible interferences due to other elements in our samples. Modifications have been introduced which have increased the sensitivity considerably, the useful range going down to 4-5 micrograms of uranium with good accuracy.

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Introduction

This work was based on the project report, MX-149 "The Determination of Small Quantities of Uranium in the Presence of Large Quantities of Thorium and Small Quantities of Iron and Copper" by J. E. Currah and F. E. Beamish (Ref. 1) and consisted mainly in testing various modifications of their method. In general we have found their procedure to be fairly good.

The colorimetric method for uranium analysis most commonly used in this laboratory employs the color developed by sodium salicylate in an acetate buffer (Ref. 2,3). However, besides the anions that form complexes with uranium, such as carbonate, phosphate, and organic acids, the cations of iron, thorium, cerium, and ruthenium interfere. Iron interferes to such an extent (1 microgram of iron is equal to 5 micrograms of uranium) that no iron-containing samples can be analyzed with this method. With many samples containing varying amounts of iron being submitted for analysis, the need for a procedure free from iron interference is clearly evident.

In the procedure outlined by Currah and Beamish, the sample is first adjusted to either pH 1.5 or pH 1 (one should be chosen and then kept constant). Stannous chloride solution is then added to reduce any iron which may be present, (ferrous ion does not form a colored complex with thiocyanate), and a quantity of ammonium thiocyanate solution pipeted in to develop the color. The mixture is diluted to 25 ml. and compared with a blank solution in a spectrophotometer at a wave length of 365 mμ. During a thorough test of this procedure, we noticed several sources of error and introduced a number of improvements in the method.

Order of Addition and Effect of Mixing

We found that the order of addition of reagents to the sample makes a small difference in the transmission. A low value for uranium content is obtained if the ammonium thiocyanate is added before the stannous chloride. W. M. Byerly noticed that a much more serious error was introduced if the sample was not shaken well after each addition of reagents. Low and erratic results are obtained, particularly if thorough mixing after addition of stannous chloride is omitted. Apparently a high local acid or stannous ion concentration destroys the thiocyanate ion and causes a higher transmission. As much as a 20% error in uranium content for 300γ U was found if the solutions were not thoroughly mixed.

Table I

The Effect of Mixing on Percent Transmission for 300 γ Uranium

Order of addition	With shaking	Without shaking
$SnCl_2$ then NH_4SCN	55.4% 55.3	62.0% 64.8
NH_4SCN then $SnCl_2$	56.1 56.3	63.7 65.0

Variation of Transmission with Wavelength

The absorption curve of the uranyl thiocyanate system was taken on a Beckmann quartz spectrophotometer and the results are shown in Figure 1. In addition the family of curves given in Figure 2 and taken on the same instrument depict the variation of a standard curve with wavelength.

These curves show that the uranyl thiocyanate system deviates from Beer's Law above 400 γ U at 380 mμ and this deviation becomes more pronounced at lower wavelengths. However, when similar curves are taken on a Coleman Model 11 spectrophotometer with a PC-6 filter, 10V battery source, and 30 mμ slit width, (Figure 3) the divergence from Beer's Law is negligible at 360 mμ (the lowest convenient wavelength obtainable on the Coleman Model 11) and in the opposite direction. For routine analytical purposes this deviation from Beer's Law does not affect the results since the method has been shown to be very reproducible. The reason why the Coleman Model 11 does not show the deviation may be due to the relatively wide slit used in that instrument. As seen from the absorption curve a 30 mμ slit covers quite a range on the steep slope where one has to work. From our experiments it is seen that Beer's Law is followed more closely at higher wavelengths. Since the 30 mμ slit includes more of these higher wavelengths than the 0.2-0.3 mμ slit width used on the Beckmann instrument, the Coleman instrument would be expected to give a straighter line. The time intensification factor (see below) was checked and found to have no effect on the above results. We have used 380 mμ with the Coleman Model 11 for routine analysis with good success. If better sensitivity is desired for very small amounts of uranium, lower wavelengths may be used. Though greater deviations from Beer's Law may be expected at wavelengths lower than 380 mμ, these still may be advantageously used for analytical purposes. Due to the great dependence of transmission on wavelength, the setting of a particular wavelength is very important.

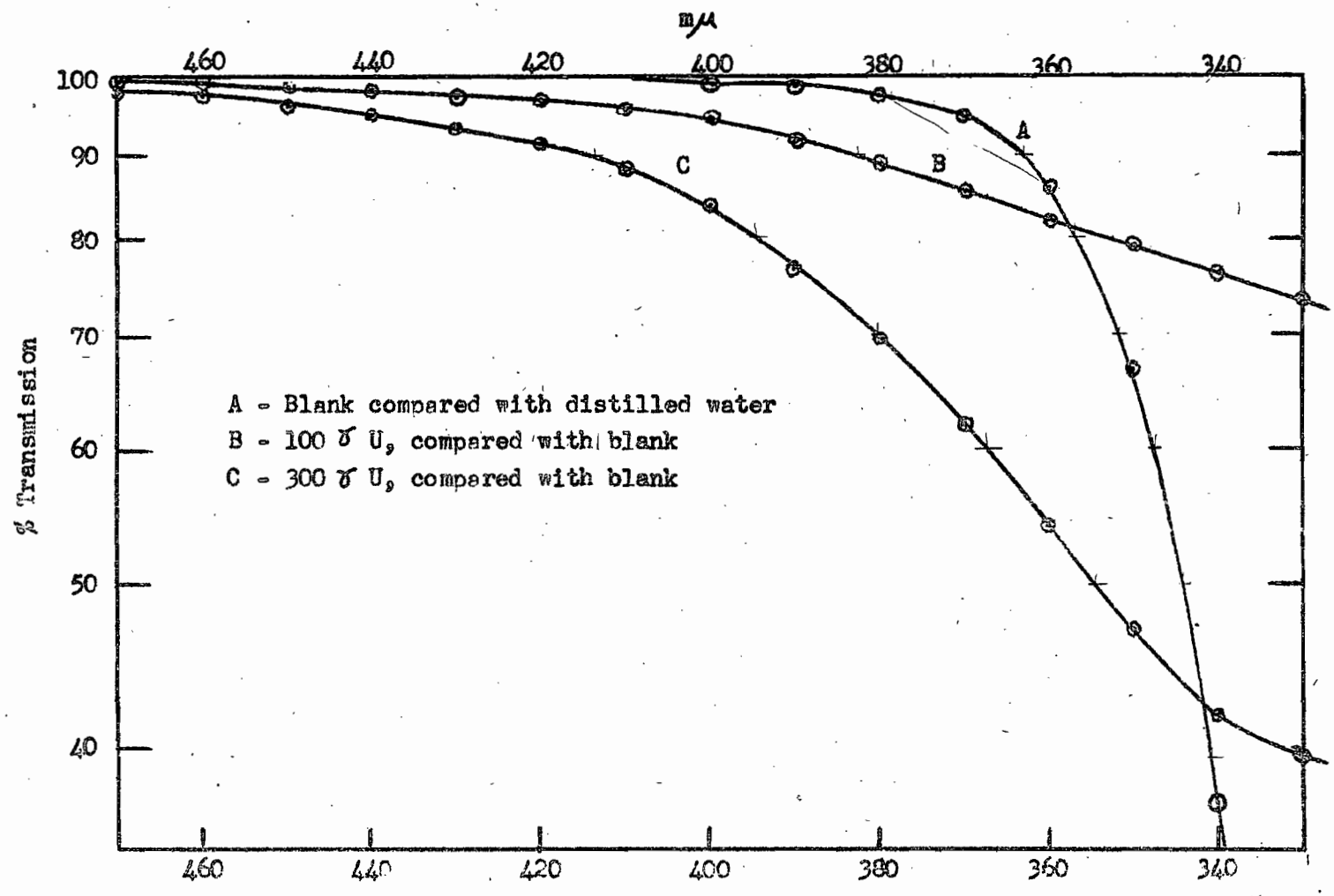

Figure 1. ABSORPTION CURVES

Procedure B. Beckmann Spectrophotometer

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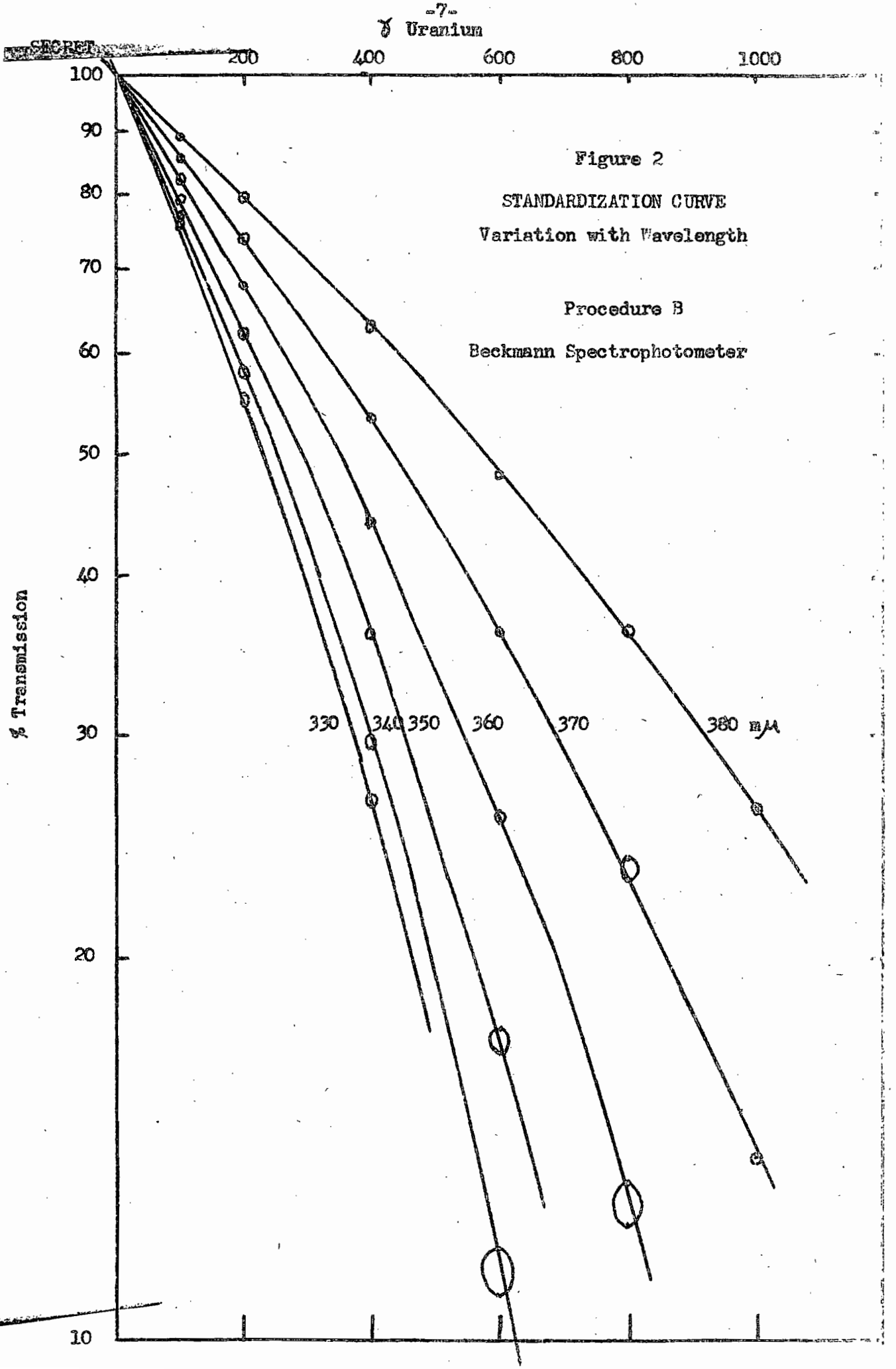

Figure 2

STANDARDIZATION CURVE

Variation with Wavelength

Procedure B

Beckmann Spectrophotometer

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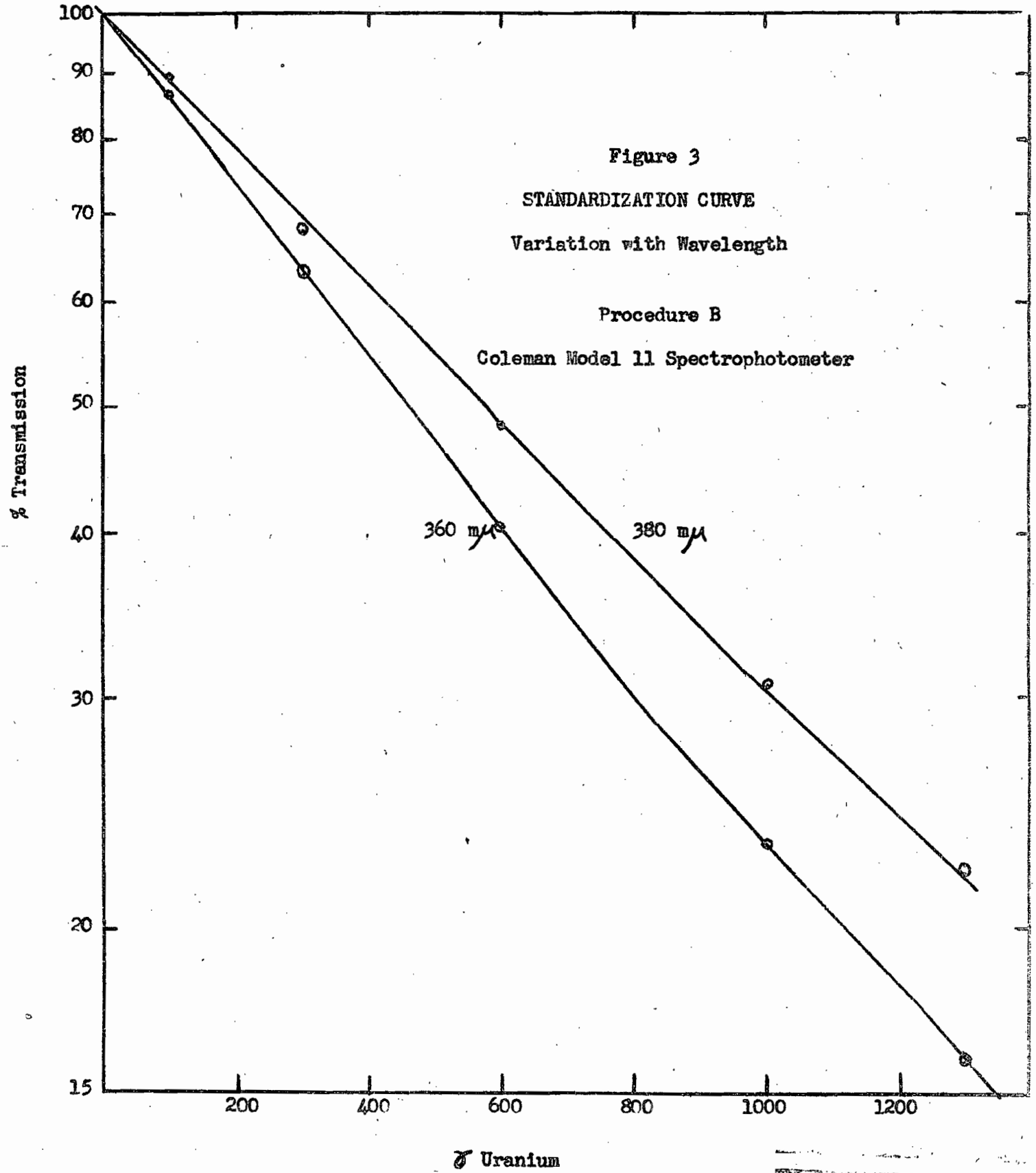

Figure 3

STANDARDIZATION CURVE

Variation with Wavelength

Procedure B

Coleman Model 11 Spectrophotometer

The Effect of Ammonium Thiocyanate Concentration

To improve the sensitivity of the procedure for small quantities of uranium, a higher concentration of ammonium thiocyanate was tried. A graph showing the decrease in transmission by increasing the amount of thiocyanate is given (Figure 4). The use of the higher concentration (10 ml 8 M NH_4SCN in a 25 ml volumetric flask) seemed worthwhile and this system was studied rather extensively. However, we found that under these conditions Beer's Law does not hold around 1000 γ of uranium.

Stability of the Ammonium Thiocyanate System with Time

It was found that there is a definite and noticeable intensification of the colored complex and blank with time. This rate of intensification is shown in an accompanying graph (Figure 5). Thus to eliminate this source of error a time limit was set for the final addition of thiocyanate, dilution, and reading of transmission. We adopted 1.5 min. as the standard time for these operations and it was used in subsequent work. Using a lower concentration of thiocyanate, (5.0 ml 8 M NH_4SCN added), the rate of intensification is smaller and less emphasis is placed on time (Figure 5). Using the lower concentration, an analysis should be completed within a half hour in order to neglect the intensification factor. To simplify the preparation of blanks for Procedure A, a stable colored solution (1.5 mg Cr^{+3}/ml as $Cr(NO_3)_3$ in 0.01 M HNO_3) was compared to freshly made blanks and used as a reference solution.

Stability of the Ammonium Thiocyanate System with Temperature

The thermal stability of the uranyl thiocyanate system was also investigated. Up to about 40°C, we found no change in the transmission of samples in a 5 minute period. Above 40°C, the rate of thiocyanate decomposition becomes very noticeable. Thus under normal conditions there is no temperature effect.

The Effect of a Longer Path and Smaller Dilution

We also used some arbitrary means to improve the sensitivity of the method to the utmost. In order to obtain a longer path than provided by the normal 13 mm. matched cuvettes, we tried a set of Coleman 5 cm. matched horizontal cells (Ref. 4). Using the 5 cm. horizontal cells and a total dilution volume of 10 ml a practical limit in sensitivity with respect to path length and uranium concentration in the final dilution was obtained. Other special apparatus requiring specialized technique might be used but would be inconvenient for routine analysis. Corresponding to the amount of sample taken, a higher concentration of thiocyanate can be used with the 10 ml volumetric flasks to improve the sensitivity. Beer's Law is followed with very low uranium concentrations (4-5 γ U) in these 5 cm. horizontal cells.

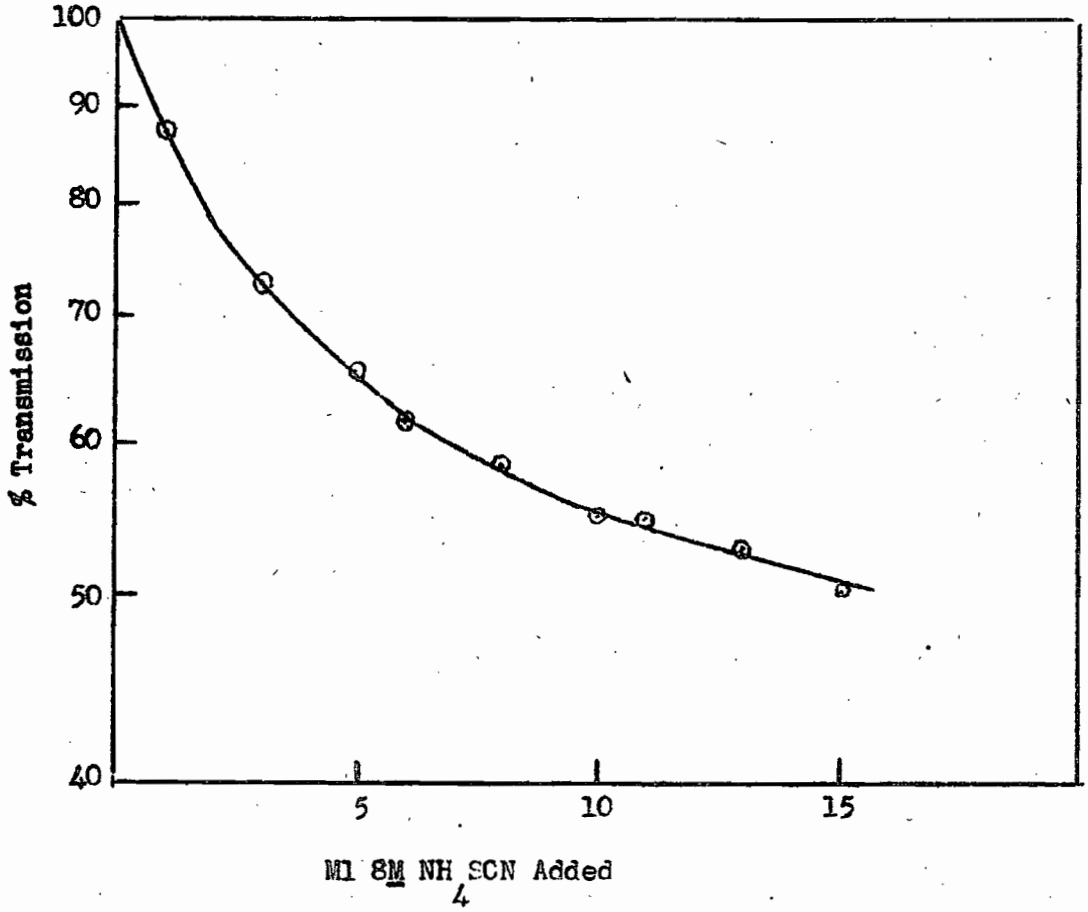

Figure 4

PERCENT TRANSMISSION VARIATION WITH AMMONIUM AMMONIUM THIOCYANATE CONCENTRATION

Coleman Model 11 360 mμ
300γ Uranium

The Effect of pH

According to their report, Currah and Beamish always adjusted their samples to pH 1.5 before addition of reagents but stated that pH 1.0 may be more satisfactory. We used pH 0.9 and also investigated the whole pH range from strongly acid (below pH 0.2) to a region (around pH 2) where Sn^{+4} hydrolyses. Our pH values are based on the final dilution since this should be a better value to use for comparison. There was no essential pH difference before and after addition of reagents at pH 1 and below. We found no change in transmission when the solution is kept within the limits pH 1 to pH 0.2. Thus quite a range in acidity can be tolerated provided the solution is kept below pH 1. From an examination of the plotted experimental points (Figure 6), it is noticed that above pH 1 the values are

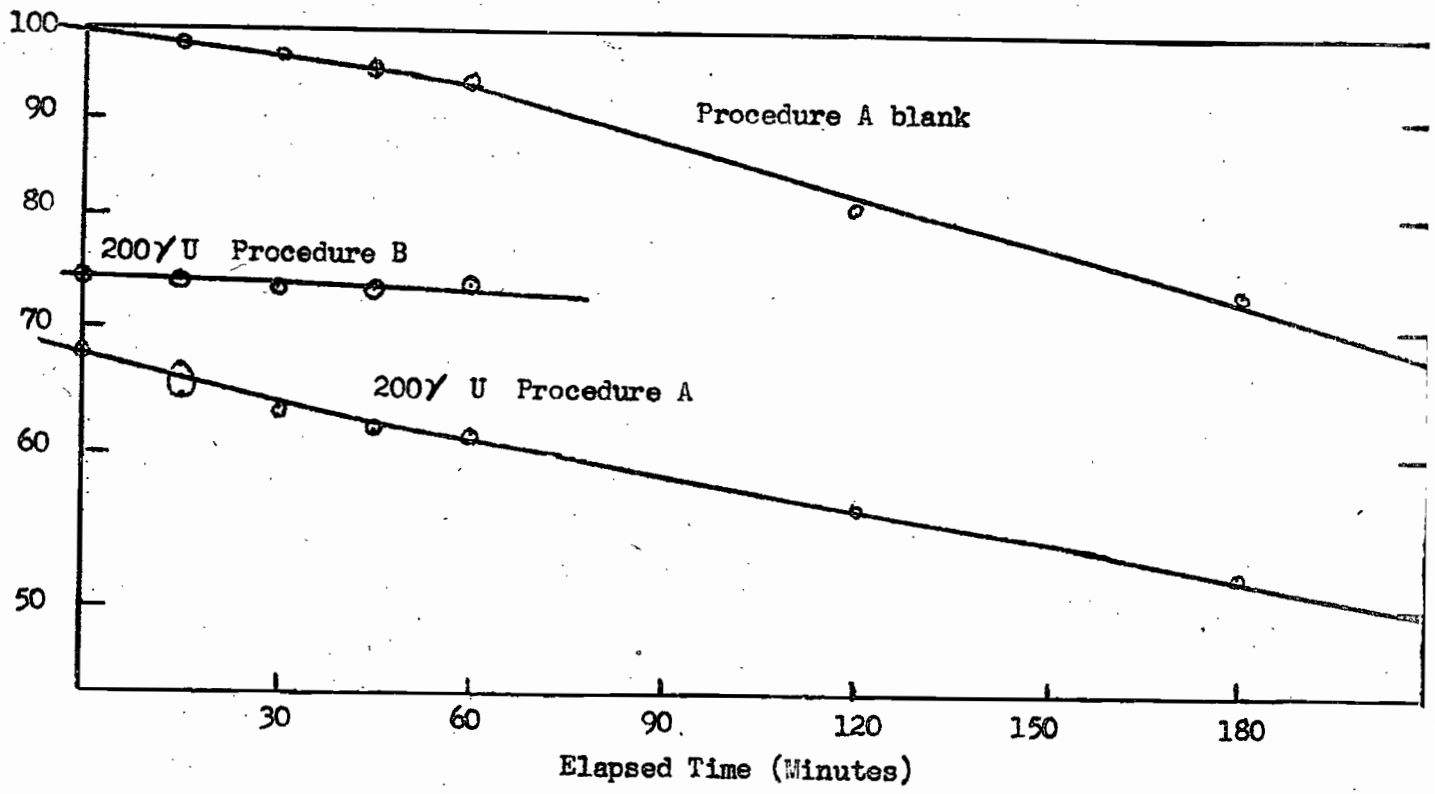

Figure 5

LOSS IN TRANSMISSION WITH TIME

Coleman Model 11

360 mμ

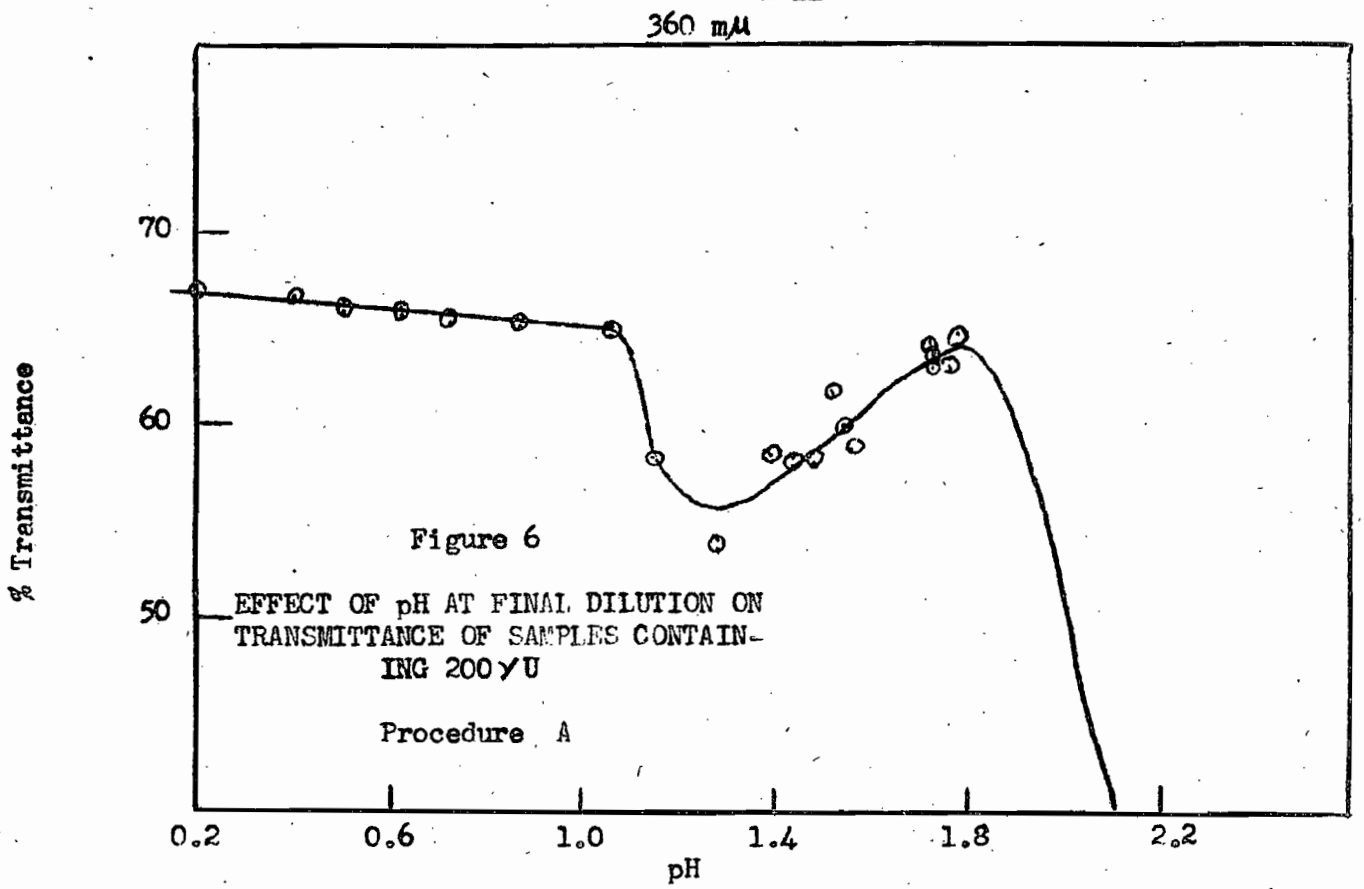

Figure 6

EFFECT OF pH AT FINAL DILUTION ON TRANSMITTANCE OF SAMPLES CONTAINING 200γU

Procedure A

erratic and unpredictable. Colloidal metastannic acid is especially noticeable around pH 2. There is a disadvantage with working at high acid concentrations in that the thiocyanate is attacked and decomposes with a color intensification. We found that up to 12 milliequivalents of acid added to a nearly neutral sample will not vary the transmission appreciably. The range pH 1 to pH 0.2 allows quite a bit of latitude, and with experience no trouble is found if pHydrion paper is used to indicate an approximate pH.

The Elimination of Iron and Carbonate Interference

We found the stannous chloride solution recommended by Currah and Beamish to be very satisfactory for the removal of iron interference and no other reducing agent was tried in our laboratories. We substantiated their claim that 2 ml of the 10% stannous chloride solution is sufficient to reduce 2 mg of ferric iron. If more than 2 mg of iron are present, more stannous chloride solution may be added. However, if more is added, a corresponding amount should be added to the blank.

Since the solution is adjusted to a pH lower than pH 1, the carbonate ion is destroyed. We tried the effect of carbonate ion and found no interference.

The Effect of Thorium and Cerium

Thorium does not interfere in the thiocyanate method up to 1.25 g of thorium in the 25 ml dilution. If a larger amount of Th is present, it can be compensated for by adding a corresponding amount to the blank as indicated by Currah and Beamish. Very little thorium (2-3 mg) can be tolerated in the sodium salicylate method so that for samples containing an unknown amount of thorium, the thiocyanate method should be used.

Cerium appears to interfere with the salicylate method but does not affect the transmission of the samples analyzed with the thiocyanate method.

The Elimination of Lead Interference

A major disadvantage to the use of the thiocyanate method is that only 50 γ of lead can be tolerated in Procedure A (10 ml of 8 M ammonium thiocyanate) and about 500 γ lead in Procedure B (5 ml of 8 M ammonium thiocyanate). For amounts of lead greater than this, 1 ml of 3 N sulfuric acid is added to precipitate $PbSO_4$. The solution is filtered through a "F" sintered glass funnel into a 25 ml volumetric flask by means of the apparatus shown in Figure 7. This worked very satisfactorily and can be applied to any similar work where filtration into a volumetric flask is needed. Two washes with dilute nitric acid are sufficient to transfer all the uranium. Stannous chloride and ammonium thiocyanate solutions are added, the mixture diluted to volume, and the transmission determined. This method has been found to remove lead to such an extent that if a standardization curve is made using the above technique with about 10 mg lead, a straight line results (Figure 8). Very good reproducibility can be obtained. The

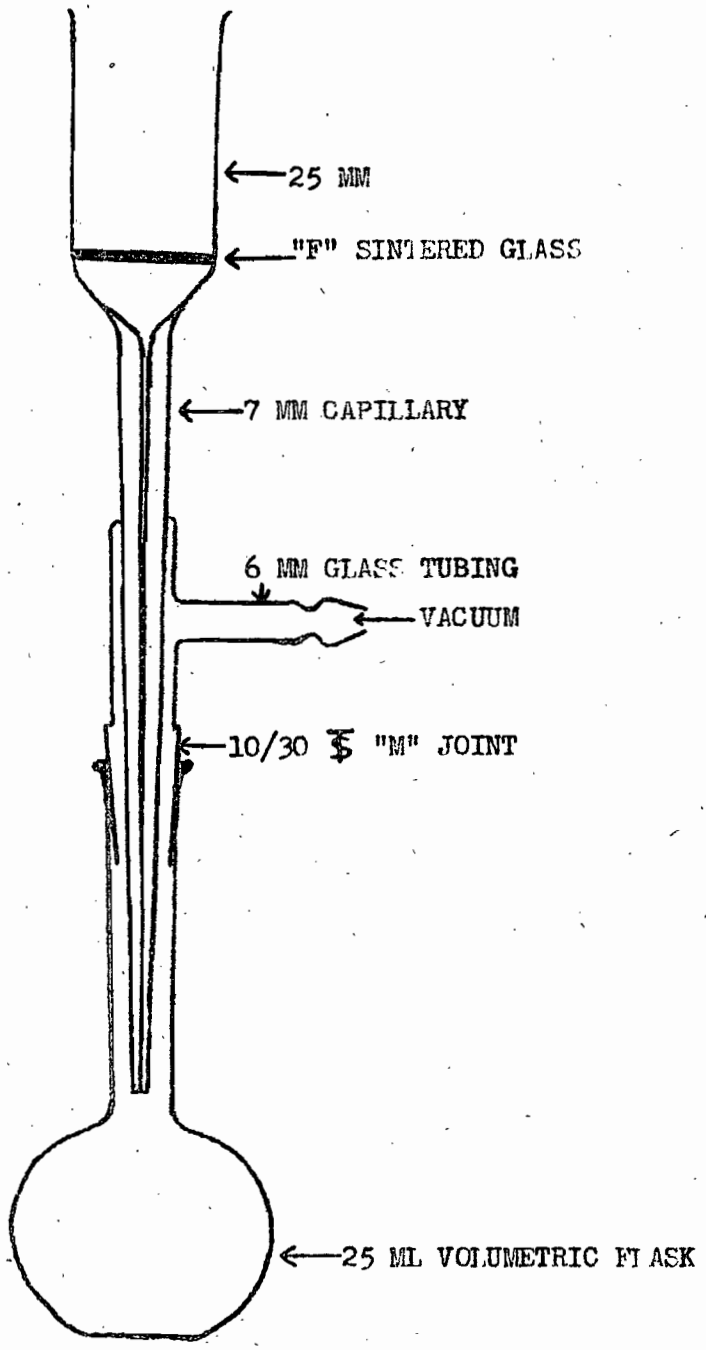

Figure 7

FILTRATION APPARATUS

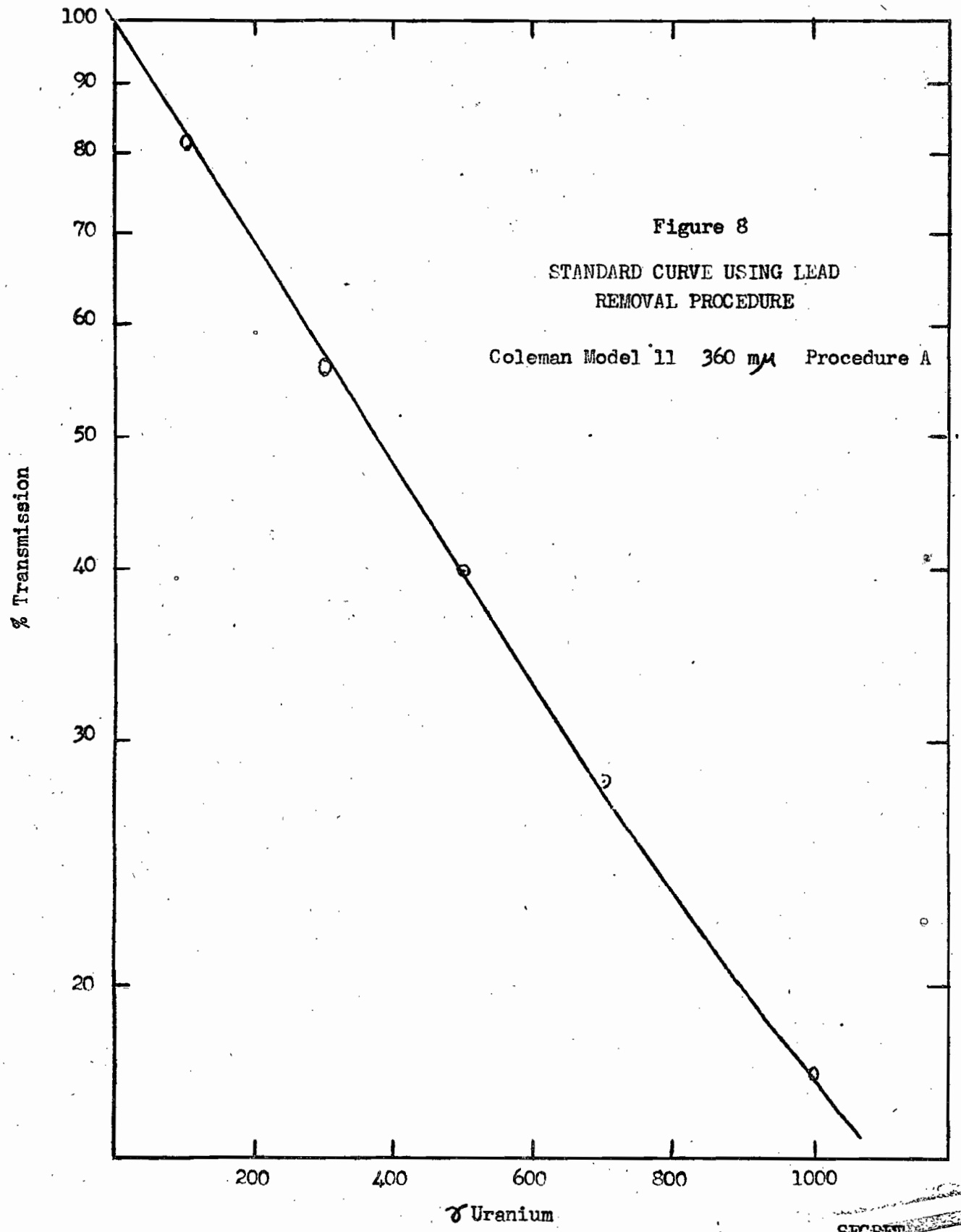

Figure 8

STANDARD CURVE USING LEAD REMOVAL PROCEDURE

Coleman Model 11 360 mμ Procedure A

method has been checked with from 1 mg to 50 mg of lead with 50 γ of uranium, and 100 γ to 1000 γ of uranium with 10 mg of lead. Within the limits of experimental error this method of lead removal is very good.

S. A. Reynolds in this laboratory has found that lead may also be removed by precipitating lead carbonate (Ref. 5). If the solution is too acid, it is partially neutralized with 6 N potassium hydroxide. Excess 50% potassium carbonate is added to precipitate the lead carbonate. The solution is filtered and the precipitate dissolved in 2 ml nitric acid. Excess 50% potassium carbonate is added to precipitate lead carbonate again. Two washes with distilled water are made. The reagents are added, the solution diluted to volume, and the transmission compared to a standard solution. This procedure has been used with good success in our laboratories with no noticeable loss of uranium.

The Elimination of Organic Matter and Hydrogen Peroxide Interference

As might be expected, organic matter interferes if present in appreciable amounts (15-20 mg.). However, it can be easily destroyed by a nitric-perchloric acid treatment. The sample is evaporated to dryness at least once on a hot plate (more nitric acid evaporations may be necessary if large amounts of organic matter are present) and then evaporated to dryness again with 0.5 ml concentrated nitric acid, 0.5 ml distilled water, and 1 ml 70% perchloric acid. The residue is dissolved in 1 ml of 1 N nitric acid and the analysis continued (Ref. 5).

The tolerated amounts of hydrogen peroxide are about 0.02 millimoles and 0.18 millimoles for Procedures A and B respectively. If the sample happens to contain larger amounts, the peroxide may be destroyed by rotating a platinum stirring rod in a hot dilute nitric acid solution for 5-10 minutes, depending on the amount of peroxide present.

The Interference of Molybdenum, Ruthenium and Tellurium

One of the serious interferences is molybdenum. Only about 5 γ Mo can be tolerated with Procedure A, while over 10 γ will give an appreciable error using Procedure B.

Another of the interferences is ruthenium, which cannot be tolerated in amounts above 10 γ. However, W. M. Byerly has found that excess amounts can be removed as RuO_4 by evaporating the solution to dryness with 1 ml 70% perchloric acid added. The residue is dissolved in 1 ml 1 N nitric acid and the analysis continued.

Tellurates do not interfere in the thiocyanate method but tellurites cannot be present at all since they are reduced to metallic tellurium. Tellurate ion seems to be fairly stable in the stannous chloride solution.

Table II

Maximum Allowable Amounts of Interfering Substances in the Determination of Uranium with Ammonium Thiocyanate

Substance	Procedure A	Procedure B
MoO_4^-	5 γ	10 γ
Ru^{+3}	10 γ	10 γ
Pb^{+2}	50 γ	500 γ
H_2O_2	0.02 mmol.	0.18 mmol.
$SO_4^=$	2 meq.	2 meq.
Cr^{+3}	1000 γ	1000 γ
Ni^{+2}	1000 γ	1000 γ

No appreciable interference was found in experiments with 1 mg amounts of Th^{+4}, Ba^{+2}, Sn^{+2}, Ce^{+3}, La^{+3}, Y^{+3}, Zr^{+4}, Be^{+2}, Fe^{+3}, Te^{+6}, Br^-, I^-, or IO_3^-.

Conclusions

The ammonium thiocyanate procedure has been shown to be very reproducible with not many interfering substances. Though it easily eliminates ferric iron, which cannot be tolerated in other methods, it is subject to other interferences. Molybdenum and ruthenium cause serious interference and not much sulfate can be tolerated. On the other hand, thorium, carbonate, and cerium have little effect on this method. The volume of ammonium thiocyanate added is critical and the wavelength setting must be watched closely.

By using a 10 ml dilution volume and a 5 cm. path length, much better sensitivity is obtained for very small amounts (5-10) of uranium than with a 25 ml dilution volume and 1.3 cm. path length. If still smaller amounts of uranium need to be determined, the analyst can go to lower wavelengths but this narrows the range of the method. For general routine analysis Procedure B is probably more useful but if other things are equal smaller amounts of uranium can be detected by using a higher concentration of thiocyanate (Procedure A). The procedures are adapted to quick and accurate (± 2%) analyses provided there are no seriously interfering ions present. Four samples in duplicate can be analyzed in about 30 minutes if no interferences are present.

Reagents and Apparatus

Ammonium thiocyanate solution: 8 M NH_4SCN, 609 gm. reagent grade ammonium thiocyanate dissolved in distilled water, diluted to 1 liter, and filtered through a "F" sintered glass funnel.

Stannous chloride solution: 10% by weight, 50 g $SnCl_2 \cdot 2H_2O$ dissolved in 50 ml conc. HCl and diluted to 500 ml. This should be filtered through a "F" sintered glass funnel.

Hydrochloric acid: 1 N HCl, C.P. concentrated hydrochloric acid diluted to volume.

Potassium hydroxide solution: 1 N KOH, reagent grade potassium hydroxide dissolved in water and diluted to volume.

Spectrophotometer: Coleman Model 11 with a PC-6 filter and a 10 V battery source.

Cuvettes: Coleman 13 mm. square or round cuvette sets, or 5 cm. horizontal cell sets. These should be perfectly clean and matched.

Recommended Procedures

A. 50-800 micrograms U Range

1) Pipette an aliquot of the sample solution into a 25 ml volumetric flask.

2) Adjust the pH of the solution to a value between pH 0.2 and pH 1.0 with 1 N HCl or 1 N KOH[a].

3) Add 2 ml 10% $SnCl_2$ solution and shake well.[b]

4) Add 10.0 ml 8 M NH_4SCN and shake well immediately.[c]

5) Dilute to volume and immediately compare[d] transmittance with a blank[e] at 360 mμ.[f]

B. 50-1200 micrograms U Range

Same as A except in 4). Add 5.0 ml 8 M NH_4SCN and shake well immediately.[g]

C. 5-150 micrograms U Range

Same as A except that a 10 ml dilution is made and the matched 5.0 cm. cells are used to compare transmittances. The volume of reagents added are modified accordingly:

(1) 1 ml 10% $SnCl_2$ solution.

(2) 2.0 ml 8 M NH_4SCN solution.

Notes: a) With experience the analyst can use pHydrion paper.

b) A 2 ml dropper can be used since a ± 10% error can be tolerated.

c) A buret or pipet should be used as only a ± 4% error can be permitted.

d) This should be compared immediately since there is an intensification of color with time. A reference solution of 1.5 mg Cr^{+3}/ml was found to be satisfactory so that there would not be an error with the blank "fading". This reference solution should be compared as often as necessary with true blanks made up and immediately compared.

e) A blank is made up with 1 ml of 1 N HCl plus the added reagents.

f) 360 mμ was about the lowest we could go on our spectrophotometer and still cover the range satisfactorily. See the discussion of the wave length setting in the report. This setting must be watched closely.

g) With the low ammonium thiocyanate concentration, the accuracy of the volume delivered becomes more important with a tolerance of about ± 2%. The use of a 5 ml pipet rather than a buret is recommended.

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4. L. A. Nutting, Book No. CL-A-74, p. 43.

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