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THE SALICYLATE METHOD FOR DETERMINING MICROGRAM AMOUNTS OF URANIUM

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THE SALICYLATE METHOD FOR DETERMINING MICROGRAM AMOUNTS OF URANIUM

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Urpo Koskela, and Ward M. Byerly**

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The work described herein was done during 1944-1945

*Present Address, National Dairy Research Labs, Oakdale, L.I., N.Y.
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I. ABSTRACT

The spectrophotometric salicylate method for the determination of uranium in solutions was used extensively at the Clinton Laboratories (former name of Oak Ridge National Laboratory) in 1944 and 1945. Although it has been largely replaced by other methods, it is still useful as a rapid method of analysis when the interferences are known.

When sodium salicylate is added to uranium in a solution that is buffered to a pH of about 8 with an ammonium acetate-ammonium hydroxide buffer, a yellow color is produced. This color can be measured on the Coleman (or Beckman) spectrophotometer. If the prescribed procedures for the respective ranges are followed, the relative standard deviation of the method is 3% in the range of 50 to 1800 micrograms of uranium and 5% in the range of 5 to 125 micrograms of uranium.

II. INTRODUCTION

The salicylate procedure described herein is a modification of an earlier one[12] that was in use at the Clinton Laboratories during 1944 and 1945. As the samples became more complex and began to contain many interferences, the thiocyanate[3,4,11] method was introduced. Later, the fluorometric[14] method became available for the determination of submicrogram amounts of uranium.

Numerous reagents have been used for the colorimetric estimation of uranium; among the more familiar are potassium ferrocyanide,[6] sodium alizarin sulfonate,[7] hydrogen peroxide,[5] 8-hydroxyquinoline,[1] and ammonium thiocyanate.[3] The ammonium thiocyanate method is very satisfactory when aluminum or iron is present. However, the amounts of reagents are critical, and a slow fading of the color limits the number of samples that can be measured against a single reference solution.

When salicylate ion is added to a solution that contains uranyl ion, a yellor or orange-red color is produced. This color has been used as an indicator in the titration of phosphoric acid with uranyl acetate.[8] Sodium salicylate has been used as a colorimetric reagent for uranium by Müller[10]. Also, Kennedy and Segre,[9] using a colorimeter and ammonium salicylate as a reagent, determined uranium in the quantity range of 5 to 500 micrograms.

The use of salicylate as a colorimetric reagent for uranium offered the advantages of allowing considerable latitude in the conditions for analysis and the amounts of reagents used without affecting the precision of the method.

A modification of previous salicylate methods was developed at the Clinton Laboratories for the analysis of numerous samples for uranium in the quantity range of 5 to 1800 micrograms by use of a 10% w/v sodium salicylate solution and ammonium acetate-ammonium hydroxide buffer.

III. SUMMARY

Uranium can be determined quantitatively in the range of 5 to 1800 micrograms with a relative standard deviation of 3 to 5% depending upon the procedure that is used. Recent measurements with a Beckman model B or DU spectrophotometer indicate improved reproducibility.

Sodium salicylate, when added to uranium in a solution that is buffered to a pH of about 8, produces a yellow color. This color intensity is proportional to the uranium concentration and can be measured spectrophotometrically.

Iron and thorium are the worst interferences; therefore, other methods must be used if samples are known to contain these cations. Small amounts of Pb^{++} and Al^{+++} can be tolerated. Anions except $PO_4^{\equiv}$ cause no interference. Peroxides and carbonates interfere but they are easily removed. Ruthenium, and organic acids and solvents can be removed by treatment with nitric and perchloric acids.

The method was used extensively in 1944 and 1945 at the Clinton Laboratories (former name of Oak Ridge National Laboratory) for rapid analyses. The amounts of reagents are not critical and the color complex is stable for at least twenty-four hours. Although the method is little used, it is still a convenient and rapid method for determining uranium when the interferences are known.

IV. SELECTION OF CONDITIONS

The method was adapted to the Coleman Model 11 spectrophotometer. It was decided to make the final volumes up to 25 ml in order that in routine work the analyst, using a pair of matched cuvettes, need but rinse out the cuvette being used for the sample solutions with a few washings of the next sample to be measured.

A 10% w/v sodium salicylate solution was used and the test solution was buffered with an ammonium acetate-ammonium hydroxide buffer (pH $\sim$7.5 to 8.0). Figure 1 shows the effect of various amounts of salicylate on the per cent transmittancy of the solution. For convenience in delivery, 5 ml was chosen as the volume of salicylate solution to be used.

Because the samples were generally acidic, it was decided to use 5 ml of the buffer. Thus, only a few drops of NH_4OH solution sufficed to make the final adjustment to a pH of about 8. Figure 2 shows the effect of pH on the per cent transmittancy of the solution.

Figure 3 shows the per cent transmittancy vs. wavelength curves for reagents vs. water, reagents and uranium vs. water, and reagents and uranium vs. reagents. Because there is no appreciable difference in the per cent transmittancy between 360 and 380 mμ, and because the Coleman spectrophotometer is unreliable at the lower wavelengths, it was decided to measure the color intensity of the uranyl salicylate complex at a wavelength of 380 mμ.

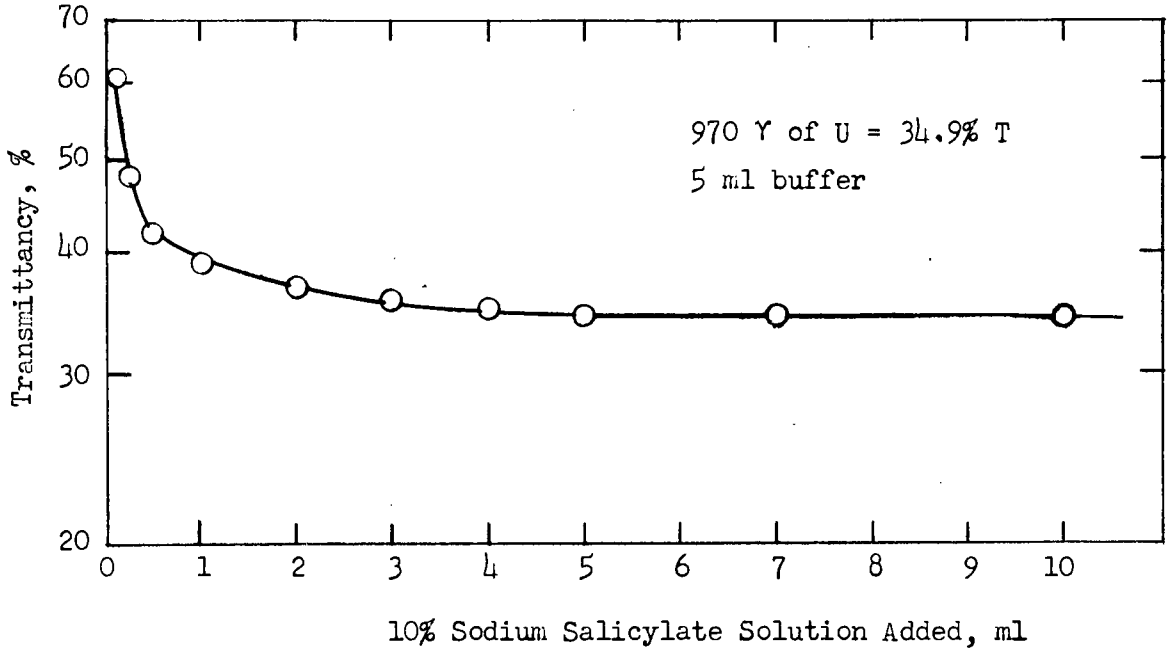

Fig. 1 - Effect of Salicylate Concentration on Color Intensity

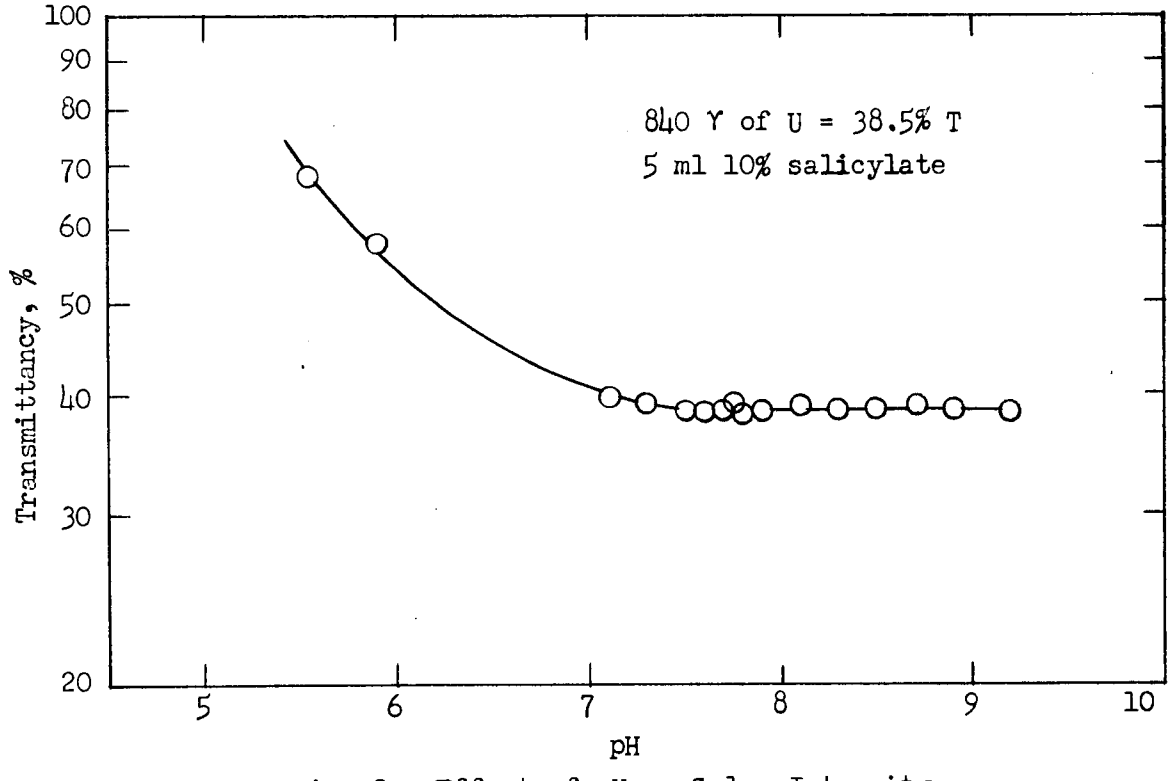

Fig. 2 - Effect of pH on Color Intensity

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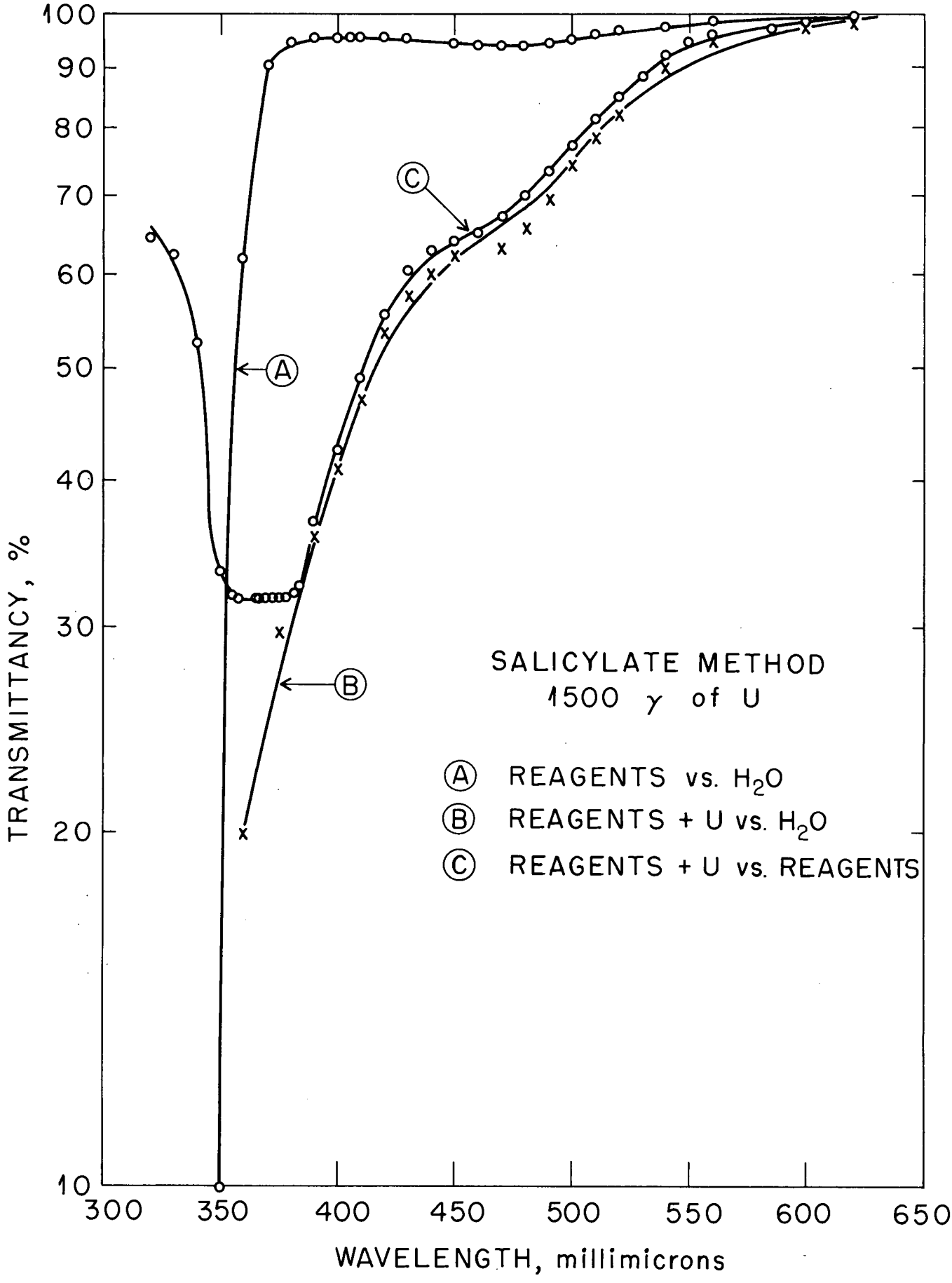

FIG. 3 – TRANSMITTANCY vs. WAVELENGTH

V. INTERFERENCES

A volume of 1 ml of concentrated H_2SO_4, HNO_3, or HCl added in the preparation of the 25-ml volume of standard uranium solution causes no interference. Phosphoric acid cannot be tolerated because of the formation of the uranyl phosphate complex.

Cations, such as Pb^{++} and Al^{+++}, can be tolerated up to the point of precipitation. Reynolds,[13] introducing about 20 mg of Pb per sample, removed the Pb by precipitating it as sulfate, filtering the solution through a sintered-glass crucible, and washing the precipitate twice with HNO_3 solution. The recovery of uranium averaged about 106%.

Iron and thorium are possibly the worst interferences and are difficult to separate; an ether-extraction separation for iron is described by Kennedy and Segre[9]. However, because the salicylate method is designed for the rapid estimation of uranium samples that contain iron and thorium should be analyzed by the thiocyanate method[11].

Carbonates readily complex with uranium. They are best removed by evaporating the sample to dryness with acid at least twice; HCl is the preferred acid because the dried residue dissolves more readily in water.

Peroxide interferes and can be removed by evaporating the sample to dryness at least twice with HCl; if the residue does not dissolve readily in water, a drop of HCl will hasten the solution of it.

Ruthenium, organic acids, and organic solvents can best be removed by fuming the sample several times with nitric and perchloric acids.

VI. RANGE AND PRECISION

By use of Coleman vertical cuvettes with the Coleman Model 11 spectrophotometer, uranium can be determined in the range of 50 to 1800 micrograms per 25 milliliters (Fig. 4). If horizontal cuvettes of 50-mm light-path length are used, uranium can be determined in the range of 5 to 150 micrograms per 10 milliliters (Fig. 5).

Because the amount of excess reagent is not critical and the method is relatively insensitive to pH changes above pH 7, the precision of the method is dependent upon the reproducibility of the instrument readings. The reproducibility of the readings is limited chiefly by the accuracy of the galvanometer, which has a precision of about 2%[2]. In the quantity range of 50 to 1800 micrograms of uranium, the relative standard deviation of the method is within 3% and within 5% in the range of 5 to 150 micrograms using the horizontal cuvettes. It is also possible to use a final dilution volume of 10 ml. By use of the vertical cuvettes, uranium in the range of 20 to 500 micrograms can be determined with a slight increase in precision (Fig. 6).

There is no evidence of color fading. The per cent transmittancy of samples measured over a period of twenty-four hours has not differed from the initial readings.

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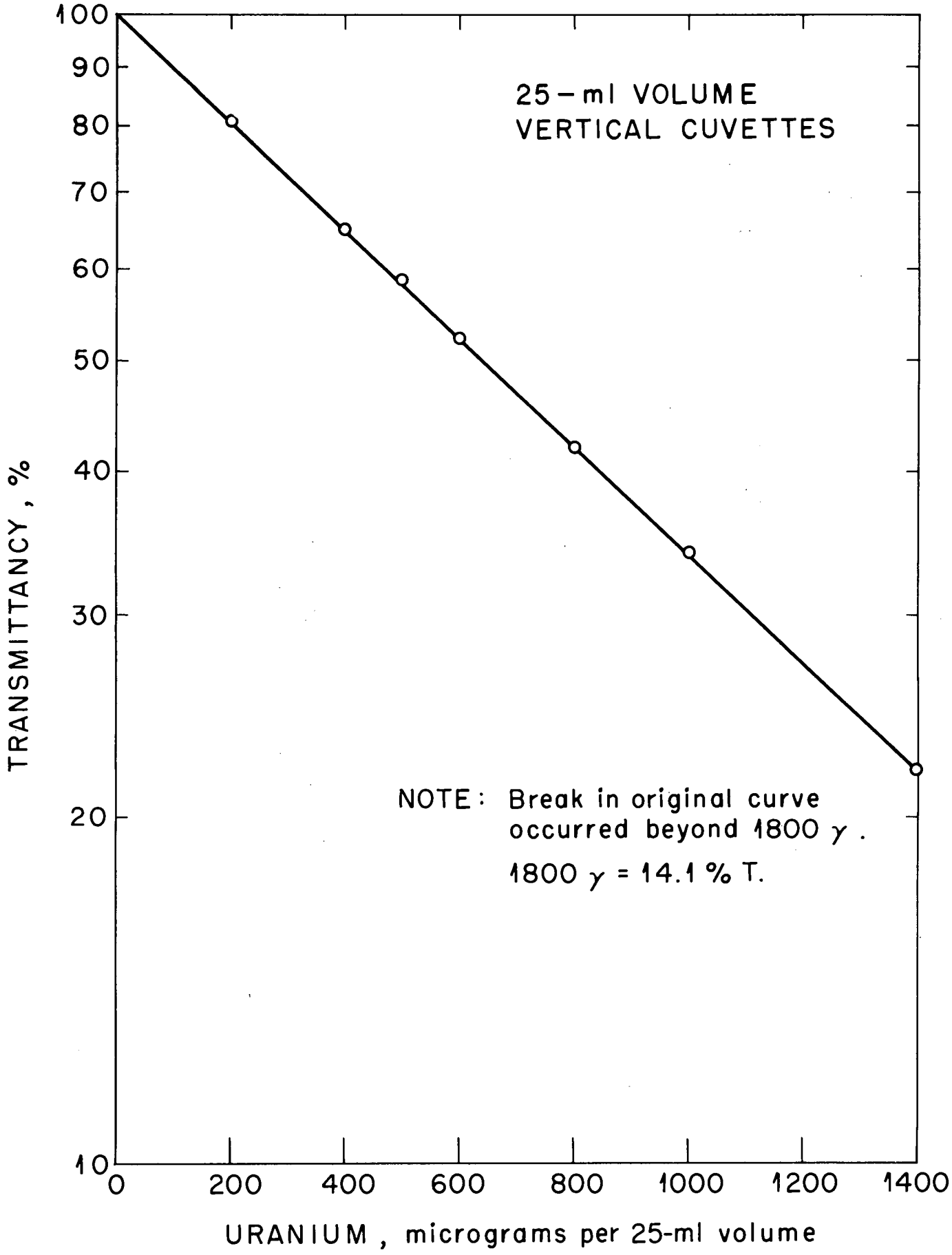

FIG. 4 – STANDARD CURVE

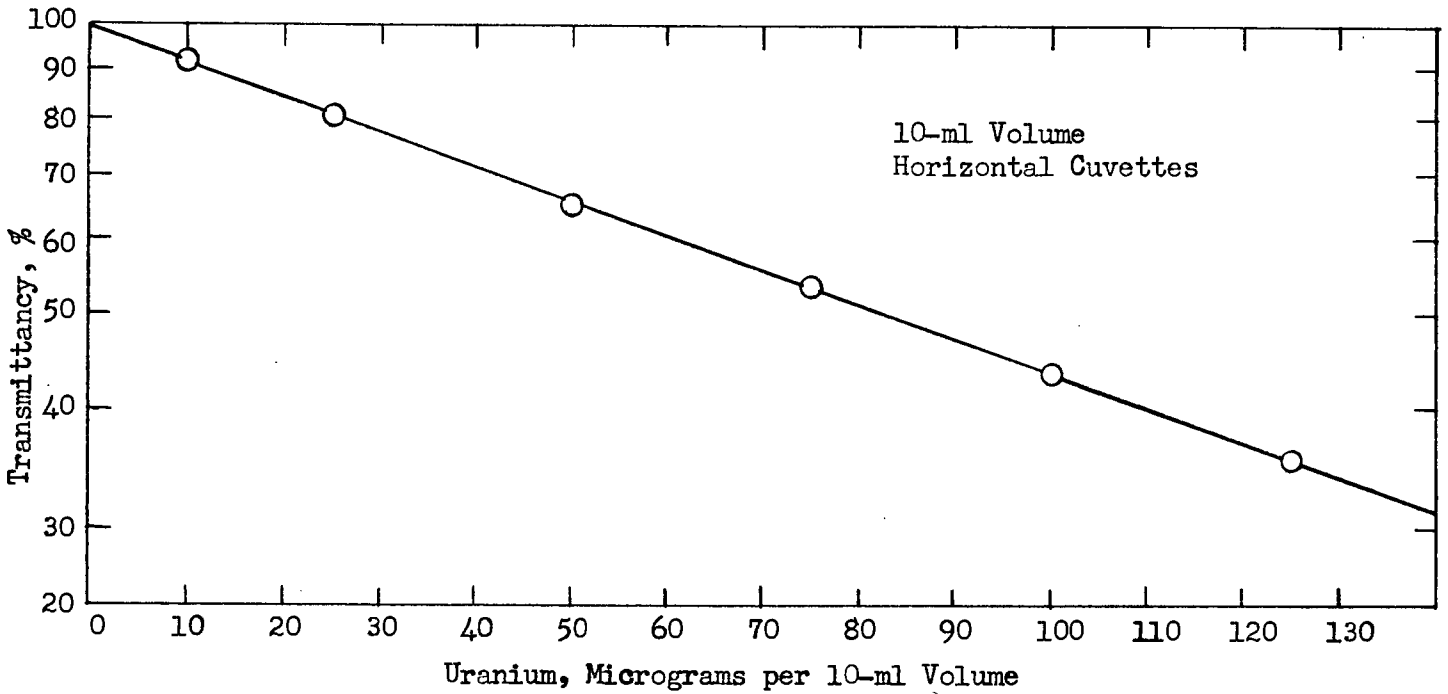

Fig. 5 - Standard Curve

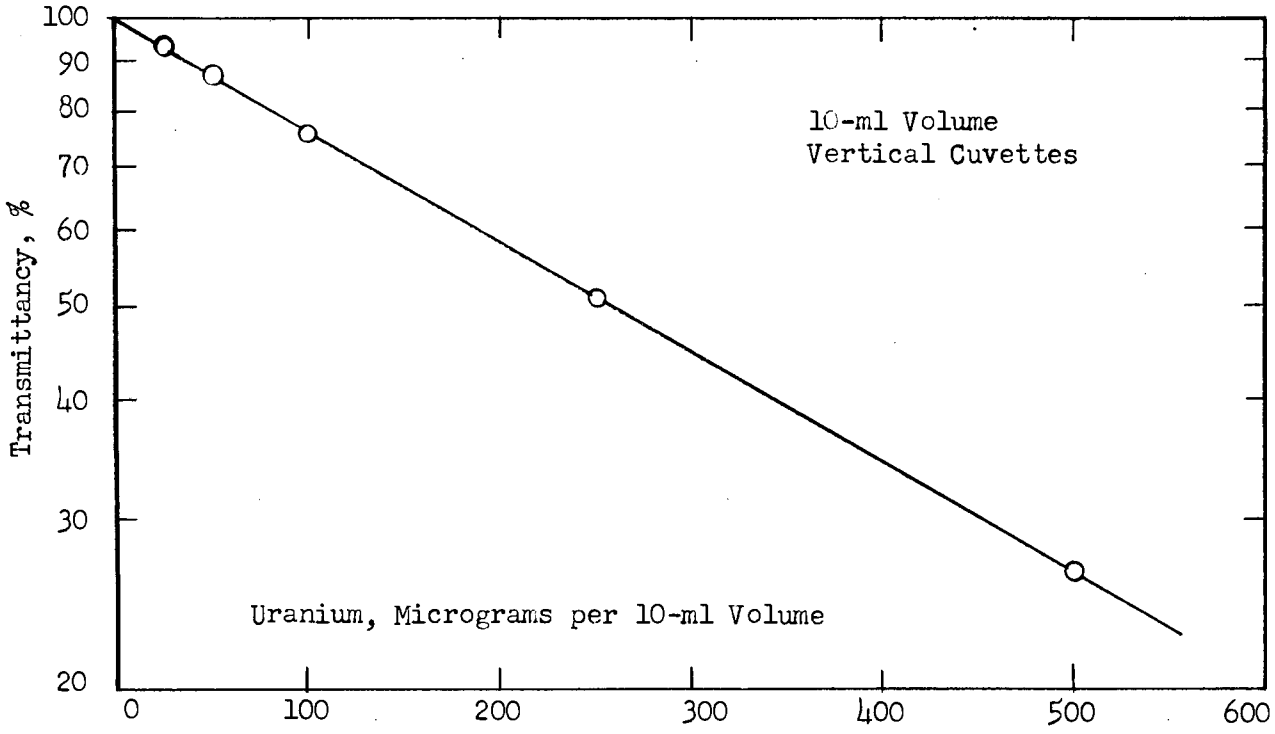

Fig. 6 - Standard Curve

VII. EXPERIMENTAL CONDITIONS

A. Reagents

1. Standard Uranium Solution:

Dissolve 21.0905 g of C.P. $UO_2(NO_3)_2 \cdot 6H_2O$ in one liter of distilled water. Standardize the solution by evaporating 10-ml aliquots to dryness in platinum evaporating dishes and igniting the residue to U_3O_8. This amount should give a stock solution of 10 mg of U/ml. A working solution of 200 µg of U/ml is used.

2. Ammonium Acetate Buffer:

Dissolve about 140 g of C.P. $NH_4C_2H_3O_2$ plus approximately 5 ml of conc. NH_4OH in one liter of distilled water (pH 7.5-8.0).

3. Sodium Salicylate Solution:

10% (w/v) in distilled water.

4. Ammonium Hydroxide Solution, concentrated.

5. Hydrion Paper.

B. Apparatus

1. Burets: 50-ml, self-filling.

2. Volumetric flasks: 10- and 25-ml with ground-glass stoppers.

3. Spectrophotometer: Coleman, Model 11, with PC-6 filter.

4. Cuvettes: Matched vertical and matched horizontal, 50-mm light-path length.

C. Procedures

1. For 50 to 1800 Micrograms of Uranium (Fig. 4)

a) Pipet a sample of appropriate size into a 25-ml volumetric flask(1).

b) Add 5 ml of buffer solution and shake(2).

c) Add 5 ml of sodium salicylate solution and shake(2).

d) Dilute the solution with distilled water to a point just below the neck of the flask and shake.

e) Adjust the pH of the solution to about 8 with NH_4OH solution(3).

f) Dilute the solution to the mark with distilled water and shake.

g) Measure the per cent transmittancy of the solution in the spectrophotometer against a reference solution of reagents only(4).

h) Determine the amount of uranium present in the sample aliquot from a standard curve prepared in the above manner.

2. For 20 to 500 Micrograms of Uranium (Fig. 6)

Follow the above procedure, except use 10-ml volumetric flasks. Accordingly, use 2 ml of the buffer solution and 2 ml of the sodium salicylate solution. Measure the solutions in the vertical cuvettes.

3. For 5 to 150 Micrograms of Uranium (Fig. 5)

For this range, use 10-ml volumetric flasks and the horizontal cuvettes. Follow the procedure (1) as modified in (2).

Notes

1) If the sample contains organic interferences or any of the above-mentioned interferences, they must first be removed. The residue is dissolved and transferred to the volumetric flask.

2) The reagents can be dispensed by using self-filling burets.

3) Hydrion paper is satisfactory for the pH measurement.

4) Measure at 380 mμ (PC-6 filter) using the vertical cuvettes and by direct reading from the galvanometer scale (p. 2 of Ref. 2).

VIII. ACKNOWLEDGEMENTS

This work is an extension of development studies by Hammand, C. W., Richards, R. W., and Moran, J. N., as reported by Parlour[12].

IX. REFERENCES

1. R. Berg, J. prakt Chem., 115, 178, (1927).
2. Coleman Electric Co., Maywood, Ill., "Directions for Model 11 Universal Spectrophotometer," Pamphlet D-142, June, 1945.
3. J. E. Currah and F. E. Beamish, MX-149, June 6, 1945.
4. Ibid., Anal. Chem., 19, 609, (1947).
5. Th. Fairley, Chem. News, 62, 227, (1890).
6. F. Feigl and R. Stern, Z. Anal. Chem., 60, 39, (1921).
7. F. G. Germuth and C. Mitchell, Am. J. Pharm., 101, 46, (1929).
8. G. Gutzeit, Helv. Chim. Acta., 12, 713, (1929).
9. J. W. Kennedy and E. Segre, CC-49, Apr. 20, 1942.
10. Müller, Chem. Ztg., 43, 739, (1919).
11. C. M. Nelson and D. N. Hume, MonC-28, Nov. 1, 1945.
12. A. K. Parlour, CN-2008, Aug. 15, 1944 (Classified).
13. S. A. Reynolds, private communication to W. M. Byerly, Sept. 9, 1945.
14. G. S. Sadowski, A. F. Stehney et al., unpublished work at Clinton Laboratories, 1946.