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DETERMINATION OF TIN IN SOLUTIONS
OF URANYL SULFATE

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Oscar Menis, D. L. Manning, R. G. Ball

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ABSTRACT

A method is described for the determination of microgram quantities of tin in solutions of uranyl sulfate. In this method, tin is separated from uranium by precipitating it as the hydroxide on an aluminum hydroxide carrier in a basic carbonate medium. The precipitate, which contains the tin with the carrier, is then dissolved in hydrochloric acid, following which the tin is determined polarographically. The method is applicable to the separation of tin in amounts as low as 2 μg from as much as 200 mg of uranium by a single precipitation. The coefficient of variation for the determination of tin in amounts ranging from 2 to 50 μg is approximately 10 per cent.

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INTRODUCTION

While in the process of making analyses of solutions of uranyl sulfate for corrosion products and other impurities, it became evident that the presence of small quantities of tin necessitated the development of a method for its determination. Since uranium interferes with both the colorimetric and polarographic methods for the determination of tin(IV), a reliable procedure for the quantitative separation of tin from uranium is a prerequisite for the estimation of tin by either method.

Before beginning any experimental work, a search of the literature was made which revealed that Rodden⁽⁶⁾ lists several methods for the separation of tin from various interferences; however, none of these methods appeared to be applicable to the separation of microgram quantities of tin from uranium. Another method in which tin is precipitated as the sulfide was recommended.

In an effort to separate tin from interfering elements, a distillation method was first examined. The tin was distilled as the tetrabromide,⁽¹⁾ then determined polarographically. The recovery of tin appeared to be quantitative in the range from 100 to 500 μg . Since the hydrogen peroxide that was used as a reagent in this experimental work was contaminated with small amounts of tin, the error due to the reagent blank became noticeable and significant in the determination of less than 50 μg of tin. For this reason, the results were both high and erratic.

A precipitation method, which proved to be quite satisfactory, was then investigated for the separation of small amounts of tin from solutions of uranyl sulfate. The method is essentially a combination of the carbonate separation of uranium from elements of the ammonium hydroxide group, as described by Rodden,⁽⁶⁾ and the method of Godar and Alexander,⁽²⁾ for the separation of tin from biological materials. In a procedure which has been adapted for use in this laboratory, tin is precipitated as the hydroxide in a basic carbonate medium with aluminum being used as a carrier. The uranium, of course, remains in solution as the complex uranyl carbonate anion. By following this procedure, tin is also separated from any cobalt, copper, chromium(VI), nickel, and molybdenum that may be present.⁽⁶⁾ Other ions that are members of the ammonium hydroxide group and that do not form carbonate complexes precipitate along with the tin.

After this method of separation was established as the most suitable for the purposes of this laboratory, methods of determining tin were studied. The two methods that are used commonly for the measurement of small quantities of tin are the polarographic⁽⁵⁾ and the dithiol spectrophotometric methods.^(1,6) The latter method is seriously limited in its application in that so many other elements interfere; therefore, a complete separation of tin is required before the method can be used successfully. In the use of the dithiol method, tin is separated from substances that interfere with the determination as the bromide by the application of a distillation technique. When the separation is complete, the excess bromide is removed by reacting it with hydrogen peroxide, following which the tin is reduced with thioglycolic acid. After the stannous-dithiol complex is formed,

its absorbancy is measured at a wavelength of 530 m μ . In addition to the limitation of this method due to interfering elements, another disadvantage is the need for the addition of a dispersant to the stannous-dithiol lake before spectrophotometric measurements can be made.

Due to the limitations of the dithiol method for the determination of tin, it was discarded in favor of the polarographic method, which does not require the complete isolation of tin before its determination. Only those substances that exhibit a reduction wave at approximately -0.55 volts versus the SCE must be removed. In view of the greater selectivity of the polarographic method and since the polarograph⁽³⁾ affords a very sensitive means of detecting microgram quantities of tin, this method appeared to be more suitable for making the final measurement in this particular application. In a supporting electrolyte that contains a sufficient amount of chloride, the stannic ion is reduced stepwise at the dropping mercury electrode.⁽⁵⁾ The first wave is due to the reduction of the stannic ion to the stannous ion with a half-wave potential of approximately -0.15 volts versus the SCE. The second wave comes about as a consequence of the reduction of the stannous ion to elementary tin at a half-wave potential of about -0.55 volts versus the SCE. The latter reduction wave is used most frequently for analytical purposes.⁽⁴⁾

In addition, the development of the procedure involved a study to ascertain the optimum conditions relating to the supporting electrolyte, the amount of aluminum carrier to use, and the maximum amount of uranium from which satisfactory separations of small quantities of tin could be achieved. The precision and reliability of the method were established by noting the

degree of recovery of known amounts of tin from solutions of uranyl sulfate which were analyzed by the procedure given in this report.

REAGENTS

1. Aluminum Nitrate Solution, 5 mg Al per ml. Dissolve 17.4 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 250 ml of water.
2. Basic Carbonate Solution. Dissolve 25 g of $(\text{NH}_4)_2\text{CO}_3$ in about 500 ml of water then transfer the solution to a 1-liter volumetric flask. Add 70 ml of concentrated NH_4OH ; then dilute this mixture to 1 liter with water. This gives a 2.5 per cent solution of ammonium carbonate in 1 N ammonium hydroxide.
3. Ethanol, 95 per cent.
4. Hydrochloric Acid, concentrated.
5. Methyl Red Solution. Dissolve approximately 0.1 g of technical-grade methyl red in 60 ml of ethanol then dilute to 100 ml with water.
6. Nitric Acid, approximately 7 M. Cautiously add 10 ml of concentrated HNO_3 to 10 ml of water. Mix thoroughly.
7. Tin(IV) Standard Solution, 20 mg per ml. Dissolve 2.00 ± 0.05 g of Mallinckrodt reagent-grade, 20-mesh, granulated tin in 100 ml of concentrated HCl . Dilute the solution to 1 liter with water. Prepare less concentrated solutions by appropriate dilutions of the stock solution.
8. Water, demineralized. Demineralized water is to be preferred over distilled water since the latter may contain certain contaminants.

APPARATUS

1. Centrifuge tubes, conical, graduated, 50-ml capacity.
2. Polarograph, ORNL High Sensitivity, Model Q-1160, with dropping mercury and saturated calomel electrodes.
3. Stirrer, platinum wire.

PROCEDURE

Transfer an aliquant that contains at least 5 μg of tin and not more than 200 mg of uranium from a solution of uranyl sulfate to a 50-ml conical centrifuge tube. Add 1 to 2 ml of a solution of aluminum nitrate, add 2 drops of the methyl red solution; then neutralize the solution with ammonium hydroxide. Re-acidify this mixture by the addition of a few drops of 7 M nitric acid; then add 40 ml of the basic carbonate reagent. After mixing the sample thoroughly, centrifuge it for five minutes. Decant the supernatant liquid; then wash the hydroxide precipitate two times with 5-ml portions of the basic carbonate reagent. Centrifuge and decant after each wash. Add 3 ml of concentrated hydrochloric acid to the precipitate; then heat the mixture gently over a burner until the precipitate dissolves. When solution is complete, cool, add 2 ml of ethanol; then dilute to 10 ml with water.

Transfer this solution to a polarographic cell; deaerate the solution with nitrogen; then record the polarogram by scanning from a potential of -0.4 up to -0.7 volts versus the SCE. Measure the diffusion current of the tin reduction wave at a half-wave potential of about -0.55 volts versus the

SCE. Plot, on rectilinear graph paper, the diffusion current versus concentration of tin in the 10-ml test volume.

EXPERIMENTAL

Effect of Aluminum in Two Supporting Electrolytes. Since it is proposed to use from 5 to 10 mg of aluminum as a carrier agent, tests were made to ascertain which of two supporting electrolytes could be used to the best advantage in the presence of relatively high concentrations of aluminum. The two electrolytes which have been reported in the literature as being suitable for use in this determination are as follows:

- 3 M NH₄Cl in 1 M HCl -by Lingane,⁽⁵⁾
- and 3 M HCl in 20 v/v per cent C₂H₅OH -by Kolthoff and Johnson.⁽⁴⁾

The results of tests on both of these electrolytes are presented in Table I.

Table I
Effect of Aluminum in Two Supporting Electrolytes
on the Diffusion Current of Tin

Conditions:

Tin, μg	43
Volume, ml	10
Diffusion current measured at, volts	- 0.55 (vs. SCE)

Aluminum	Diffusion Current, μg	
mg	3 M NH ₄ Cl-1 M HCl	3 M HCl-20% C ₂ H ₅ OH
0	0.246	0.190
1	0.220	0.184
5	0.176	0.184
10	0.150	0.184

It is readily apparent from the data in Table I that the presence of different amounts of aluminum does not appreciably affect the diffusion current of tin when hydrochloric acid in ethyl alcohol is used as the supporting electrolyte. It is evident, however, that a pronounced decrease in the diffusion current occurs when aluminum is added to a mixture of 3 M ammonium chloride and 1 M hydrochloric acid.

The Effect of Hydrochloric Acid. Since a noticeable increase in the diffusion current of tin occurred in the solution of ammonium chloride and hydrochloric acid when aluminum was added, an effort was made to determine if the concentration of acid caused this change. Hydrochloric acid in concentrations from 1 to 7 M was the medium which was used in this phase of study. From this experimental work, it was found that the diffusion current of tin is independent of the concentration of acid from 2 to 6 M. When the concentration of acid is outside this range, however, the diffusion current decreases. Although 2 to 6 M hydrochloric acid can be used with no serious effects on the diffusion current, 3 M hydrochloric acid was chosen for subsequent experiments, since the agar salt bridge deteriorates at higher acid concentrations.

These results are in essential agreement with those of Kolthoff and Johnson.⁽⁴⁾ They were concerned, however, with the determination of the optimum conditions for the formation of the first reduction wave of tin. In this laboratory, the experimental work was carried out in an effort to determine the applicability of the second reduction wave of tin for analytical purposes.

The Effect of Aluminum Carrier on the Separation of Tin From Uranium.

Since the method of separation of tin from uranium involved the use of an aluminum carrier, several tests were made to determine the effect that aluminum has on the precipitation and recovery of tin. In these tests attempts were made to separate 42 micrograms of tin from 50 mg of uranium in the presence of different amounts of aluminum carrier. It was found that tin is not recovered if aluminum is absent. A recovery of only 10 per cent of the tin was realized when 1 mg of aluminum was present; while however, in the presence of 5 to 10 mg of aluminum, the recovery of tin was quantitative. It is concluded, therefore, that at least 5 mg of aluminum must be present before a quantitative separation of tin from uranium in a basic carbonate medium is possible .

The Effect of Varying Concentrations of Uranium on the Recovery of Tin.

In order to establish the maximum concentration of uranium from which tin can be separated satisfactorily, 25 μ g of tin in test solutions that contained various amounts of uranium up to a maximum of 300 mg was separated by means of the recommended procedure, following which the tin was determined polarographically. Typical polarograms are shown in Figure 1. It was found that quantitative recovery of tin from as much as 200 mg of uranium can be achieved with a single precipitation. When the amount of uranium in the test solution was of the order of 200 mg or more, a single precipitation was not sufficient for the separation of tin from uranium; consequently, a double and sometimes a triple precipitation was necessary. Under these conditions the recovery of tin was consistently low. Apparently, the loss of tin was due to solubility effects which become significant when multiple

precipitations are made. A pronounced decrease in the quantity of stannic and aluminum hydroxides was observed each time more than one precipitation was made. For this reason, the aliquant of uranyl sulfate that is used for analysis must contain no more than 200 mg of uranium so that the tin can be separated by a single precipitation.

Calibration Curve and Diffusion Current Constant. A standard curve was established for the determination of tin by processing known amounts of tin according to the recommended procedure in the presence of and in the absence of uranium. The diffusion current constant, K , was also calculated from the following relationship:

$$K = \frac{I_d}{Cm^{2/3} t^{1/6}}$$

Where K = diffusion current constant

I_d = observed diffusion current, μa

C = concentration of the tin, millimolar

m = mass of mercury flowing from the dropping mercury electrode
in one second, mg

t = drop time of the dropping mercury electrode in seconds.

The results are presented in Table II. Plots of typical polarograms and of the calibration curve of tin are presented in Figures 1 and 2, respectively.

Table II
Diffusion Currents of Tin Following a
Basic Carbonate Separation From Uranium

Conditions:

Volume, ml	10
Aluminum, mg	5
Medium, 3 M HCl, 20 per cent Ethanol	
Capillary characteristics, ($m^2/st^{1/6}$)	2.07
Temperature, °C	25 ± 0.5

Tin μg	Diffusion Current, μa		Diffusion Current Constant, K	
	A	B	A	B
1.7	0.008	0.008	2.78	2.78
2.5	0.012	0.010	2.84	2.36
4.2	0.014	0.019	2.38	2.68
8.5	0.033	0.030	2.29	2.10
17.0	0.065	0.068	2.25	2.36
25.5	0.097	0.095	2.29	2.24
42.5	0.198	0.184	2.76	2.55
85	0.396	0.394	<u>2.76</u>	<u>2.74</u>
		\bar{X}	2.54	2.48
	Coefficient of Variation, Per Cent		11	10

A = Uranium present, 50 mg.

B = Uranium absent

From the data presented in Table II, it is indicated that the polarographic technique is a sensitive means for the measurement of small quantities of tin. A linear relationship exists between the diffusion current and the concentration of tin over the range that was studied. The calibration curve was reproducible to about 10 per cent. The close agreement between the diffusion current constants for tin with and without uranium, reported in Table II, indicate that no interference is encountered from as much as 50 milligrams of uranium.

The Recovery of Tin From Uranyl Sulfate Solutions. In order to ascertain the reliability of the method for the recovery of small amounts of tin, test solutions of the uranyl sulfate were analyzed for tin before and after standard additions of tin. The recovery of the tin, based on the amount that was initially present plus the amount added, was then calculated. The results are presented in Table III.

Table III

Recovery of Tin From Uranyl Sulfate Solutions

<u>Tin, μg</u>		<u>Diffusion Current, μa</u>	<u>Total Tin, μg</u>		<u>Recovery, Per Cent</u>
<u>Initially Present⁽¹⁾</u>	<u>Added</u>		<u>Present</u>	<u>Found</u>	
5.5	8.5	0.053	14.0	14.5	105
8.5	8.5	.060	17.0	16	94
Not detected	8.5	.026	8.5	7.0	82
2.2	17	.058	19.2	15.4	80
Not detected	17	.060	17	16	94
Not detected	17	.075	17	20	117
Not detected	17	.065	17	17.5	<u>103</u>
				Average	96
Coefficient of Variation					10

(1) Established by the basic carbonate, polarographic method prior to the standard addition of tin.

The results of the tests that are summarized in Table III indicate that the polarographic method, following the separation from uranium by a basic carbonate precipitation, is an effective method for the determination of microgram quantities of tin. In unknown test solutions of uranyl sulfate whose initial tin content was negligible, the recovery of tin thus added was essentially quantitative. Several of the solutions contained detectable amounts of tin which augmented the amount added. The amount of tin initially present was determined by the method under test; consequently, a degree of uncertainty exists with respect to the total amount of tin which was present in these samples. The test results for samples that contained tin initially

must therefore be considered as supporting rather than conclusive evidence of the reliability of the method. The precision and reliability of the method for the determination of tin in amounts ranging from 2 to 50 μg , as tested with unknown samples, is thus of the same order of 10 per cent as that established for the calibration curve.

Interferences. No interference was encountered in solutions of uranyl sulfate which contained microgram quantities of corrosion products such as iron, nickel, and chromium. Earlier work⁽²⁾ on the polarography of tin in the presence of these metals indicated that a metal to tin ratio of about 5 to 1 can be tolerated without interference. Lead interferes seriously; however, it was not present in any of the samples.

SUMMARY

A reliable method was developed for the estimation of microgram quantities of tin in solutions of uranyl sulfate. In the application of this method, tin is first separated from uranium by precipitation with basic carbonate with aluminum hydroxide being utilized as a carrier, following which the precipitate of stannic and aluminum hydroxides is dissolved in hydrochloric acid. After this precipitate is properly dissolved, the tin is determined by a polarographic method. In this method, the diffusion currents of the doublet wave for the reduction of stannic tin to the stannous ion and of stannous tin to the elementary metal are determined in a hydrochloric-ethyl alcohol medium. The diffusion current of the second wave which occurs at a half-wave potential of -0.55 versus the standard calomel electrode is utilized in measuring the quantity of tin

which is present in the sample. This polarographic method is satisfactory for the estimation of 2 to 50 micrograms of tin in a final volume of ten ml. The coefficient of variation is of the order of ten per cent.

ACKNOWLEDGEMENT

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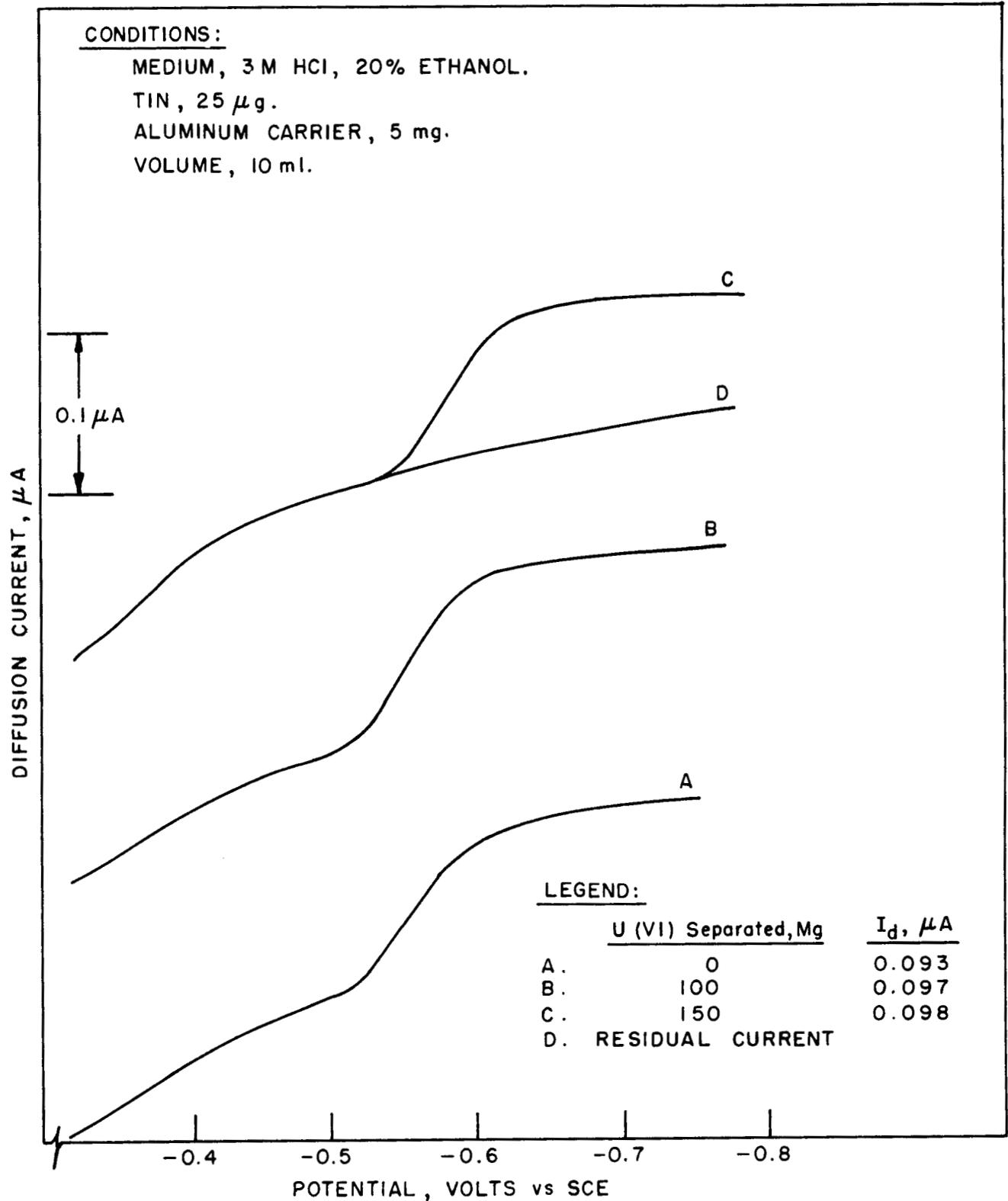


FIGURE I. POLAROGRAMS OF TIN (IV) IN 3M HYDROCHLORIC ACID FOLLOWING A BASIC CARBONATE SEPARATION FROM URANIUM (VI)

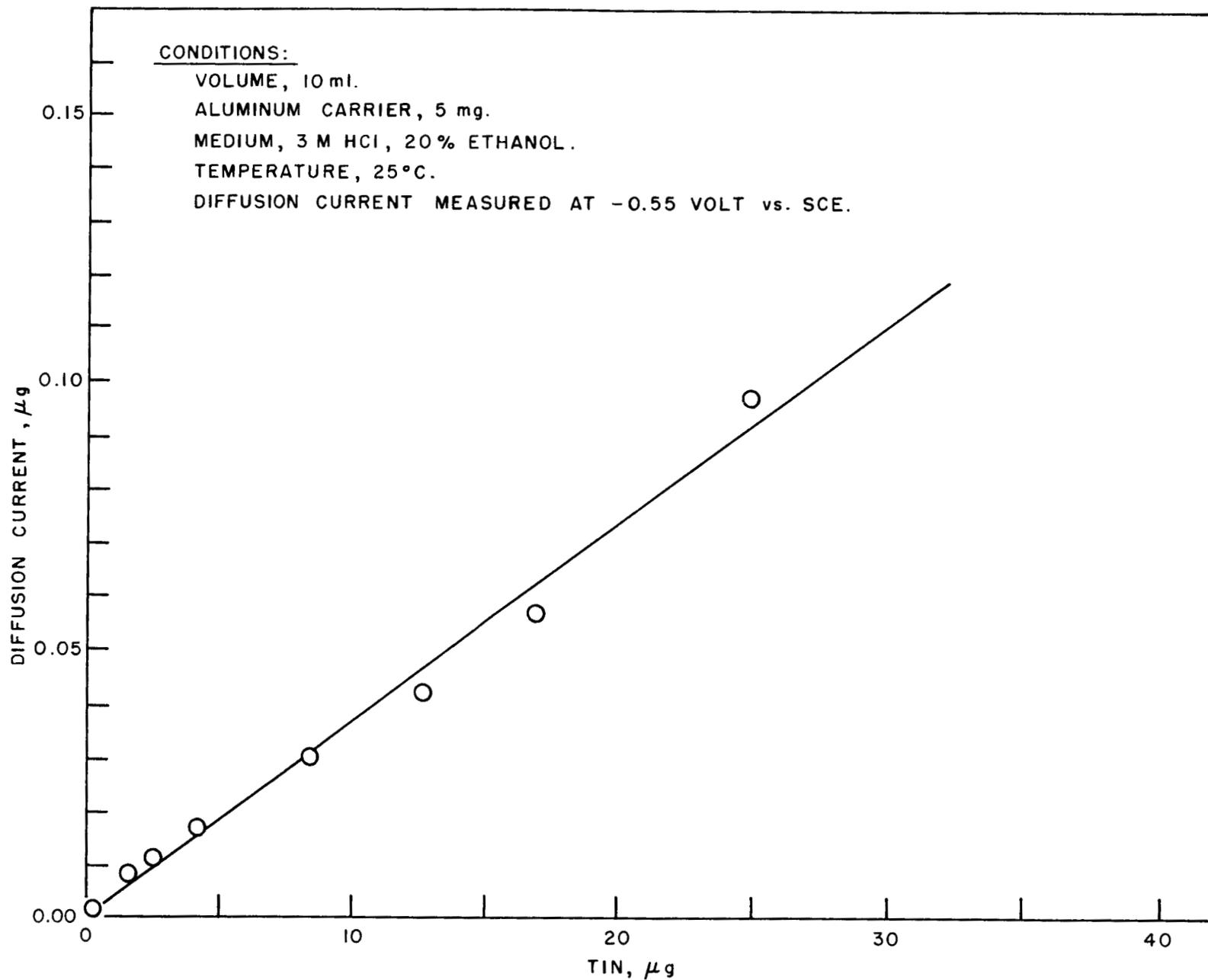


FIGURE 2. CALIBRATION GRAPH FOR THE POLAROGRAPHIC DETERMINATION OF TIN(IV)