SPECTROPHOTOMETRIC DETERMINATION OF TIN (IV)

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ABSTRACT

A coprecipitation study required a rapid and accurate method for the determination of small quantities of tin.

The reaction between tin (IV) and hematoxylin at pH 0.8 produces a red color with an absorption maximum at approximately 515 mu for 0.1 to 14 milligrams of tin per liter. Beer's Law is not completely followed but the curve obtained is reproducible and easily prepared. The effects due to the presence of other ions have been noted. Analyses of some standard alloy samples indicate an error of the order of ±1%.

The method presents possibilities for the analysis of tin in non-ferrous materials. It should also be useful for the determination of tin in trace quantities as in water analysis.

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INTRODUCTION

In the course of a study of the coprecipitation of manganese (II) on basic stannic sulfate precipitated from homogeneous solution, it was found necessary to have a sensitive and convenient method for the determination of small amounts of tin (IV).

Relatively few methods have been proposed for the colorimetric determination of tin (IV). Various authors (5, 15, 18) have recommended the use of dithiol and thioglycolic acid to determine up to 80 micrograms of tin (IV) in a volume of 10 ml.

Gentry and Sherrington (7) have recommended the extraction of stannic 8-hydroxyquinolinate with chloroform from a solution at pH 2.5 to 5.5 and subsequent photometric measurement of the chloroform layer. Morrison (13) reported that stannic cupferrate can be extracted by chloroform from aqueous solution; if a color is developed in the chloroform phase it may be suitable for photometric determination. However, no work has appeared on this latter application.

Tin (IV) has also been determined colorimetrically by reduction to tin (II) and subsequent reaction with a number of heteropoly molybdates to produce a blue solution (1, 10, 17).

Thionalide produced a turbidity with tin (IV) and has been proposed as the basis for a turbidimetric procedure (2). Recently,

another turbidimetric procedure using 3-nitro-4-hydroxybenzene-arsonic acid (11) has been introduced for the determination of 0.1 to 0.2 mg. of tin (IV) in a 20-ml. volume.

Qualitative reagents for tin (IV) such as resorcinol (3) and cacotheline (6, 15) have also been studied for the analytical determination but with little success.

Charlot (4) reported that hematoxylin, a reagent commonly used for the determination of aluminum, reacts with tin (IV) at pH 4.5; earlier Tartakovskii (17) had utilized hematoxylin in a method for the determination of tin (II). This paper describes a spectrophotometric method employing the reaction between tin (IV) and hematoxylin, but at pH 0.8, for the determination of 0.1 to 14 milligrams of tin per liter.

EXPERIMENTAL

1. Preliminary

Although the dithiol method is the most widely used for the colorimetric determination of tin (IV), it was found to be unreliable because of the formation of turbidities due to the decomposition of the mixed dithiol-thioglycolic acid reagent. Decomposition was noted in alcoholic (18) as well as in dilute sodium hydroxide solution (5). Furthermore, the color due to the tin complex was also unstable leading to additional turbidities. The use of agar and gelatin to stabilize the color was unsuccessful. However, some investigators (12, 19) have been able to stabilize the color with other dispersing agents.

Attempts to extract the red complex with various solvents were also unsuccessful because no characteristic absorption band appeared in either the ultra-violet or visible range.

The procedure reported by Gentry and Sherrington for the extraction of tin (IV) oxinate and the photometric determination of the chloroform phase could not be reproduced. An attempt to find a characteristic absorption band with the chloroform extract of stannic cupferrate (13) also failed.

Attempts to adapt qualitative reagents such as resorcinol (3), thymol (3), pyrogallol (3) and cacotheline (6, 15) for quantitative determinations were unsuccessful.

2. Spectral Curve

The reaction of hematoxylin with tin (IV) produces a red color, the exact shade of which depends upon the quantity of tin present and pH (see section 4 below). Figure 1 shows the spectral absorption curve for the reagent, and also for the reagent with varying amounts of tin, under the conditions described in the subsequent procedure. There is a maximum at 515 mu for the tin-hematoxylin complex; with amounts of tin (IV) less than 500 micrograms per 50 ml. this maximum is not so well-defined and appears as a break or plateau. With 700 micrograms the maximum shifts to 525 mu.

3. Calibration Curve

Figure 2 shows a calibration curve prepared as directed in the recommended procedure. Although Beer's law is not completely followed the curve is reproducible and easily prepared.

4. Stability of Hematoxylin Reagent

Although Houghton (9) reported that a 0.005 N hydrochloric acid solution of hematoxylin was stable for two months, this could not be verified. Charlot (4) used a 0.2% hematoxylin solution in 95% ethanol but this solution also proved to be unstable. However, a

0.1% hematoxylin solution in 95% alcohol and 0.005N in hydrochloric acid was found to be stable for approximately 15 hours. The subsequent decomposition of this reagent is not evident in the blank but reaction with known amounts of tin gave high results.

Hematoxylin from different sources gave different absorbancy measurements thus requiring a calibration curve for each batch.

5. Development of Color

Figure 3 indicates that the full development of the color varies with the amount of tin present, up to 1 hour being necessary for 700 micrograms.

It was found that 5 ml. of 0.1% reagent in 95% ethyl alcohol was a suitable quantity of reagent. With smaller volumes of reagent an insufficient color was developed; with larger quantities of reagent, the blank correction becomes excessive.

6. Effect of pH

It was observed that the reagent itself responded to variations in pH so the procedure had to be rigorously standardized, as described below, to work at a reproducible pH of 0.80. At lower pH values the blank absorbancy became excessive with respect to a given quantity of tin, thereby decreasing the sensitivity and the accuracy. At higher pH values, stannic acid might precipitate.

7. Interfering Metal Ions

The interferences of various cations were investigated and the results are summarized in Table 1. Suitable quantities of cation and tin (IV) were treated as directed in the recommended procedure.

TABLE 1.

Interference of Cations with Determination of Tin (IV)[a]

Cation[b]	Remarks
NH_4^{+1}	no interference
Mg^{+2}	" "
Pb^{+2}	" "
Cu^{+2}	" "
Co^{+2}	" "
Ni^{+2}	" "
Zn^{+2}	" "
Mn^{+2}	" "
UO_2^{+2}	" "
Al^{+3}	" "
Fe^{+3}	serious interference
Sb^{+3}	" "
Bi^{+3}	slight interference
Cr^{+3}	no interference
Ti^{+4}	serious interference
Ce^{+4}	no interference
Th^{+4}	" "

a. 50 micrograms of tin present.

b. 250 micrograms of each cation taken.

No attempt was made to study the removal of serious interferences. The method presents possibilities for the analysis of non-ferrous materials as well as for water analysis.

RECOMMENDED PROCEDURE

1. Reagents and Equipment

a. Hematoxylin, Eastern Chemical Corporation, Newark, New Jersey.

b. Ethyl alcohol, 95%

c. Sulfuric acid, concentrated, reagent grade

d. Hydrochloric acid, concentrated, reagent grade

e. Tin, metallic, Kahlbaum, or J. T. Baker, C. P., 30 mesh

f. C.P. salts of ions investigated for interferences

g. Beckman Model B Spectrophotometer; 1.002 cm. Corex cells

2. Preparation of Solutions

a. Hematoxylin reagent, 0.1%

Weigh out 0.100 grams of dry reagent and transfer to a 150 ml. beaker. Add 25 ml. of alcohol (95%) and 1 drop of concentrated hydrochloric acid; heat just below boiling. Cool and then filter into a 100 ml. volumetric flask. Add 15 ml. of alcohol to the original beaker and warm; cool and filter into the volumetric flask. Repeat this washing procedure twice. Finally remove the filter paper from the funnel and place in the beaker. Warm with two 15 ml. portions of alcohol, then cool and filter into the volumetric flask. Dilute the solution with alcohol to the proper volume. Store in an amber bottle away from direct sunlight.

b. Tin Solution

Treat 1.0 gram of metallic tin with 400 ml. of concentrated hydrochloric acid at a low temperature (40°C.) until all the solid dissolves. Cool, transfer to a ground-glass liter bottle, dilute to approximately 1 liter, and slowly bubble chlorine gas through for thirty minutes. Pass filtered air through the solution to remove the excess chlorine and standardize gravimetrically (8). This solution will correspond to about 1 mg. of tin per ml.

To prepare a standard solution transfer 10.00 ml. to a 100 ml. volumetric flask, add 10 ml. concentrated hydrochloric acid and dilute to volume. This latter solution will contain about 100 micrograms of tin (IV) per ml. and may be stored indefinitely.

3. Calibration Curve

To prepare the calibration curve transfer 5, 10, 20, 30, 40, 50, 60 and 70 ml. of standard tin solution to 100 ml. beakers and

perform the procedure described in section 4 below. These points will correspond to approximately 50, 100, 200, 300, 400, 500, 600 and 700 micrograms of tin (IV). Determine the absorbancies at 515 mu against pure water; subtract the absorbancy of the blank. Plot corrected absorbancies against amount of tin.

4. Procedure for Analysis

Transfer a quantity of unknown solution containing from 50 to 7,000 micrograms of tin (IV) to a 100-ml. beaker and add 5 ml. of concentrated sulfuric acid. Cover the beaker and then evaporate on a hot plate, using an indented stirring rod to prevent bumping, until fumes are observed. Remove from hot plate and allow to cool. Wash down watch glass and then cool the solution to room temperature. Transfer to a 100 ml. volumetric flask and dilute to volume. Transfer duplicate 10.00 ml. aliquots to 50 ml. volumetric flasks, then add 5.00 ml. of 0.1% hematoxylin reagent and dilute to 50.00 ml. Allow the color to develop for one hour and determine the absorbancy at 515 mu. Prepare a blank in a similar manner. Subtract the blank absorbancy from the observed absorbancy and determine the quantity of tin present from the calibration curve.

DISCUSSION AND RESULTS

This method has been very satisfactorily applied to the determination of tin (IV) in the coprecipitation study mentioned previously. The aqueous solution contained tin (IV), manganese (II), urea, ammonium chloride, ammonium sulfate, hydrochloric and sulfuric acids.

In comparison to the dithiol procedure, this method has a wider range, appears to be more reproducible, and suffers from less interferences. From the operator's point of view, the unpleasant odors of the dithiol and the thioglycolic acid are also avoided.

This procedure was also applied to the analysis of some tin-bearing alloys. The results are tabulated in Table II. The alloy was weighed into a 50-ml. Pyrex centrifuge tube and then dissolved at room temperature with 10 ml. of 1:1 nitric acid added in 2 to 3 ml. increments. The sample was then digested at 80°C for 15 minutes and afterwards centrifuged for 15 to 30 minutes. The supernatant liquid was removed and the precipitate washed 2 to 4 times with 20-ml. portions of 5% ammonium sulfate solution. The precipitate was dissolved by heating with 15 ml. of concentrated hydrochloric acid for 3 to 4 minutes at 100°C. The solution was transferred to a 150 ml. beaker, 5 ml. of sulfuric acid was added, and the solution then analyzed by the recommended procedure. In the case of the Bureau of Standards cast bronze sample, however, 25 ml. of sulfuric acid was added with a final dilution being made to 500 ml. instead of 100 ml.

Table II

Analyses of Tin Alloys

Sample	Weight of Alloy Taken gram	Composition %	Tin Found %	Difference %
Bureau of Standards, Sheet Brass No. 37	0.5000	1.013 Sn,[a,b]	1.028 1.028	+1.5 +1.5
Bureau of Standards, Cast Bronze No. 52a	0.4000	7.83 Sn,[c]	7.74 7.81	-1.2 -0.25
Standard Sample Co., Ames, Iowa. Brass No. 59	0.5000	0.58 Sn,[d,e]	0.56 0.58	-3.5 ±0.0

a. B of S certificate states "this value (0.013%) is almost certainly a little low." B of S chemist reported 1.03% tin.

b. 0.964 Pb, 70.29 Cu, 26.89 Zn, 0.29 Fe, 0.52 Ni.

c. 88.17 Cu, 3.17 Zn, 0.013 Pb, 0.05 Fe, 0.73 Ni, 0.003 Sb, 0.02 Mn, 0.003 As, 0.015 Ag, 0.001 Si, 0.002 S, 0.001 P

d. 0.63 Pb, 66.03 Cu, 3.95 R_2O_3, 28.74 Zn, 0.35 Ni

e. Method of analysis unknown.

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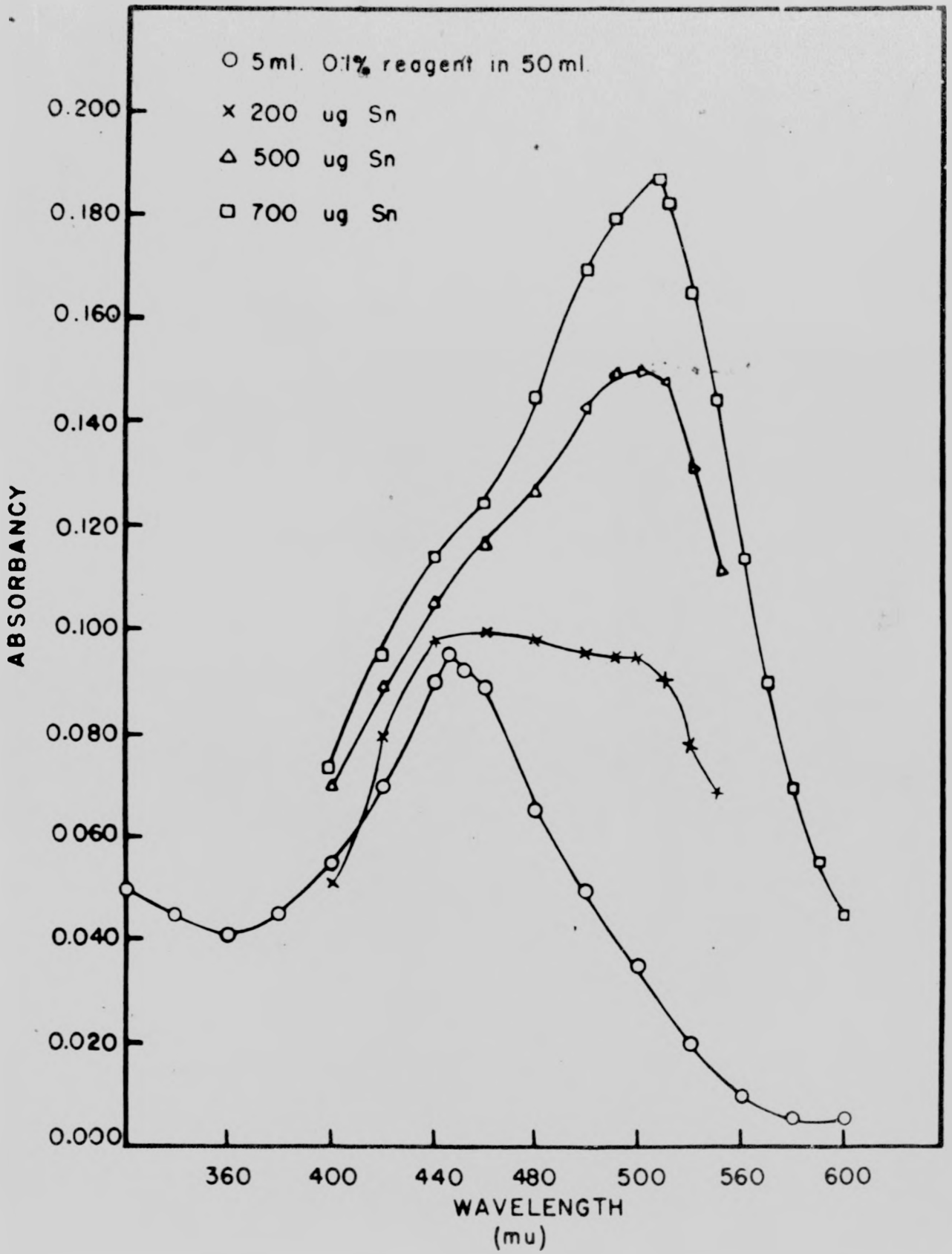

FIGURE 1. ABSORPTION CURVES OF TIN-HEMATOXYLIN

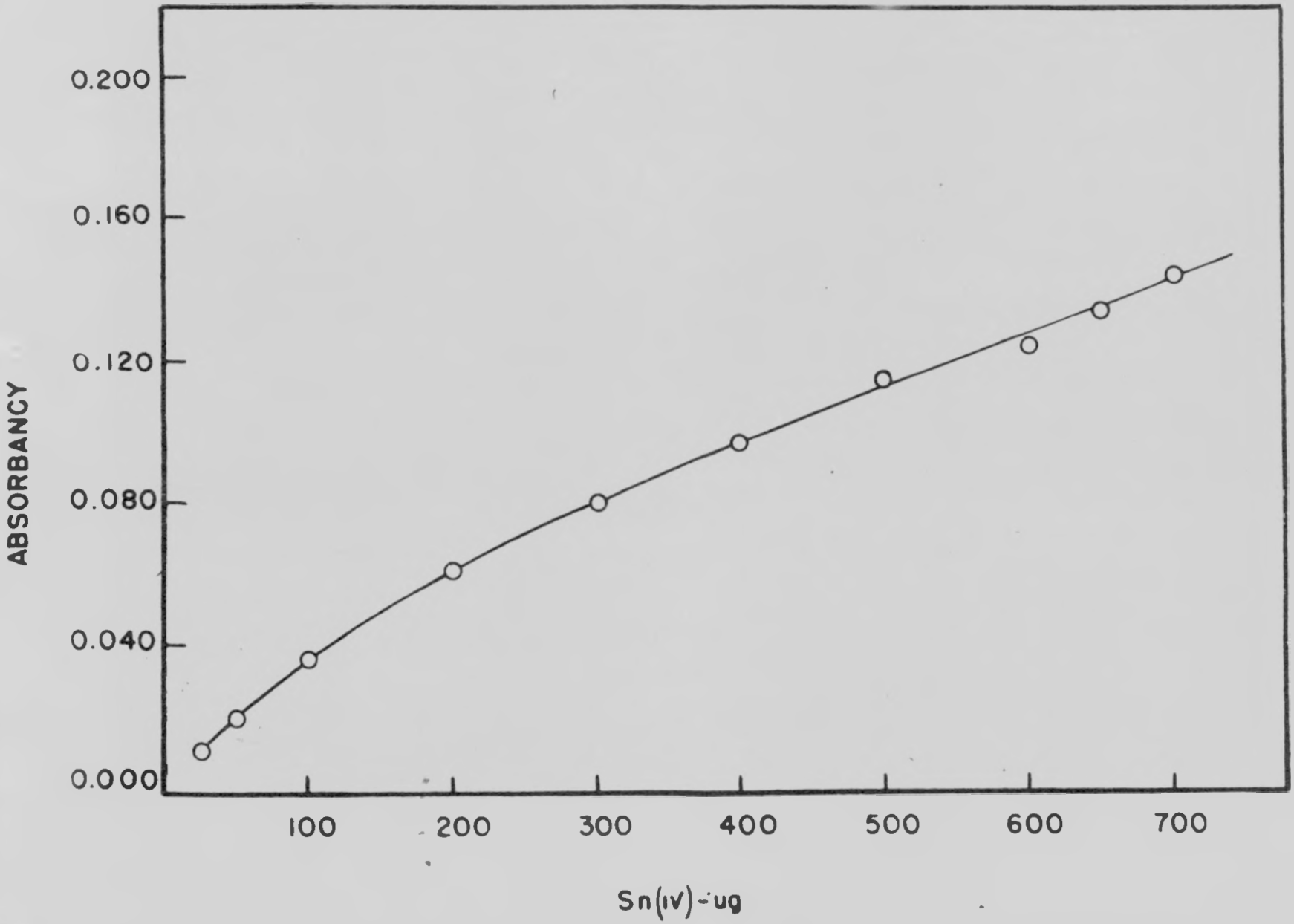

FIGURE 2. CALIBRATION CURVE

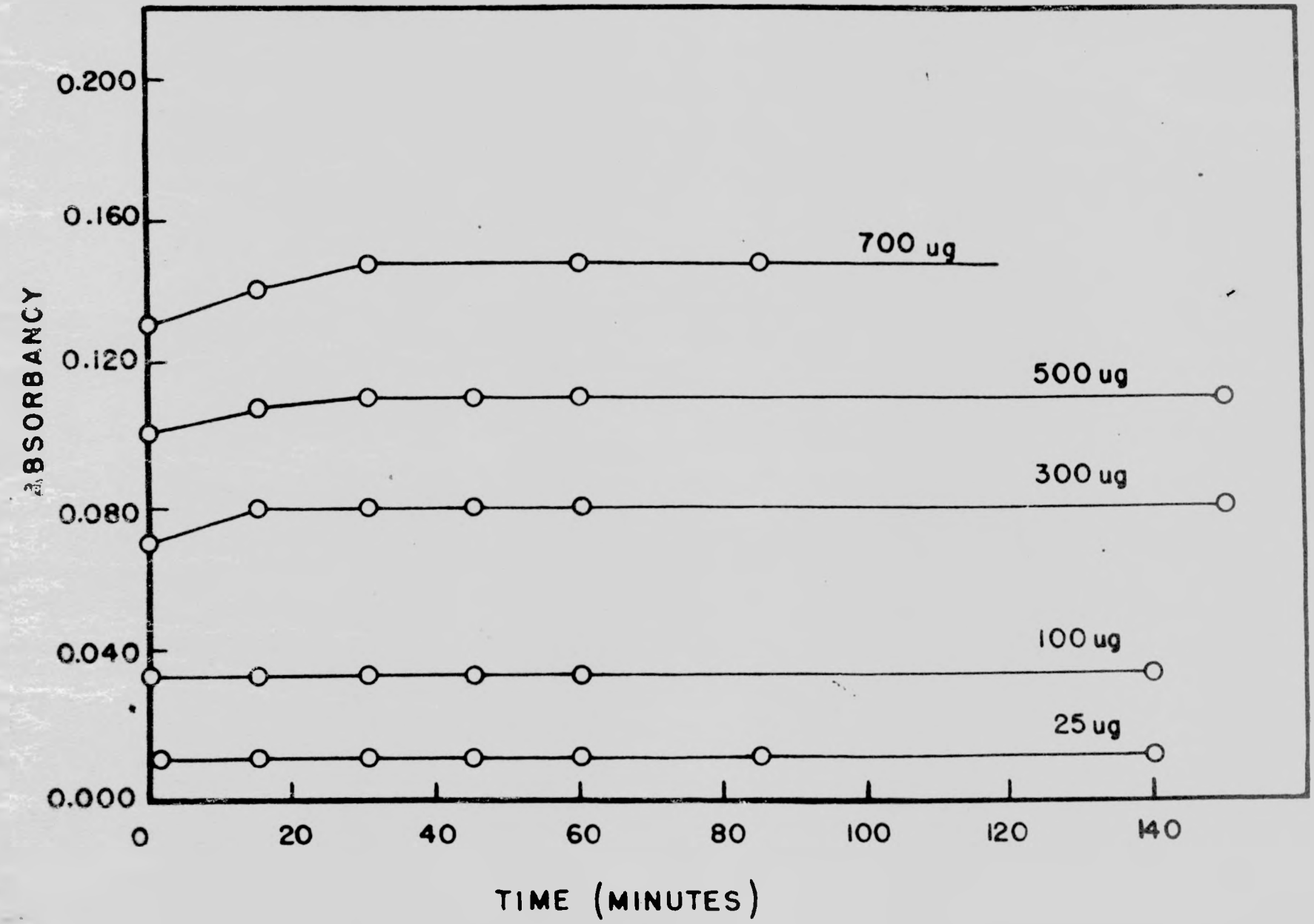

FIGURE 3. TIME FOR COLOR DEVELOPMENT