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Characterization of a photosensitive tin(II) compound

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CHARACTERIZATION OF A
PHOTOSENSITIVE TIN(II) COMPOUND

by

Paul J. Sewall

A Thesis

Presented to the Graduate Committee
of Lehigh University

in Candidacy for the Degree of
Master of Science
in Metallurgy and Materials Science

Lehigh University

1969

CERTIFICATE OF APPROVAL

This thesis is accepted and approved in partial fulfillment of the requirements for the degree of Master of Science.

13 May 1950
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ABSTRACT

A process for the selective deposition of metals on substrates was recently developed. The process utilizes an invisible film of a photosensitive tin(II) compound which is deposited on a substrate by immersing it in an acid (HCl) solution of stannous chloride and then rinsing it in deionized water. This study was undertaken to characterize the unknown photosensitive compound and to investigate the effects of the surrounding atmosphere (particularly relative humidity and oxygen) on the photochemical reaction rate.

X-ray fluorescence analysis indicated that approximately $4 \mu\text{g./cm.}^2$ of tin was deposited and that the molar ratio of tin to chlorine was greater than 9 to 1. No x-ray diffraction peaks were observed for the unknown and thus direct identification by this method was not possible. Electron microscopy and diffraction revealed that the freshly deposited film consisted of a mixture of SnO and SnO₂ with particle sizes ranging from approximately 50 to 150 Å. The electron diffraction pattern of the film after exposure to ultraviolet light indicated that it consists of SnO₂.

In the characterization of the unknown, it was discovered that the ultraviolet absorption of the film decreased as the reaction proceeded. This gave a means of measuring the reaction rate. In ambient conditions the time to half-exposure was found to be a linear function of relative humidity. Similar measurements in a nitrogen flushed atmosphere indicated that the reaction rate is dependent on the partial pressure of oxygen.

INTRODUCTION

A. Selective Metal Deposition

This study was undertaken to clarify some of the steps of a process for the selective deposition of metals on substrates. The printed circuit industry uses a number of different methods to obtain metal patterns on various substrates but the processes in wide use at this time have some disadvantages. Some techniques begin with a substrate completely coated with the desired metal and then by photography, printing or other methods, a protective coating is placed over those areas where the metal pattern is desired. The exposed metal is then etched away resulting in the desired pattern. A large amount of the metal is wasted (usually more than half) and the disposal of the used etchant is often a significant problem. These difficulties and others such as poor line definition are often properties of the various methods in wide use today.

A process was recently developed¹ that overcomes these difficulties to a great extent. The basis of this process is a photochemical reaction in which a tin(II) compound is oxidized when it is exposed to ultraviolet light in air giving a tin(IV) compound. In the selective deposition process, a substrate is immersed in an acid (HCl) solution of stannous chloride, rinsed in an overflow bath of deionized water and then excess water is blown off the substrate with nitrogen. The result is an invisible film of an unknown tin(II) compound on the substrate. A mask is then placed over the substrate and desired areas are exposed to ultraviolet light. Areas which are

not exposed remain covered with the tin(II) compound while the exposed areas are converted to a tin(IV) compound. The substrate is then immersed in an acid (HCl) solution of palladium chloride and the tin(II) compound reduces the palladium² and it is deposited on the areas of the substrate that are coated with the tin(II) compound. Palladium is not deposited on the exposed areas that are coated with the tin(IV) compound. The substrate is next rinsed and then immersed in an electroless plating solution and the palladium serves as a catalyst for the deposition of copper or nickel. The electroless metal pattern is usually thin but it can be built up by a subsequent electroplating step. The overall process does not waste copper and uses only trace amounts of tin and palladium. In addition, the resolution of the metal pattern is excellent.

B. Statement of the Problem

Many of the steps of the selective metal deposition process, such as, electroplating and electroless deposition, have been in use for some time and are fairly well characterized commercial processes.³ However, the fact that the compound deposited on a substrate from a stannous chloride solution is photosensitive is a recent discovery and therefore the photochemical process is worthy of investigation. A thorough understanding of the reaction requires the characterization of the photosensitive compound (for brevity this tin(II) compound will be referred to as X) and an investigation of the reaction mechanism. At best, the characterization of X should give the composition, structure, amount, particle size, particle distribution and the ultraviolet

absorption spectrum of the compound in situ. The study of the photochemical reaction should also measure the effect of the surrounding atmosphere on the reaction rate. This information can be obtained by varying the atmospheric composition (particularly oxygen and relative humidity) provided that a means is available for measuring the reaction rate.

C. Methods for Characterizing X

The unknown, X, is a good reducing agent indicating that it contains tin in the +2 valence state². The unknown film probably contains some tin(IV) as an impurity^{4,5,6} because tin(II) chloride is slowly oxidized by dissolved oxygen in aqueous hydrochloric acid solutions⁷. The compound is formed under conditions of increasing pH and thus it could be a basic salt, such as $\text{Sn(OH)Cl}\cdot\text{H}_2\text{O}$, which forms as a precipitate in aqueous solutions of stannous chloride⁸ if the pH is between 1.14 and 4.5 or it could be a hydrous oxide, such as $5\text{SnO}\cdot 2\text{H}_2\text{O}$, which forms when the pH of a stannous salt solution is raised above 6.3⁴. If the pH is between 4.5 and 6.3, a mixture of the two compounds is observed.⁸

Because the film consists of a very small quantity of X, standard analytical techniques for determining composition^{9,10} are not applicable. It is therefore necessary to use indirect measurements to characterize X. The x-ray diffraction patterns of hydrous tin(II) oxide^{4,11,12} and basic tin(II) chloride⁸ can be compared with the x-ray and electron diffraction patterns of the unknown. X-ray fluorescence analysis can be used to determine the amount of tin and chlorine

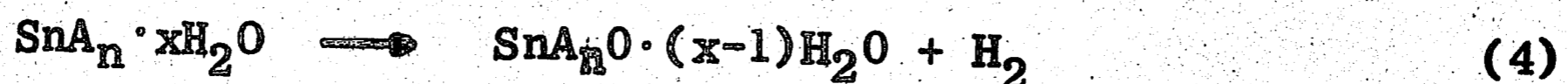
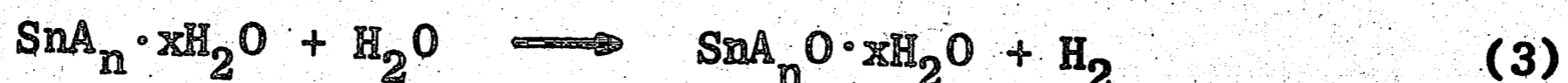
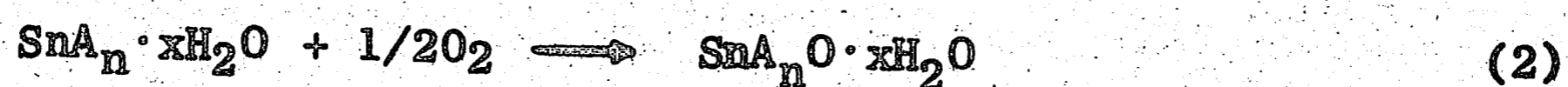
in the film. The ultraviolet and infrared absorption spectra of the unknown can be compared with those of known compounds. Also, the particle size and distribution can be determined by electron microscopy.

D. Photo-oxidation of X

There are three known valence states of tin^{5,6}. In the pure metal the valence is zero and in compounds tin occurs in the +2 and +4 valence states. The photo-oxidation of X can be expressed by the partial reaction



The composition of X may be expressed by the general formula $\text{SnA}_n \cdot x\text{H}_2\text{O}$ where A_n has a valence of -2 (A_n^{-2}) and x is a positive number or zero. Some of the possible reactions can be written, i.e.,



Equation (2) represents the oxidation of X by atmospheric oxygen, Equation (3) by free water and Equation (4) represents the oxidation of X by water of hydration⁴. These are three possible mechanisms for the oxidation process, however, it could be complicated by several other events. The reaction may actually proceed by a combination of these mechanisms and the product may be further hydrated or dehydrated.

Thermodynamic data are available for the case in which A_n represents oxygen.^{13,14} The data are as follows:

<u>Sn(OH)₂</u>	$\Delta F^{\circ} = -117.6$ Kcal./mole	
	$\Delta H^{\circ} = -138.3$ Kcal./mole	$\Delta S^{\circ} = 23.1$ cal./°k.
<u>Sn(OH)₄</u>	$\Delta F^{\circ} = -227.5$ Kcal./mole	
	$\Delta H^{\circ} = -270.5$ Kcal./mole	$\Delta S^{\circ} = 29$ cal./°k.

However, the compositions given with the data are not in agreement with recent analytical results^{4,5,6,11} and thus the use of this information in making predictions about the possible reactions is questionable.

In the characterization of X, it was discovered that its optical density decreases as the photochemical reaction proceeds. This behavior may be explained using Lambert's Law¹⁵ which states that light is absorbed as

$$\frac{dI}{I} = -Kdx$$

where x is the absorber thickness and K is a constant of the absorber at a particular wavelength. The number of moles of absorber in a film of cross section A is

$$m = \rho Ax$$

where ρ is given in moles/cm³. Thus

$$x = \frac{m}{\rho A}$$

and

$$dx = \frac{dm}{\rho A}$$

Lambert's Law can then be written as

$$\frac{dI}{I} = -\frac{K}{\rho A} dm = -K' dm$$

and integration gives

$$I = I_0 e^{-K'm}$$

For two absorbing species, namely, a tin(II) and a tin(IV) compound and assuming no exchange interaction^{16,17,18}

$$I = I_0 e^{-K'_2 m_2} e^{-K'_4 m_4}$$

or

$$\frac{I_0}{I} = e^{K'_2 m_2} e^{K'_4 m_4}$$

Optical density is defined as

$$D = \log_{10}(I_0/I)$$

and therefore

$$D = \frac{K'_2 m_2 + K'_4 m_4}{\ln(10)}$$

If the total amount of tin is constant then

$$m_2 + m_4 = m_T = \text{constant}$$


and thus

$$D = \frac{K'_2 m_2 + K'_4 (m_T - m_2)}{\ln(10)}$$


$$D = \frac{(K'_2 - K'_4) m_2 + K'_4 m_T}{\ln(10)}$$

(5)

It is then seen that the optical density is a linear function of the number of moles of the tin(II) compound present. This then provides a means of measuring the variation of X with time as the reaction proceeds. The ability to determine the reaction rate by measuring the optical density of the unknown as a function of exposure time



allows a study of some of the factors that influence the reaction. The effect of atmospheric oxygen can be observed by making the measurements in an inert atmosphere such as nitrogen and comparing the results with those obtained in air. Similarly, the effect of surface moisture can be determined by measuring the reaction rates at various relative humidities in air.



EXPERIMENTAL PROCEDURE

I. Characterization of Unknown

A. Ultraviolet Absorption of Unknown

An invisible film of the unknown was deposited on a clean fused quartz slide by immersing it in a tin solution (10 g. of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.8 ml. of concentrated HCl in 100 ml. of deionized water) for 3 minutes and then rinsing it in an overflow bath of deionized water for 5 minutes. Excess water was then blown off the slide with nitrogen. The ultraviolet absorption due to the unknown was measured using the Model 14 Cary Spectrophotometer. The sample was then exposed to ultraviolet light (approximately 5 mw./cm.^2) from a mercury lamp ($2,537 \text{ \AA}$) for 6 minutes and the ultraviolet absorption due to the film was measured again. Figure 1 shows the optical density of the unknown before and after exposure.

In some cases a visible film was deposited on the slide (particularly if the sample was rinsed gently). The ultraviolet absorption of such a sample is shown in Figure 2. The reflectance of the sample was also measured and is shown in Figure 3.

B. Ultraviolet Absorption of Other Compounds

The absorption spectra of other samples were measured for comparison with the unknown. Hydrous tin(II) oxide⁵ was prepared by adding NaOH to the tin solution (10 g. of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.8 ml. of HCl in 100 ml. of deionized water) until the pH was 8.4. The precipitate was washed with water and applied to a clean quartz slide. The ultraviolet optical density of the compound was measured before and after exposure to ultraviolet light. The results are in Figure 4.

A slightly visible film was deposited on quartz by immersing the slide in a solution of stannous sulfate (10 g. SnSO_4 and 0.9 ml. concentrated H_2SO_4 in 100 ml. of deionized water) and then rinsing it in an overflow bath of deionized water for 1 minute. Excess water was removed with nitrogen and the ultraviolet absorption of the film was measured before and after exposure to ultraviolet light. The procedure was completely analogous to that used in preparing the unknown except that the tin solution contained sulfate ions rather than chloride ions. The results are shown in Figure 5.

Hydrous SnO_2^{19} was prepared by adding sodium hydroxide to a water solution of stannic chloride pentahydrate until the pH was 4.0. The ultraviolet absorption of the precipitate was measured. The results are shown in Figure 6 for both invisible and visible films.

C. X-ray Diffraction

Both visible and invisible films of the unknown on quartz were examined with a diffractometer and with a universal camera. No diffraction peaks were observed with the diffractometer. A diffuse band corresponding to d-spacings in the range of 2.32 to 1.99 Å was consistently observed with the universal camera. However, this band was also observed for clean quartz slides that were not coated with the unknown film. No other diffraction peaks were observed.

The unknown, X, is formed under conditions of increasing pH during the rinsing step. For this reason, bulk precipitates were prepared by increasing the pH of tin solutions. A solution was prepared which consisted of 10 g. of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.7 ml. of concentrated HCl in 100 ml. of deionized water. Sodium hydroxide was

added slowly to give a pH of 8.2. The white precipitate was placed in a capillary tube and mounted in a Debye-Scherrer camera. The x-ray film was loaded by the Straumanis method and the sample was exposed for 6 hours with CuK_α radiation. Table 1 gives the observed d-spacings and intensities.

The above procedure was repeated using a tin solution that initially consisted of 10 g. of SnSO_4 and 5 ml. of concentrated H_2SO_4 in 100 ml. of deionized water. The results are given in Table 2.

D. X-Ray Fluorescence Analysis

Standards for tin and chlorine were prepared by applying known amounts of the elements to filter paper mounted on quartz slides. A NaCl solution (331.31 mg. Cl/100 ml. of deionized water) and an acid solution of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (23.405 mg. Sn/100 ml. of deionized water) were used to prepare the chlorine and tin standards respectively. Fluorescent intensity was measured for SnL_α and ClK_α using a chromium target and a PET crystal. The SnL_α and ClK_α intensities were measured for each of the slides before applying tin or chlorine to establish background levels. Five standards were prepared for tin and five for chlorine by applying various amounts of the standard solutions to the slides. The SnL_α and ClK_α intensities were then measured again. Figures 7 and 8 show the fluorescent intensity (corrected for background) versus the amount of the tin and chlorine respectively. The amounts of tin and chlorine in the deionized water were also measured by x-ray fluorescence and they were observed to be negligible compared to the amounts on the standard slides.

Samples of the unknown on quartz were then prepared by immersing a quartz slide in a tin solution consisting of 10 g. of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.7 ml. of concentrated HCl in 100 ml. of deionized water. They were then rinsed either in a fixed volume or an overflow bath of deionized water for various times. The amounts of tin and chlorine were measured before and after applying the film. The results are listed in Table 3.

E. Electron Microscopy and Diffraction

The unknown was deposited on a carbon substrate by immersing it in a tin solution consisting of 10 g. of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.8 ml. of concentrated HCl in 100 ml. of deionized water. Samples were next rinsed for 15 seconds in each of two 500 ml. beakers of deionized water. The samples were then allowed to dry in air which required approximately 5 minutes. The electron diffraction data are given in Table 4* and the corresponding transmission micrograph is presented in Figure 9.

Other samples were prepared in the manner described above and then exposed to high intensity ultraviolet light for two minutes. The electron diffraction data are listed in Table 5* and the corresponding transmission micrograph is presented in Figure 10. The diffraction bands observed for the films before and after exposure are quite broad and therefore the diffraction data are given in terms of ranges of d-spacings.

*

The very diffuse bands due to carbon are not included.

F. Other Analytical Techniques

The infrared absorption of the unknown was measured in transmission and by total internal reflectance using the Model IR7 Beckman Spectrophotometer. The unknown did not show measurable absorption in the range of 600 to 4,000 cm^{-1} .

Samples of the unknown deposited on glass were analyzed in a nitrogen flushed chamber using the Model 950 du Pont Thermogravimetric Analyzer. No mass changes attributable to the unknown were observed in the range of 25 to 200° C. The most sensitive scale of the instrument (0.2 mg./in.) was used.

II. The Photochemical Reaction

A. Effect of Relative Humidity

As mentioned previously, the optical density of the film can be used to measure the reaction rate for the oxidation of X. A convenient apparatus for such measurements should provide a closed chamber in which the relative humidity can be controlled and an optical arrangement by which the sample can be exposed to high intensity ultraviolet light and also provide a means for measuring the optical density of the sample. For these reasons a combined cover plate and sample holder was made for the sample chamber of the Model 14 Cary Spectrophotometer. The apparatus is illustrated schematically in Figure 11. The major features are:

1. The sliding sample holder allows the sample to be inserted without opening the chamber.
2. The sample is held at 45° with respect to the spectrophotometer beam and with the beam of the exposure lamp. (A quartz window transmits the light from the source into the chamber.)
3. The push-button is used to close the shutter of the spectrophotometer when the exposure lamp is on thus protecting the photodetector.
4. A direct reading hygrometer measures the relative humidity in the chamber.
5. Dry air is fed through the gas scrubber filled with deionized water and then into the chamber. A small beaker is inverted over the inlet of the chamber to prevent a direct air flow over the sample.

All samples were deposited on clean quartz slides by immersing the slide in the tin solution (10 g. of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.8 ml. of concentrated HCl in 100 ml. of deionized water) and then rinsing in an overflow bath of deionized water for 1 minute. The excess water was then removed from the slide with nitrogen. The sample was placed in the chamber of the spectrophotometer and held in the controlled atmosphere for 10 minutes before the exposure process was initiated. During this time, the absorption spectrum of the film was measured and the relative humidity and temperature in the chamber were recorded. After the 10 minute interval, the optical density of the film was measured at 2,500 Å and then the pen of the spectrophotometer was turned off and the shutter closed. The sample was then exposed to the light from the mercury lamp for a fixed time. (The lamp was on at all times to eliminate the variation of intensity during warm-up. A sheet of black paper was used as a manual shutter for the source.) After this, the shutter of the spectrophotometer was opened and the recorder pen activated to measure the optical density of the film after exposure. The above sequence was repeated several times to obtain the optical density as a function of exposure time. All of the optical densities reported are for the film only. The absorption due to the quartz was eliminated by using a double beam arrangement in which the standard was a clean quartz slide. The zero absorption baseline was established with a clean slide in the sample position.

Table 6 lists the optical density and total exposure times for invisible films at various relative humidities. This data is for invisible films only. In other instances the films were visible

(reflective) white coatings non-uniformly distributed over the surface. More will be said about the visible films below.

B. Effect of a Nitrogen Flushed Atmosphere

To gain some insight into the mechanism of the photoreaction, samples were exposed in a nitrogen flushed atmosphere. The flow rate of nitrogen into the chamber was 35 S.C.F.M. and the relative humidity was controlled by diverting a portion of the gas through the gas scrubber filled with deionized water. The time to half-exposure is listed in Table 7 as a function of how long the sample was held in the atmosphere before exposure and the relative humidity of the atmosphere. Again, the data are for invisible films only.

ANALYSIS OF EXPERIMENTAL RESULTS

I. Characterization of UnknownA. Ultraviolet Absorption of Unknown

There are two important pieces of information to be obtained by an analysis of the absorption spectra of the film when freshly deposited and after exposure. First, the true absorption spectrum of X will define the limits of the action spectrum of the photochemical oxidation of the substance. This is based on the Grotthus-Draper Law which states that "...only radiations which are absorbed by the reacting systems can result in a photochemical reaction."²⁰ Secondly, the absorption spectrum can be compared with those of known films to assist in establishing the identity of the unknown.

A determination of the true absorption spectrum of X is complicated by two factors. It is difficult to prepare a pure tin(II) compound due to oxidation in air and the diffuse reflectance of samples with large quantities of X (visible films) give optical density spectra which include the effects of both absorbance and reflectance.

The optical density of the film shown in Figure 1 indicates that the absorption of an exposed sample is negligible for wavelengths greater than 3,200 Å. The previously derived relationship for the optical density of the film states that

$$D = \frac{(K'_2 - K'_4)m_2 + K'_4 m_T}{\ln(10)} \quad (5)$$

The fact that the optical density decreases upon exposure indicates that the molar absorption coefficient of the tin(II) compound, K'_2 , is greater than the molar absorption coefficient for the tin(IV) compound, K'_4 . Also, K'_4 is at least negligible for wavelengths greater than $3,200 \text{ \AA}$ since the absorption of the exposed sample is zero in this region. (It should be noted that this result does not depend on the complete oxidation of X).

The above result implies that any absorption for wavelengths greater than $3,200 \text{ \AA}$ is due entirely to X. The unexposed film does not show appreciable absorption above $3,600 \text{ \AA}$ and thus X does not appreciably absorb light for wavelengths greater than $3,600 \text{ \AA}$.

The above analysis applied to an invisible film. An unexposed visible film has an optical density spectrum which is linear from $4,000 \text{ \AA}$ to about $3,600 \text{ \AA}$ (Figure 2). For wavelengths less than $3,600 \text{ \AA}$, the optical density increases in a manner quite similar to invisible films before exposure. The difference between the two types of films can be explained by attributing the linear portion of the spectrum for the visible film to a diffuse reflectance (Figure 3) rather than to true absorption. This gives very close agreement between the true absorption spectra of the two types of films. Similarly, the differences between the optical densities for exposed visible and invisible films can be accounted for by the reflectance of the visible films. The linear portion of the optical density spectrum for exposed visible films extends from $4,000$ to about $3,000 \text{ \AA}$ and then the optical density increases in a manner quite similar to the exposed invisible

films.

B. Ultraviolet Absorption of Other Compounds

The ultraviolet optical density of hydrous tin(II) oxide (Figure 4) is similar to that of a visible film of X (Figure 2) in two respects. The spectra are similar in shape and the known compound shows a decrease in absorption upon exposure to ultraviolet light as does the unknown. In the reflectance region of the spectra, both visible films of the unknown and hydrous tin(II) oxide show an increase in reflectance upon exposure. This effect may be due to a change in the refractive index of the scattering particles during the photochemical reaction.

The primary reason for determining the absorption of a film deposited from a stannous sulfate solution is to clarify the role that the chloride ion plays in the absorption and photochemical processes. The optical density of this type of film (Figure 5) is very similar to that observed for the unknown before and after exposure.

It is quite likely that the product of the photo-oxidation of X is hydrous SnO_2 . A comparison of Figure 6 and the optical density curves for the unknown after exposure (Figures 1 and 2) reveals that they are similar.

C. X-ray Diffraction

The absence of x-ray diffraction peaks attributable to films of the unknown on quartz is probably due to three factors, i.e., diffuse scattering by the substrate, the small particle size of X and the small amount of X present.

The diffraction patterns for the precipitates formed by increasing the pH of a stannous chloride dihydrate solution (Table 1) or a stannous sulfate solution (Table 2) agree closely with the pattern for hydrous tin(II) oxide⁴ ($5\text{SnO}\cdot 2\text{H}_2\text{O}$). Exposure times of 6 hours were required to obtain all of the diffraction lines.

D. X-ray Fluorescence Analysis

The amounts of tin and chlorine deposited on a quartz substrate vary considerably (Table 3) depending on the rinsing method. However, two points are clear; the amount of chlorine deposited is heavily dependent on the volume of rinse water used and also, for the rinsing method generally used (overflow bath with a flow rate of 800 to 1200 ml. of deionized water per minute), the number of moles of chlorine deposited is an order of magnitude less than the number of moles of tin deposited.

If it is assumed that the compound deposited is $5\text{SnO}\cdot 2\text{H}_2\text{O}$ and that it is distributed in a uniform film over the entire surface, then the film thickness can be determined. The area of the substrate examined by x-ray fluorescence is 2.42 cm^2 and the density of hydrous tin(II) oxide¹² is 4.71 g./cm^3 . The estimated film thickness for Sample No. 2 (Table 3) is thus

$$t = m/\rho A$$

$$t = \frac{709.5\text{ g./mole}}{593.5\text{ g. Sn/mole}} \times \frac{9.62\ \mu\text{g. Sn}}{(4.71\text{ g./cm}^3)(2.42\text{ cm}^2)}$$

$$t = 101\ \overset{\circ}{\text{A}}$$

E. Electron Microscopy and Diffraction

Before attempting to use the data obtained with the electron microscope, the factors that may cause changes in X from its usual state should be considered. Samples for the electron microscope were prepared on a carbon substrate that is supported in a copper grid. The effects of this substrate as opposed to a clean quartz slide can be of two types. First, the copper may have a chemical effect on X and secondly the surface energy of the carbon may have an effect on the particle size, shape, and distribution of X that is different from that of quartz. Another factor that is probably significant is that the sample is examined in a high vacuum and thus any free water on the surface is evaporated and the unknown is probably dehydrated due to beam heating. For these reasons, the characteristics of X as revealed by the electron microscope may be considerably different than the same characteristics when the compound is in an ambient environment on a quartz substrate.

A better understanding of the electron diffraction patterns can be obtained if the particle size is first determined. The transmission electron micrograph shown in Figure 9 shows particles or aggregates (the dark areas) on carbon (light areas) that range in size from approximately 50 to 250 Å. There is no apparent morphology to the aggregates, however, the coating is reasonably uniform with void areas generally less than 1000 Å in length and 250 Å in width.

To analyze the effect of particle size on the diffraction pattern, a mean particle size of 150 Å is a reasonable choice. For an ideally collimated monochromatic beam, the angles, θ_1 and θ_2 which

correspond to complete destructive interference for a particular diffraction angle θ are given by²¹

$$t(\sin \theta_1 - \sin \theta_2) = \lambda \quad (6)$$

where t is the particle size measured perpendicular to the incident beam. The diffraction angle θ is given by²¹

$$\lambda = 2d \sin \theta \quad (7)$$

and differentiating (7) with respect to d gives

$$\frac{d\theta}{dd} \lambda = - \frac{\lambda}{2d^2 \cos \theta} \doteq - \frac{\lambda}{2d^2} \quad (8)$$

since $\theta \doteq 0$. Replacing differentials by finite increments in equations (6) and (8)

$$\lambda \doteq t (\theta_1 - \theta_2) = t \delta\theta$$

and

$$\delta\theta \doteq - \frac{\lambda}{2d^2} \delta d.$$

Combining these results it is seen that

$$\delta d \doteq - \frac{2d^2}{t} \quad (9)$$

where δd is the range of d -spacings that would be observed for a particular d -spacing under ideal conditions. As an example, for $d = 3.00 \text{ \AA}$ and $t = 150 \text{ \AA}$, the expected range of observed d -spacing is

$$\delta d = - \frac{2(3.00 \text{ \AA})^2}{150 \text{ \AA}} = - 0.12 \text{ \AA}.$$

Thus, considerable line broadening due to particle size can be expected.

The electron diffraction pattern of the unknown after exposure to ultraviolet light (Table 5) is illustrated in Figure 14 (a). In Figure 14 (b), the eight most intense lines of SnO_2 ²² are shown for comparison. The strong similarity between the two patterns is apparent if line broadening due to particle size is taken into consideration. The only dissimilarity is that the SnO_2 pattern has a line at 2.37 \AA and a corresponding band is not shown for the unknown after exposure. There are two factors that account for this apparent difference. First, the integrated intensity of this band is expected to be less than the other four bands (Figure 14 (b)) and therefore it is difficult to observe. Secondly, the carbon substrate exhibits a broad diffraction band centered at 2.18 \AA which adversely affects the film contrast and makes it difficult to observe a weak band in this region. With these problems in mind, it is reasonable to conclude that the compound is SnO_2 . The particle size can be estimated with equation (9) and the observed range of d-spacings for each band (Table 5). Such a calculation (Table 8), gives particle sizes in the range of 50 to 75 \AA .

The electron diffraction pattern (Table 4) of the unknown before exposure is illustrated in Figure 15 (a) and the nine most intense lines of SnO ²³ are shown in Figure 15 (b) for comparison. The extremely broad band between 2.61 and 3.58 \AA cannot be attributed to pure SnO even when line broadening is considered. However, a mixture of SnO and SnO_2 (Figure 14) would produce this wide band. This implies that the stannous compound is partially oxidized during sample preparation.

II. Photochemical Reaction

A. The Effect of Relative Humidity

The reaction rate was measured for different relative humidities by measuring the optical density of invisible films as a function of total exposure time (Table 6). After several minutes of exposure the optical density reaches a constant value and further exposure causes no noticeable decrease. A good fit to the data is of the form

$$D(t) = A + Be^{-t/\tau} \quad (10)$$

where $D(t)$ is the optical density and A and B are constants illustrated by Figure 12 (a). The same data is plotted on a logarithmic scale in Figure 12 (b) as $D(t) - A$ versus total exposure time. The plots clearly illustrate the exponential decrease of optical density with exposure time. By combining equations (5) and (10).

$$A + Be^{-t/\tau} = \frac{(K_2' - K_4')m_2 + K_4'm_T}{\ln(10)} \quad (11)$$

Since A is a constant, it is equal to the constant portion on the right

$$A = \frac{K_4'm_T}{\ln(10)} \quad (12)$$

and equating the transient terms gives

$$Be^{-t/\tau} = \frac{(K_2' - K_4')m_2}{\ln(10)} \quad (13)$$

It is thus seen that the moles of tin(II) compound present is proportional to the transient portion of the optical density.

Differentiation of (13) gives

$$-\frac{B}{\tau} e^{-t/\tau} = \frac{K_2' - K_4'}{\ln(10)} \frac{dm_2}{dt}$$

or

$$\frac{dm_2}{dt} = -\frac{m_2}{\tau} \quad (14)$$

indicating that the reaction is first order in m_2 .

The time-constant, τ , of the reaction is dependent on the relative humidity. The time required for the number of moles of X to decrease to one-half of the initial value is

$$t_{0.5} = 0.693 \tau$$

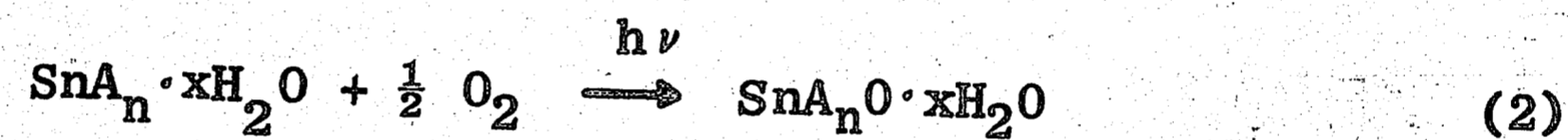
which corresponds to $D(t) - A$ equal to one-half of its initial value. In Figure 13 the time to half-exposure is plotted versus the relative humidity of the air in which the sample was exposed. Also shown are a best line fit (obtained by linear regression) and 90% confidence intervals for individual points. The null hypothesis that $t_{0.5}$ is independent of relative humidity can be rejected at the 0.001 confidence level ($T = -20.9$ with 6 degrees of freedom). The coefficient or correlation (-0.9932) indicates that the fit to the experimental data is quite good. The resulting relationship is

$$t_{0.5} = 7.4 - 0.084 x (\text{Rel. Hum.}) \text{ min.}$$

It should be noted that the relationship applies in the range over which the data were taken (27% to 79% relative humidity) and may not be valid elsewhere.

B. The Effect of a Nitrogen Flushed Atmosphere

When an invisible film of X was exposed in a chamber flushed with nitrogen (35 S.C.F.M.), the photochemical reaction rate was much lower than in air. For samples that were held in the nitrogen atmosphere for 17 min. before exposure, the time to half-exposure ranged from 17.8 min. at 13% relative humidity to 8.1 min. at 61% (Table 7). The time to half-exposure in air at 61% relative humidity was 2.3 min. (Figure 13). This difference indicates that the reaction rate is a function of the partial pressure of oxygen and that a reaction of the type



occurs.

The time that the sample is held in the nitrogen atmosphere prior to exposure also has an effect on the reaction rate (Table 7). The time to half-exposure increased with hold time at a constant relative humidity. This indicates that oxygen (adsorbed and/or dissolved) was slowly removed from the film due to the low partial pressure of oxygen in the nitrogen flushed atmosphere.

CONCLUSIONS

I. Characterization of Unknown

The unknown is a photosensitive tin(II) compound which is deposited as an invisible film on a substrate by immersing it in an acid (HCl) solution of stannous chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), rinsing in an overflow bath of deionized water and then removing excess water. X-ray fluorescence analysis indicates that approximately $4 \mu\text{g./cm.}^2$ of tin is deposited and that the molar ratio of tin to chlorine is greater than 9 to 1. The x-ray diffraction patterns for the unknown gave no diffraction peaks and thus direct identification was not possible by this method. However, bulk precipitates were prepared by increasing the pH of stannous chloride solutions in a manner analogous to the conditions under which the unknown is formed and the resulting precipitates were found to be hydrous tin(II) oxide ($5\text{SnO} \cdot 2\text{H}_2\text{O}$). Electron microscopy and diffraction reveal that the freshly deposited film consists of a mixture of stannous oxide (SnO) and stannic oxide (SnO_2) with particle sizes ranging from approximately 50 to 150 \AA . The electron diffraction pattern of the film after exposure to ultraviolet light indicates that it consists of stannic oxide (SnO_2). Beam heating and the high vacuum in which the samples were examined probably caused drying and dehydration.

The above results indicate that the photosensitive tin(II) compound is a hydrated tin(II) oxide. Other qualitative data that support this result are:

1. A photosensitive film can be deposited using an acid (H_2SO_4) solution of stannous sulfate (SnSO_4) in a procedure identical with

that used to produce the unknown. The resulting film exhibits ultraviolet optical density spectra very similar to the unknown before and after exposure. These results show that chloride ion is not essential to producing a photosensitive film.

2. Hydrrous tin(II) oxide ($5\text{SnO} \cdot 2\text{H}_2\text{O}$) is photosensitive and its ultraviolet optical density spectra before and after exposure are similar to visible (reflective) films of the unknown.

II. Photochemical Reaction

The fact that the ultraviolet absorption of the film decreases* as the photochemical reaction proceeds gives a means of measuring the reaction rate. In ambient conditions the time to half-exposure is found to be a linear function of relative humidity and thus (at constant temperature) a linear function of the partial pressure of water in the air.²⁴ Similar measurements in a nitrogen flushed atmosphere indicate that the reaction rate is dependent on the partial pressure of oxygen in the atmosphere. Lower reaction rates are observed as the hold time in the nitrogen atmosphere before exposure is increased indicating the gradual removal of dissolved and/or adsorbed oxygen from the surface.

The exact mechanism of the photoreaction is unknown, however, three factors have a direct effect on the formation of an activated complex²⁵ which results in the photochemical oxidation of the film,

*Estimated values of the molar adsorption coefficients for the tin(II) and tin(IV) compounds are calculated in the Appendix.

i.e., surface water, dissolved and/or adsorbed oxygen and the adsorption of ultraviolet light of energy greater than 79 Kcal./mole (wavelength less than $3,600 \text{ \AA}$).

The surface water may be reduced in the photoreaction or it may be involved in an intermediate process in which it serves simply as a medium that provides dissolved oxygen at the reaction site.

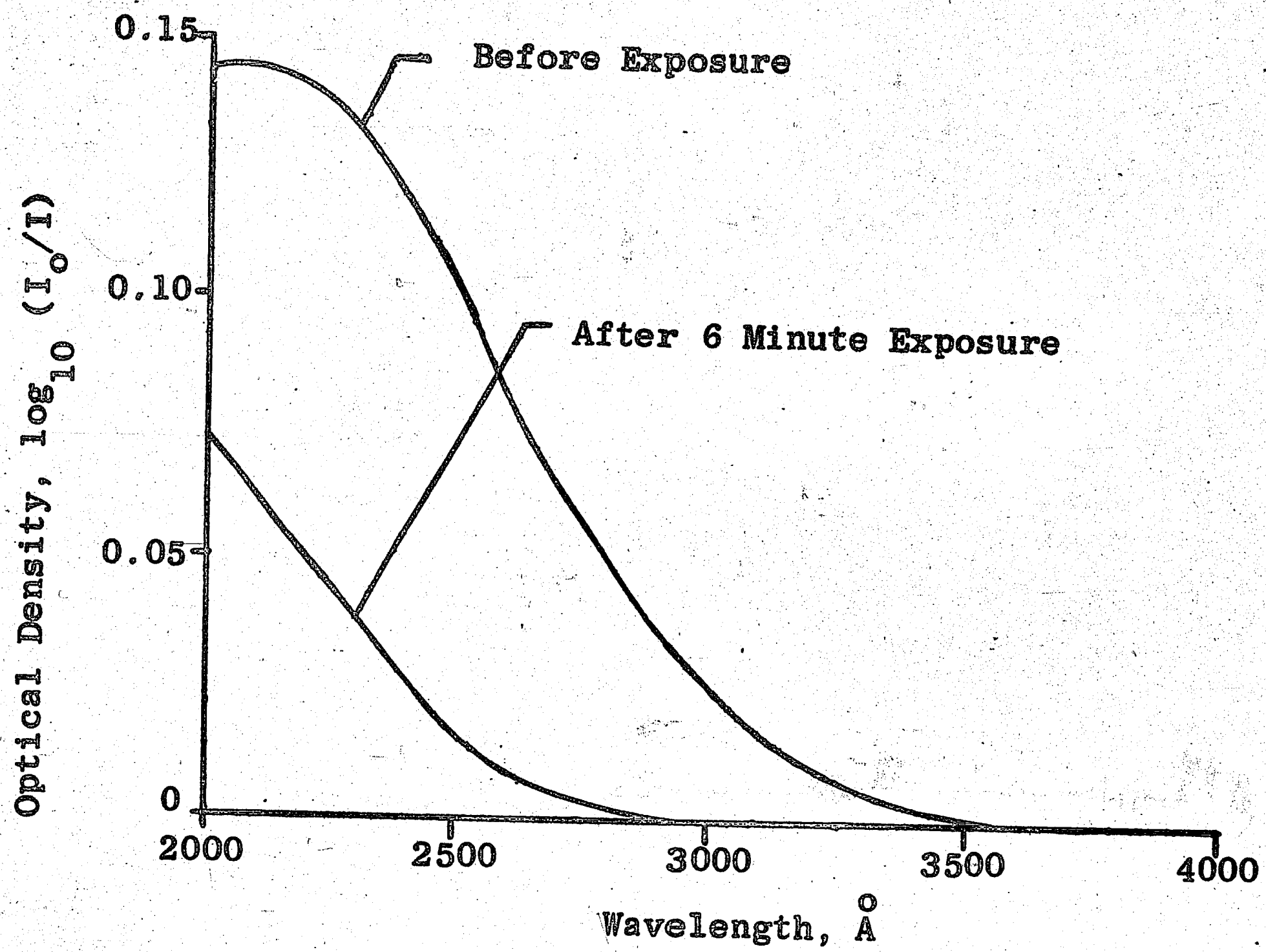


FIGURE 1. Optical Density Versus Wavelength for an Invisible Film of the Unknown on a Quartz Substrate Before and After Exposure.

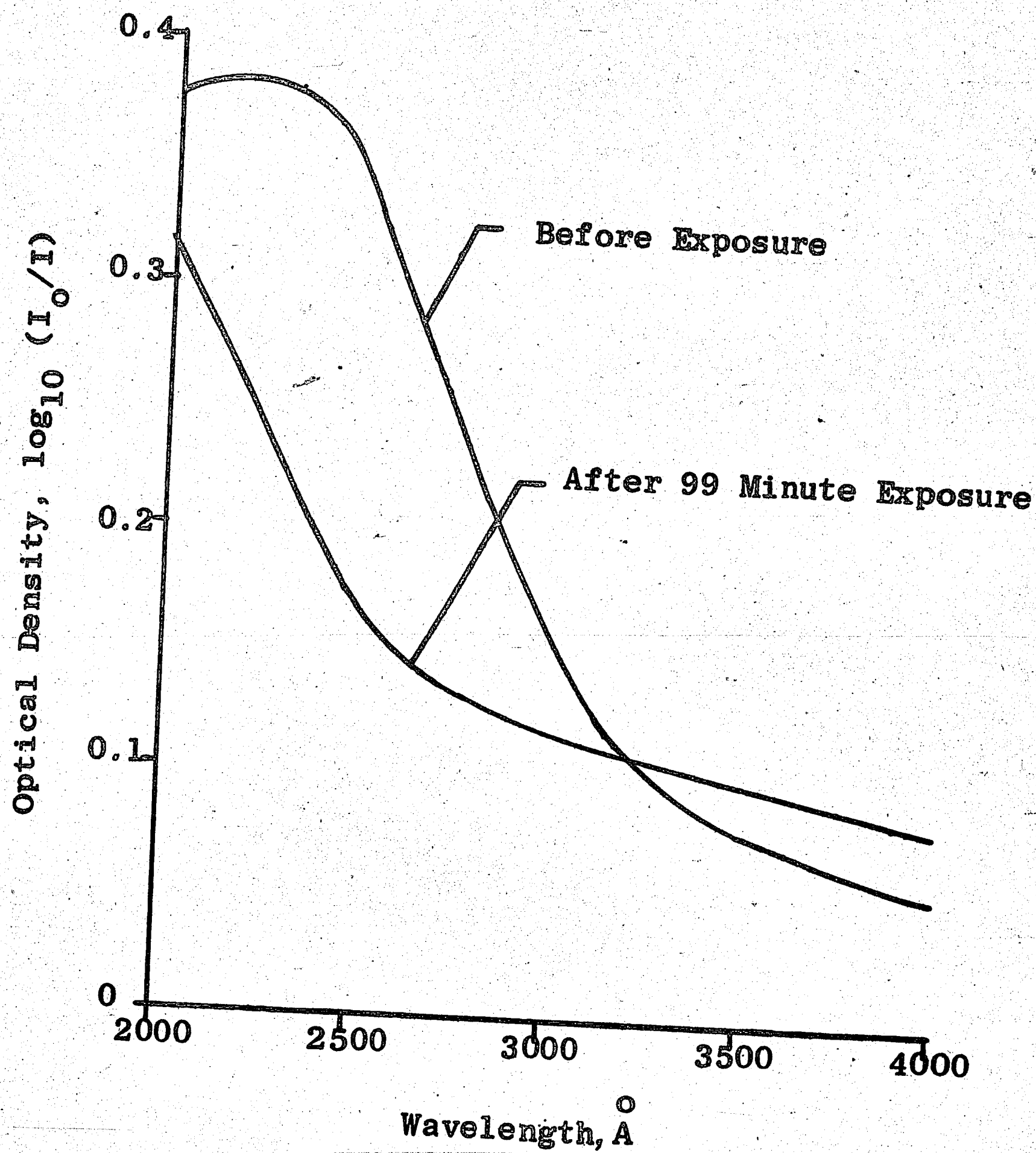


FIGURE 2. Optical Density Versus Wavelength for a Visible Film of the Unknown on a Quartz Substrate Before and After Exposure.

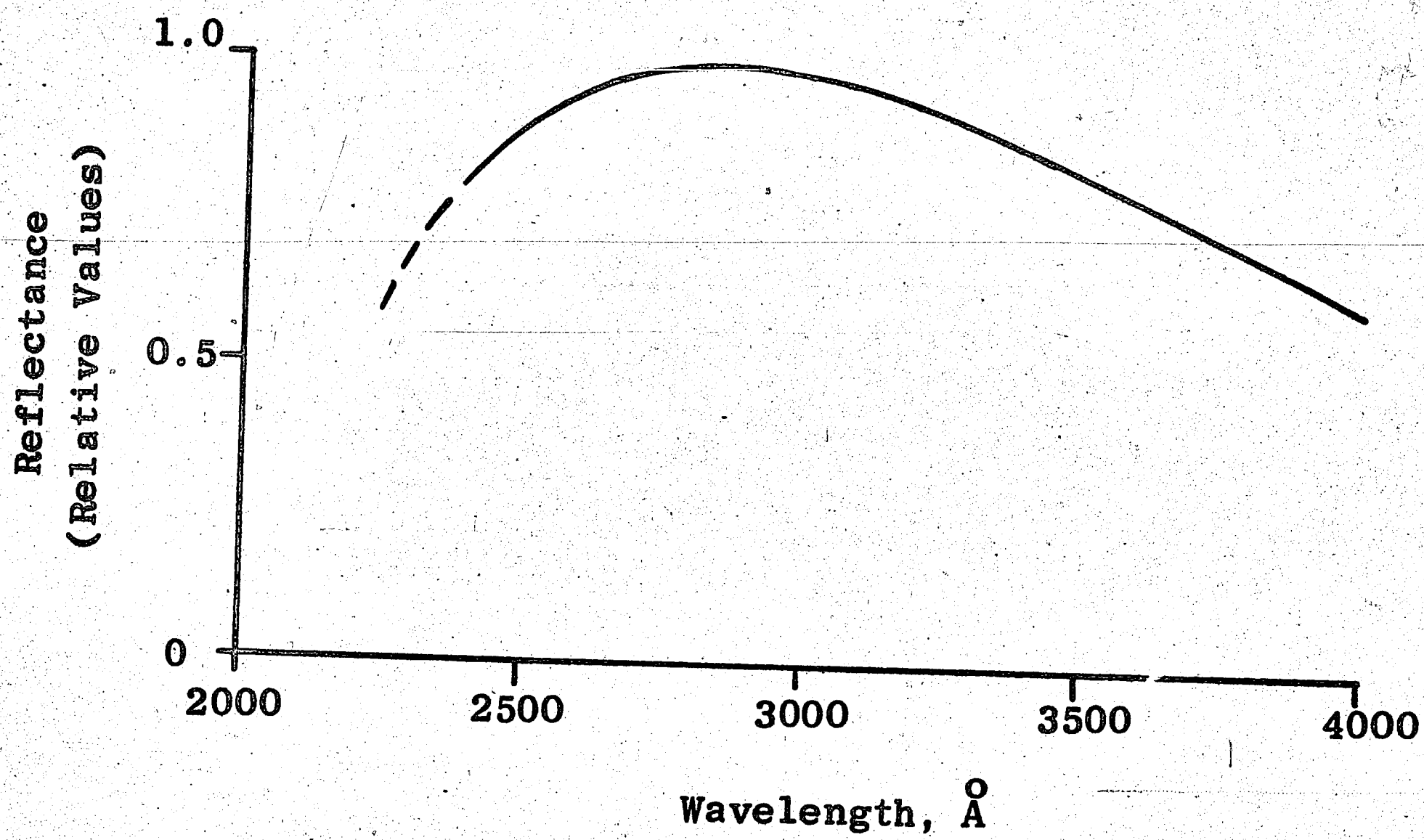


FIGURE 3. Reflectance Versus Wavelength for a Visible Film of the Unknown on a Quartz Substrate.

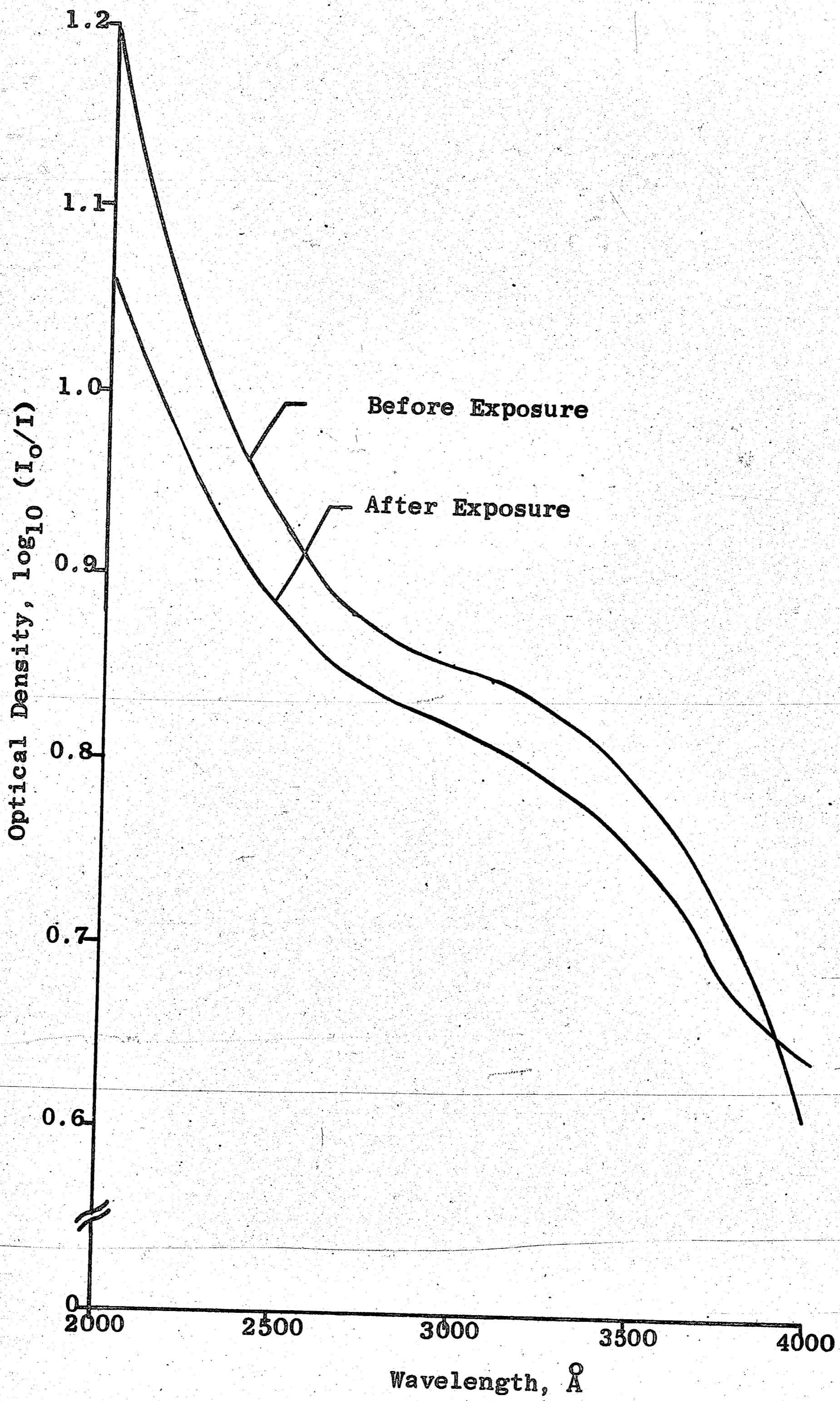


FIGURE 4. Optical Density Versus Wavelength for Hydrous Tin(II) Oxide on a Quartz Substrate Before and After Exposure.

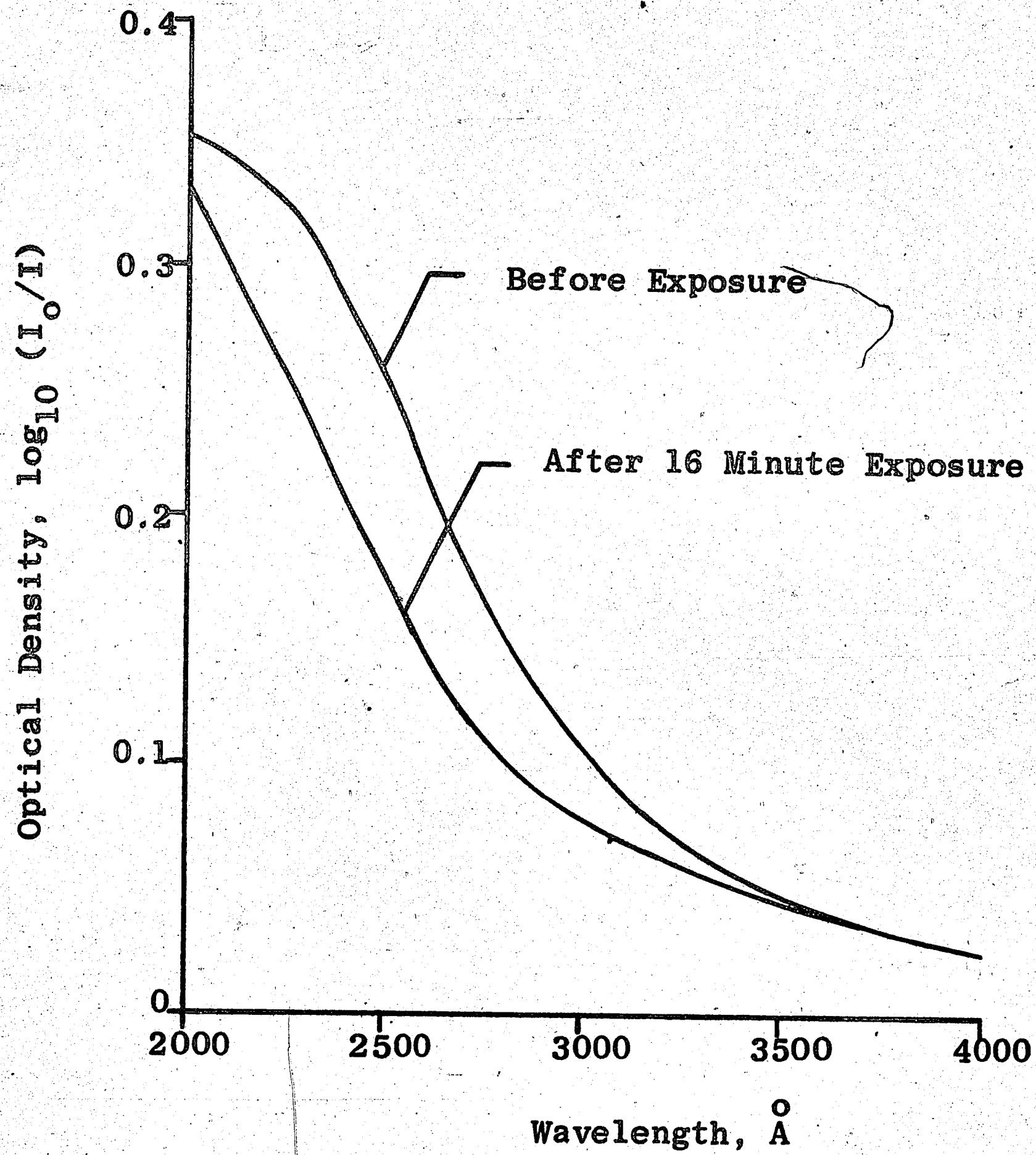


FIGURE 5. Optical Density Versus Wavelength for a Visible Film Deposited on Quartz using a Stannous Sulfate Solution.

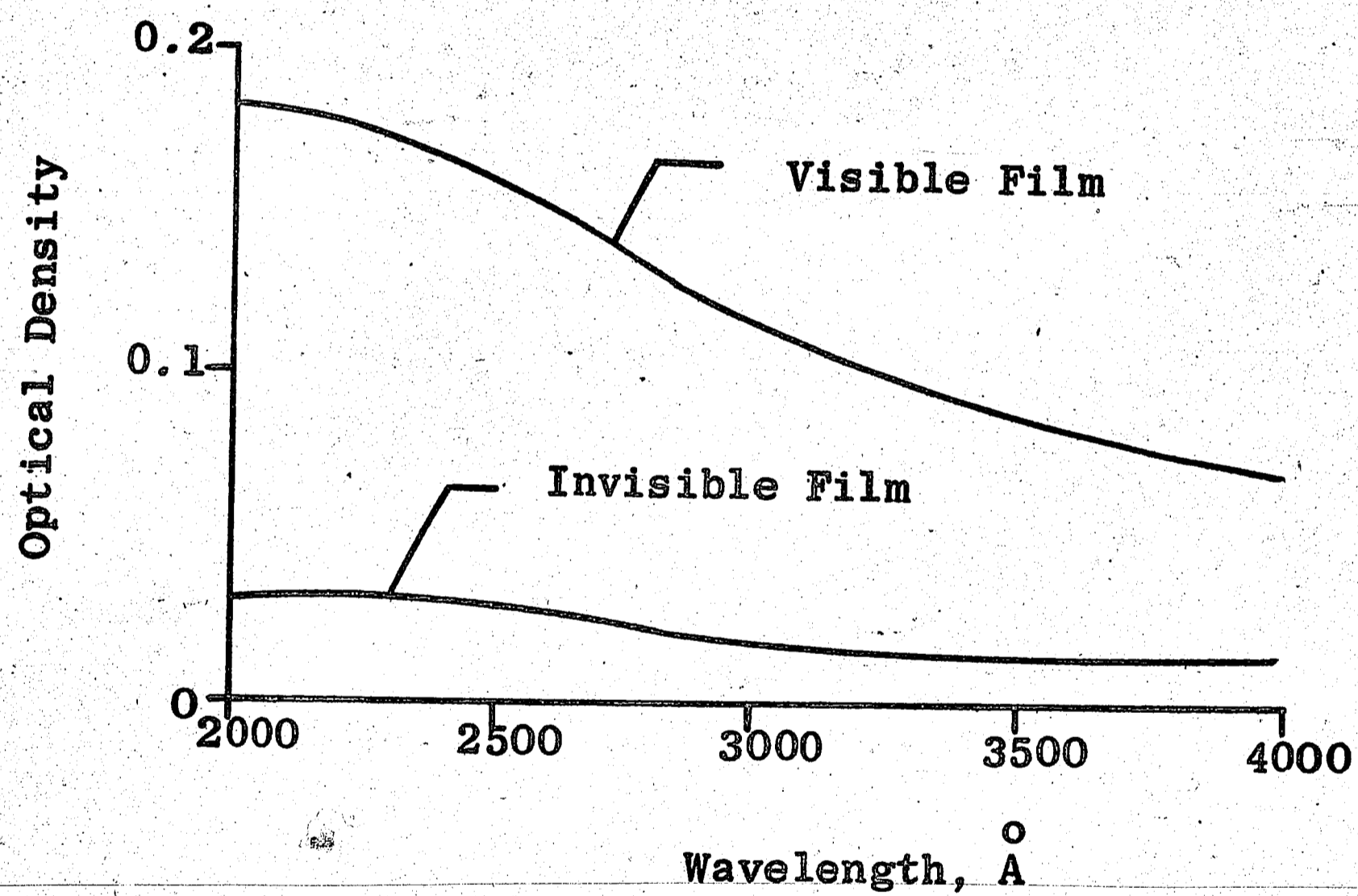


FIGURE 6. Optical Density Versus Wavelength for Visible and Invisible Films of Hydrous SnO_2 .

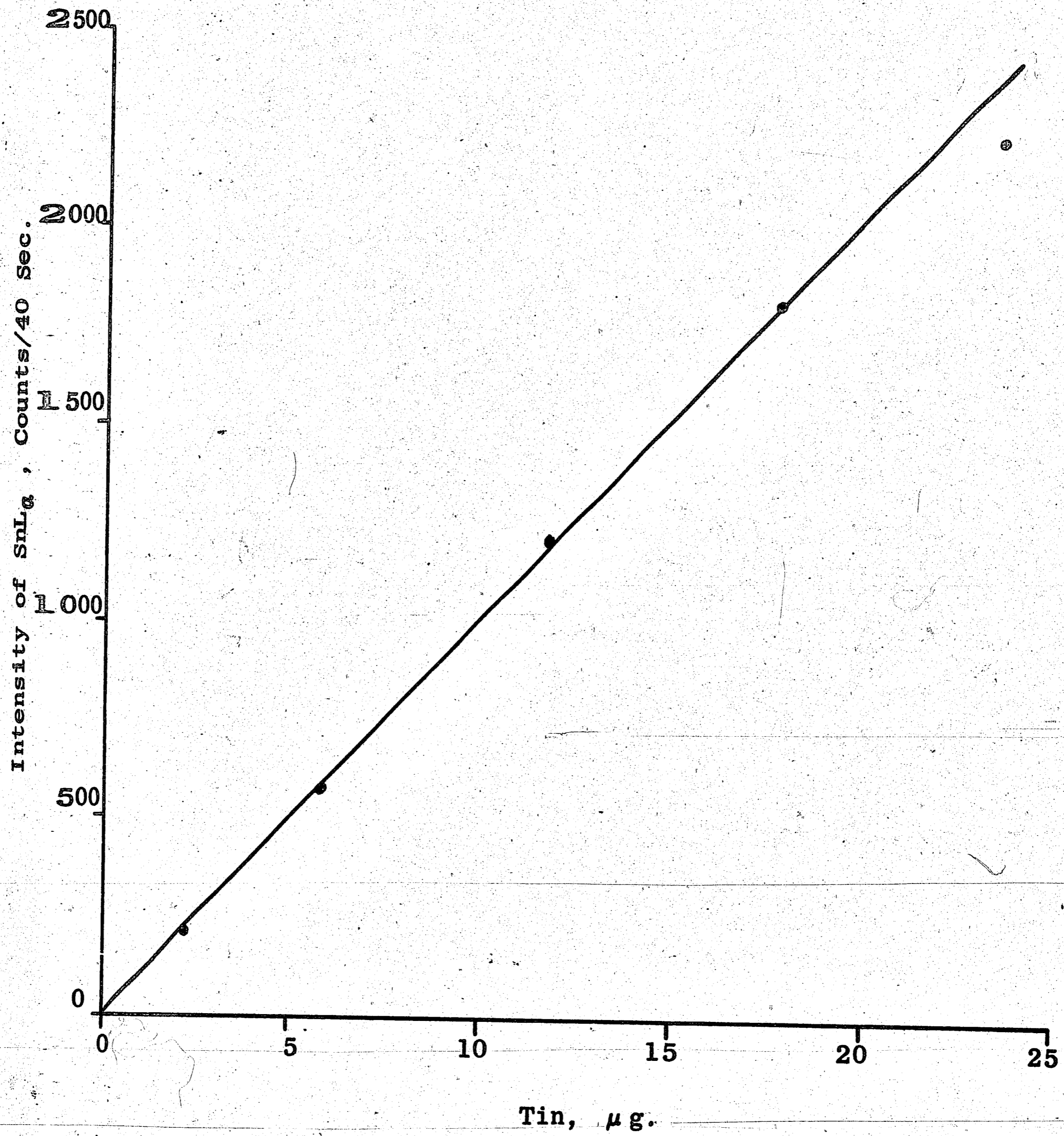


FIGURE 7. Fluorescent Intensity Versus Amount of Tin for Tin Standards.

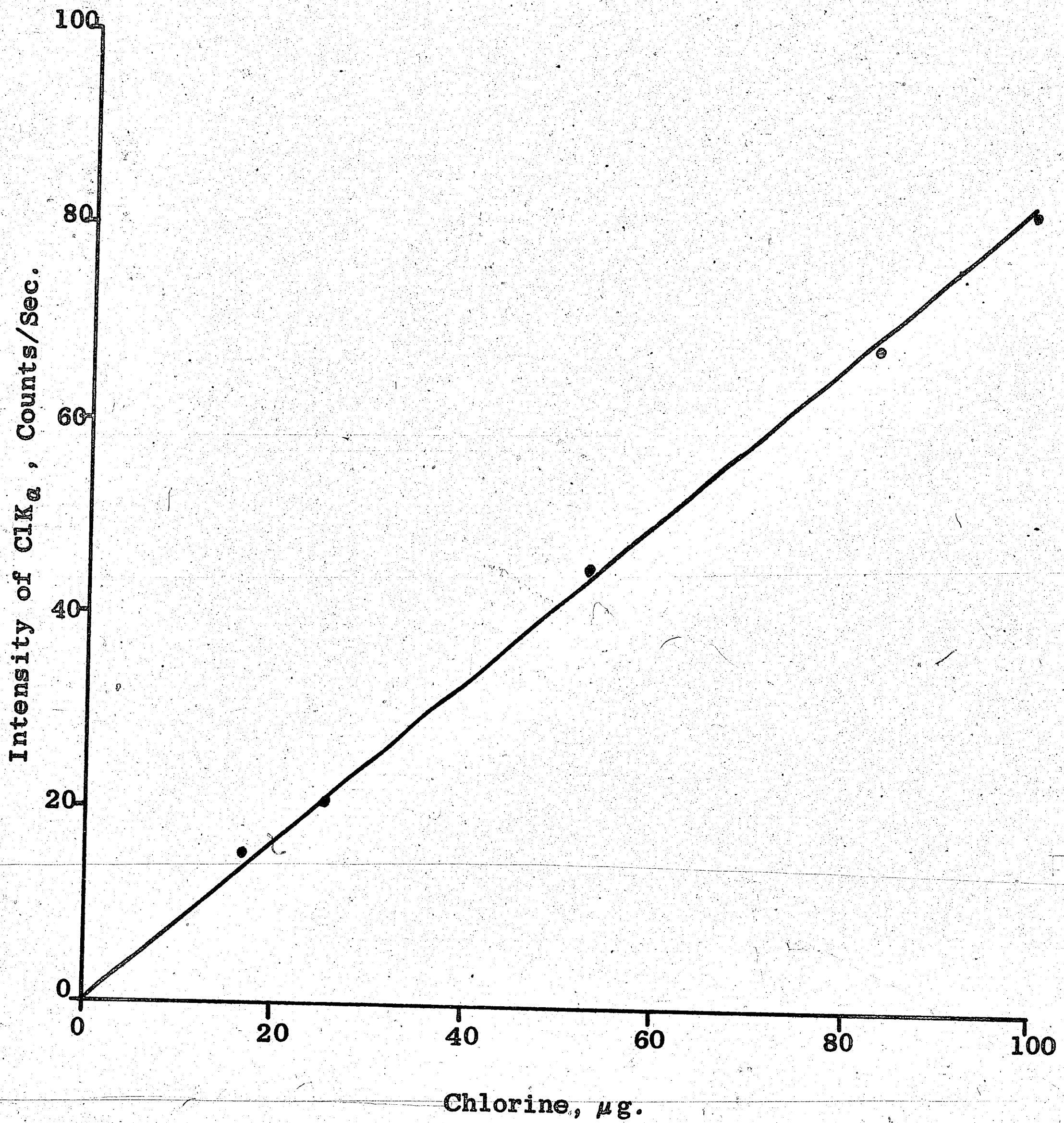


FIGURE 8. Fluorescent Intensity Versus Amount of Chlorine for Chlorine Standards.



500 ⁰/_A

FIGURE 9. Transmission Electron Micrograph of the Unknown (dark areas) on a Carbon Substrate (light areas) Before Exposure.



500 Å

FIGURE 10. Transmission Electron Micrograph of the Unknown on Carbon after 2 Minute Exposure with Ultraviolet Light.

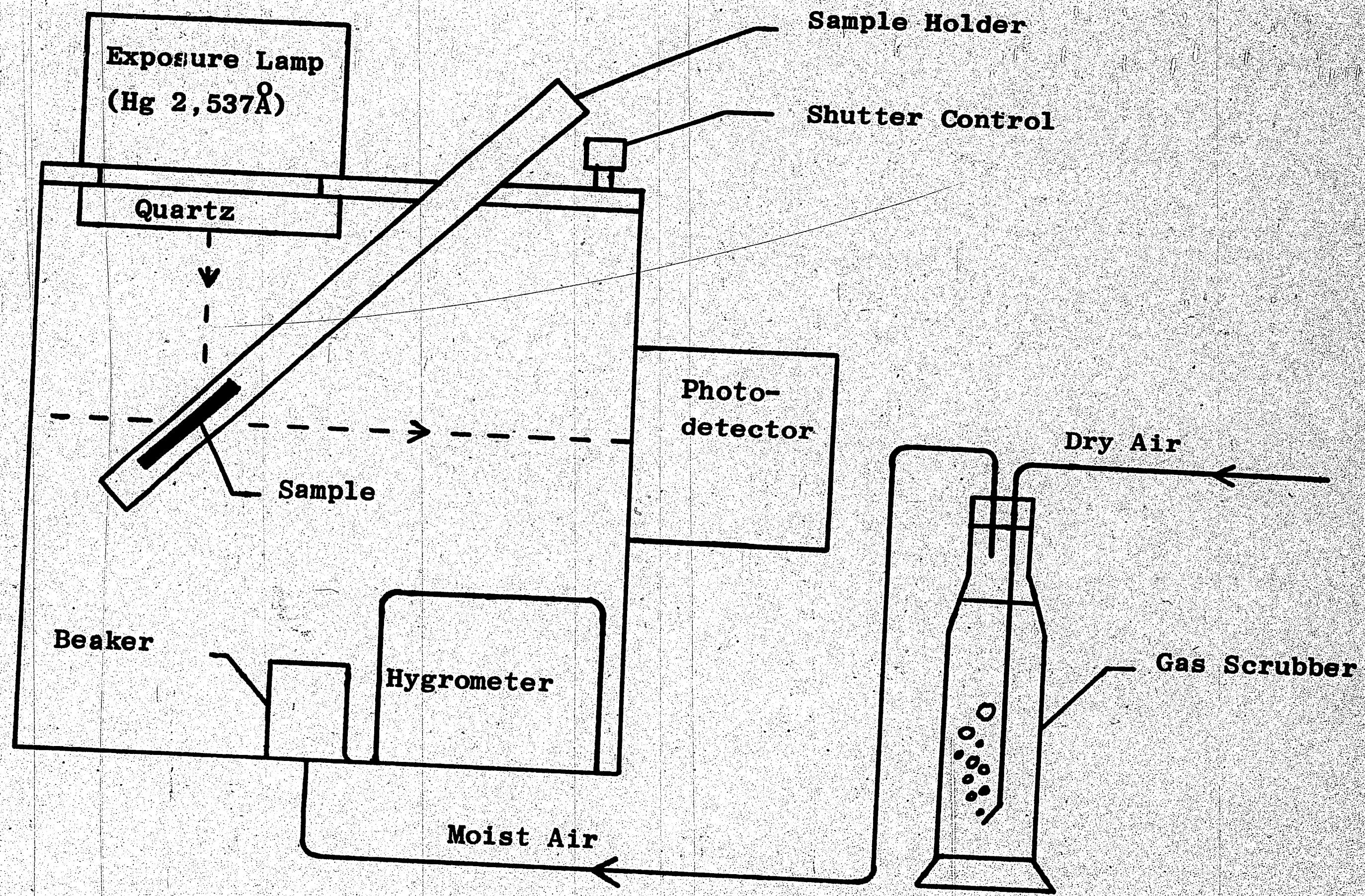


FIGURE 11. Schematic Illustrated of the Apparatus used to Measure the Photochemical Reaction Rate.

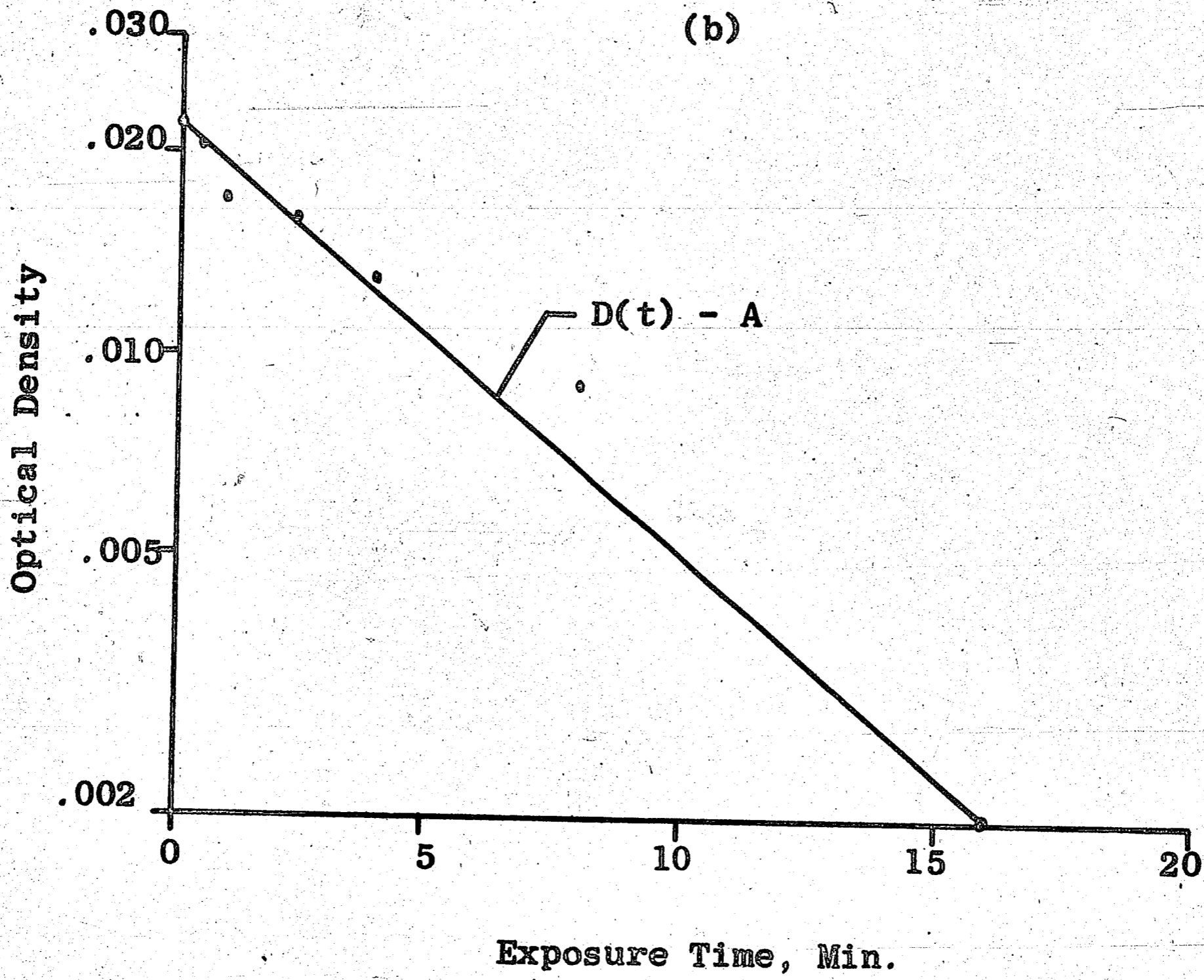
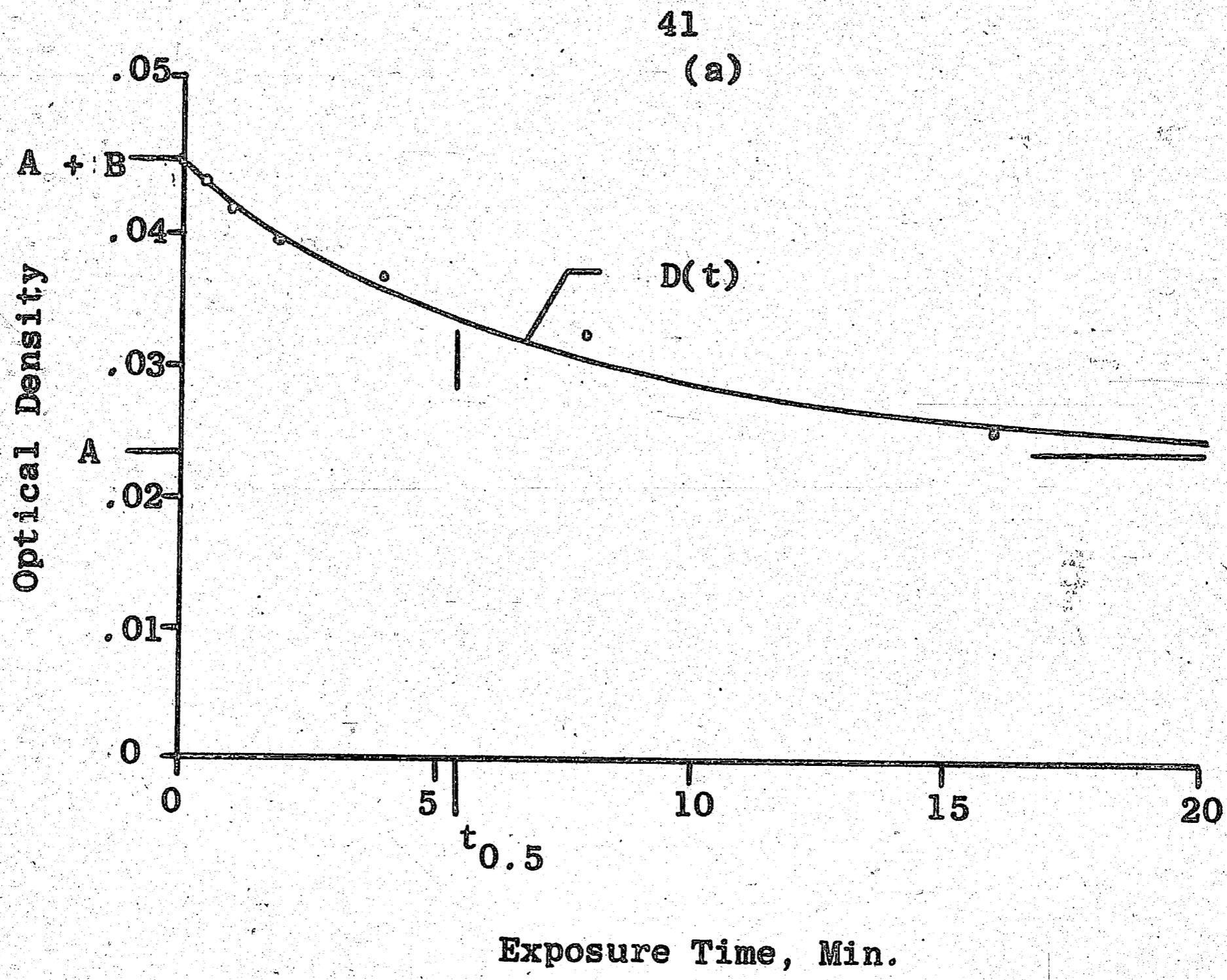


FIGURE 12. (a) Optical Density Versus Exposure Time for an Invisible Film.
(b) The Transient Portion of the Optical Density Plotted on a Logarithmic Scale.

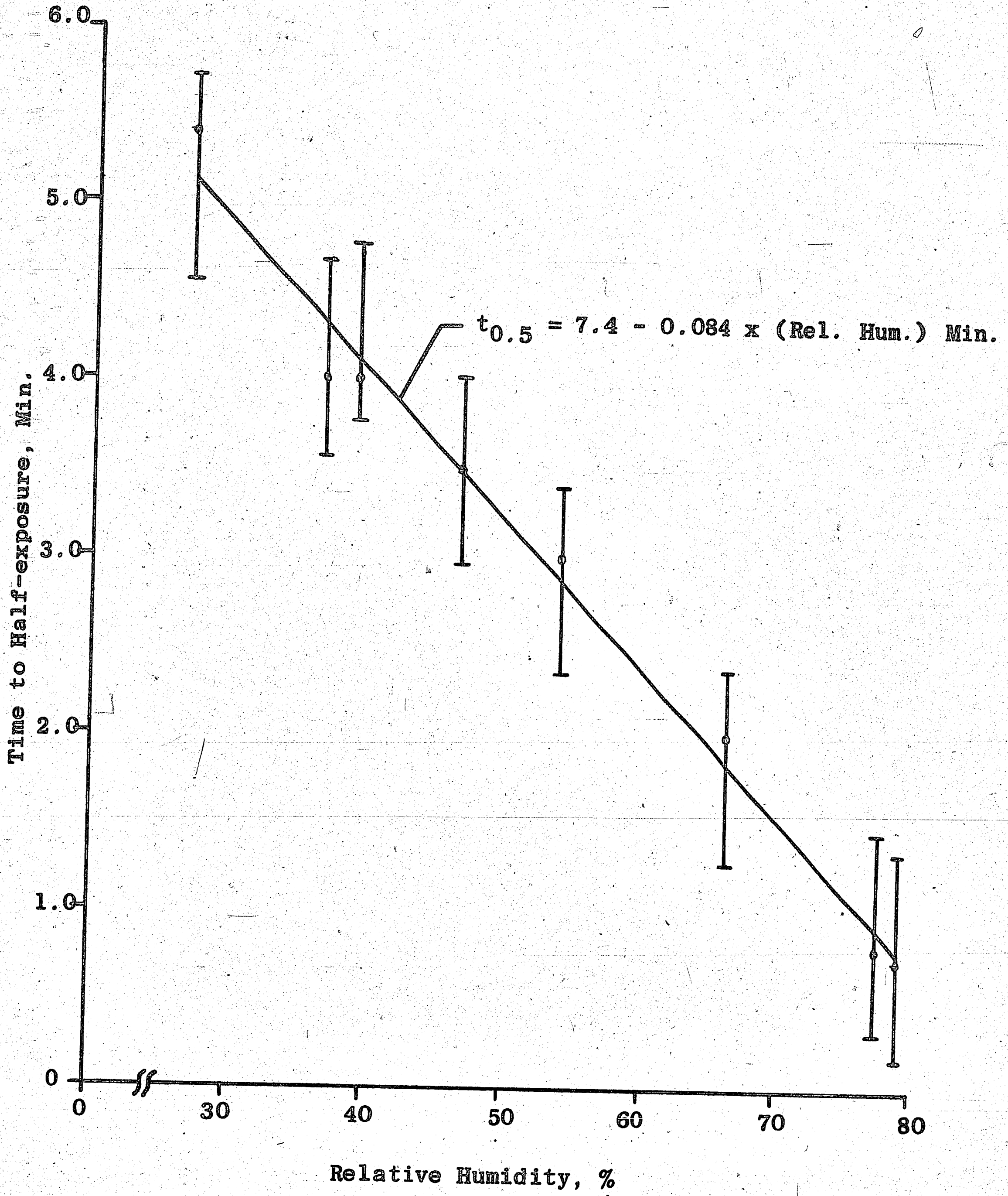


FIGURE 13. Time to Half-exposure Versus Relative Humidity for Samples Exposed in Air. The Line of Regression and 90% Confidence Intervals for Individual Readings are also Shown.

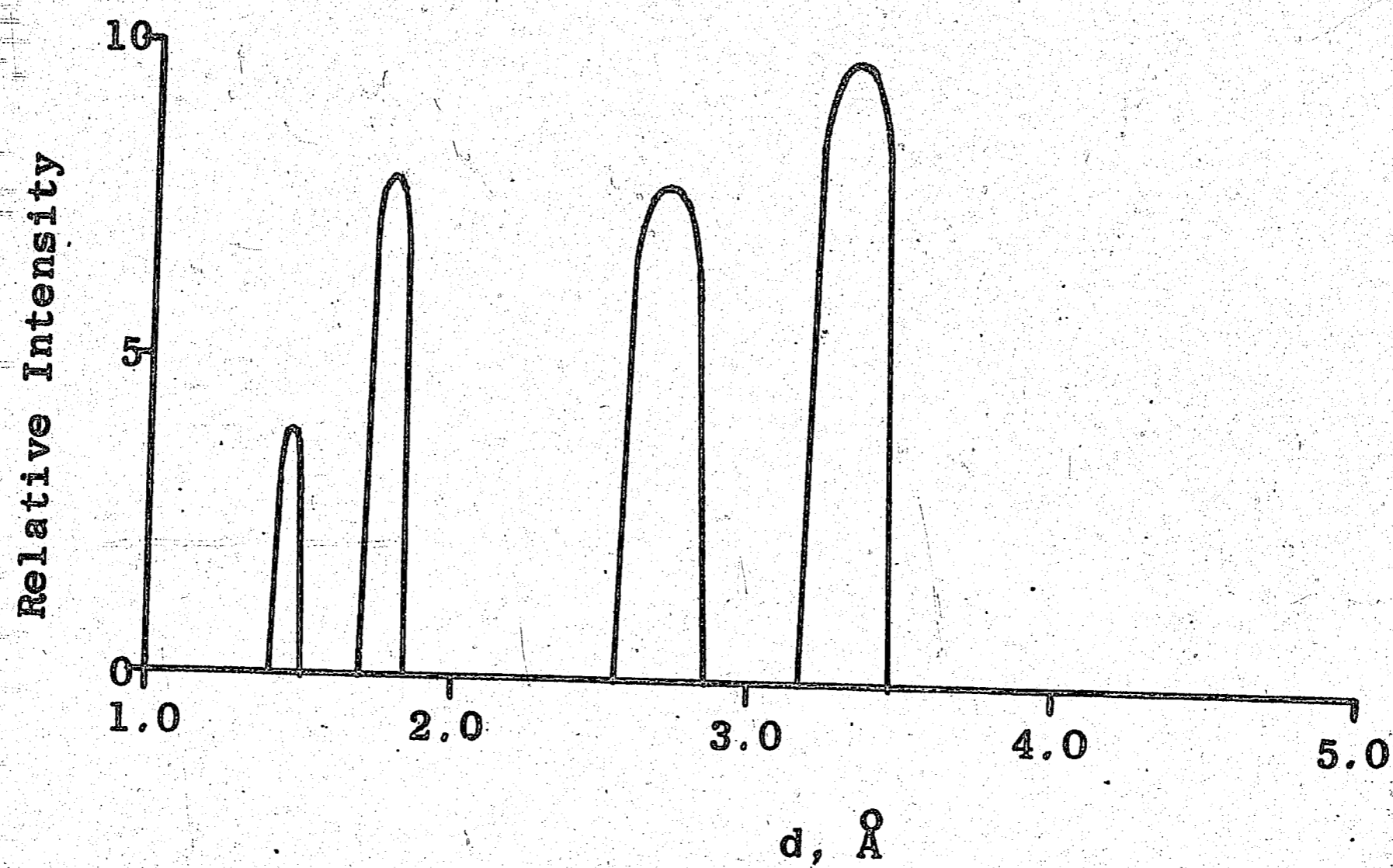


FIGURE 14 (a) Observed d-spacings for Unknown after Exposure (Sample 165-8).

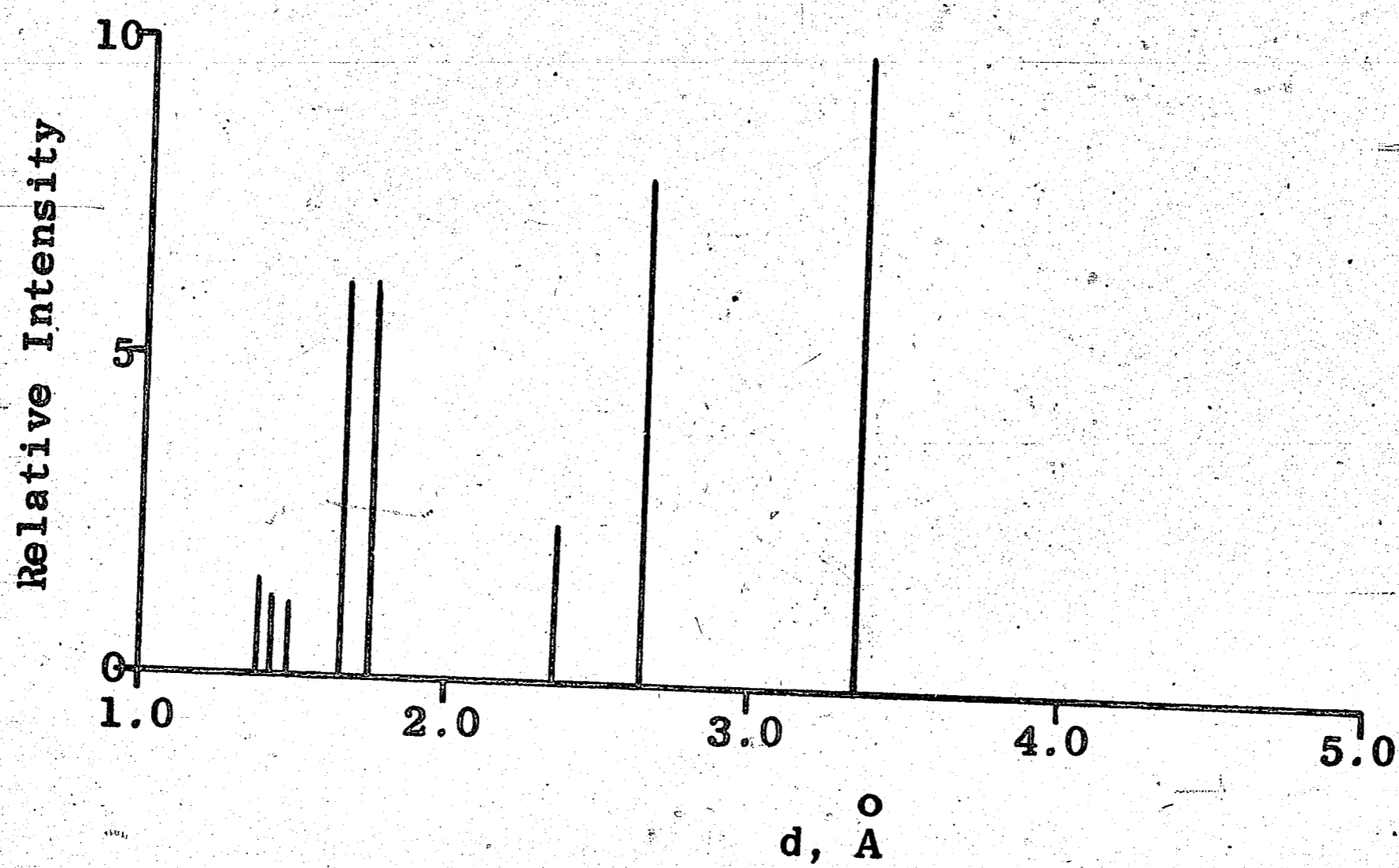


FIGURE 14 (b) X-ray Diffraction Data for SnO₂.

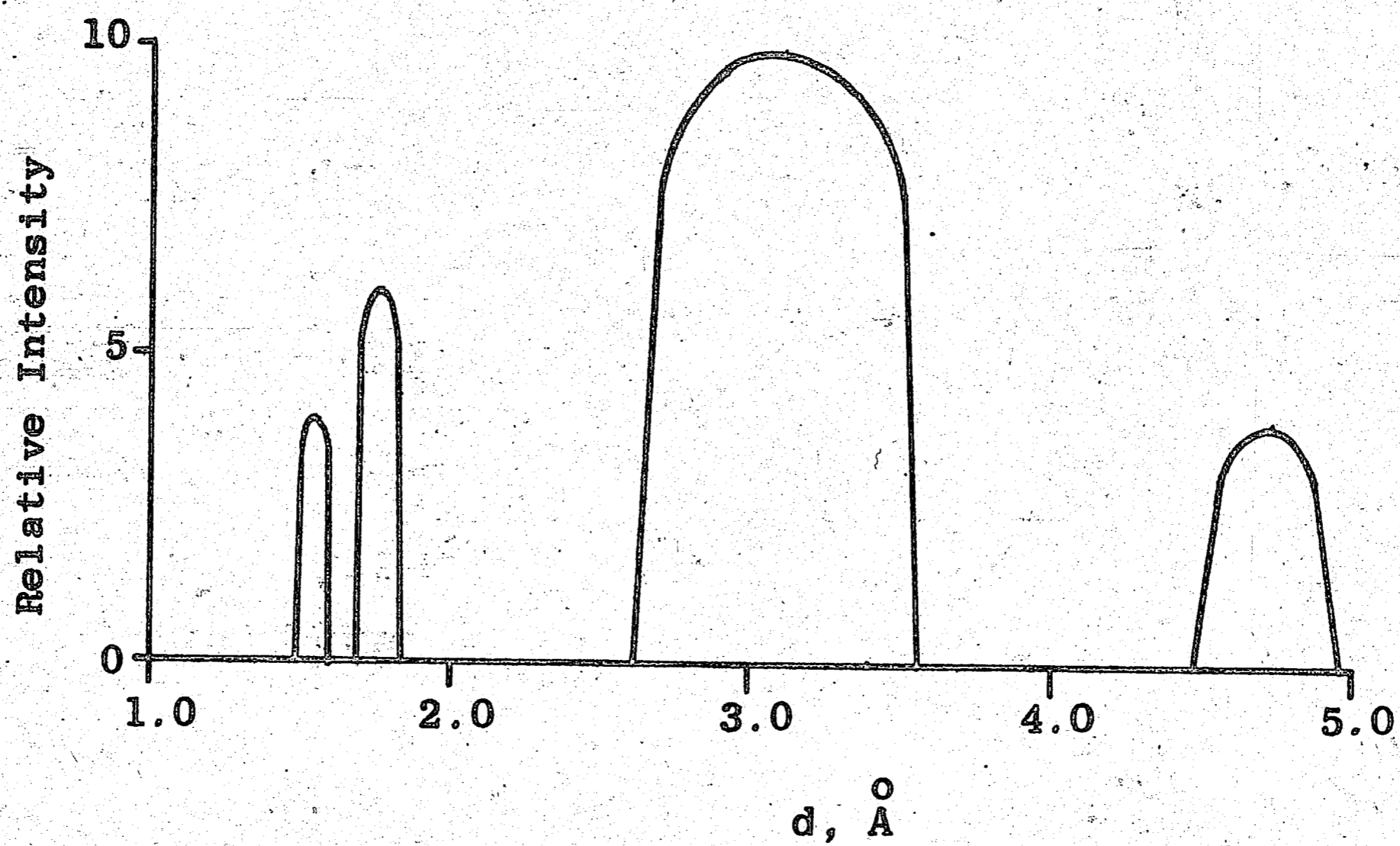


FIGURE 15 (a) Observed d-spacings for Unknown (Sample 165-5).

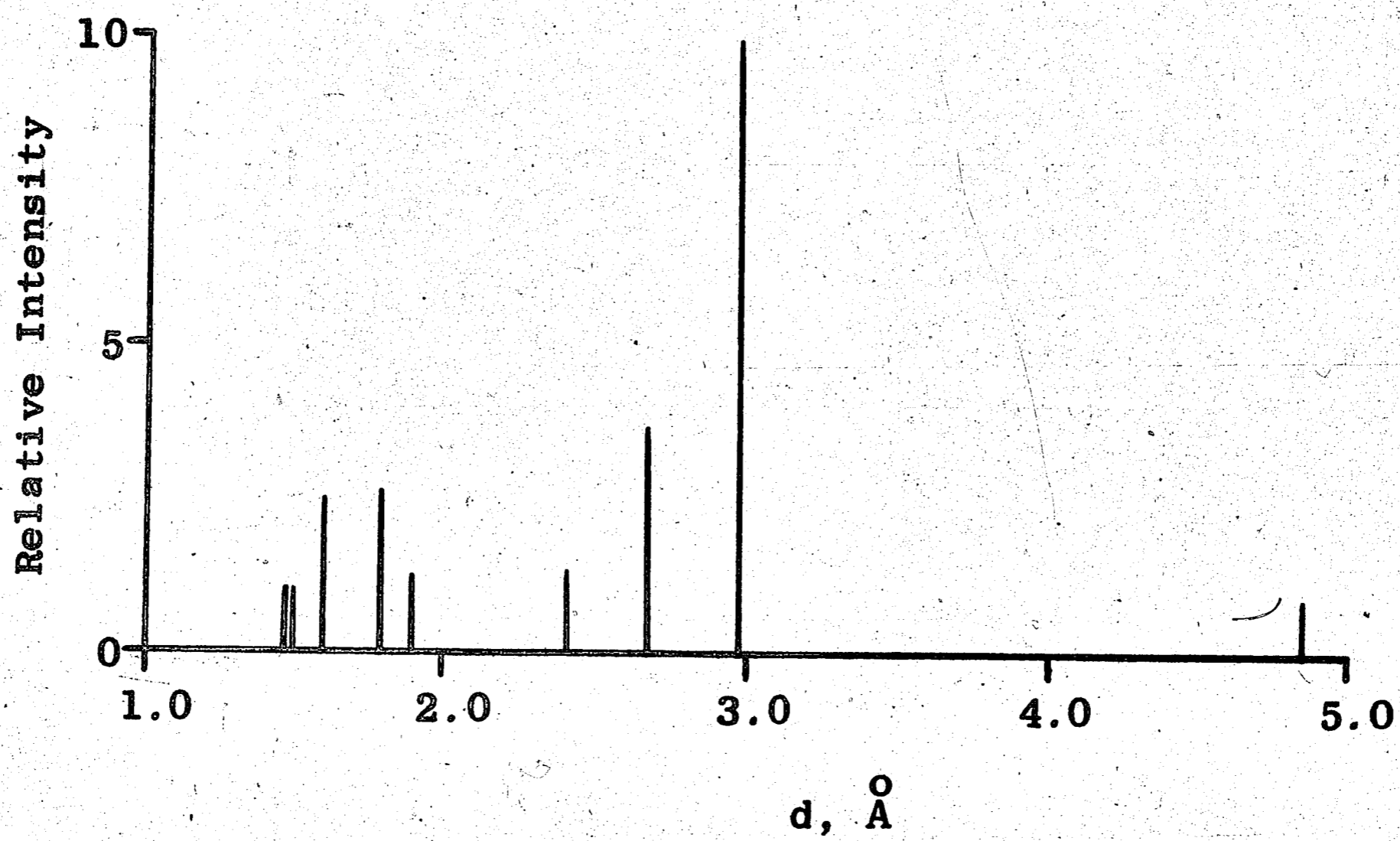


FIGURE 15 (b) X-ray Diffraction Data for SnO.

TABLE 1

X-ray diffraction data for the precipitate from a $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ solution.

$d, \text{\AA}$	$I/I_1, \text{ visual}$	$d, \text{\AA}$	$I/I_1, \text{ visual}$
5.98	40	1.98	20
5.62	40	1.78	20
4.55	20	1.74	10
3.56	100	1.69	10
3.31	60	1.62	10
3.00	70	1.568	10
2.80	90	1.474	10
2.51	50	1.197	10
2.41	20	1.126	10
2.28	10	0.8645	30
		0.8400	30

TABLE 2

X-ray diffraction data for the precipitate from a SnSO_4 solution.

<u>d, Å</u>	<u>I/I₁, visual</u>	<u>d, Å</u>	<u>I/I₁, visual</u>
5.96	40	1.93	30
5.59	40	1.91	30
4.54	20	1.82	10
3.54	100	1.77	20
3.30	60	1.73	10
2.98	80	1.68	10
2.80	90	1.62	10
2.50	40	1.561	10
2.40	30	1.533	10
2.28	20	1.471	10
1.98	10	1.397	10
		1.196	10
		1.119	10
		0.8647	30
		0.8399	30

TABLE 3

Amount of tin and chlorine deposited for various rinsing methods.

<u>Sample No.</u>	<u>Cl, μg</u>	<u>Sn, μg</u>	<u>moles of Cl \div moles of Sn</u>
1	0.258	9.03	0.10
2	0.077	9.62	0.03
3	0.385	11.60	0.11
4	2.608	20.10	0.43
5	-0.436	0.76	--
6	0.615	1.10	1.87

<u>Sample No.</u>	<u>Rinse Time</u>	<u>Type of Rinse</u>
1	1.0 min.	overflow, 1200 ml./min.
2	1.0 min.	overflow, 1200 ml./min.
3	1.5 min.	overflow, 800 ml./min.
4	0.5 min.	fixed volume, 400 ml.
5	5.0 min.	fixed volume, 5 beakers (250 ml. each)
6	0.5 min.	fixed volume, 250 ml.

TABLE 4

Electron diffraction data for the unknown on carbon before exposure.

Sample 165-5

<u>Band</u>	<u>d-spacing range, Å</u>	<u>d in center of band</u>	<u>I</u>
1	4.97 to 4.48	4.72	4
2	3.58 to 2.61	3.05	10
3	1.84 to 1.71	1.77	6
4	1.60 to 1.505	1.55	4

TABLE 5

Electron diffraction data for the unknown deposited on carbon and then exposed to ultraviolet light for 2 minutes (Sample 165-8).

<u>Line</u>	<u>d max, Å</u> ^o	<u>d min, Å</u> ^o	<u>d avg, Å</u> ^o	<u>I, visual</u>
1	3.47	3.17	3.32	10
2	2.84	2.56	2.70	8
3	1.84	1.71	1.78	8
4	1.52	1.43	1.48	4

TABLE 6

Optical density at 2500 Å versus total exposure time for invisible films in air at various relative humidities. (Temp.=24.5± 1.5° C).

<u>time, min.</u>	<u>Optical Density</u>			
	<u>(27.0%)</u>	<u>(36.5%)</u>	<u>(39.0%)</u>	<u>(46.5%)</u>
0	.0455	.0405	.0480	.0810
.5	.0440	.0375	.0460	.0750
1.0	.0420	.0360	.0450	.0750
2.0	.0395	.0340	.0420	.0700
4.0	.0365	.0310	.0350	.0640
8.0	.0325	.0240	.0310	.0570
16.0	.0255	.0220	.0260	.0510
26.0	.0235	.0210	.0250	.0490

<u>time, min.</u>	<u>Optical Density</u>			
	<u>(54.0%)</u>	<u>(66.3%)</u>	<u>(77.4%)</u>	<u>(79.0%)</u>
0	.0645	.0810	.0720	.1020
.25	.0625	.0740	.0650	.0930
.5	.0610	.0710	.0625	.0860
1.0	.0590	.0660	.0550	.0795
2.0	.0560	.0565	.0495	.0720
4.0	.0510	.0460	.0460	.0670
8.0	.0445	.0390	.0440	.0650
16.0	.0415	.0320	.0435	.0640

TABLE 7

Time to half-exposure for films in a nitrogen flushed atmosphere (35 S.C.F.M.). Each sample was held in the atmosphere for a "hold time" before being exposed.

<u>Relative Humidity</u>	<u>Hold Time, min.</u>	<u>t_{0.5}, min.</u>	<u>Sample No.</u>
47%	5	5.6	1/30/69-6
47%	10	6.5	1/30/69-1
46%	17	10.6	4/5/69-1
61%	17	8.1	1/25/69-1
13%	17	17.8	1/25/69-2

TABLE 8

Estimated particle sizes (t) for a film (Sample 165-8) after exposure to ultraviolet light.

<u>Line</u>	<u>δd, $\overset{\circ}{\text{A}}$</u>	<u>d, $\overset{\circ}{\text{A}}$</u>	<u>t, $\overset{\circ}{\text{A}}$</u>
1	-0.30	3.32	73
2	-0.28	2.70	52
3	-0.13	1.78	49
4	-0.09	1.48	49

APPENDIX

Estimated Values of K'_2 and K'_4 at 2,500 Å

If certain assumptions are made, estimated values of K'_2 and K'_4 can be calculated using

$$D = \frac{(K'_2 - K'_4)m_2 + K'_4 m_T}{\ln(10)} \quad (5)$$

The assumptions to calculate K'_4 are:

1. After long exposure times m_2 is zero and $m_4 = m_T$.
2. The average amount of tin present is $4\mu\text{g./cm.}^2$
3. One mole of the tin(IV) product of the reaction contains one mole of tin.
4. The average value of D for fully exposed films is 0.0334.

This is obtained by averaging the final values of D listed in Table 6.

The total area of the unknown consists of two layers (one on each side of the quartz) with diameters of 1.26 cm. Thus the amount of tin in moles is

$$m_T = \frac{4\mu\text{g. Sn/cm.}^2}{118.7 \text{ g. Sn/mole}} \cdot 2\pi \left(\frac{1.26\text{cm.}}{2}\right)^2 = 0.084\mu\text{mole}$$

When m_2 is zero (5) reduces to

$$D = \frac{K'_4 m_T}{\ln(10)}$$

and thus

$$K'_4 = \frac{(0.0334)(2.303)}{0.084 \times 10^{-6} \text{ mole}} = 9.2 \times 10^5/\text{mole.}$$

The assumptions to calculate K'_2 are:

1. One mole of the tin(II) compound contains one mole of tin.
2. The average value of D for unexposed films is 0.668. This is obtained by averaging the initial values of D in Table 6.
3. The freshly prepared film consists of 100% tin(II) compound (Case I) to 50% tin(II) compound (Case II). This wide range is used to account for oxidation during sample preparation.

For Case I, m_4 is zero and since $m_2 + m_4 = m_T$ (5) reduces to

$$D = \frac{K'_2 m_T}{\ln(10)}$$

and thus

$$K'_2 = \frac{(0.0668)(2.303)}{0.084 \times 10^{-6} \text{ mole}} = 1.84 \times 10^6 / \text{mole}.$$

For Case II, $m_2 = m_4 = m_T/2$ and (5) reduces to

$$D = \frac{(K'_2 + K'_4)m_T/2}{\ln(10)}$$

and thus

$$K'_2 = \frac{2(0.0668)(2.303)}{0.084 \times 10^{-6} \text{ mole}} - 9.2 \times 10^5 / \text{mole} = 2.76 \times 10^6 / \text{mole}.$$

The ratio of K'_2 to K'_4 is thus in the range of 2.0 to 3.0.

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