

THE STRUCTURE AND
OPTICAL PROPERTIES OF GOLD
BLACK -- A GOOD SOLAR
RADIATION ABSORBER

A THESIS
PRESENTED TO
THE FACULTY OF THE DEPARTMENT OF PHYSICS
UNIVERSITY OF HOUSTON

IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE
MASTER OF SCIENCE

BY
CHARLES MICHAEL DOLAND

AUGUST 1977

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ABSTRACT

Samples of gold black were prepared under a variety of conditions. The structural and optical properties of the gold blacks were measured and are compared to the Drude theory. The properties of the gold blacks are also correlated to the conditions of preparation of the gold black samples.

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I INTRODUCTION

In recent years, the continual depletion of oil and gas reserves has generated interest in alternate energy sources. The sun is one of the most promising of these alternate energy sources. Solar energy reaches the Earth as radiant energy which must be converted into some other form of energy for most applications. Thermal energy is one of the most commonly used forms of energy, and conversion of solar radiant energy to heat energy is easily accomplished. The research described herein was undertaken in order to better understand the processes which could be used to effectively convert solar radiant energy to useful heat energy.

Of the many schemes for utilization of solar energy, the methods which seem most practical for immediate implementation are generally systems employing conversion of solar energy to thermal energy. Many small, low efficiency systems of this type have been produced for various purposes, including a number of solar water heaters which are presently on the market for home use.¹ A large scale, high efficiency solar-thermal system called the central receiver system is presently under study by several institutions.² Each solar-thermal system uses a medium, called a solar radiation absorber, which converts incident radiant energy into heat energy. The efficiency of a solar-thermal system is strongly dependent on the properties of the solar radiation absorber used in the system. For this reason, there is considerable interest in development of materials which are good radiation absorbers.

Previous work has shown that a class of materials termed "metal blacks" have properties which make them possible candidates for use as solar radiation absorbers. Metal blacks consist of small particles of a conductor in a low density structure of connected particles. Most metal blacks can be produced by the technique of inert gas evaporation. With this technique, metal blacks with a range of properties can be produced by preparing the samples under different evaporation conditions. The following experimental work was carried out on one of the most extensively studied metal blacks, gold black:

- (i) gold black samples were produced under controlled conditions,
- (ii) the structure of the samples was studied, and
- (iii) several structural and optical properties of the samples were measured for different conditions of preparation.

The results of the experiments were compared to theoretical predictions.

II PURPOSE

In this section, the role of solar radiation absorbers in the utilization of solar energy is briefly discussed. First, the characteristics of solar radiation available at the surface of the Earth are presented. The different types of solar energy systems are briefly described, and the requirements for a good solar radiation absorber are discussed.

A. Solar Radiation

The spectrum of the radiation emitted by the sun can be approximated by blackbody radiation for about 5760° K. There are many features of the solar spectrum which are neglected in this approximation, including absorption lines in the visible to near ultraviolet, emission lines in the ultraviolet to soft x-ray regions, and nonthermal radio emission. These features are caused by the structure of the solar atmosphere, and they are not very important for the utilization of solar energy since about 98% of the radiant energy from the sun is in the wavelength region of 0.25 to $3.0\text{ }\mu\text{m}$.³ Above the Earth's atmosphere, the energy flux of solar radiation is about 1.36 kilowatts per square meter. This value is called the solar constant, and it is denoted by K.

The Earth's atmosphere has a significant effect on the solar radiation arriving at the surface. We distinguish two different components of solar radiation at the surface of the Earth. One component is the direct radiation, which is the radiation which has passed through the

Earth's atmosphere without being scattered. Indirect radiation, the other component, is the scattered radiation. The indirect radiation is diffuse, coming from the entire sky, while the direct component is well collimated, since the disk of the sun has an angular diameter of about one half of a degree of arc at the Earth's surface.

In addition to scattering by air molecules, water droplets, and airborne particles, solar radiation is also absorbed by air molecules. This absorption affects both direct and indirect radiation. The wavelength regions where the molecular absorption is most important are the near ultraviolet and near infrared regions. The absorption in these regions is mainly due to carbon dioxide (CO_2), water vapor (H_2O), and ozone (O_3), and the concentrations of these constituents of the Earth's atmosphere may vary.

The amount of air through which incident radiation must travel before reaching the surface of the Earth depends on many factors, including the position of the sun in the sky, the altitude of the observation point, and the weather conditions. This quantity is a minimum when the sun is at the zenith, and this value is called one air mass (written AM1) for an observation point at sea level under standard conditions. The position of the sun in the sky depends on the time of day, the season, and the latitude of the observation point.

Weather can strongly alter the amount of direct radiation at a point, as when a cloud passes between the point and the sun, reducing direct radiation to near zero. It can also affect the concentrations of particles and water droplets in the air, as well as the amount of

Table 1Characteristics of Direct Solar Radiation

<u>Characteristic</u>	<u>Above Atmosphere</u>	<u>Typical Surface</u>
Air Mass	AM0	AM2
Total Energy Flux	1360	755 $\frac{\text{watts}}{\text{m}^2}$
98% Energy Limits (Spectral)	0,25 to 3,0	0,30 to 2,0 μm

air (the number of air masses) through which the incident solar radiation must pass. Because of the variability of the weather and other factors affecting the amount of sunlight reaching the surface of the Earth, there is no fixed value for the energy flux available at the surface. An average value representing daytime conditions for a cloudless area is the flux for air mass two (AM2), about 755 watts per square meter, here denoted by K_2 . For this air mass, about 98% of the radiant energy has wavelengths between 0.30 and 2.0 μm .⁴ See Table 1 for a summary of characteristics of solar radiation.

B. Solar Energy Systems

Types of Systems

There are many types of systems which have been suggested as possible methods for utilization of solar energy. These systems may be classified by the form of energy to which the solar radiation is first converted, as follows:

- (a) photovoltaic systems,
- (b) photochemical systems,
- (c) solar-thermal systems, and
- (d) indirect systems.

The fourth class includes systems which make use of the effects of solar radiation on the environment, rather than using the solar radiation directly.

Photovoltaic systems involve the direct conversion of solar radiation to electrical energy. Such systems have the advantage of being

very simple and reliable. Silicon photocells with efficiencies of about 15% can be produced at present,⁵ and gallium arsenide (GaAs) photocells of higher efficiency may be developed in the near future. However, both types are limited to theoretical maximum efficiencies of about 25%.⁶ Due to the high cost of materials, these systems are expensive, about \$2000 per square meter for silicon, and more for GaAs. Another drawback is that the direct current output of these devices must be converted to alternating current for transmission along the conventional power grid. There are possibilities for improvements in the future, however. The use of polycrystalline cells may dramatically reduce costs, and the use of concentration with high efficiency cells may result in a slightly more complicated system with a substantially lower cost.

The systems of the second class utilize conversion of solar radiation to chemical energy, with subsequent release of the chemical energy, possibly at a different time or place. This type of system has received less attention in the past than the other types, so there is little information about the feasibility of such systems. Further research on light activated reactions may determine the possibilities for use of these systems.

The third class includes systems which initially convert solar radiant energy to heat energy. The resulting thermal energy may be used for many different purposes, including, for example, space heating or electrical power generation. A large variety of systems, delivering heat at many different temperatures, is contained in this class. These systems are discussed more fully below.

Some power generation systems which are not usually associated with solar energy are actually in the fourth class. Hydroelectric power generators, for example, draw power from the flow of water, which is an indirect result of solar radiation. Wind power, which has been successfully used in the past for a few applications, is another example. The variability of winds and high cost per unit output of wind powered generators are drawbacks, but attempts are being made to solve these two problems.⁷ A scheme to use the thermal gradient of the oceans utilizes solar energy collected over a large area, but this system has an extremely low Carnot efficiency and also has the problem of transportation of the energy from the floating power plant to the user.⁸ A final example of a system in this class is the bioconversion of solar energy to chemical energy. Plants would be grown and subsequently burned to yield heat energy. Even very high yield crops have extremely low conversion efficiencies, although the initial capital cost of such a system is expected to be low. Furthermore, a substantial time period is required after initiation of a project of this type before useful energy is available.

Solar-Thermal Systems

It is well known that solar radiation is easily converted to heat energy. On a sunny day, black or darkly colored objects may become quite hot to the touch. The conversion of solar energy to heat energy by a solar absorber is the basis of the solar-thermal systems. Different systems can provide heat at a wide variety of temperatures for different applications.

Solar-thermal systems providing heat at low temperatures (25° to 50° C above ambient) can be used for space heating. Slightly higher temperatures (50° to 75° C above ambient) are needed for home water heating. Solar produced steam, at temperatures up to 300° C, could be used to provide process heat for industry. Conventional steam powered electrical generators could operate using solar heat at temperatures of 250° C to about 600° C. The higher temperatures are desirable because of the higher Carnot efficiencies possible at these temperatures. Another possible use for solar heat is for thermochemical energy conversion. Temperatures as high as 1000° C may be required, but the resulting chemical energy may be able to be easily stored or transported to the user. The storage feature is particularly desirable, since all solar energy systems collect energy only during the daytime.

The temperature at which heat can be extracted from a solar energy collector depends on the balance of energy incident on the collector and the energy flow out of the collector. The incident energy flux may be increased by the use of concentrations, i.e., reflecting or refracting solar radiation from a large area onto a smaller area. The energy flow out of the collector is the sum of the useful heat energy extracted from the collector and the following types of losses:

- (a) reflection.
- (b) reradiation, and
- (c) convection.

The last two of these types of losses are temperature dependent, the losses increasing as the collector temperature is increased in both cases.

Since the first two types of losses involve the optical properties of the collector, a few relevant parameters are introduced here. The spectral reflectivity $R(\lambda)$ and spectral emissivity $e(\lambda)$ for a given surface are related to the solar reflectivity R_s and thermal emissivity $e(T)$ for a given temperature T as follows:

$$R_s = \int_0^\infty F(\lambda) R(\lambda) d\lambda / \int_0^\infty F(\lambda) d\lambda \quad (1)$$

$$e(T) = \int_0^\infty G(\lambda, T) e(\lambda) d\lambda / \int_0^\infty G(\lambda, T) d\lambda \quad (2)$$

where $F(\lambda)$ is the solar spectral distribution function, and $G(\lambda, T)$ is the Planck blackbody radiation spectral distribution function for the temperature T . Note that $F(\lambda)$ is significantly different from zero only for λ between 0.3 and 2.0 μm for AM2 radiation.

The Planck blackbody distribution function is given by:

$$G(\lambda, T) = 2 h c^2 \lambda^{-5} [\exp(hc/\lambda kT) - 1]^{-1} \quad (3)$$

where h is Planck's constant, c is the velocity of light in a vacuum, and k is Boltzmann's constant. We also note that

$$e(\lambda) = 1 - R(\lambda). \quad (4)$$

We define the solar absorptivity A_s of a surface as follows:

$$A_s = 1 - R_s = \int_0^\infty F(\lambda) [1 - R(\lambda)] d\lambda / \int_0^\infty F(\lambda) d\lambda \quad (5)$$

The concentration ratio C of a collector system is defined to be the ratio of the energy flux incident on the collector surface to the flux available at the Earth's surface normal to the direction of the sunlight.

The efficiency of conversion of solar energy to heat energy is given by the thermal output of the system divided by the incident radiant energy. In general, with proper design of the collector, losses due to convection can be reduced to values from one to ten percent of the incident energy. Reflection losses can also be reduced to ten percent or less. Thus, thermal reradiation limits the temperature of operation of the collector in most cases. For flat plate collectors (for which C is about one), which are perfect black bodies ($R_s = 0$, $e(\lambda) = e(T) = 1$), the collector is limited to approximately 100°C for AM2 radiation. Somewhat higher temperatures may be obtained by reducing $e(T)$, while keeping A_s near one, but the efficiency of flat plate collectors is low if they are operated at temperatures exceeding 100°C even if the selective surfaces presently available are used. Temperatures exceeding 300°C can only be obtained by use of concentration of the incident radiation. High concentration ratio systems will probably be able to deliver heat efficiently at temperatures over 400°C , and reasonably high Carnot efficiencies can be realized at these temperatures.

Central Receiver Concept

A type of solar-thermal system presently under consideration having a very high concentration ratio is called the central receiver system. This system employs a large number of independently directed heliostats which reflect sunlight onto a central radiation receiver. The field of heliostats will be large (one square kilometer or larger),

so that the central receiver will need to be mounted on a tower 100 to 500 meters tall. Concentration ratios of up to 1000 should be obtainable for a large system, so that collector temperatures in the range of 250 to 700° C will be possible.²

The central receiver concept has a number of advantages, some of which have already been mentioned. Since all of the solar-thermal energy conversion takes place at the central receiver, this system does not require extensive circulation of the working fluid as in distributed systems. In addition, the cost will not be as high as for most solar energy systems, since conventional steam powered generation equipment could be used for generation of electrical power with such a system, and the heliostats can be made of a low cost reflecting material. This type of system may also be able to power a thermal-chemical conversion process, which could provide a means of energy storage.

Central receiver systems also have a number of disadvantages. Each heliostat must be provided with a mechanical drive to track the sun on two axes, and the cost of these devices may be a substantial portion of the total system cost. The central receiver will need to be constructed to withstand severe thermal cycling, as when clouds pass over the heliostat field or at sunrise and at sunset. The frequency of cycling may be high in cloudy or occasionally cloudy regions, but even in areas with no clouds, there will be at least one thermal cycle per day. One of the major problems of a central receiver system used for the generation of electrical power is the need for some type of energy storage. Solar energy is available for use in such a system only on clear days,

so an alternate energy source is needed at nights and on cloudy days. Methods under consideration for this storage include thermal energy storage and thermal-chemical energy conversion.

The thermal power available from a central receiver system depends on several factors. The effective area of the heliostats normal to the direction of the incident radiation is denoted by A_h . We let R_h stand for the solar reflectance of the heliostats, and let E be the efficiency with which the central receiver converts the incident solar radiation into heat energy. Then, the total power available at the central receiver P_{th} is given by the following equation:

$$P_{th} = K_2 A_h R_h E \quad (6)$$

where we have assumed AM2 incident radiation. Since the heliostat cost is expected to be the major cost for such a system,² a modest improvement of 5% in E , for example, can reduce the system cost by about 5% for a fixed thermal output. The value of R_h will be a tradeoff between cost, durability, and reflectivity, while the cost of the central receiver radiation absorber will probably be small.

C. Solar Radiation Absorbers

Interaction of Radiation with a Medium

The interaction of electromagnetic radiation with a material can be described by the complex dielectric function $\epsilon(\omega)$ of the material, where ω is the angular frequency of the radiation. The imaginary part of $\epsilon(\omega)$ can be related to the conductivity σ of the medium by the equation (in Gaussian units):

$$\text{Im}[\epsilon(\omega)] = 4 \pi \sigma / \omega \quad (7)$$

The reflection coefficient or reflectivity $R(\omega)$ and the absorption coefficient $\alpha(\omega)$ are of particular interest for conversion of radiation to thermal energy. The reflection coefficient for a plane wave normally incident on a plane surface between media characterized by $\epsilon(\omega)$ and $\epsilon'(\omega)$ is given by the following equation:

$$R(\omega) = \left| (\sqrt{\epsilon} - \sqrt{\epsilon'}) / (\sqrt{\epsilon} + \sqrt{\epsilon'}) \right|^2 \quad (8)$$

The radiant energy flux S of the wave transmitted through the boundary is given by the equations:

$$S = S_0 [1 - R(\omega)] e^{-\alpha(\omega) z} \quad (9)$$

$$\alpha(\omega) = 2 \omega \operatorname{Im}[\sqrt{\epsilon'(\omega)}] / c$$

where S_0 is the incident energy flux, $[1 - R(\omega)]$ is the transmission coefficient of the surface, and z is the distance from the plane boundary between the two media. We have assumed that there is no absorption in the first region, i.e., $\epsilon(\omega)$ is real. Equations (9) are valid for oblique angles of incidence as well, if the correct reflection coefficient is used.

Efficiency of a Solar Radiation Receiver

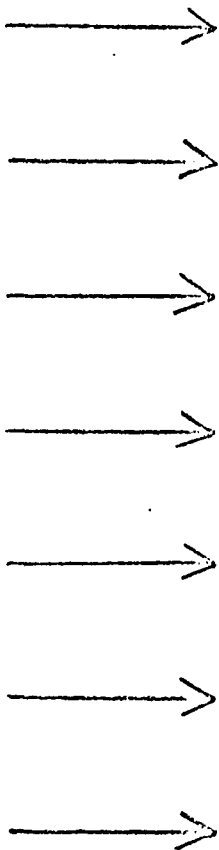
We next consider the factors which determine the efficiency with which a solar radiation absorber converts radiant energy to thermal energy. We consider the model of a radiation receiver pictured schematically in Figure 1. Solar radiation is incident on the solar absorbing film of thickness t coating the radiation receiver. The incident radiation interacts with the solar absorber and is partially converted into thermal energy. This energy is transferred by conduc-

Figure 1

Schematic Diagram of Radiation

Receiver Surface

Solar
Radiation



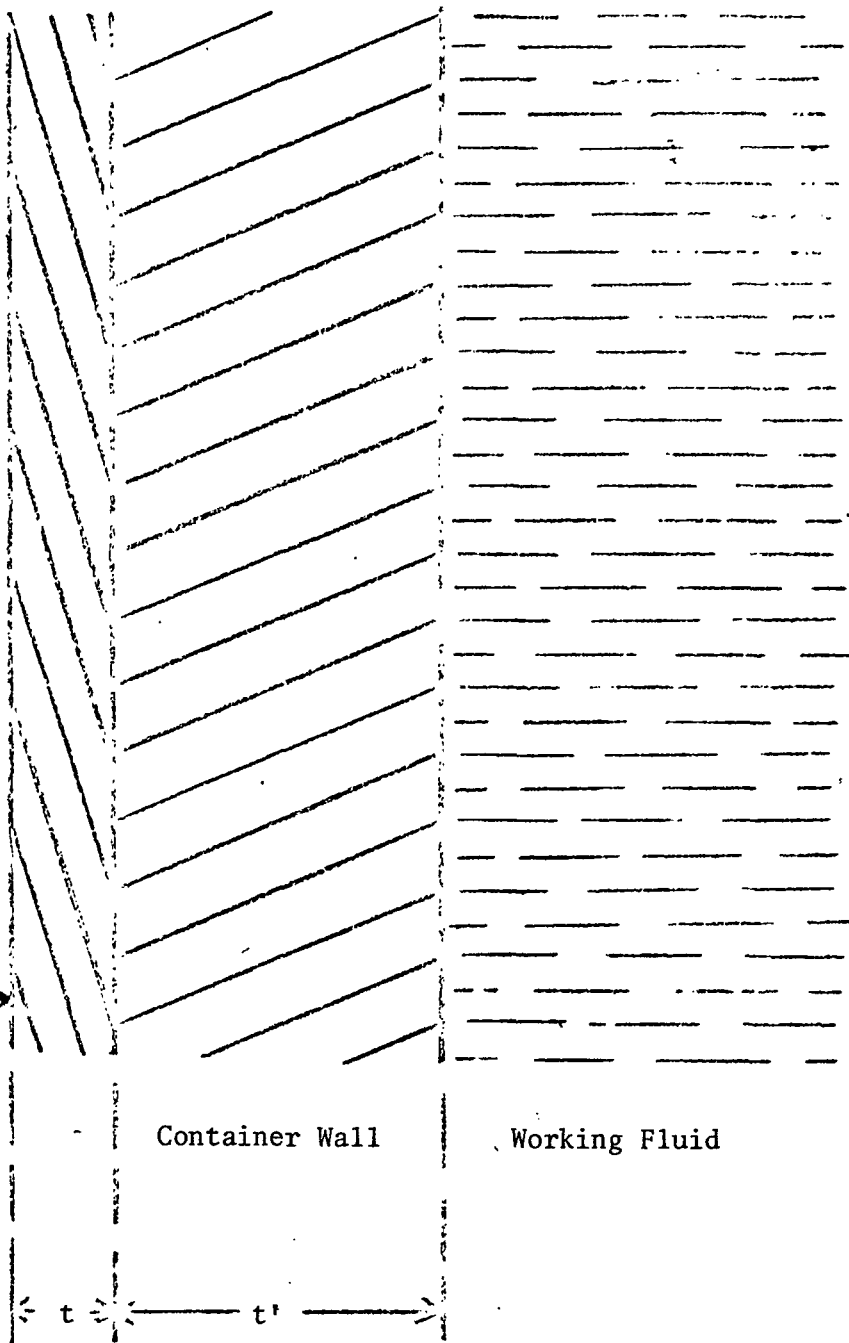
Solar Radiation
Absorber



Container Wall

Working Fluid

t t'



tion through the solar absorber film and container wall into the working fluid. We consider here the efficiency with which the incident radiant energy is converted to thermal energy in the working fluid.

There are several mechanisms by which energy can be lost from the radiation receiver, as mentioned above. A portion of the incident radiation will be reflected from the receiver. The absorber surface will also lose energy by radiation and convection, since it is at an elevated temperature. Note that it is desirable to minimize the temperature drop from the absorber surface to the working fluid for the following reasons:

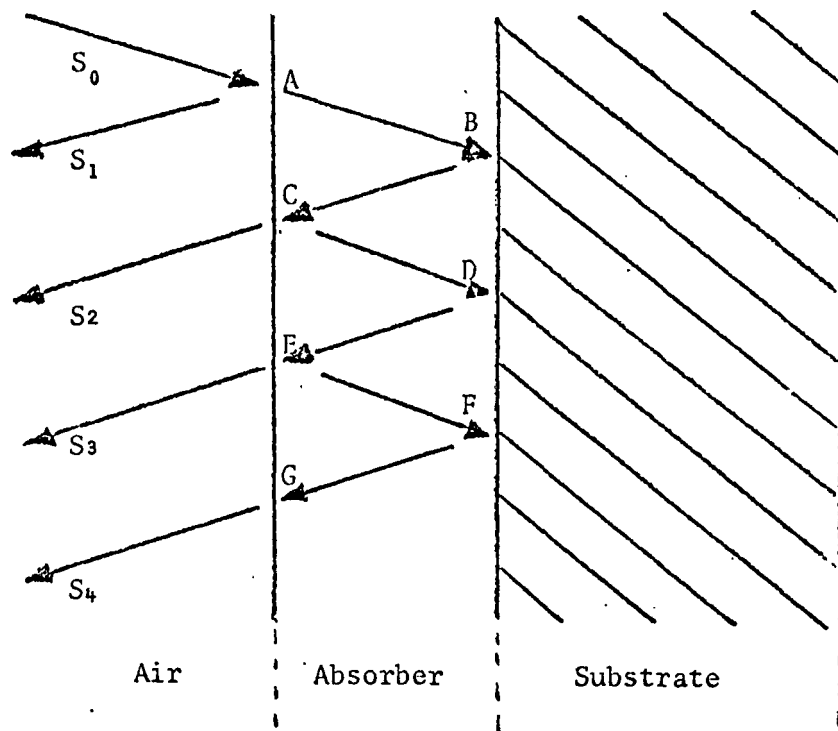
- (i) the energy lost by convection and radiation will be minimized, and
- (ii) the absorber material will be required to withstand a lower temperature for a given working fluid temperature.

The fraction of the incident solar radiation reflected from the radiation receiver (denoted by R_s) depends on the optical properties of the container wall and the absorber, and on the thickness t of the absorbing film. As shown in Figure 2, we consider multiple reflections from the absorber-air and absorber-substrate surfaces. For simplicity, we consider only one wavelength of radiation at a time, and let R represent the reflection coefficient of the receiver surface for this wavelength of light. The reflection coefficient for the absorber-air interface is denoted by R_a , and R_c denotes the reflection coefficient from the absorber-substrate surface. The substrate is considered to be opaque, and α is the absorption coefficient of the absorber.

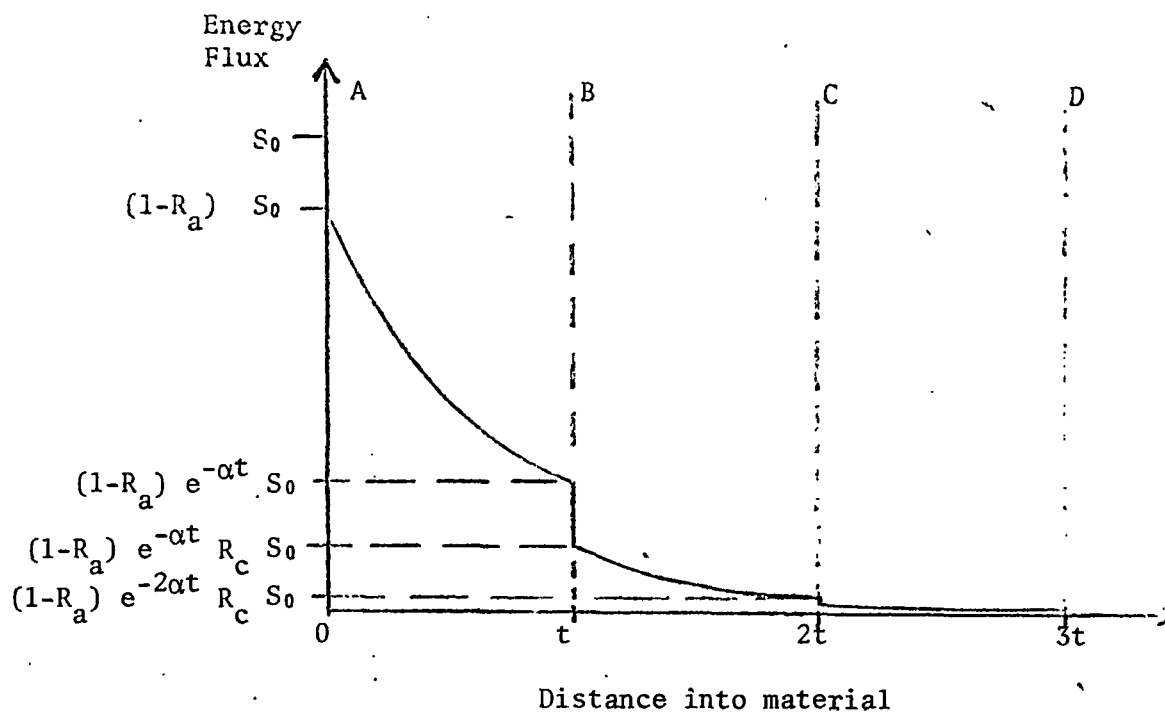
Figure 2

(a) Multiple Reflections at the Collector Surface

(b) Energy Flux in the Film



(a)



(b)

Let $S_1, S_2, S_3, \dots$ represent the energy flux in the various reflected beams, as shown in Figure 2. We can neglect interference between the beams, if we require that $S_2 \gg S_3 \gg S_4 \gg \dots$, although we could have used interference to control R if this condition was not satisfied. (Antireflection coatings generally use this interference to reduce the reflection coefficient of a surface.) We then have the following equations:

$$\begin{aligned} S_1 &= R_a S_o \\ S_2 &= (1 - R_a)^2 R_c e^{-2\alpha t} S_o \\ &\vdots \\ S_n &= (1 - R_a)^2 R_c^{n-1} e^{-2(n-1)\alpha t} S_o \\ &\vdots \end{aligned}$$

Hence $S_n \ll S_2$ for all $n > 2$ if $R_c e^{-2\alpha t} \ll 1$. Since R_c is less than or equal to one, this condition is met if the following inequality is satisfied:

$$\alpha t \gg 1 \quad (10)$$

Then, neglecting interference between S_1 and S_2 we obtain:

$$\begin{aligned} R &= (S_1 + S_2) / S_o \\ R &= R_a + (1 - R_a)^2 R_c e^{-2\alpha t} \end{aligned} \quad (11)$$

From this equation, it is evident that R_c is relatively unimportant compared to R_a if condition (10) is satisfied.

If we let T_a be the temperature of the absorber surface, and let S_c be the power loss per unit area due to convection, then the efficiency E of the receiver is given by the equation:

$$E = 1 - R - (S_c/S_o) - \sigma e(T) T^4 \quad (12)$$

where $\sigma = 5.669 \times 10^{-8}$ watts $m^{-2} \text{ } ^\circ K^{-4}$.

Criteria for a Good Solar

Radiation Absorber

The incident radiant flux at a solar collector surface determines not only the temperatures achievable by the system, but also some of the requirements for the solar radiation absorber. In order to be brief, only extremes of radiant flux are considered. At the low end of the scale is the low concentration ratio regime, having C approximately equal to one. At the other extreme, we consider a central receiver system, with C equal to about 500.

For the low concentration ratio regime, low cost flat plate or fixed concentrating collectors can be used for low temperature applications. For temperatures above about 100°C , selective absorbers are necessary. A selective absorber is a material which has a higher reflectance in the infrared than in the visible, resulting in a value of A_s higher than $e(T)$. Selective absorbers can be produced by several techniques. One technique employs a good infrared reflector coated with a film which is transparent in the infrared, but a good radiation absorber in the visible. The net result is a good absorber for visible wavelengths and a reflector for the infrared, as desired.⁹

The central receiver system will require substantial capital investments, but temperatures of 400°C or higher will be possible, allowing fairly high Carnot efficiencies. For such a system, the maximum efficiency possible is desirable to best utilize the large investment. The high temperatures and large energy fluxes through the absorber severely limit the types of materials which may be used as solar radiation absorbers.

One problem associated with solar absorbers for high fluxes is the need for high thermal conductivities. Referring to Figure 1, the temperature drop T_d across the absorber is given by:

$$T_d = S_o \cdot t / K_a \quad (13)$$

where S_o is the energy flux at the absorber, t is the absorber thickness, and K_a is the thermal conductivity of the absorber. We have assumed that most of the radiation is absorbed near the surface of the absorber, and this is justified if equation (10) is satisfied. For a central receiver system with $C = 500$, $S_o = K_2 C = 3.77 \times 10^5$ watts per square meter. Requiring that $T_d \leq 50^\circ \text{C}$, then

$$S_o \cdot t / K_a \leq 50^\circ \text{C}. \quad (14)$$

Since we also require that $t \geq 1/\alpha$, the absorber material must satisfy the following requirement:

$$\alpha K_a \geq S_o / T_d = 7340 \text{ watts m}^{-2} \text{ }^\circ\text{C}^{-1}. \quad (15)$$

We can summarize the criteria for a solar absorber for a central receiver system as follows:

- (i) $R_a(\lambda) \ll 1$ over the solar spectrum,
- (ii) $K_a \alpha(\lambda) \geq 7.34 \times 10^3 \text{ watts m}^{-2} \text{ }^\circ\text{C}^{-1}$ over the solar spectrum, and
- (iii) the material must be able to withstand temperatures of about 500°C or higher and severe thermal cycling.

Note that for a central receiver system having a black absorber at 500°C , the radiated energy flux of $\sigma T^4 = 20.2$ kilowatts per square meter is small compared to the incident flux of 377 kilowatts per square meter, so that a selective absorber is not needed. Higher concentration ratios will result in a smaller percentage radiation loss, but higher values of K_a are required. At lower concentration ratios, selective surfaces may be required for a high thermal efficiency at these temperatures.

III BACKGROUND -- METAL BLACKS

A. Description

Metal blacks are a class of materials which have some of the properties desired for a good solar radiation absorber. As the name implies, these materials appear black, that is, they reflect little of the visible light incident on them. Since the solar spectrum peaks near the center of the visible spectrum, they have high solar absorptances. The optical properties of the metal blacks are strongly related to the structure of these materials.

A number of different metal blacks have been produced by several different techniques, but they appear to have similar structures. Metal blacks are low density materials, consisting of small electrically conducting particles. There is electrical contact between the particles in most of the blacks. The presence of insulating materials in a metal black can cause substantial changes in the optical properties of the material. Metal blacks may have densities of about 10^{-2} to 10^{-3} of the pure metal density.

An approximation to the complex dielectric function for a metal black of low electrical conductivity is derived in Appendix A. The result is the following:

$$\epsilon(\omega) = 1 + \delta_a + f \delta_o - \frac{4 \pi \sigma g \gamma_o'}{(\omega^2 + \gamma_o'^2)} + i \frac{4 \pi \sigma g \gamma_o'^2}{\omega(\omega^2 + \gamma_o'^2)} \quad (16)$$

(valid for $\lambda = .35$ to $2.5 \mu\text{m}$ and $g\sigma \ll 4.3 \times 10^{14} \text{sec}$) where

$1 + \delta_a$ is the dielectric function of air (assumed real),

f is the packing fraction of the black,

δ_o is a parameter of order unity,

σ is the d.c. electrical conductivity of the pure metal,

ω is the angular frequency of the radiation,

γ_o' is the effective damping coefficient for the free electrons in the metal black, and
 g is a parameter such that $g\sigma$ is the conductivity of the metal black.

Here, $\delta_a = 5.6 \times 10^{-4}$, and $\gamma_o' = (f/g) \gamma_o$, where γ_o is the damping coefficient for free electrons in the pure metal. The damping coefficient γ_o is related to the relaxation time τ by $\gamma_o = 1/\tau$. Equation (16) is only an approximation, since such effects as polarization of the material and inter- and intra-band transitions have been neglected.

In Appendix A, the above equation is used to calculate expressions for $R(\omega)$ and $\alpha(\omega)$ for a metal black. The results are the following:

$$R(\omega) = \frac{1}{4} \left[\left(\frac{f \delta_o}{2} - \frac{2 \pi \sigma g \gamma_o'}{\omega^2 + \gamma_o'^2} \right)^2 + \left(\frac{2 \pi \sigma g \gamma_o'^2}{\omega(\omega^2 + \gamma_o'^2)} \right)^2 \right] \quad (17)$$

$$\alpha(\omega) = \frac{4 \pi \sigma g \gamma_o'^2}{c(\omega^2 + \gamma_o'^2)} \quad (18)$$

In order to obtain an approximate value for γ_o' to simplify these equations, we consider the values of f and g for one of our samples.

For sample #18a, $f = 6.86 \times 10^{-3}$, and $f/g = 960$. Hence, $\gamma_o' = 6.80 \times 10^{16} \text{ sec}^{-1}$. We consider the near infrared range, where ω is between 7.54×10^{14} and $2.69 \times 10^{15} \text{ sec}^{-1}$. Then ω^2 is much smaller than $\gamma_o'^2$, so we can neglect ω^2 compared to $\gamma_o'^2$. With this approximation, we obtain the following:

$$R = \frac{1}{4} \left[\left(\frac{f \delta_o}{2} - \frac{2 \pi \sigma g}{\gamma_o'} \right)^2 + \left(\frac{2 \pi \sigma g}{\omega} \right)^2 \right] \quad (19)$$

$$\alpha = \frac{4 \pi \sigma g}{c} = \frac{4 \pi \sigma}{c} \frac{f}{(f/g)}, \quad (20)$$

for $\lambda = .7$ to $2.5 \text{ } \mu\text{m}$. Since $2 \pi \sigma / \gamma_o' = 66.0$ and $f/g = 960$, we find:

$$R = \frac{1}{4} \left[\left(\frac{f \delta_0}{2} \right)^2 + \left(\frac{2 \pi \sigma g}{\omega} \right)^2 \right] \quad (\lambda = .7 \text{ to } 2.5 \text{ } \mu\text{m}) \quad (21)$$

The second term in the brackets is small, except for long wavelengths, since $2 \pi \sigma / \omega$ is less than or equal to 537. For sample #18a, we expect $R = \frac{1}{16} f^2 \delta_0^2 = 2.94 \times 10^{-6} \delta_0^2$. Low reflection coefficients are characteristic of metal blacks, although reported reflection coefficients may be as high as about one percent.

B. Methods of Production

Several techniques may be used to produce metal blacks. Some metal blacks may be produced by evaporation of the metal in an inert gas. Others can be made by electrodeposition from an appropriate solution. Carbon black, which can be considered a metal black since carbon is a good conductor, can be collected as soot from an acetylene flame.

The first technique, inert gas evaporation, may be carried out in the laboratory as follows: A sample of the metal is placed inside a chamber which can be filled with a high purity inert gas at a pressure of about 1 to 10 torr. Then, the sample is heated in the inert gas until evaporation begins. Small droplets of metal condense out of the vapor and coalesce. The resultant particles are collected on a cooled substrate. The formation of these particles is described in reference 10.

There are a number of advantages afforded by this technique. Many different types of metal blacks may be produced by this method, including aluminum, antimony, gold, silver, and zinc,¹¹ and others may be added to this list in the future. The metal blacks prepared by inert gas evaporation are extremely clean, since they are prepared

in a closed chamber filled with a high purity inert gas. Most of the data available on metal blacks at present pertains to samples produced by this technique.

Electrodeposition has been used to produce metal black samples of high melting point materials. This method uses an electric current to deposit small particles of the metal from a solution onto an electrically conducting substrate. Platinum black samples have been produced by this technique for catalysis research as well as for the absorption of radiation.¹¹ Recently, a type of chromium black produced by electrodeposition has generated interest as a possible high temperature solar radiation absorber.¹²

Carbon, in the form of graphite, is a good conductor of electricity, having a conductivity of about 1.15×10^{-3} times that of silver, the metal having the highest electrical conductivity. Small particles of carbon can be produced by burning acetylene in air. The soot from such a flame can be easily collected on a substrate. This technique is undoubtedly the simplest and least expensive of the three mentioned here.

C. Review of Prior Data

Particle Data

There is a substantial amount of published data concerning the sizes of particles produced by inert gas evaporation under different conditions. Most particles formed in this manner have diameters from 50 Å to 1 μm , and some of the larger particles display crystal habits. The sizes of the particles in a sample are generally found by the examination of transmission electron microscope (TEM) photographs.

Inert gas evaporated particles of many metals have been produced, including the following: aluminum, antimony, beryllium, bismuth, cadmium, chromium, cobalt, copper, gold, iron, lead, magnesium, manganese, nickel, silver, tin, and zinc. The evaporations have been done in helium, argon, xenon, and nitrogen.^{10,11,13-16}

Previous experiments have shown that the size of the particles depends on the evaporant temperature and material, and on the pressure and type of inert gas. For a given evaporant, particle size increases with increasing evaporant temperature, or with increasing inert gas pressure or gas molecular weight. A probable mechanism for formation of the observed particles is described in reference 10. The mechanism involves homogeneous nucleation of small droplets of metal near the vapor source, with subsequent liquidlike coalescence of the small droplets of metal into the particles which are observed. The authors assume that the coalescence stage is the dominant factor in determination of the size distribution of the particles collected on the substrates. The experimentally determined qualitative dependence of the particle sizes on the evaporation conditions is consistent with this mechanism.

In addition, this mechanism predicts a log-normal distribution of particle diameters for spherical particles. The log-normal distribution is a distribution such that the logarithm of the particle diameters is Gaussian. This distribution is discussed more fully in Appendix B. The normalized distribution function $f(x)$ can be expressed as follows;

$$f(x) = [2 \pi \ln \sigma]^{-1} \exp\left[-\frac{1}{2} \left(\frac{\ln(x/x_0)}{\ln \sigma}\right)^2\right] \quad (22)$$

where x_0 is the median particle diameter, σ is the geometric standard deviation, and $f(x) \Delta x$ is the probability that a particle will have a diameter between x and $x + \Delta x$. The probability that a particle has a diameter between x_1 and x_2 is given by the following equation:

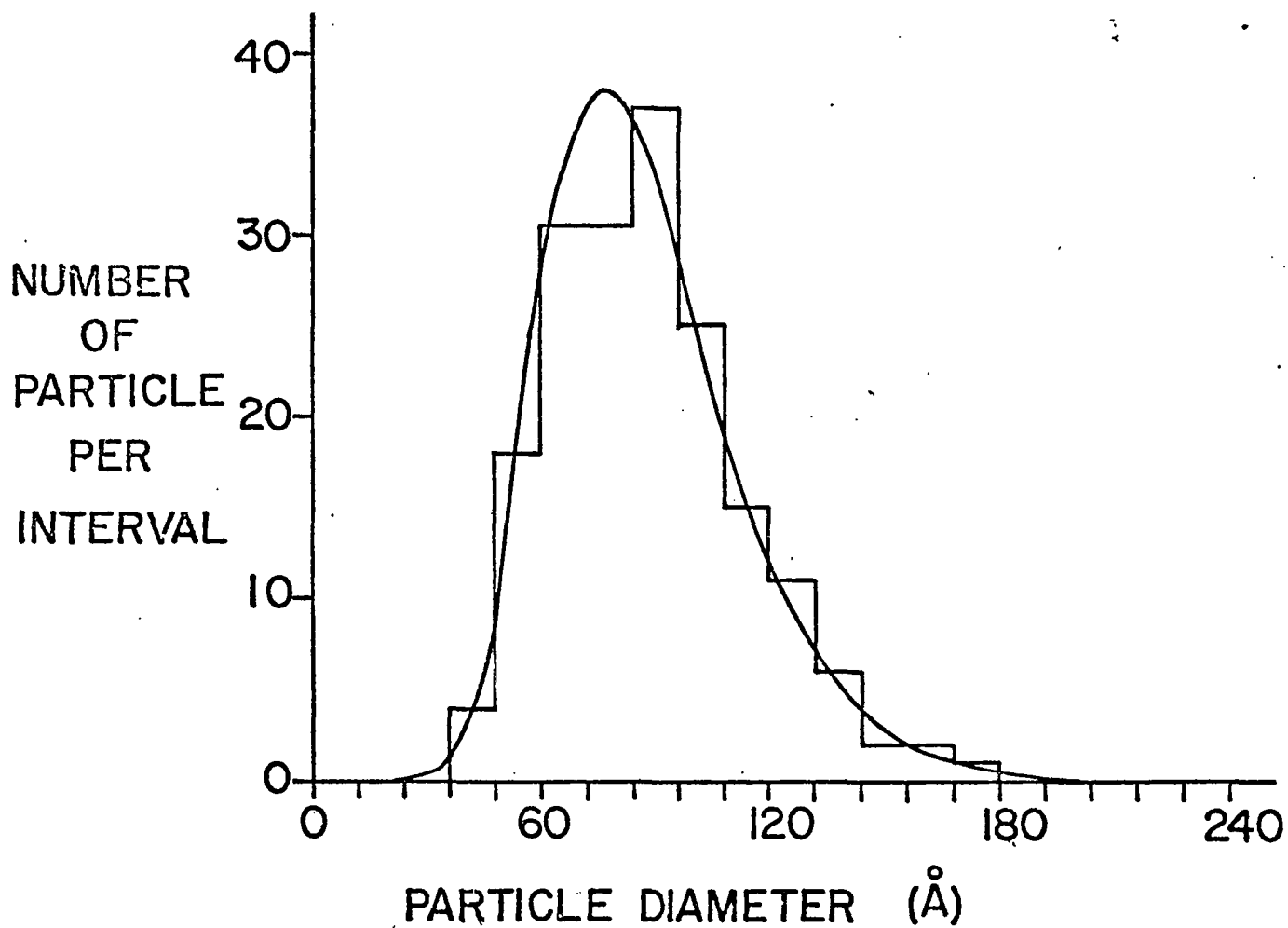
$$P(x_1, x_2) = \int_{\ln x_1}^{\ln x_2} f(x) d(\ln x) = \int_{x_1}^{x_2} \frac{1}{x} f(x) dx \quad (23)$$

Figure 3 depicts a histogram of particle sizes in a gold black sample we prepared and also a log-normal curve which was fit to the data. The method for a determination of x_0 and σ for a log-normal fit to experimental data is described in Appendix B. There is substantial data in the literature which supports the log-normality of diameters of inert gas evaporated particles, for materials which do not exhibit crystalline shapes. It has been suggested by the authors of reference 10 that for all inert gas evaporated particles, $\sigma = 1.48 \pm .12$, and we will compare our data with this empirical result.

It is worthwhile to mention that the particle size data described above pertains to individual particles, not particles in metal blacks. In the black, the particles are in contact with each other, and there is generally electrical contact through the medium. Layers of insulating oxides on the particles may also prevent adhesion between them, and it will certainly cause a change in the optical properties of the material. Although relatively few blacks have been produced by inert gas evaporation, the work on individual particles indicates that many more types of metal blacks may be able to be produced using this technique.

Figure 3

Histogram of particle sizes for sample #16.
A log-normal distribution is also plotted for comparison.



Physical Properties

A measure of the quantity of material in a metal black film is needed to compare different metal black samples. The thickness of a film is not a good measure of the amount of material in a film due to the variability of the packing fraction of the metal blacks. Hence, we use the area mass density M of a film as a measure of the quantity of gold black in a film. Typical values of M for most metal black films are from 10 to 200 $\mu\text{g cm}^{-2}$. Metal black films with higher area densities have been produced, but they are nearly opaque, so that optical transmission measurements are difficult to carry out.

The packing fraction f is of interest, since it appears in the expression (16) for $\epsilon(\omega)$. The packing fraction is the fraction of the volume of the material occupied by the metal. Since the density of the air can be neglected, f is also the ratio of the density of the metal black to the density of the pure metal. Harris reports a value of about 2×10^{-3} for f for some of his gold blacks.¹⁷ Packing fraction data is unavailable for other blacks.

Since the d. c. electrical conductivity appears in expression (16) also, it is of interest to measure this quantity for metal black samples. The conductivity $g\sigma$ of a metal black sample can be calculated from the area resistivity ρ_A and thickness t of the film as follows:

$$g\sigma = \rho^{-1} = [\rho_A t]^{-1} \quad (24)$$

where ρ is the resistivity of the metal black film. Area resistivities of about 300 to 5000 $\Omega/\square$ have been reported for gold blacks, and higher values have been noted for antimony blacks.¹¹

Some gold and antimony samples have been prepared in gases containing small concentrations of oxygen. These samples are called gold smokes or antimony smokes to distinguish them from the metal blacks. The smokes have area resistivities about 10^3 times higher than that of the blacks. This is probably due to the deposition of tungsten oxide or antimony oxide along with the pure metal. The presence of the insulating oxides alters the structure of the material and also changes the optical properties of the sample.

Optical Properties

The optical properties of many inert gas evaporated metal blacks have been examined. The properties which can be directly measured by various instruments are the spectral reflectance $R(\omega)$ and spectral transmittance $T(\omega)$. The reflectance of a sample will be the same as the bulk material provided that there is no reflection from the substrate. This can be accomplished by making the sample sufficiently thick. The transmittance of a sample is given by the following equation:

$$T(\omega) = T_s(\omega) e^{-\alpha(\omega) t} \quad (25)$$

where $T_s(\omega)$ is the transmittance of the substrate, t is the sample thickness, and $\alpha(\omega)$ is the absorption coefficient of the sample. Here, we assume that the reflection from the metal black surface is negligible, and that the reflectance from the substrate is not affected by the presence of the metal black. These assumptions are quite accurate for most metal blacks.

We can measure the area density M of a film more accurately than we can measure the film thickness t . Therefore, the mass absorption coefficient $\alpha_m(\omega)$ is more useful for comparing different samples of the same material than the linear absorption coefficient $\alpha(\omega)$. The mass absorption coefficient $\alpha_m(\omega)$ is defined by the following:

$$M \alpha_m = t \alpha.$$

Hence,

$$\alpha_m = \alpha t / M = \alpha / D_b = \alpha / (f D) \quad (26)$$

where D_b is the density of the black, and D is the density of the pure metal. We can substitute the expression for α given in equation (20) into the above to obtain the following:

$$\alpha_m = \frac{4 \pi \sigma}{c D} \frac{1}{(f/g)} \quad (27)$$

so that only the ratio (f/g) need be obtained to calculate $T(\omega)$ using the measured values of the gold black parameters. The equation for $T(\omega)$ is then given by the following:

$$T(\omega) = T_s(\omega) e^{-\alpha_m(\omega) M} \quad (28)$$

We distinguish between several different types of measurements of $R(\omega)$; one can measure the specular reflectance, the diffuse reflectance, or the total reflectance. Similarly, we distinguish between direct transmittance, diffuse transmittance, and total transmittance. The optical properties calculated in Appendix A assume a perfectly flat boundary between media, which results in only direct transmittance and specular reflection. The diffuse components of $R(\omega)$ and $T(\omega)$ are due to nonuniformities of the surface of the metal black samples. These nonuniformities must have sizes on the order of the wavelength of the light or larger to cause this effect.

Available data indicate that the reflectance of gold black samples is between 0.5 and 1.0% in the visible range (0.4 to 0.7 μm), but it is not clear whether corrections need to be made to this data to account for possible reflections from the substrates. In this wavelength region, the measured reflectance is essentially entirely diffuse. Far infrared (20 to 450 μm) reflectances are significantly higher, and the reflectance is mostly specular for these wavelengths. Reflectance data for metal blacks other than gold is scanty.

Transmittance data for gold blacks was also available for the visible region. The direct transmittance shows a maximum near 0.5 μm , with a decrease toward shorter wavelengths. Between 0.5 and 0.7 μm , the direct transmittance of a gold black is nearly constant. At longer wavelengths, the transmittance decreases. Diffuse transmittance measurements indicate that diffuse transmittance is nearly constant over the range 0.4 to 0.7 μm , and about 20% of the total transmittance.

For a gold black with $M = 100 \text{ } \mu\text{g cm}^{-2}$, total transmittance increases from about 10% at .254 μm to about 20% from 0.5 to 0.7 μm , and decreases to a minimum of about 7% near 7 μm . Transmittance rapidly increases for longer wavelengths. Silver blacks show similar infrared transmittance. The antimony smokes and gold smokes, however, have nearly 100% transmittance for wavelengths between 2.0 and 15 μm . This high infrared transmittance is attributed to the presence of insulating oxides in these samples.

The thermal properties of metal blacks are also of interest for solar energy applications, as mentioned in Section II. It has been

shown that gold blacks are not stable at temperatures of several hundred degrees centigrade. Prolonged exposure to temperatures of 150 ° C or higher results in an increased infrared specular reflectance R and an increased area resistivity ρ_A . Higher temperatures cause large increases in the reflectance of the blacks. In addition, since metal blacks have such low densities, the conductivities of metal blacks are expected to be small compared to metals, although data on this was not previously available.

IV EXPERIMENTAL

A. Scope of Experimental Work

General

The experimental work described herein involved three stages. The first stage was the production of test gold black samples under controlled conditions. Next, the samples were carefully examined in order to determine the composition and structure of the material. During the final stage, gold black samples which were produced under different conditions were studied in order to determine the dependence of some of the properties of the gold blacks on the conditions under which they were produced.

Production of Gold Black Samples

The method of inert gas evaporation was chosen for production of the metal black samples because:

- (i) clean samples are produced, and
- (ii) the evaporation conditions can be easily regulated and varied over wide ranges.

The cleanliness of the samples was particularly important for the examination of the composition and structure of the gold blacks. The conditions to be varied were the inert gas pressure, the evaporation temperature, and the substrate temperature. Gold was chosen as the evaporant since it can be readily evaporated at temperatures of 1500 to 1600° C, and it does not attack tungsten, so that filaments or evaporation boats made from tungsten can be used. In addition, gold is stable from oxidation in air at, and substantially above room temperature. A large body of data on gold black is also available.

Examination of Composition and Structure

The composition and structure of the gold black samples were examined using several techniques. A scanning electron microscope (SEM) was used to examine the gross structure of the samples. Energy dispersive analysis of the fluorescence x-rays by the SEM was used, along with electron scattering for chemical analysis (ESCA), for the determination of sample composition. The SEM was also used to find the thicknesses of the samples. A transmission electron microscope (TEM) was used for the determination of particle sizes and for studying structural features on a finer scale than possible with the SEM.

Measurement of Properties

The physical, electrical, and optical properties of each sample were measured. The area density M and thickness t of each sample was measured, so that the packing fraction f could be obtained. Measurement of the thickness t of each film was particularly difficult for the thinner samples, resulting in fairly large percentage uncertainties for t . The area resistivity ρ_A of each sample was measured. The electrical conductivity of the black σ_b may then be calculated from ρ_A and t using equation (24):

$$\sigma_b = 1 / (\rho_A t) \quad (24)$$

The optical properties of interest were the spectral reflectance $R(\lambda)$ and the spectral transmittance $T(\lambda)$ for each sample. The reflectance was measured for selected thick samples and the transmittance was measured for all samples. All optical measurements were carried out for the wavelength region of 0.35 to 2.4 μm . Only total reflectances and total transmittances were measured.

B. Experimental Apparatus and Procedures

Production of Gold Black Samples

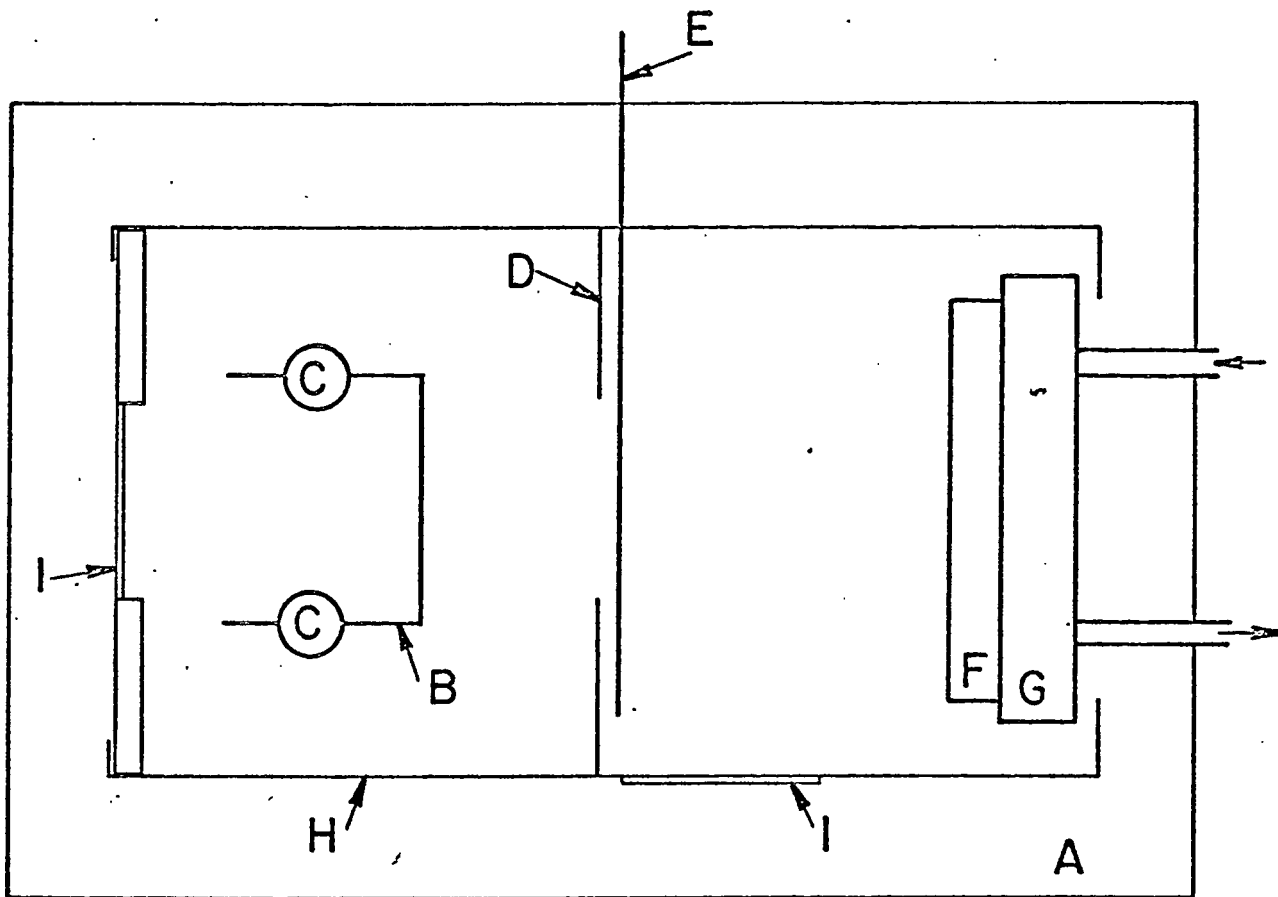
The gold black samples were produced by inert gas evaporation in a manner similar to that described by Harris.¹¹ Two slightly different techniques were employed. The earlier samples were produced by evaporation from a hot filament, with subsequent deposition on cooled substrates located about 10 cm from the filament in a horizontal direction. The 0.030 inch diameter tungsten filament was bent into a "V" shape mounted with the apex down, and high purity gold was evaporated from a drop at the apex of the filament. A mask and shutter were also included on the apparatus to control the deposition of the gold black on the substrate. The apparatus was contained within a vacuum bell jar into which helium gas could be introduced at various pressures. A removable cover with replacable windows was used to prevent excessive contamination of the chamber by gold particles. The apparatus is pictured diagrammatically in Figure 4.

The second technique was a modification of the first which was used in order to obtain more uniform samples and a more accurate measurement of the evaporation temperature. This method was intended to correct a slight vertical variation of film thickness on the largest substrates. The second technique used vertical evaporation from a tungsten boat. The substrates were placed directly above the gold vapor source. We believe that this geometry minimizes the effects of gravity and convection on the uniformity of the gold black films. This geometry also allows a different method for the measurement of the evaporation temperature. The remainder of the apparatus was unchanged.

Figure 4

Diagram of the Evaporation Apparatus

- A - base plate
- B - filament
- C - insulated posts
- D - mask
- E - shutter
- F - substrate holder
- G - coolant chamber
- H - removable cover
- I - window



Four methods were used to measure the temperature of the gold vapor source. The first involved the use of an optical pyrometer to determine a current-temperature calibration for a given filament. Then, gold was loaded onto the filament and filament current was monitored during the evaporation. The temperature of the filament was obtained from the current-temperature calibration. Different calibration curves were needed for the different helium pressures used due to the varying amount of convective cooling of the filament by the helium. This method was the least accurate, since the emissivity of the tungsten filament was not accurately known; the gold also affected the temperature of the filament.

To obtain more accurate temperature measurements, a tungsten - 5% rhenium / tungsten - 26% rhenium (W-5%Re/W-26%Re) thermocouple was spot welded to the apex of the filament. During an evaporation, the gold globule completely engulfed the thermocouple junction. At elevated temperatures, however, the gold alloyed with the thermocouple wires, changing the temperature-potential calibration for the thermocouple. An approximate temperature was obtained by assuming a linear temperature-potential calibration, with the melting point of gold used as a standard for the calibration during each evaporation.

The third method of temperature measurement was used on samples produced using the vertical geometry. A W-5%Re/W-26%Re thermocouple was spot welded onto the bottom of the tungsten boat. Accurate temperature readings could not be obtained consistently using this method because gold vapor condensed onto the thermocouple wires

and alloyed with them, affecting the thermocouple calibration as before, Shielding the thermocouple from the gold vapor proved to be difficult, so a fourth method was used to measure the evaporation temperature of the remainder of the samples.

The final technique employed a spot photometer which measured the brightness of the bottom of the tungsten boat. The first portion of the light path was in a narrow tube, so that gold particles would be deposited on the walls of the tube before reaching the mirror which reflected the image of the bottom of the boat into the spot photometer. The optical path is indicated in Figure 5. The mirror M was made to be replacable in case some gold became deposited on it after several evaporations. A temperature calibration curve was made using a W-5%Re/W-26%Re thermocouple spot welded to the top of an empty boat.

The gold black samples were deposited on several types of substrates: 25 mm square glass cover slips, 12 mm diameter polished aluminum disks, and formvar coated 400 mesh copper TEM grids. The glass slide deposits were used for measurements of area resistivity ρ_A , area density M, film thickness t, optical properties, and particle sizes by x-ray diffraction. The aluminum disks were used for the SEM measurements of surface morphology and composition. The formvar coated copper grids were examined using the TEM to determine the detailed structure of the material and the sizes of the component particles.

Figure 5

Evaporation Temperature Measurement

Using a Spot Photometer

W - tungsten boat

M - mirror

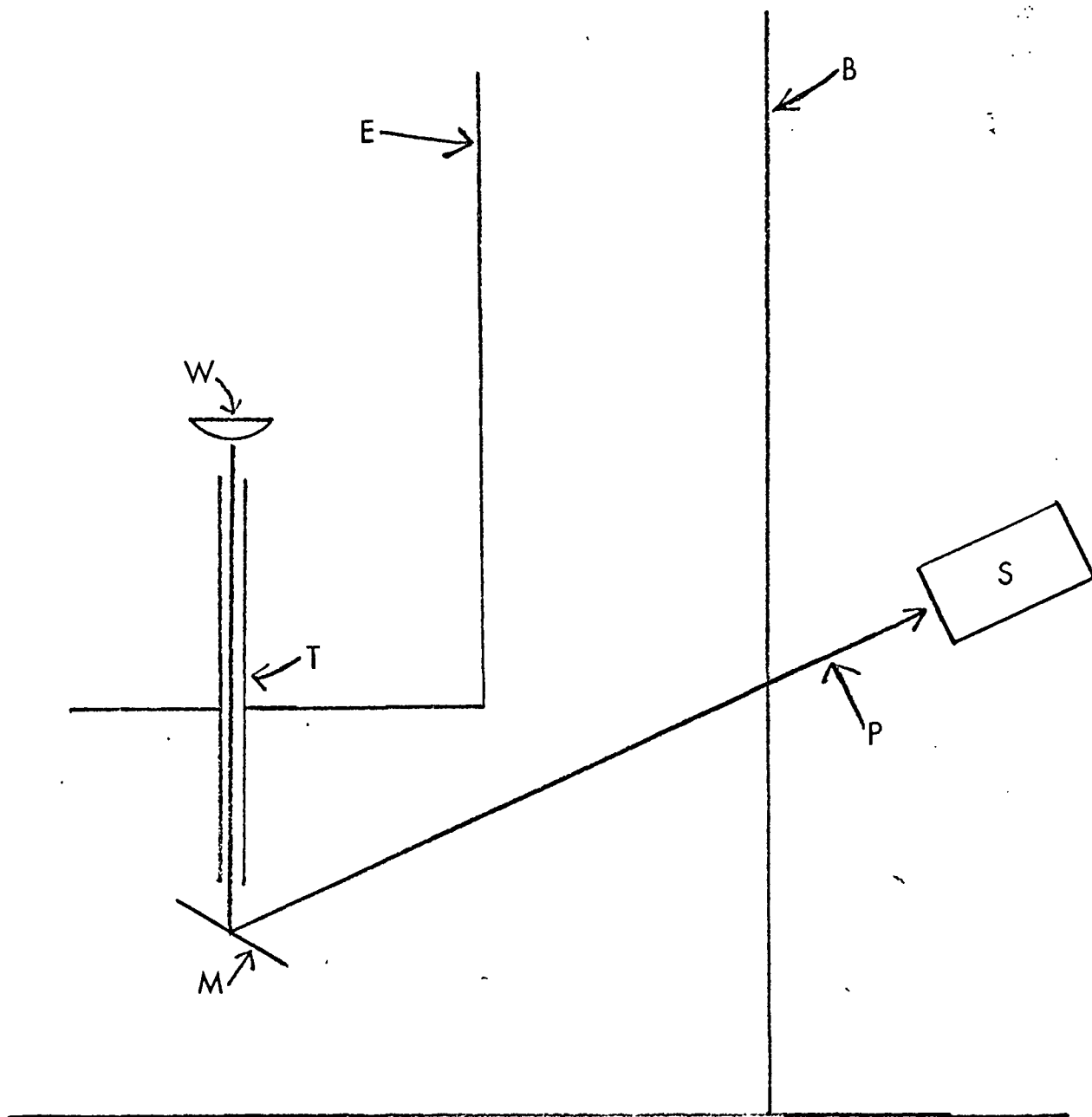
T - metal tube

B - glass bell jar

S - spot photometer

E - evaporation enclosure

P - light path



The following procedure was used to prepare the samples: A suitable quantity of 99.95 to 99.99 % pure gold was placed on the filament or in the boat. The bell jar was evacuated and the gold sample was outgassed. After a pressure of about 5×10^{-7} torr was reached, 99.999 % pure helium was admitted into the chamber. The leak rate of the chamber was about 1.5×10^{-4} torr hr⁻¹. The gold was then heated to the desired temperature and the shutter was opened. When the deposition was finished, the shutter was closed; the gold vapor source was then allowed to cool. The substrate holder and evaporation source were allowed to come to thermal equilibrium with their surroundings for 15 to 30 minutes, before air was admitted to the chamber for removal of the substrates.

Examination of Composition and Structure

Two instrumental methods were used to ascertain the composition of the gold black samples. Fluorescence x-ray analysis on the SEM was used to check for impurities of atomic number higher than sodium. ESCA was used to insure that lower atomic number impurities were absent as well. These two techniques are discussed briefly in Appendix C.

The structure of the samples was examined using different instruments for different size ranges. The roughness of the surface of gold black samples can be seen in a light microscope. The resolution of a light microscope is limited by the wavelength of the light, which is about 5000 Å. Much more detail could be seen using the Cambridge

S4-10 SEM. This microscope has a maximum resolution of about 100 Å. Even finer details were visible in photographs taken using a Hitachi HS-8 TEM, which has a resolution of 12 Å at best. The principles of operation of these microscopes are described briefly in Appendix C.

The samples deposited on the glass slides and aluminum disks were examined in the SEM. The aluminum disks could be directly mounted on the microscope stage, but the glass slides were too large for the stage. To view these samples, the slides were broken after all other measurements on these substrates were completed. Each piece of a slide could be mounted on a sample holder for the SEM. The samples must remain electrically neutral under the primary electron beam to obtain good pictures, so the samples must have electrical contact with the stage to bleed off excess charge. An electrically conductive paint was used to insure electrical conductivity between gold black samples on glass slides and the sample holders, which were made of aluminum. In addition, most of the samples on glass slides were sputter-coated with a layer of gold about 100 Å thick. This gold coating serves two purposes:

- (i) it insures electrical conductivity between the sample and the sample holder, and
- (ii) it improves image quality by decreasing the depth of penetration of the secondary electrons.

Individual gold particles were visible on the TEM photographs. The particle sizes were measured directly from photographic enlargements of the TEM negatives. Particle size distributions were obtained by measuring many particles on each photo. In order to see individual particles or small groups of particles, the gold black coatings on the TEM grids needed to be very thin. These thin deposits were obtained by placing the grids away from the axis of the deposition, and the mask served to reduce the amount of gold reaching these grids. In order to compare particles sizes found in this manner to the particle sizes on the glass substrates, we measured the average particle sizes of some of the samples on glass slides using x-ray diffraction. The results obtained by the two methods are in fair agreement. See Table 2.

Measurement of Gold

Black Properties

The physical properties of the samples which were measured were the sample thickness t and packing fraction f . The packing fraction f is the ratio of the gold black density to the density of pure gold. The density of each sample was found by dividing its area density M by the sample thickness t . The area density was obtained by weighing the glass substrates before and immediately after the deposition of the gold black of known area. The weights were accurate to about $5 \mu\text{g}$ and the sample was about 6 cm^2 . Thus, the area density measurements were accurate to about $2 \mu\text{g cm}^{-2}$. It was found that the mass of a gold black film was stable in air, changing by less than 10% over a period of about three weeks.

Two different techniques were used to measure sample thicknesses. The first technique, which could only be used for relatively thick deposits, involved focusing a Leitz metallographic microscope alternately on the "top" of the film and on the substrate surface. The movement of the focusing knob, calibrated to read the distance the stage was moved, gives the film thickness to an accuracy of about 3 μm . The second method employed the SEM as shown in Figure 6. An edge of the gold black film is viewed at a high angle to the normal, and the apparent height of the film, t' , is corrected for the viewing angle θ by the following formula:

$$t = t' / \sin \theta \quad (29)$$

These measurements are difficult to carry out due to the roughness of the surface of the gold black samples. An example of the very feathery nature of a gold black surface is shown in Figure 7, one of our thinner samples.

The conductivities of our samples were calculated from measured values of the area resistivity ρ_A and thickness t of the gold black films. The area resistivity of each film was found by depositing bright gold electrodes along two opposite sides of the 25 mm square glass substrates before the gold black depositions. After the gold black was deposited on a substrate, the resistance between the electrodes was measured to determine ρ_A . It is believed that the conductivities we measured were lower than the actual conductivities, due to the non-uniformity of the surface of a gold black. This effect is most important for the thinnest samples, which appear to consist of nearly isolated clumps, with relatively few bridges between the clumps, as shown in Figure 8.

Figure 6

Measurement of Sample Thickness

Using the SEM

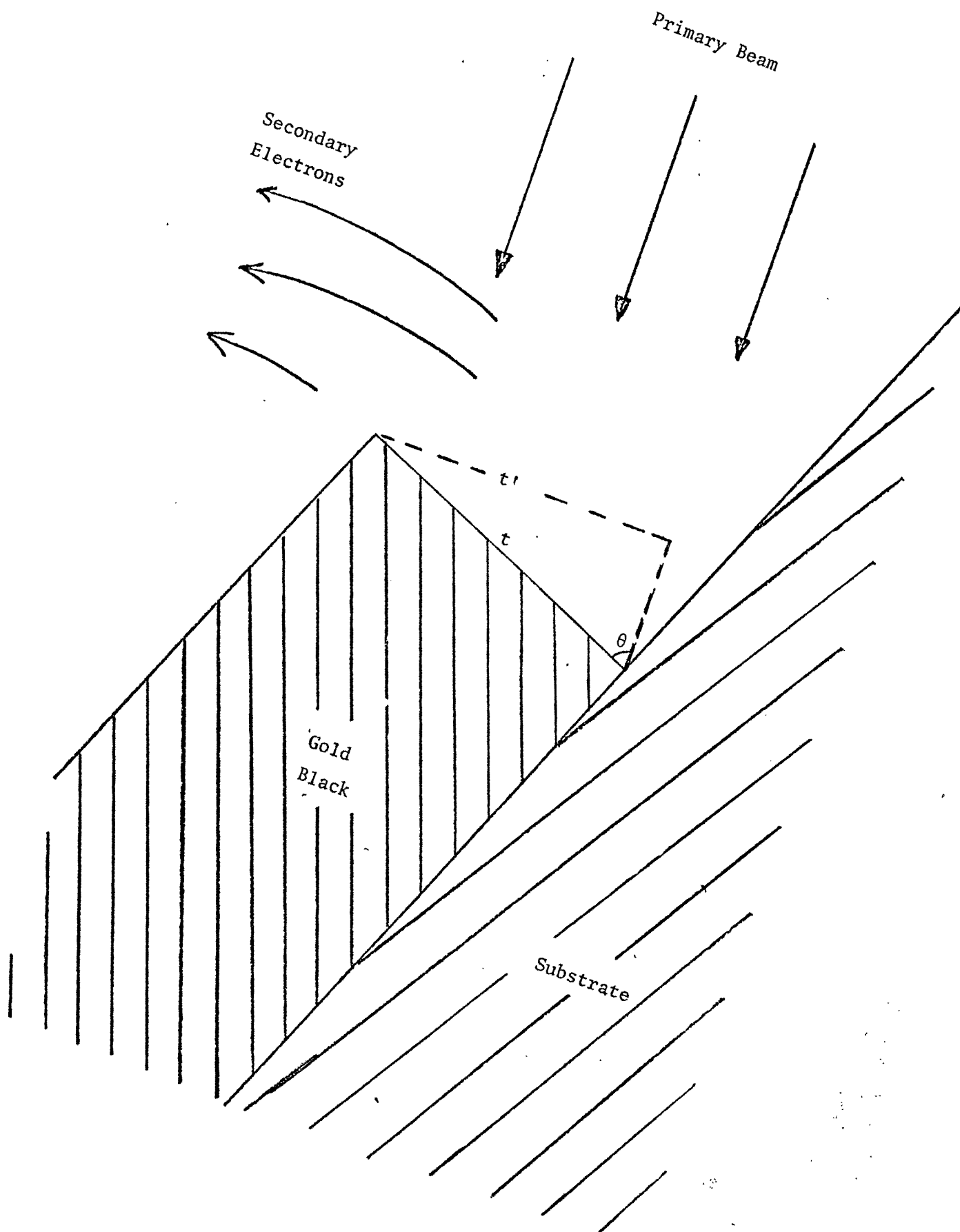


Figure 7

SEM photo of a gold black sample. Note the feathery nature of the surface of the material.

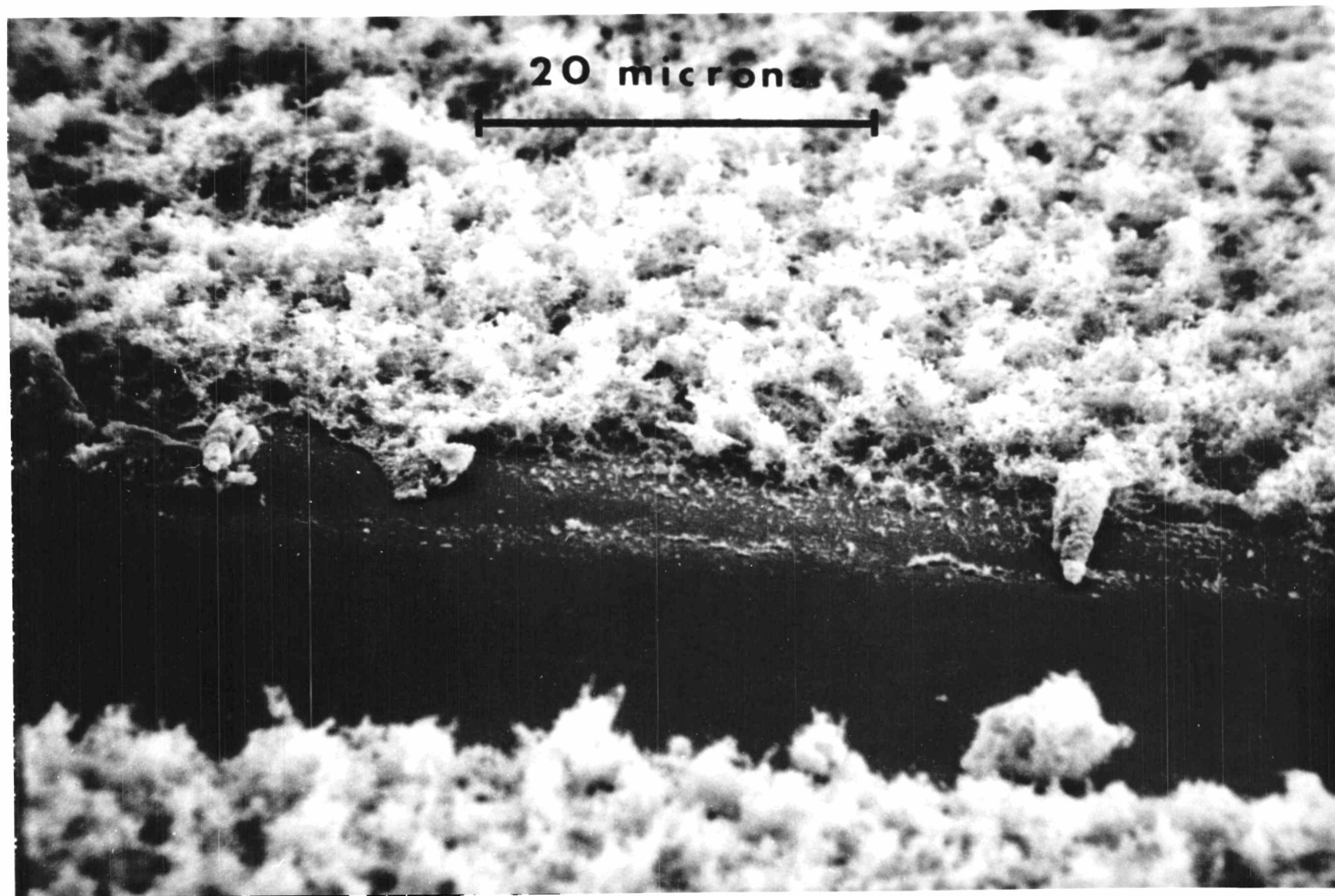
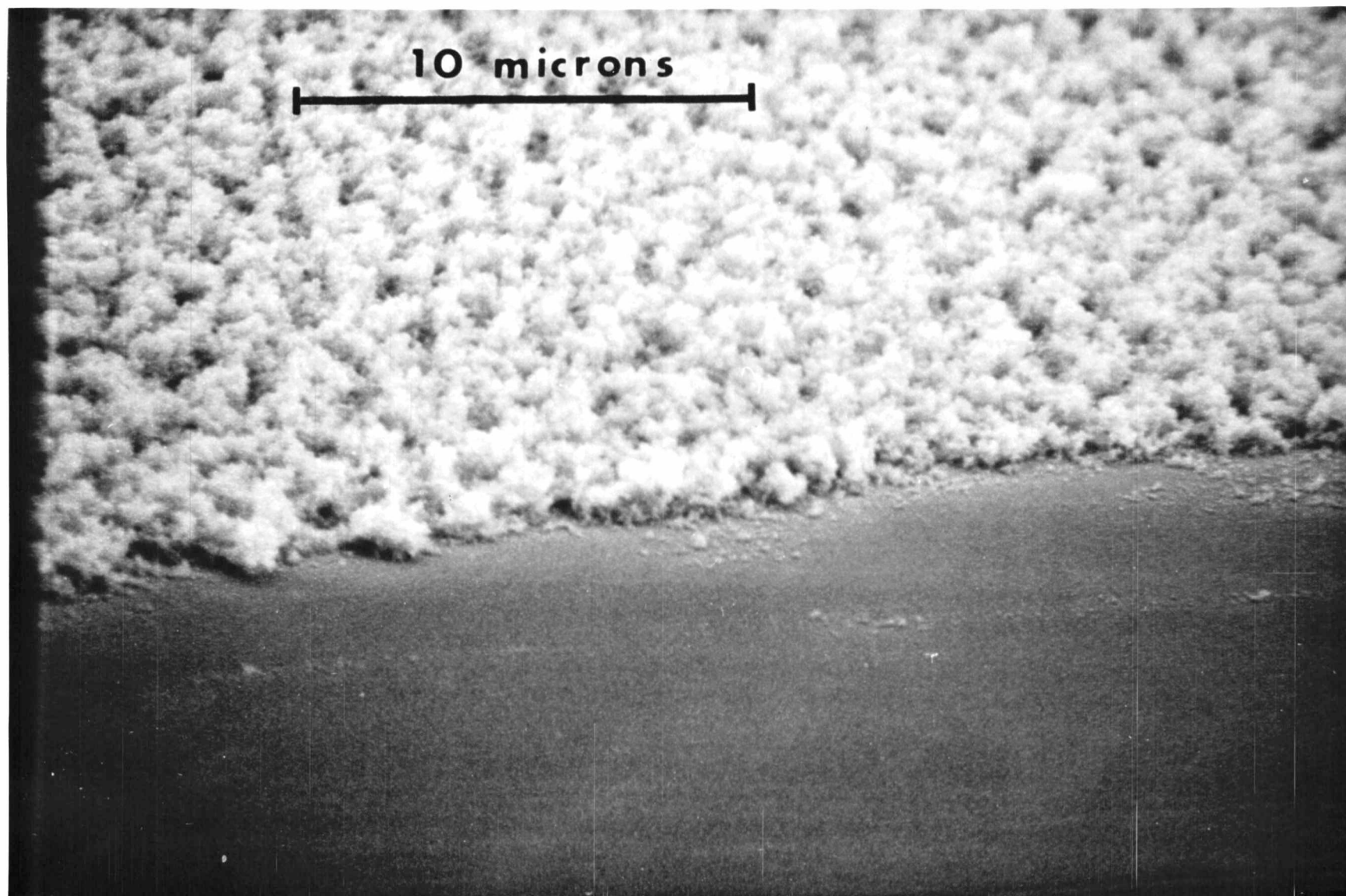


Figure 8

SEM photo of a thin gold black sample, The gold black tends to adhere into clumps having diameters between one and two microns for this sample.



The optical measurements were carried out on the samples deposited on the 25 mm square glass substrates. The measurements were done using a Beckman DK-2A spectrophotometer, with an integrating sphere. Total (specular and diffuse) reflectance measurements were carried out on some of the thicker samples. Total transmittance was measured for all samples. A transmittance curve for the glass substrates was also recorded to correct the transmittance measurements. The transmittance of the glass was between 91% and 92% over the range of 0.40 to 2.4 μm , dropping to 90% at 0.35 μm . This instrument is accurate to 1% on the 0 to 100 % scales and to 0.1% on the 0 to 10 % scales.

V RESULTS AND CONCLUSIONS

A. Composition and Structure

Composition

The characteristic x-ray analysis on the SEM detected only gold in our gold black samples, with a sensitivity limit of 100 ppm. A few samples of gold smoke were prepared, and x-ray analysis of these samples indicates substantial amounts of tungsten, possibly in the form of tungsten oxide. ESCA analysis of the gold blacks also showed mostly gold, but small amounts of oxygen and carbon were also present. ESCA measurements on gold foil show similar carbon and oxygen peaks, indicating that these impurities are probably due to the exposure of the gold blacks to air rather than being part of the gold black material.

Structure

As shown in the SEM photos of Figures 9 and 10, the large scale structure of the gold blacks is that of a spongy material of low density. These photos are of thick samples, and the roughness of the top surface is not as apparent as in Figures 7 and 8, which are SEM photos of two of the thinner samples we produced. A higher magnification SEM photo giving an indication of the small scale structure is shown in Figure 11. It can be seen that the gold black consists of a network of small particles adhering to each other to form chains. This photo is of a feathery projection from the top of a gold black film.

Figure 9

SEM photo of a thick gold black film peeled off a glass slide. The lower surface of the film is nearly flat, while the upper surface is rougher.

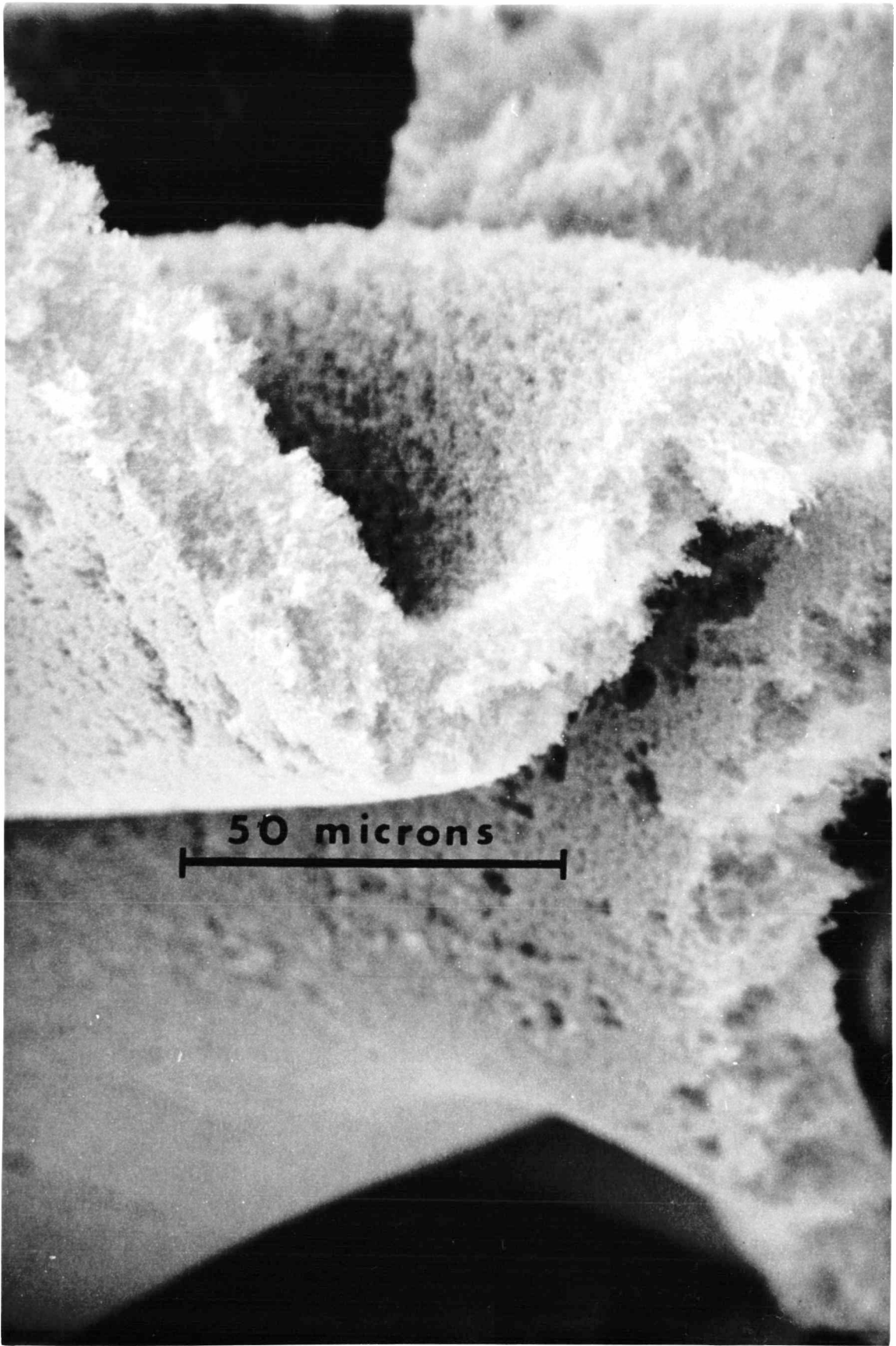


Figure 10

SEM photo of a thick gold black film. The
sponge-like nature of the material is evident
in this photograph.

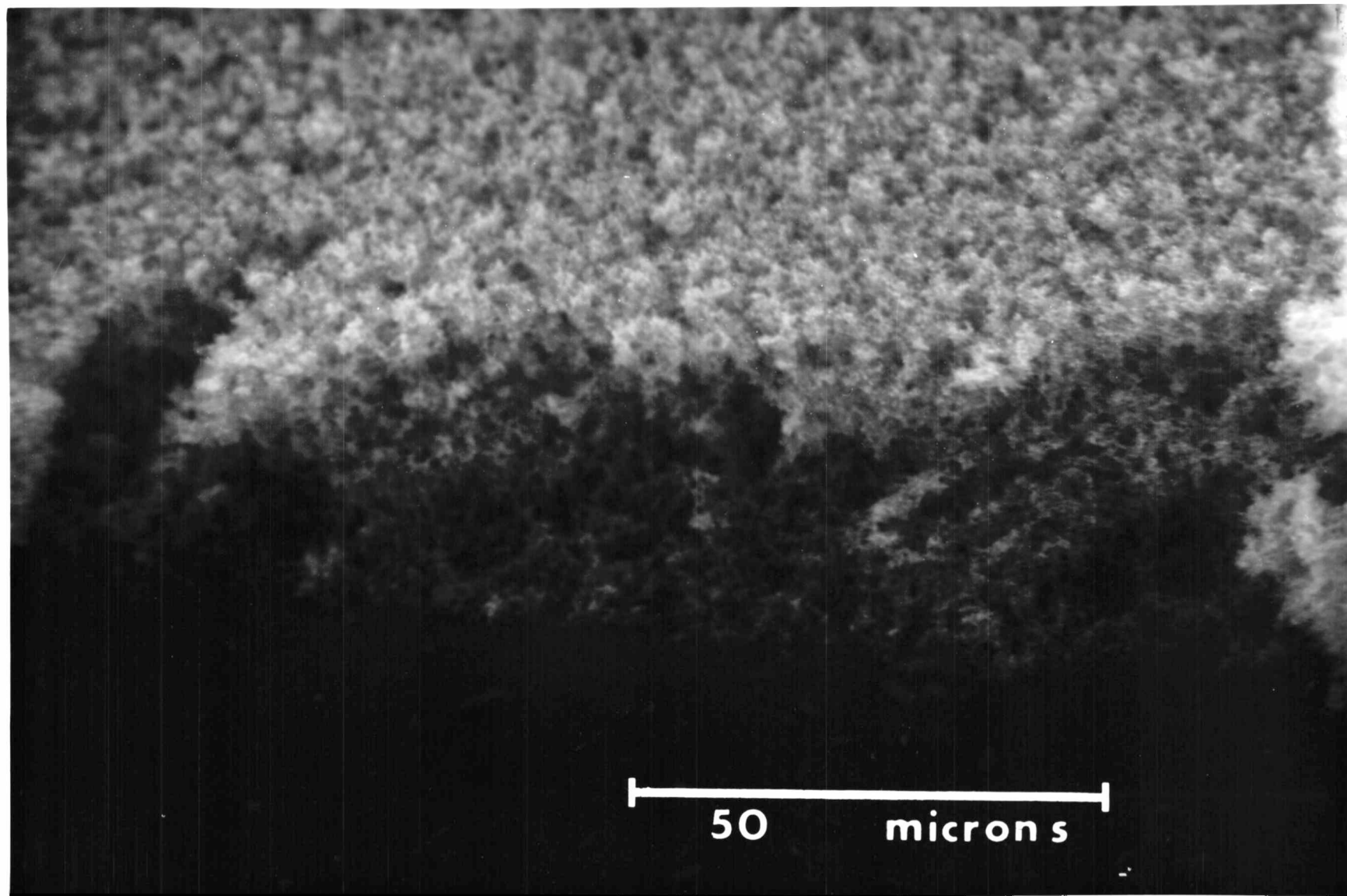


Figure 11

A high magnification (about 100,000X) SEM photo of the edge of a gold black sample. The filamentary structure of the gold black material can be seen, but the SEM is unable to resolve individual gold particles.

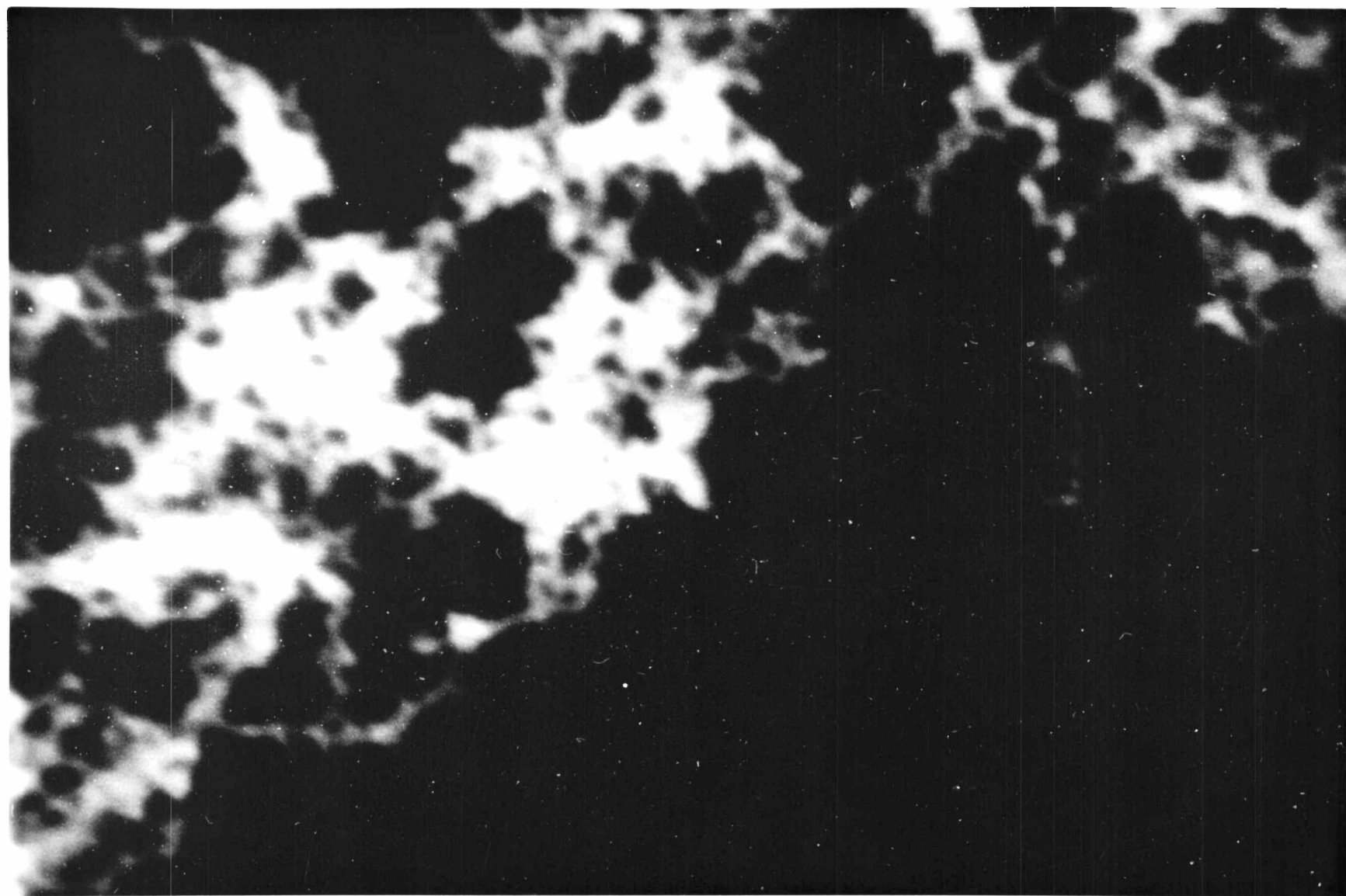


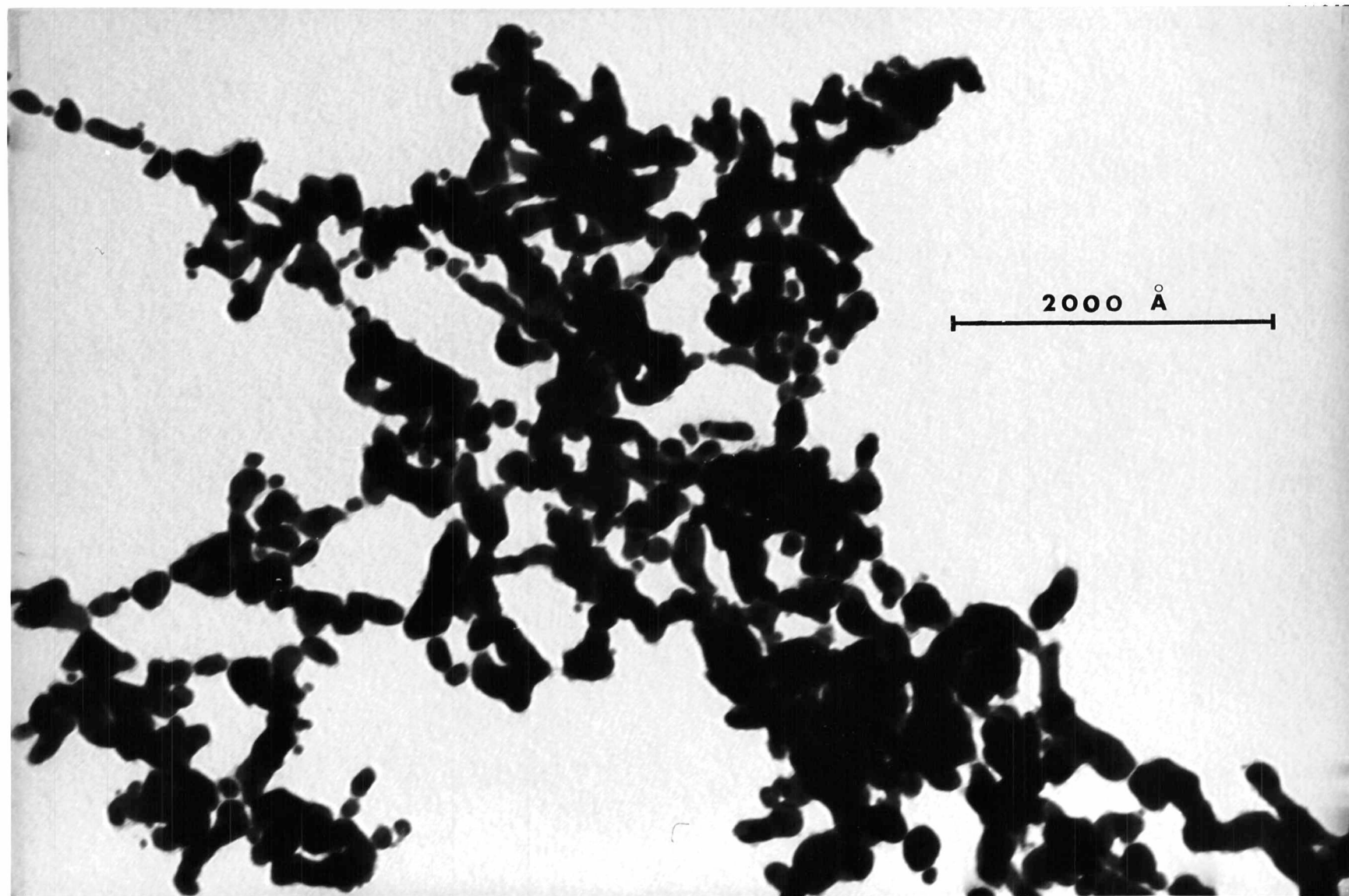
Figure 12

TEM photo of a gold black sample, showing strands
which make up the spongy gold black network.



Figure 13

TEM photo of thin gold black sample,
showing gold particles adhering to
each other.



The SEM does not have sufficient resolving power to examine these gold particles in detail, so TEM photos of the gold particles on the TEM grids were studied to gain information on the small scale structure of the gold blacks. TEM photos show that the nearly spherical gold particles adhere to each other to form cross linked and branched chains, but it is impossible to unambiguously determine the area of contact between adjacent particles due to the limiting resolution of the TEM. Figures 12 and 13 are TEM photos which show this structure.

Examination of particle sizes determined from the TEM photos showed that the particles generally obey a log-normal distribution, as discussed in section III C. Figure 14 is a log-probability plot of one of the samples, showing excellent agreement with the log-normal distribution. The corresponding sample distribution histogram and log-normal curve are shown in Figure 3 for comparison. The log-normal distribution is discussed briefly in Appendix B. Table 2 lists median particle diameters for several samples, as determined from the TEM photos and as determined by the x-ray diffraction technique. The two methods give results in fair agreement, considering that the limiting resolution of the TEM is 12 Å. Also note that particle sizes determined from the TEM photos are generally smaller than those determined by the other technique. This may be due to the fact that the TEM photos are used to find the median particle diameter, while the other method yields some sort of average or effective particle size.

Figure 14

Log-probability plot of sample #16. This sample has $x_0 = 84$ A and $\sigma = 1.35$. A histogram of the sample distribution appears in Figure 3, along with a log-normal curve for comparison.

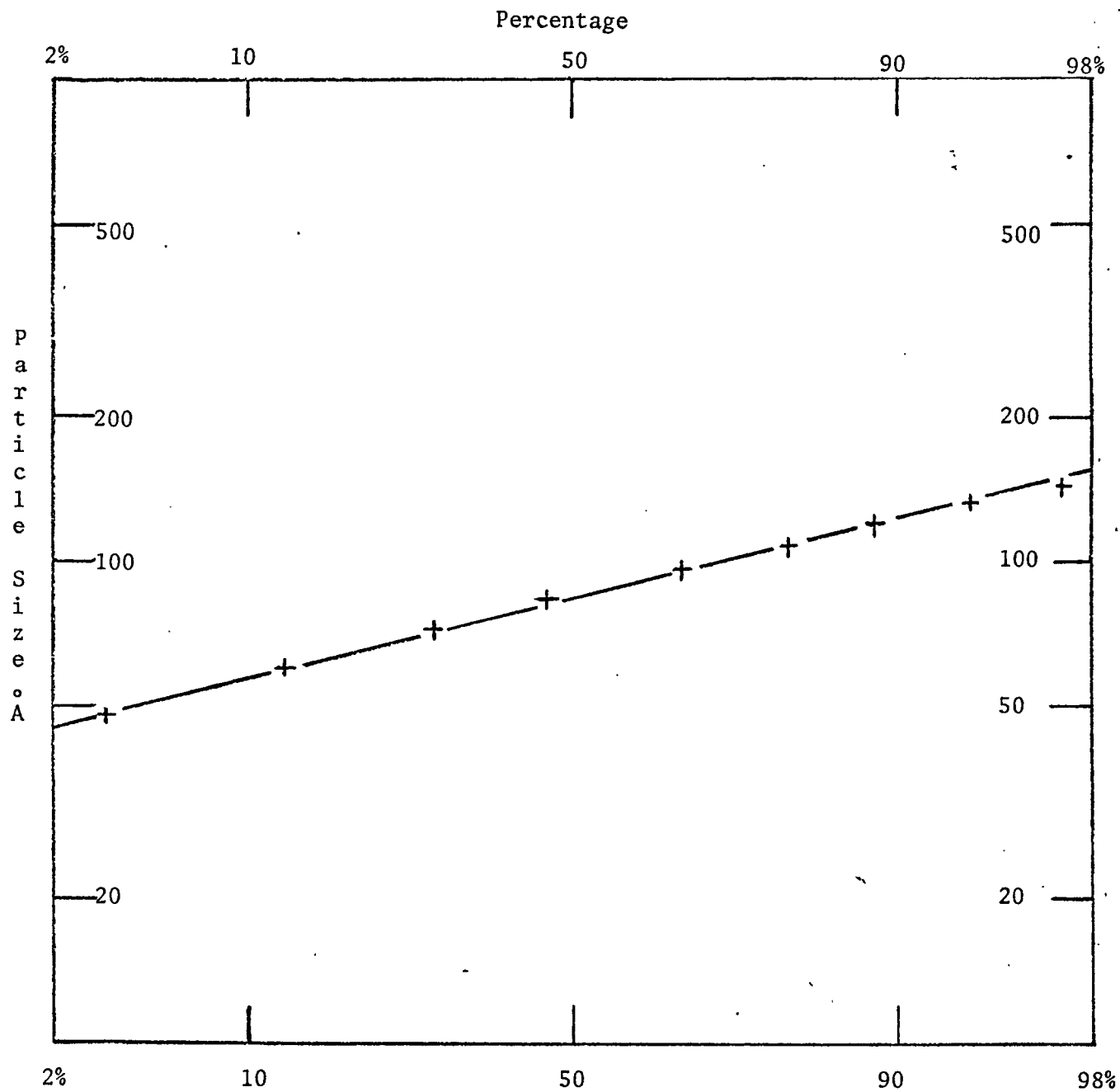


Table 2

Sample Number	Particle Size ($\text{\AA}$)	
	<u>from x-ray diffraction</u>	<u>from TEM photos</u>
14a	91	(59.5) *
14b	91	
15a	96	71
15b	70	
16a	94	84
16b	91	
18a	83	70
18b	—	

* Samples 14a and 14b have a structure which appears different from most of the other gold blacks which we prepared. See section V of the text.

The particle size distributions for the samples produced at the lower pressures were qualitatively different from the others. A large number of very small particles (less than 30 Å diameter) were seen on these photos. In addition to the small particles, there was a distribution of larger particles in these samples. We excluded particles with diameters less than about 35 Å; the remaining particles formed a log-normal distribution. This type of distribution indicates that the coalescence of atomic clusters into larger particles may be taking place over a large region, extending to the substrates. This is to be expected, since the size of the coalescence region should increase with decreasing pressure.

The samples prepared at the lowest pressures and evaporation temperatures did not have the appearance of a gold black. These samples had densities of 0.1 to 0.25 times that of gold, and they looked much like bright gold deposits. The TEM and SEM photos of these samples showed nearly solid gold films, with numerous cracks or breaks. This seems to indicate that under these conditions, the atomic clusters coalesce on the substrates to form a nearly solid gold film. There may be a difference between the samples on the glass or aluminum substrates and the TEM grids, however, due to the poor thermal contact between the Formvar coatings on the TEM grids and the substrate holder, possibly resulting in higher temperatures at the TEM grids.

B. Properties of Gold Blacks

The samples which we prepared are listed in Table 3, which describes the evaporation conditions for each sample. For all samples except 29, the substrates were cooled to about 10°C . For sample 29, the substrates were cooled to about -162°C , but this did not appear to affect any of the properties we measured. The measured values of area mass density M , thickness t , and area resistivity ρ_A are listed in Table 4 for all samples, along with experimental values for f and f/g for selected samples. Median particle diameters x and geometric standard deviations σ are listed in Table 5 for most samples. The results of the optical measurements are given in Appendix D for all samples.

The transmittance curves for samples 26 and 29 are characteristic of gold smokes. Substantial amounts of tungsten were detected in sample 26 using the characteristic x-ray analysis on the SEM. Samples 15, 16, and 19 also show an increase in transmittance as wavelengths increase above $.7\text{ }\mu\text{m}$, which may indicate the presence of small amounts of tungsten oxide in these samples. The tungsten may have escaped detection in the SEM due to the low area density of these samples. For samples of area density less than about $50\text{ }\mu\text{g}/\text{cm}^2$, the aluminum in the substrates was the principal source of characteristic x-rays, due to penetration of the primary electron beam through the gold black films.

Table 3

Sample Number	Vapor Source	Evaporation Conditions		Pressure torr
		Temperature Measurement	Evaporant Temperature	
8	Filament	A	1540 C	.5
9	Filament	A	1540 C	2
10	Filament	A	1540 C	5
11	Filament	A	1540 C	10
14	Filament	B	1485 C	1
15	Filament	B	1510 C	20
16	Filament	B	1507 C	20
17	Filament	B	1515 C	2
18	Filament	B	1510 C	5
19	Filament	B	1513 C	.5
21	Boat	C	1600 C	5
22	Boat	C	1600 C	5
26	Boat	C	1400 C	5
27	Boat	D	1500 C	5
28	Boat	D	1600 C	5
29	Boat ²	D	1500 C	5

- Notes: 1. Methods of temperature measurement are
 A: temperature-current calibration of filament
 B: thermocouple spot welded to filament
 C: thermocouple spot welded to boat
 D: photometer observation of boat.
 See the text for further detail.
2. During this evaporation, the substrates were cooled to about -162 C.

Table 4

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Properties of Samples

Sample Number	M $\mu\text{g}/\text{cm}^2$	t μm	ρ_A $\Omega/$	f	f/g	g
8a	92.5	0.18	3.7	.266	7.26	.0366
8b	101	0.18	5.2	.248	11.1	.0223
9a	217	5.0	31.3	.0224	144	.000156
9b	191	7.3	35	.0135	142	.0000951
10a	210	18.3	34.2	.00594	152	.0000391
10b	305	36.5	28.3	.00432	183	.0000236
11a	190	31	61.0	.00317	246	.0000129
11b	262	41.3	44.6	.00328	248	.0000132
14a	30	0.84	595	.0184	379	.0000486
14b	29.1	0.98	818	.0154	505	.0000305
15a	55.2	3.5	--	.00816	--	--
15b	44.3	2.8	--	.00819	--	--
16a	84.3	6.3	--	.00693	--	--
16b	97.8	7.0	--	.00723	--	--
17a	22.2	0.64	5400	.0180	2543	.00000708
17b	22.9	0.93	13800	.0127	6704	.00000189
18a	42.4	3.2	1067	.00686	960	.00000715
18b	45.8	3.65	1249	.00649	1213	.00000535
19a	21.8	0.076	--	.148	--	--
19b	21.5	0.104	--	.107	--	--
21a	7.90	0.03	--	.136	--	--
21b	8.07	0.03	--	.139	--	--
22a	25.4	1.31	1499	.0100	808	.0000124
22b	26.2	1.99	1488	.00681	827	.00000823
26a	55.1	0.640	--	.0446	--	--
26b	40.9	0.601	--	.0352	--	--
27a	44.6	2.26	--	.0102	--	--
27b	55.6	1.84	--	.0156	--	--
28a	48.4	2.32	670	.0108	688	.0000157
28b	49.5	2.98	729	.00860	765	.0000112
29a	42.3	0.835	--	.0262	--	--
29b	36.3	0.802	--	.0234	--	--

Table 5
Particle Data

<u>Sample Number</u>	<u>Particle Diameter ($\text{\AA}$)</u>	<u>Geometric Standard Deviation σ</u>
9	64	--
10	80	1.33
11	96	1.36
14	(59.5)	(1.26)
15	71	1.38
16	84	1.35
17	(50)	(1.41)
18	70	1.39
21	49.5	1.34
22	61	1.31
27	42	1.39
28	56	1.36

Data in parentheses correspond to sample distributions which do not entirely agree with a log-normal distribution.

From Table 5, we find that for the gold black samples we prepared, $\sigma = 1.36 \pm .05$, somewhat smaller than the value of $1.48 \pm .12$ suggested by the authors of reference 10. We next consider the effects of a change of the evaporation temperature T or pressure P on the median particle size x . We expect that an increase in T will increase the density of metal droplets in the coalescence region due to the increased vapor pressure. Thus, we expect more coalescence events and hence larger particles for a higher value of T . For higher pressures P , we expect better confinement of the metal droplets in the coalescence region, again resulting in larger particles. Data in references 10 and 12 are in agreement with these qualitative statements. A plot of x against P appears in Figure 15 for two different evaporation temperatures. From Tables 3 and 5, we find that samples 27 and 28 indicate an increase in x with increasing T . Hence, our data are also in agreement with the above statements.

We next note that there is a correlation between median particle diameter x and the packing fraction f . It appears that f decreases with increasing particle size. Figure 16 is a plot of f on a log scale against x on a linear scale. Values of x are from the TEM photos, and they are accurate to about $10 \text{ \AA}$ while f is accurate to about 20 %. A straight line on this plot passes near many of the experimental points. An exponential relationship between f and x would yield such a line. These data are not sufficiently precise to claim a strict exponential dependence, but f clearly decreases rapidly with increasing particle size.

Figure 15

Semilog plot of particle diameter x against inert gas pressure P . It is seen that x increases with increasing pressure.

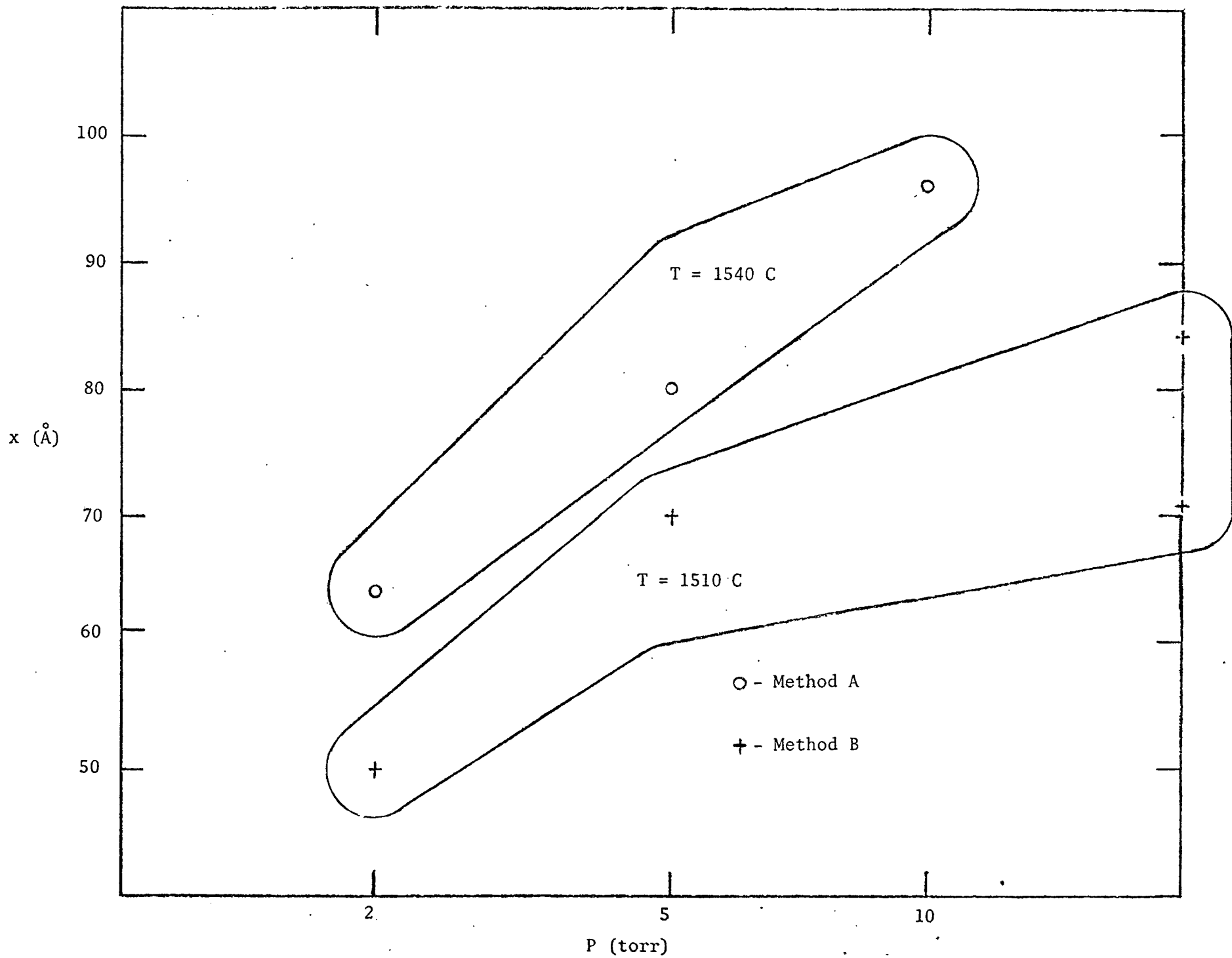
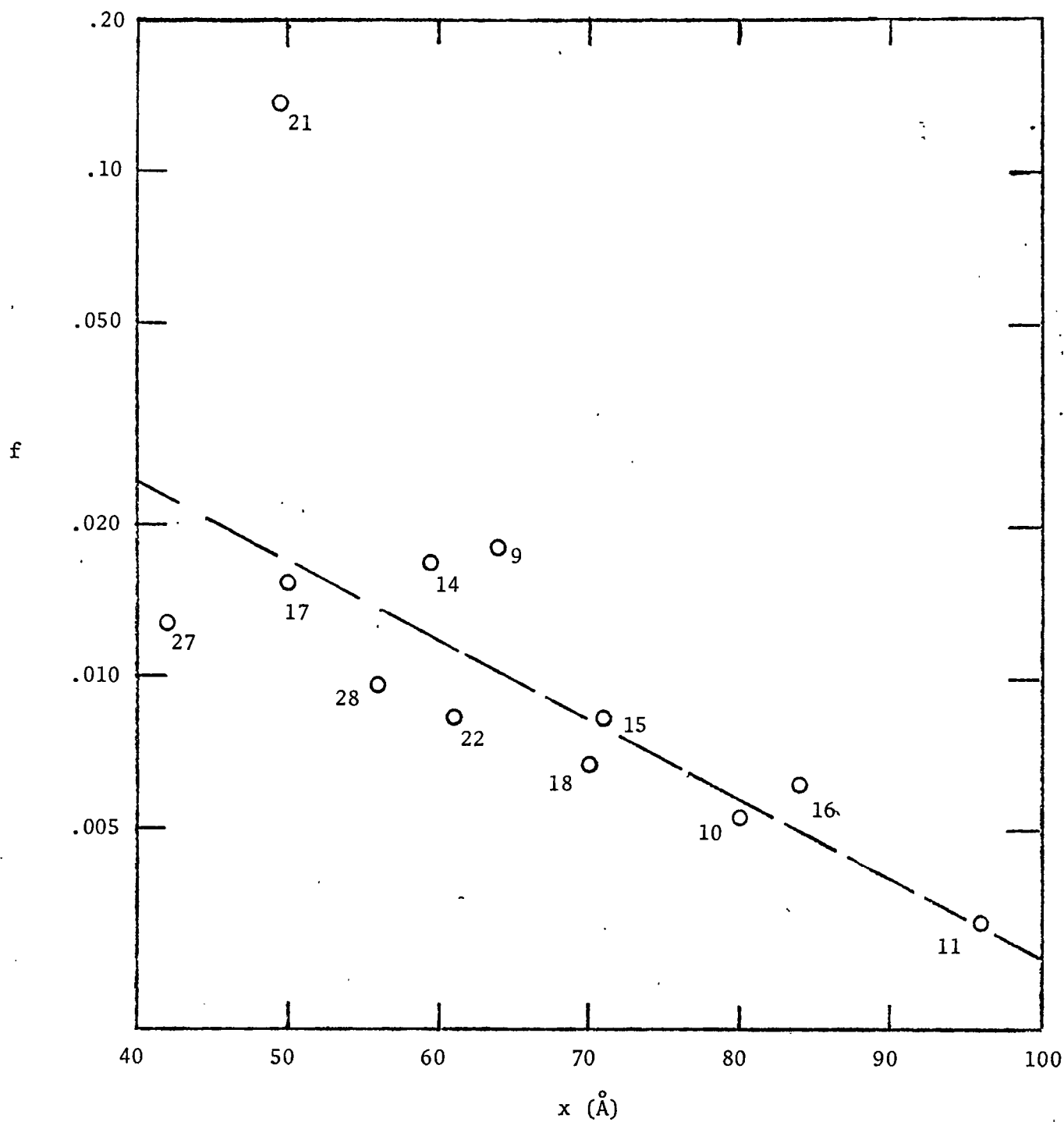


Figure 16

Semilog plot of packing fraction f against particle diameter x . A line is drawn which passes near many of the points. Numbers indicate the sample number of each point.



The dependence of f on x may be due to the sintering of the particles forming the gold black. The chain-like structure of the gold blacks is due to the adhesion between gold particles which reach the substrate. For the small gold black spheres, we expect that sintering will be mainly due to surface diffusion, and that the ratio of the neck radius r to the sphere radius a will obey the equation:¹⁹

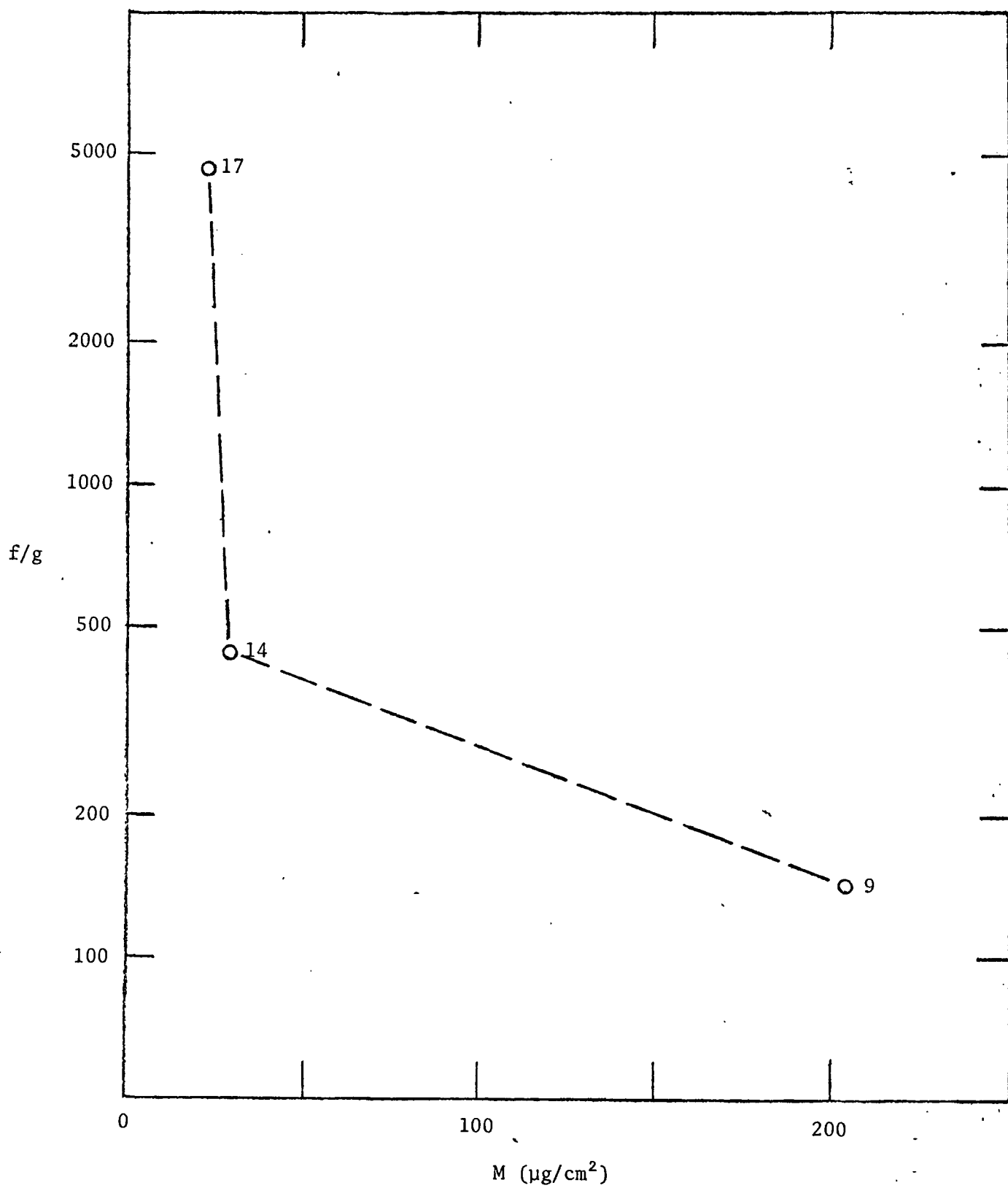
$$\frac{d}{dt}\left(\frac{r}{a}\right) = k(T) / \left[\left(\frac{r}{a}\right)^6 a^3\right] \quad (30)$$

where $k(T)$ is a function only of the temperature T and the composition of the particles. See Figure 19 for an illustration of the radii a and r . Thus, gold black films with smaller particles tend to sinter more than films with larger particles, giving rise to a decrease in f with increasing x . This does not explain why the dependence is nearly exponential, however. This sintering of small particles may also account for the change in optical and electrical properties of gold blacks after heating as noted in reference 11.

From the data for samples 8, 9, 10, and 11, we observe that the ratio f/g increases with decreasing f . Samples 9, 10, and 11 have similar values for M . It can also be seen that for a fixed packing fraction f , the ratio f/g increases with decreasing M . This effect is illustrated in Figure 17. The effect is only significant for values of M below about $50 \mu\text{g}/\text{cm}^2$. As pointed out in section IV B, this effect is thought to be caused by the nonuniformity of the gold black surface, reducing measured values of g below the actual values of g for the samples. The data plotted in Figure 17 support this conclusion.

Figure 17

Semilog plot of the quantity f/g
against area mass density M for
three samples having similar values
for the packing fraction f . Points
are labelled by sample numbers.



Next, we compare the values of the mass absorption coefficient α_m calculated from equation (27) to the measured values of α_m .

$$\alpha_m = \frac{4\pi\sigma}{c D} \frac{1}{(f/g)} \quad (27)$$

Since equation (27) is valid only if ω^2 is much less than $\gamma_0'^2$, we compare the calculated values of α_m with the experimental values for a low angular frequency ω . We choose $\lambda = 2.0 \mu\text{m}$ as the wavelength for comparison. Note that the experimental values of α_m can be calculated from equation (28):

$$T(\omega) = T_s(\omega) e^{-M\alpha_m} \quad (28)$$

$$\alpha_m = M^{-1} \ln(T_s / T_{\text{exp}}) \quad (31)$$

where T_{exp} is the experimentally determined transmittance at $2.0 \mu\text{m}$, and T_s is the transmittance of the glass substrates at $2.0 \mu\text{m}$.

The calculated and experimental values of α_m are tabulated in Table 6 for all samples, for which acceptable measurements of ρ_A and T could be obtained. The thinnest samples have essentially infinite area resistivities, while the thickest samples have too little transmittance to measure. Area densities M are also listed in Table 6. We note that in all cases, the calculated value of α_m is less than the experimental value, with the greatest disagreement for the samples having the lowest area densities. We let the ratio R_α be defined by:

$$R_\alpha = \frac{\alpha_m \text{ (measured)}}{\alpha_m \text{ (calculated)}} \quad (32)$$

A plot of R_α as a function of M appears in Figure 18. R_α is very large for values of M less than about $25 \mu\text{g}/\text{cm}^2$. This supports our claim that the measured values of f/g are less than the actual values for the thin samples. There may also be contributions to α_m due to

Table 6Comparison of Mass Absorption Coefficients

<u>Sample Number</u>	<u>Transmittance %</u>	α_m (cm ² /μg)		<u>M μg/cm²</u>
		<u>measured</u>	<u>calculated</u>	
9a	< 1	> .0208	.0609	217
9b	< 1	> .0236	.0618	191
10a	< 1	> .0215	.0577	210
10b	< 1	> .0148	.0480	305
11a	< 1	> .0238	.0357	190
11b	< 1	> .0172	.0354	262
14a	33	.0340	.0232	30
14b	36.5	.0316	.0174	29.1
17a	49	.0281	.00345	22.2
17b	44	.0320	.00131	22.9
18a	29.5	.0267	.00915	42.4
18b	26	.0275	.00724	45.8
22a	41.5	.0311	.01087	25.4
22b	43	.0288	.01062	26.2
28a	21.5	.0299	.0128	48.4
28b	27.5	.0243	.0115	49.5

Figure 18

Plot of R_α against area mass density

M. Here, R_α is defined by:

$$R_\alpha = \frac{\alpha_m \text{ (measured)}}{\alpha_m \text{ (calculated)}}$$

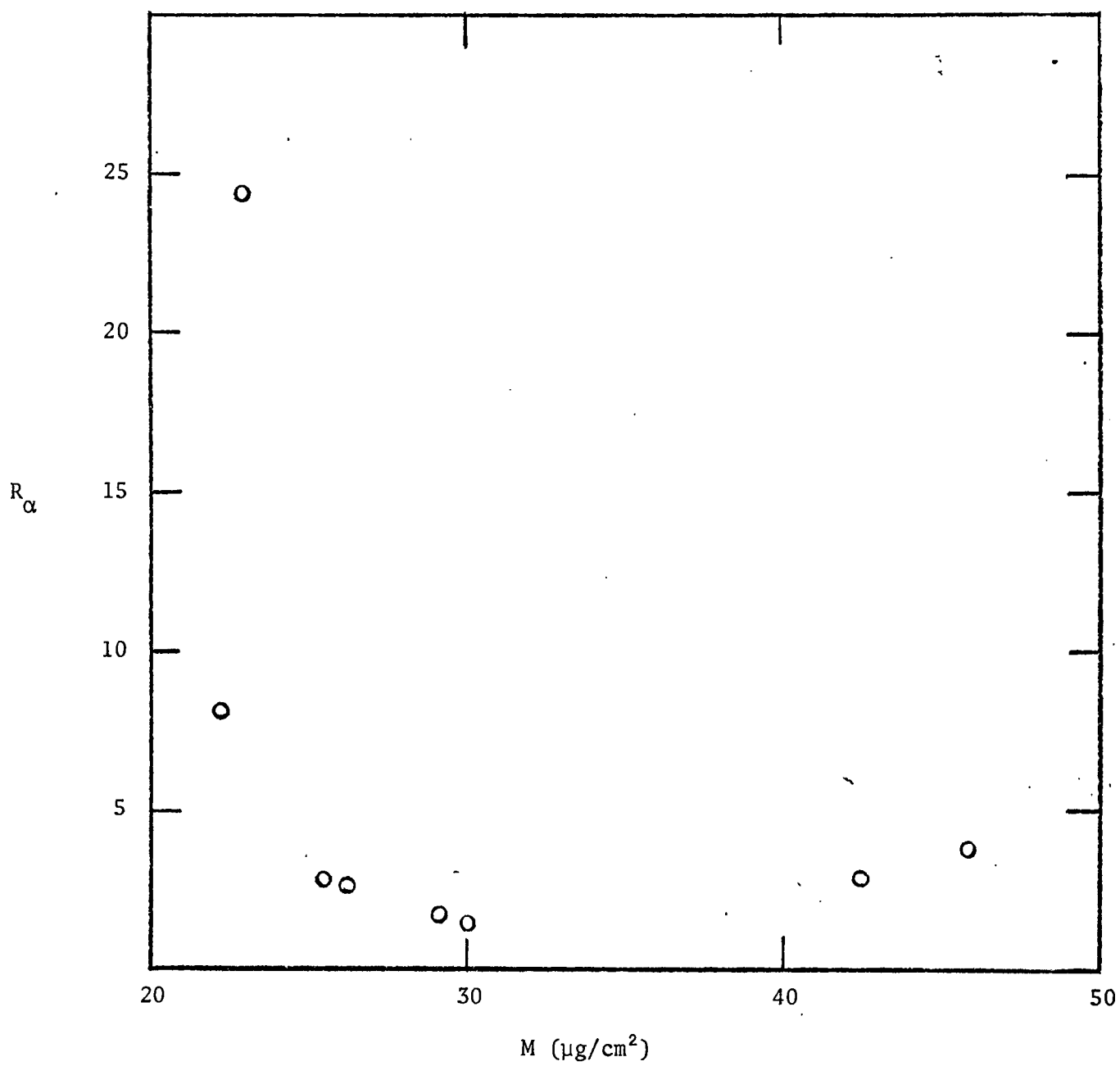
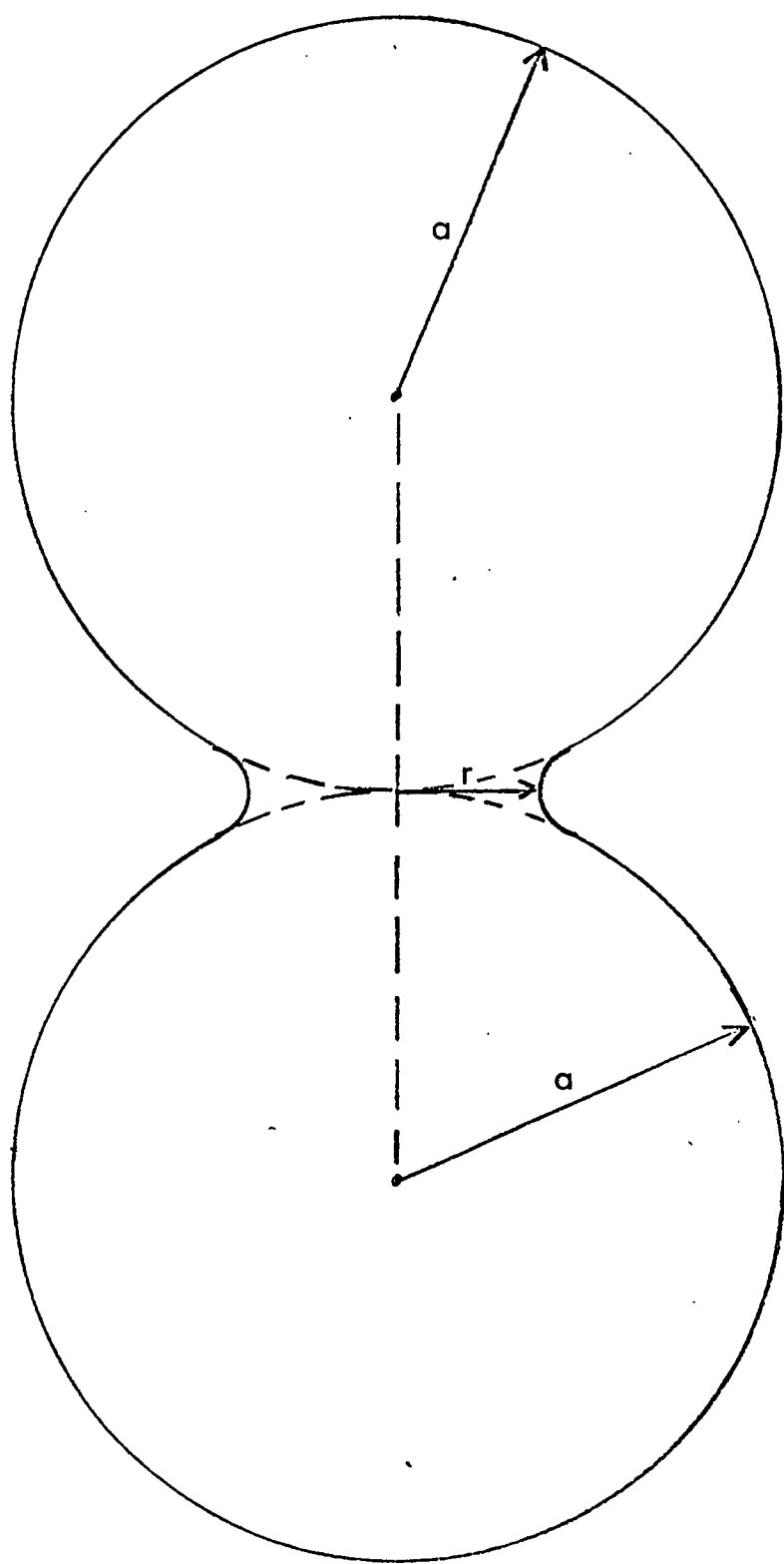


Figure 19

Sintering of Metal Spheres



polarization of the gold black material,¹⁸ accounting for the difference between the theoretical and experimental values of α_m for thick samples.

C. Conclusions

Our experimental work has confirmed the dependence of particle sizes on the evaporation conditions suggested by the authors of references 10 and 12: Particle diameter x increases with

- (i) increasing evaporant vapor pressure, and
- (ii) increasing inert gas pressure.

We have also noted that the packing fraction f of a gold black decreases approximately exponentially with increasing particle diameter x for x between about 40 and 100 Å. Thus, we can control the packing fraction f of gold black samples, by producing particles of the size required to give the desired packing fraction f .

For solar energy applications at high solar fluxes, we require a solar absorber with a high absorption coefficient α and a high thermal conductivity K_a . Specifically, the condition is given by:

$$\alpha K_a \geq 7.34 \times 10^3 \text{ watts m}^{-2} \text{ C}^{-1} \quad (15)$$

For sample 14, for example, we have

$$g = f / (f/g) = 0.0184 / 379 = 4.85 \times 10^{-5}, \text{ and}$$

$$\alpha = (1/t) \ln(T_s / T_{\text{exp}}) = 1.12 \times 10^6 \text{ m}^{-1}.$$

We make the approximation that the thermal conductivity of the gold black is given by the equation:

$$K_a = g K_g \quad (33)$$

where K_g is the thermal conductivity of pure gold. We then obtain

$K_a = (4.85 \times 10^{-5}) (3.15 \text{ watts m}^{-1} \text{ C}^{-1}) = 1.53 \times 10^{-4} \text{ watts m}^{-1} \text{ C}^{-1}$,
 so that $\alpha K_a = 171 \text{ watts m}^{-2} \text{ C}^{-1}$, much lower than the required amount.

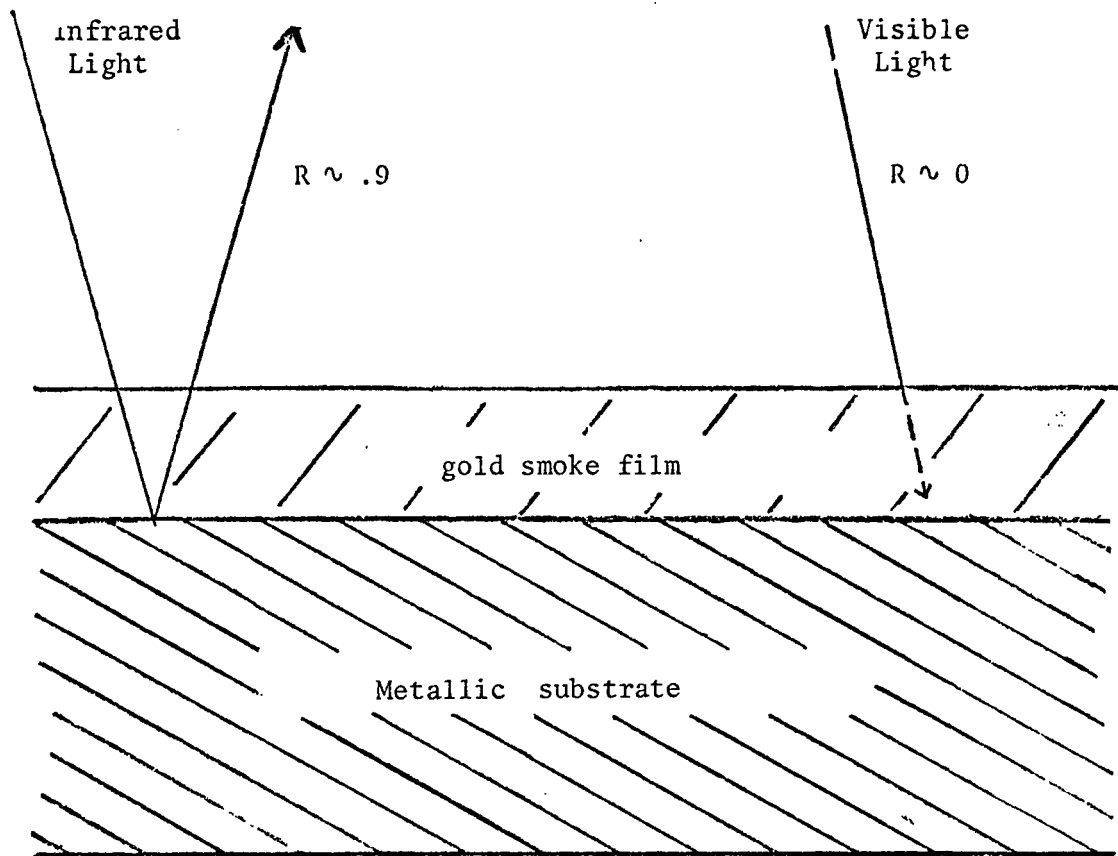
Thus, we find that these gold black samples would be unsuitable for high concentration ratio solar absorbers. The approximation used for the thermal conductivity is valid, since it assumes that the same geometrical factors cause the reduction of thermal conductivity that reduce the electrical conductivity.

We also note that these gold black samples would severely sinter at the temperatures expected in such applications, causing an increase in the reflection coefficient of the material. In fact, the sintering would be most severe for the samples with the smallest particles because of the inverse cube dependence on a in equation (30). Thus, the gold blacks having the highest values of f would be most easily damaged by exposure to high temperatures.

There may be other ways to produce metal blacks having packing fractions of 0.01 to 0.10, while using larger particles. One possibility is to carry out the evaporations under conditions which give large particles, while maintaining the substrates at a temperature sufficient to cause significant sintering of the particles, yielding metal blacks with the desired values of f . Another possibility is to begin with a metal surface and remove a portion of the surface material by etching or ion bombardment, creating a structure similar to our gold blacks. Note that packing fractions above 0.01 may result in a reflection coefficient too high for a solar absorber, particularly if the conductivity of the material is high.

It is interesting to note that gold smokes may be suitable for use for low concentration ratio selective absorbers. A material with a high infrared reflectance (a metal, for example) coated with a gold smoke is shown schematically in Figure 20. Since the gold smoke has nearly 100% transmittance in the infrared, the system will have a high infrared reflectance, and hence a low thermal emissivity for temperatures up to about 1000 °C. The gold smoke, however, will absorb most of the incident solar radiation, since the solar spectrum peaks in the visible, where the transmittance of the gold smoke film is near zero for a sufficiently thick film. See reference 9 for a discussion of selective solar radiation absorbers.

Figure 20
Schematic Diagram of a Selective Absorber



Appendix A

Calculation of the Optical Properties of a Metal Black (Drude Model)

We consider a metal black with a packing fraction f , defined by

$$f = \frac{\text{volume of metal in metal black}}{\text{total volume of metal black}} \quad (\text{A.1})$$

We let σ represent the d. c. conductivity of the pure metal, and let σ_b denote the d. c. conductivity of the metal black. We define the parameter g by the equation:

$$g = \sigma_b / \sigma \quad (\text{A.2})$$

The dielectric function $\epsilon(\omega)$ of a material may be expressed as follows:²⁰

$$\epsilon(\omega) = 1 + 4\pi \frac{Ne^2}{m} \sum_n f_n [\omega_n^2 - \omega^2 - i \omega \gamma_n]^{-1} \quad (\text{A.3})$$

where each term in the sum represents the contribution from a harmonically bound electron with resonance angular frequency ω_n and damping coefficient $m \gamma_n$. The constants f_n are oscillator strengths, and they satisfy the sum rule:

$$\sum_n f_n = Z \quad (\text{A.4})$$

where Z is the atomic number of the material. The atomic density is N , and e and m denote the charge and mass of the electron, respectively. This expression is not exactly correct, even for pure materials, since the difference between the applied field and the average field is neglected.

For a conductor, there is a contribution to $\epsilon(\omega)$ from free electrons.

If we denote this term by a subscript zero, we obtain the following:

$$\epsilon(\omega) = 1 + 4 \frac{\pi}{m} N e^2 \left[\sum_{n>0} \frac{f_n}{\omega_n^2 - \omega^2 - i \omega \gamma_n} - \frac{f_0}{\omega^2 + i \omega \gamma_0} \right]$$

We can rewrite this equation as follows:

$$\epsilon(\omega) = \epsilon_0(\omega) + i \frac{4 \pi N e^2 f_0}{m \omega (\gamma_0 - i \omega)} \quad (A.5)$$

where

$$\epsilon_0(\omega) = 1 + 4 \frac{\pi}{m} N e^2 \sum_{n>0} \frac{f_n}{(\omega_n^2 - \omega^2 - i \omega \gamma_n)} \quad (A.6)$$

If we consider the low frequency limit, where ω is much less than all of the nonzero resonance angular frequencies, then ϵ_0 is essentially constant. The low frequency behavior of a conductor can also be expressed by the following equation:

$$\epsilon(\omega) = \epsilon_0 + i \frac{4 \pi \sigma}{\omega} \quad (A.7)$$

Thus, we identify $N e^2 f_0 / m \gamma_0$ as the d. c. conductivity of the material. Solving for γ_0 gives

$$\gamma_0 = \frac{N e^2 f_0}{m \sigma}$$

It has been shown that the damping constant γ_0 for optical frequencies is 1.7 times the d. c. value.²¹ Thus, we have the following equation:

$$\gamma_0 = 1.7 N e^2 f_0 / m \sigma \quad (A.8)$$

We now consider the case of the metal black, letting $\epsilon_a(\omega)$ represent the dielectric coefficient of the air which occupies most of the space in the black. From equation (A.3), we find that contributions to $\epsilon(\omega)$ are proportional to the atomic density of the material, so that

$$\epsilon(\omega) = (1 - f) \epsilon_a(\omega) + f \epsilon_0(\omega) + i \frac{4 \pi N e^2 f_0 f}{m \omega (\gamma_0 - i \omega)} \quad (A.9)$$

where we have let $m \gamma_o'$ represent the effective damping coefficient for the free electrons in the metal black. We note that both $\epsilon_a(\omega)$ and $\epsilon_o(\omega)$ are independent of ω if ω is sufficiently small. The quantity f_o represents the number of free electrons per metal atom. The d. c. conductivity of the metal black is given by the following equation:

$$\frac{N e^2 f_o f}{1.7 m \gamma_o'} = g \sigma = g \frac{N e^2 f_o}{1.7 m \gamma_o}$$

Hence, $g / \gamma_o = f / \gamma_o'$, so that

$$\gamma_o' = \gamma_o (f/g) \quad (A.10)$$

This implies that the effective damping coefficient $m \gamma_o'$ for the black is greater than the value for the metal, since f/g is greater than one. This is partially due to the larger number of collisions suffered by the electrons in the small metal black particles. A complete description of this effect is involved, so we treat the parameter g as an experimentally determined constant. Equation (A.9) can be rewritten as follows:

$$\epsilon(\omega) = (1-f)\epsilon_a(\omega) + f \epsilon_o(\omega) + i \frac{4 \pi g \sigma}{\omega(1 - i \omega / \gamma_o')} \quad (A.11)$$

where γ_o' is given by equation (A.10). Then

$$\epsilon(\omega) = (1-f) \epsilon_a(\omega) + f \epsilon_o(\omega) - \frac{4 \pi g \sigma \gamma_o'}{(\omega^2 + \gamma_o'^2)} + \frac{4 \pi g \sigma \gamma_o'^2}{\omega (\omega^2 + \gamma_o'^2)} \quad (A.12)$$

We can use this expression to calculate approximate values of the reflection and absorption coefficients of the metal black. We first note that $\sqrt{\epsilon_a(\omega)} = 1.00028$, over the spectral range of interest (0.35 to 2.5 μm). We regard $\epsilon_a(\omega)$ and $\epsilon_o(\omega)$ as constants, and let $\delta_a = \epsilon_a - 1 = 5.6 \times 10^{-4}$ and $\delta_o = \epsilon_o - 1$. We expect that δ_o is of order unity.

$$\begin{aligned}
(1-f) \epsilon_a(\omega) + f \epsilon_o(\omega) &= (1-f) (1 + \delta_a) + f (1 + \delta_o) \\
&= 1 - f + \delta_a - f \delta_a + f + f \delta_o \\
&= 1 + \delta_a + f \delta_o.
\end{aligned}$$

We have neglected a term of order $f \delta_a$ compared to one. Hence,

$$\epsilon(\omega) = 1 + \delta_a + f \delta_o - \frac{1}{2} \frac{\pi g \sigma \gamma_o'}{(\omega^2 + \gamma_o'^2)} + i \frac{4 \pi g \sigma \gamma_o'^2}{\omega (\omega^2 + \gamma_o'^2)} \quad (\text{A.13})$$

It can be shown that the following relations are always true:

$$\frac{\gamma_o'}{\omega^2 + \gamma_o'^2} < \frac{1}{\omega} \text{ and } \frac{\gamma_o'}{\omega(\omega^2 + \gamma_o'^2)} < \frac{1}{\omega}$$

For the spectral region under consideration, ($\lambda = .35$ to $2.5 \mu\text{m}$), ω is between 7.5×10^{14} and $5.4 \times 10^{15} \text{ sec}^{-1}$. Furthermore, $\sigma \leq 6 \times 10^{17} \text{ sec}$, the conductivity of silver, the most electrically conductive metal, and g is of order 10^{-5} . Thus, $4 \pi g \sigma / \omega \ll 1$. We can then make the expansion:

$$\begin{aligned}
\sqrt{\epsilon(\omega)} &= \{\text{Re}[\epsilon(\omega)] + i \text{Im}[\epsilon(\omega)]\}^{1/2} \\
&= \sqrt{\text{Re}[\epsilon(\omega)]} \times \{1 + i \frac{\text{Im}[\epsilon(\omega)]}{\text{Re}[\epsilon(\omega)]}\}^{1/2} \\
&= \sqrt{\text{Re}[\epsilon(\omega)]} \times \{1 + \frac{1}{2} i \frac{\text{Im}[\epsilon(\omega)]}{\text{Re}[\epsilon(\omega)]}\}
\end{aligned}$$

since $\{\frac{\text{Im}[\epsilon(\omega)]}{\text{Re}[\epsilon(\omega)]}\}^2 \ll 1.0$, provided $g\sigma \ll 4.3 \times 10^{14} \text{ sec}$. Then

$$\sqrt{\epsilon(\omega)} = \sqrt{\text{Re}[\epsilon(\omega)]} + \frac{1}{2} i \frac{\text{Im}[\epsilon(\omega)]}{\sqrt{\text{Re}[\epsilon(\omega)]}}$$

where $\sqrt{\text{Re}[\epsilon(\omega)]}$ is approximately given by the following equation:

$$\sqrt{\text{Re}[\epsilon(\omega)]} = 1 + \frac{1}{2} [\delta_a + f \delta_o - 4 \pi g \sigma \gamma_o' / (\omega^2 + \gamma_o'^2)]$$

Hence, neglecting products of terms small compared to one, we obtain

$$\sqrt{\epsilon(\omega)} = 1 + \frac{1}{2} (\delta_a + f \delta_o) - \frac{2 \pi g \sigma \gamma_o'}{(\omega^2 + \gamma_o'^2)} + i \frac{2 \pi g \sigma \gamma_o'^2}{\omega (\omega^2 + \gamma_o'^2)} \quad (\text{A.14})$$

We calculate R and α as follows:

$$R = \left| \frac{\sqrt{\epsilon} - \sqrt{\epsilon_a}}{\sqrt{\epsilon} + \sqrt{\epsilon_a}} \right|^2$$

$$\sqrt{\epsilon} - \sqrt{\epsilon_a} = \left[1 + \frac{1}{2} (\delta_a + f \delta_o) - \frac{2 \pi g \sigma \gamma_o'}{(\omega^2 + \gamma_o'^2)} + i \frac{2 \pi g \sigma \gamma_o'^2}{\omega (\omega^2 + \gamma_o'^2)} \right] - \left(1 + \frac{1}{2} \delta_a \right)$$

$$\sqrt{\epsilon} - \sqrt{\epsilon_a} = \frac{1}{2} f \delta_o - \frac{2 \pi g \sigma \gamma_o'}{(\omega^2 + \gamma_o'^2)} + i \frac{2 \pi g \sigma \gamma_o'^2}{\omega (\omega^2 + \gamma_o'^2)}$$

$$\sqrt{\epsilon} + \sqrt{\epsilon_a} = 2 + \delta_a + \frac{1}{2} f \delta_o - \frac{2 \pi g \sigma \gamma_o'}{(\omega^2 + \gamma_o'^2)} + i \frac{2 \pi g \sigma \gamma_o'^2}{\omega (\omega^2 + \gamma_o'^2)}$$

$$\sqrt{\epsilon} + \sqrt{\epsilon_a} \approx 2$$

Thus, we obtain the following expression for $R(\omega)$:

$$R(\omega) = \frac{1}{4} \left[\left(\frac{f \delta_o}{2} - \frac{2 \pi g \sigma \gamma_o'}{(\omega^2 + \gamma_o'^2)} \right)^2 + \left(\frac{2 \pi g \sigma \gamma_o'^2}{\omega (\omega^2 + \gamma_o'^2)} \right)^2 \right] \quad (A.15)$$

$$\alpha = 2 \frac{\omega}{c} \text{Im}[\sqrt{\epsilon(\omega)}] = 2 \frac{\omega}{c} \frac{2 \pi g \sigma \gamma_o'^2}{\omega (\omega^2 + \gamma_o'^2)}$$

$$\alpha(\omega) = \frac{4 \pi g \sigma \gamma_o'^2}{c(\omega^2 + \gamma_o'^2)} \quad (A.16)$$

for $\lambda = .35$ to $2.5 \mu\text{m}$. Note that the above results are valid only

for metal blacks of low electrical conductivity, having $g\sigma \ll 4.3 \times 10^{14} \text{ sec}$.

Appendix B

Log-Normal Distribution

The characteristics of the log-normal distribution function are discussed briefly in this appendix. We define a distribution of a parameter x to be log-normal if the logarithm of x obeys a gaussian distribution. The normalized gaussian distribution function $g(y)$ is given by the equation:

$$g(y) = [\sqrt{2\pi} \sigma_y]^{-1} \exp[-(y - y_0)^2 / 2 \sigma_y^2] \quad (B.1)$$

where y_0 is the mean value of y , and σ_y is the standard deviation of y . Thus, we have the following equations:

$$y_0 = \int_{-\infty}^{+\infty} y g(y) dy \quad (B.2)$$

$$\sigma_y^2 = \int_{-\infty}^{+\infty} (y - y_0)^2 g(y) dy \quad (B.3)$$

We also have the normalization condition for $g(y)$, given by :

$$\int_{-\infty}^{+\infty} g(y) dy = 1 \quad (B.4)$$

We let y be the logarithm of x to obtain the log-normal distribution function $f(x)$.

$$f(x) = g(\ln x)$$

$$f(x) = [\sqrt{2\pi} \sigma_y]^{-1} \exp[-(\ln x - y_0)^2 / 2 \sigma_y^2] \quad (B.5)$$

We note that the normalization becomes the following:

$$\int_{-\infty}^{+\infty} g(y) dy = \int_{\ln 0}^{\ln \infty} f(x) d(\ln x) = 1$$

We do not characterize the log-normal distribution by the mean y_0 and standard deviation σ_y of $\ln x$. Instead of y_0 , we use the median value of x , denoted by x_0 , which is more convenient. The median x_0 ,

of the distribution is given by the following equation:

$$\int_{\ln 0}^{\ln x_0} f(x) d(\ln x) = 1/2$$

$$\int_{-\infty}^{\ln x_0} g(y) dy = 1/2$$

Clearly, we obtain

$$\ln x_0 = y_0 \quad (B.6)$$

The geometric standard deviation σ , which is used in favor of σ_y , is the ratios of values of x whose logarithms differ by one standard deviation σ_y . Hence, we obtain the equation:

$$\ln \sigma = \sigma_y \quad (B.7)$$

Substitution of these parameters into equation (B.5) yields the following:

$$\begin{aligned} f(x) &= [\sqrt{2\pi} \ln \sigma]^{-1} \exp[-(\ln x - \ln x_0)^2 / 2 \ln^2 \sigma] \\ f(x) &= [\sqrt{2\pi} \ln \sigma]^{-1} \exp[-\frac{1}{2} (\frac{\ln(x/x_0)}{\ln \sigma})^2] \end{aligned} \quad (B.8)$$

The probability that a particle has a diameter in the range $x_1 < x < x_2$ can be expressed as follows:

$$\begin{aligned} P(x_1, x_2) &= \int_{\ln x_2}^{\ln x_1} f(x) d(\ln x) \\ P(x_1, x_2) &= \int_{\ln x_2}^{\ln x_1} \frac{1}{x} f(x) dx \end{aligned} \quad (B.9)$$

If we let $x_1 = 0$, we obtain the probability that a particle has a diameter less than x_2 , as follows:

$$\begin{aligned} P(x_2) &= P(0, x_2) = \int_0^{x_2} \frac{1}{x} f(x) dx \\ P(x_2) &= [\sqrt{2\pi} \ln \sigma]^{-1} \int_0^{x_2} \frac{1}{x} \exp[-\frac{1}{2} (\frac{\ln(x/x_0)}{\ln \sigma})^2] dx \end{aligned} \quad (B.10)$$

From the definition of the error function, we can express $P(x)$ as follows:

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-t^2} dt$$

$$\operatorname{erf}(\infty) = 1 \quad \operatorname{erf}(0) = 0$$

$$\text{Let } t = \frac{\ln(x/x_0)}{\sqrt{2} \ln \sigma}; \quad \frac{dx}{dt} = \sqrt{2} \ln \sigma x$$

$$P(x) = [\sqrt{2} \pi \ln \sigma]^{-1} \int_{-\infty}^t \sqrt{2} (\ln \sigma) e^{-t^2} dt$$

$$P(x) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{t_0} e^{-t^2} dt \quad \text{where } t_0 = \frac{\ln(x/x_0)}{\sqrt{2} \ln \sigma}$$

$$P(x) = \pi^{-1/2} \int_{-\infty}^0 e^{-t^2} dt + \pi^{-1/2} \int_0^{t_0} e^{-t^2} dt$$

$$P(x) = \frac{1}{2} \operatorname{erf}(\infty) + \frac{1}{2} \operatorname{erf}(t_0)$$

$$P(x) = \frac{1}{2} [1 + \operatorname{erf}(t_0)] ; \quad t_0 = \frac{\ln(x/x_0)}{\sqrt{2} \ln \sigma} \quad (\text{B.11})$$

Log probability paper is calibrated in a probability scale along one axis and in a logarithmic scale along the other axis. Since t_0 and $\ln x$ are linearly related, a plot of a log-normal distribution on log probability paper yields a straight line. Figure 14 is a log probability plot for one of our samples. Note that the values of x_0 is the value of x at the point where the experimental line crosses the 50% probability line. The value of the geometric standard deviation σ is given by the ratio x_1/x_0 , where x_1 is the value of x where the experimental line crosses the vertical line corresponding to the probability:

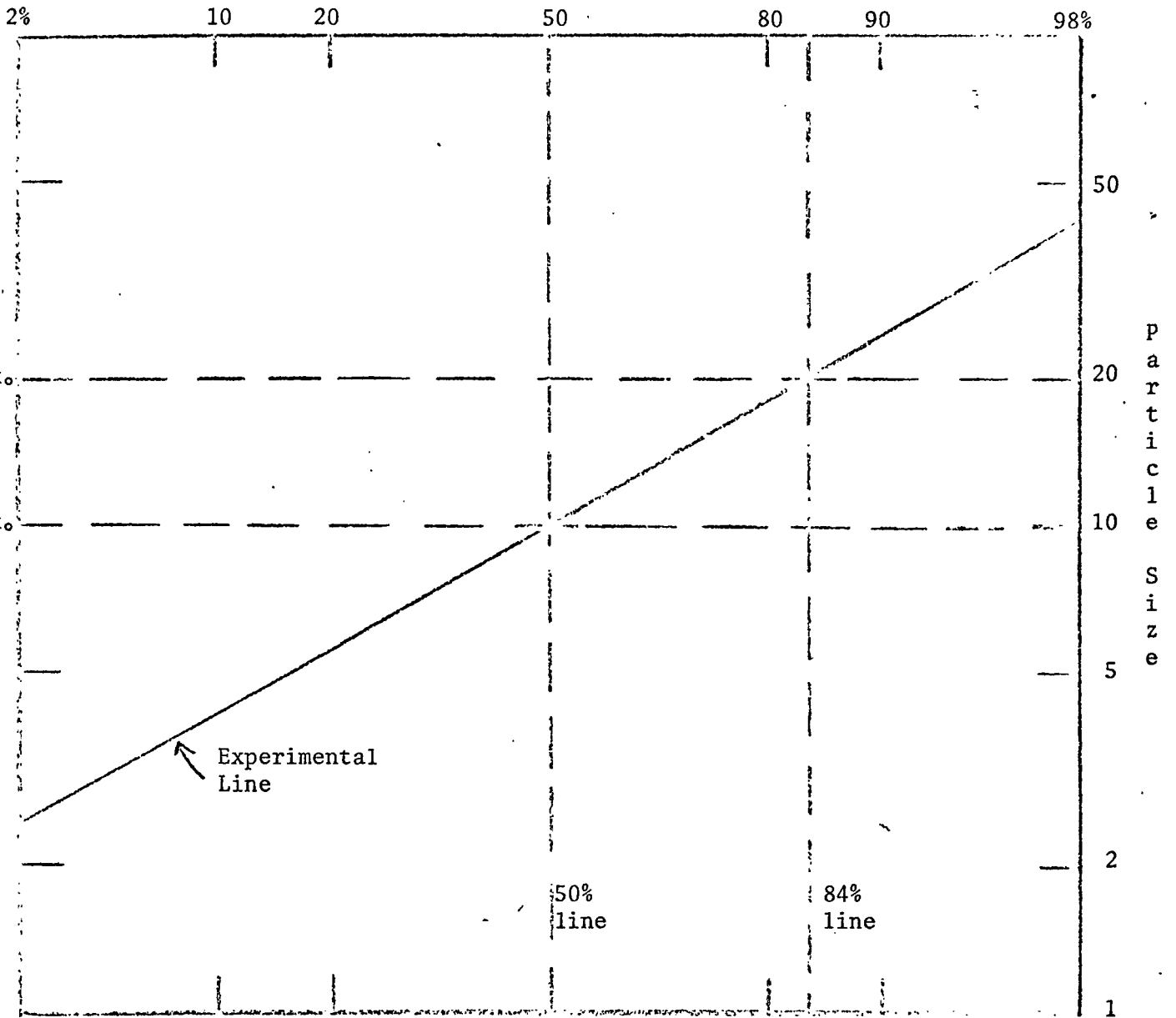
$$P(x) = \frac{1}{2} [1 + \operatorname{erf}(1/\sqrt{2})] = .841 = 84.1\%.$$

An example of the determination of x_0 and σ from a log-probability plot is given in Figure 21.

Figure 21

Sample log-probability plot showing the method used to find x_0 and σ . For this plot, $x_0 = 10$ and $\sigma = 2$.

Percentage



Appendix C

Review of Analytical Techniques

Transmission Electron Microscope (TEM)

In many ways, transmission electron microscopes are similar to conventional light microscopes. Figure 22 is a schematic diagram of a typical TEM. Electrons which are emitted from a hot filament are accelerated by a potential difference between the anode and the filament of about 40 to 1000 kilovolts. The resulting electron beam is focused by a condenser lens onto the sample. The beam transmitted through the sample is refocused to form an image of the sample by the objective lens. The projector lens magnifies this image and projects it onto a fluorescent screen for direct viewing, or onto a photographic emulsion to be recorded.

The lenses in an electron microscope differ considerably from the glass lenses used in ordinary light microscopes. Two different types of lenses may be used, electrostatic lenses or magnetic lenses. The electrostatic lenses focus the electron beam by subjecting it to an axially symmetric electric field. Magnetic lenses use axially symmetric magnetic fields to alter the electron paths. It can be shown that both of these types of lenses have the same effects on the electron beam that glass lenses have on light beams, at least for electrons which travel nearly along the optic axis.²² The various apertures used to stop stray electrons are not included in Figure 22.

Commercial transmission electron microscopes are able to achieve magnifications of about 10^5 , and minimum distances resolvable of about 10 Å under optimal conditions. The gold particles in our samples have

Figure 22

Schematic Diagram of a
Transmission Electron Microscope

E - electron source

H - high voltage connection

A- anode

B - electron beam

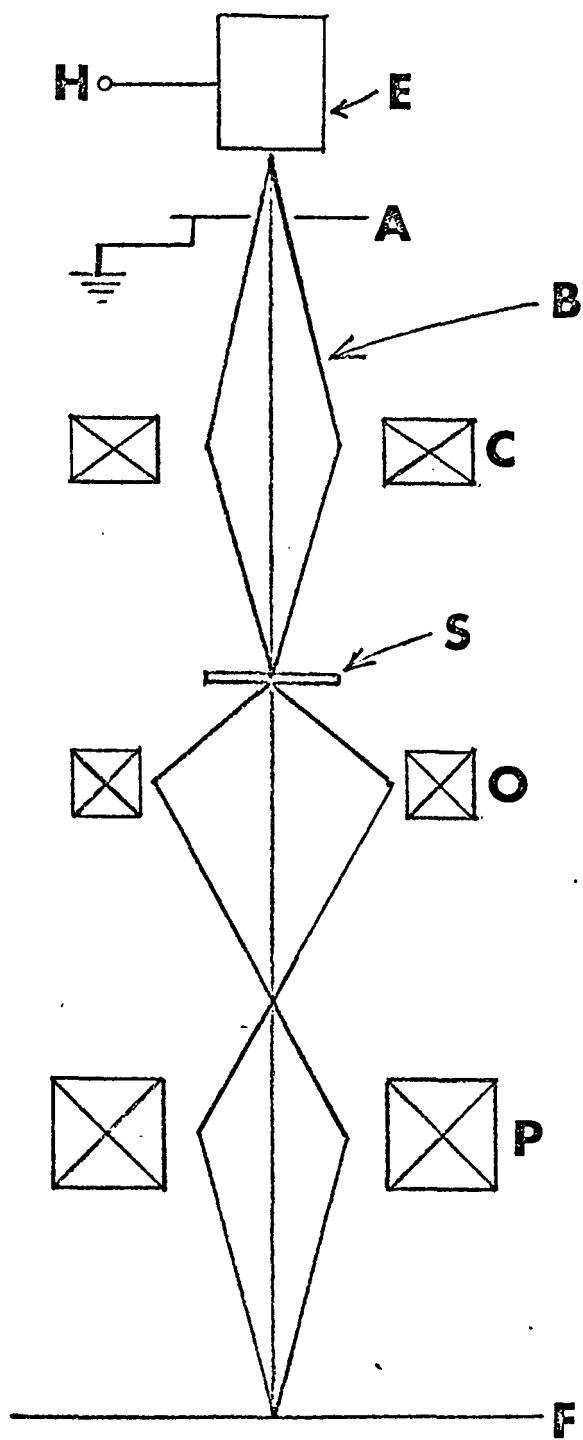
C - condenser lens

S - sample

O - objective lens

P - projector lens

F- fluorescent screen or film



sufficient opacity to obtain good contrast between particles and the Formvar film, so that high resolution photographs could be obtained. The TEM photos of our samples were all brightfield images. Some samples were seen to coalesce due to heating from the primary electron beam, but this effect was only seen in the denser samples. This coalescence may be the mechanism which causes the change in the optical properties of samples which are heated.

Scanning Electron Microscope (SEM)

The SEM uses the interaction of a small diameter electron beam with a point on a surface to form a image of that point. The electron beam is scanned across the sample in a raster pattern and a measure of the interaction at each point is reproduced on a cathode ray tube (CRT), building an image of the sample surface point by point. Several different types of interactions may be used to form the image, including:

- (i) backscattering of primary electrons,
- (ii) secondary electron emission, and
- (iii) characteristic x-ray emission.

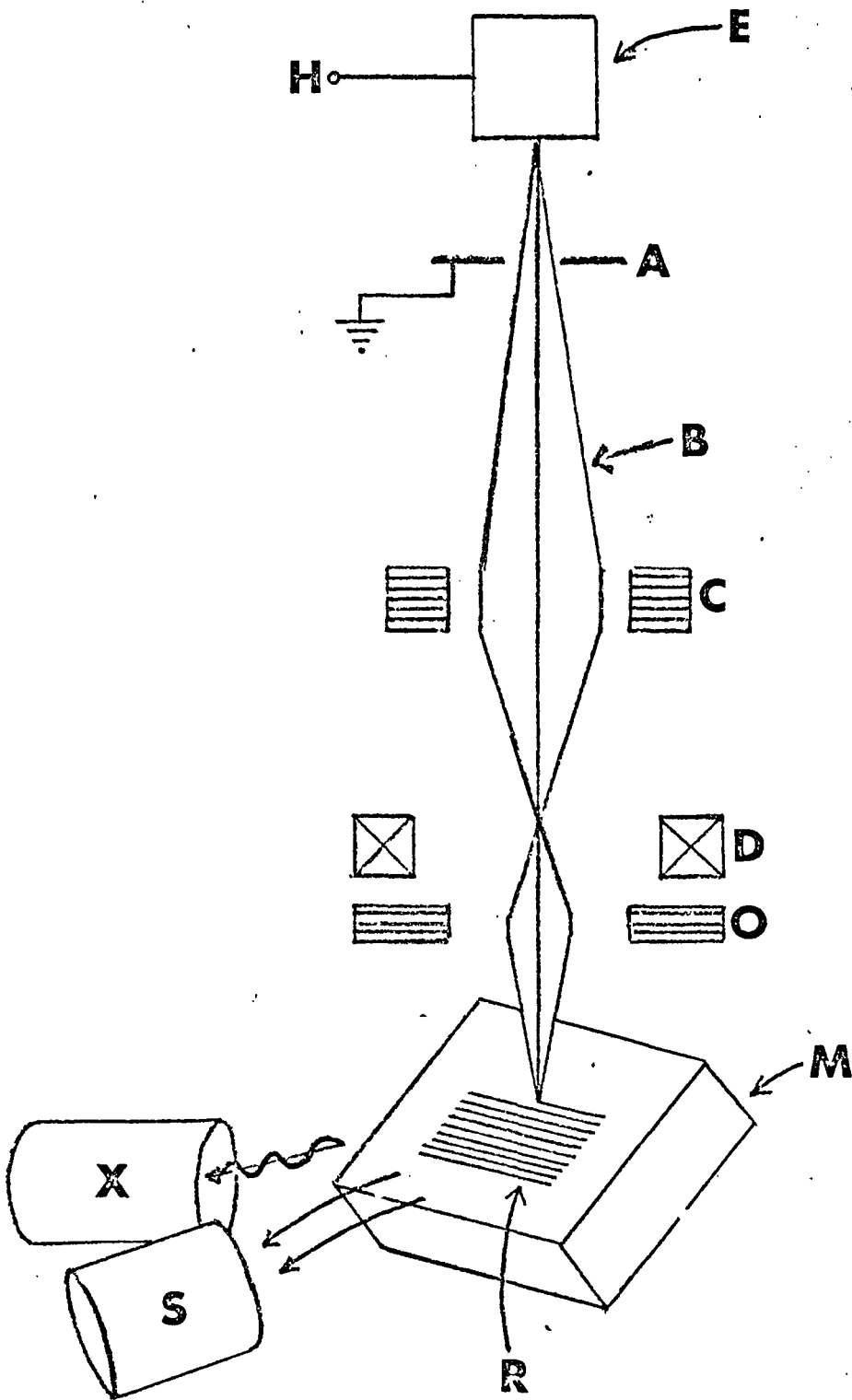
These different types of signals give different information about the sample. Figure 23 is a schematic diagram of this type of instrument.

The secondary electrons have energies on the order of 5 eV, and they can travel only short distances through the sample without being absorbed (typically about 10 to 50 Å). Hence, secondary electrons are emitted only from a region about 50 Å deep, having a diameter approximately equal to the primary beam diameter. The secondary electrons can be collected to produce a signal which controls the brightness

Figure 23

Schematic Diagram of a
Scanning Electron Microscope

- H - high voltage connection
- E - electron source
- A - anode
- B - electron beam
- C - condenser lens
- D - deflection coils
- M - movable stage holding sample
- R - raster pattern
- S - secondary electron collector
- X - x-ray detector



of the image points on the CRT. This type of imaging generally yields the highest resolution obtainable with the SEM of about 50 to 100 Å, because of the small size of the region of secondary electron emission.

The intensity of secondary electron emission depends on many factors, including primary beam voltage, the sample material and crystalline form, and the topography of the sample surface. In Figure 24a, the region of secondary electron emission from a flat surface is pictured. Figure 24b shows that projections above a flat surface give a higher secondary electron signal level due to the increased volume from which secondary electron emission can be detected. A hole or depression in a sample causes a decrease in secondary electron signal as shown in Figure 24c, due to absorption of the secondary electrons before they can escape from the hole. Therefore, secondary electrons give a high resolution picture of surface topography.

Backscattered electrons originate from a larger region of the specimen (1000 Å to 1 μm diameter), so the resolution of images formed using the backscattered electron intensity is slightly poorer. Some backscattered electrons may enter the secondary electron collector, but the intensity of backscattered electrons in the secondary electron collector is negligibly small. Backscattered electrons may be collected by a separate detector, and the resulting signal may be used to emphasize differences in composition of the sample from point to point. Some SEM's have the capability to combine the secondary electron and backscattered electron signals to produce different images of a given sample.

Fluorescence x-rays are emitted from a region of the specimen even larger than that of the backscattered electrons. Usually, x-ray intensity signals are not used to form an image, but rather used to perform an elemental analysis of the sample at some point. This is

Figure 24

Effects of Topography on Secondary
Electron Emission in the SEM

- (a) flat surface
- (b) projection
- (c) depression

M - sample material

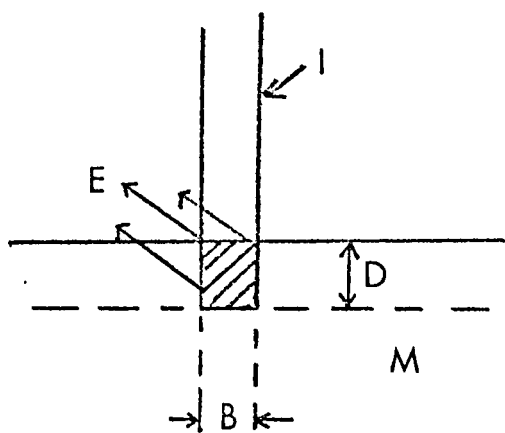
I - incident (primary) electron beam

B - primary beam diameter

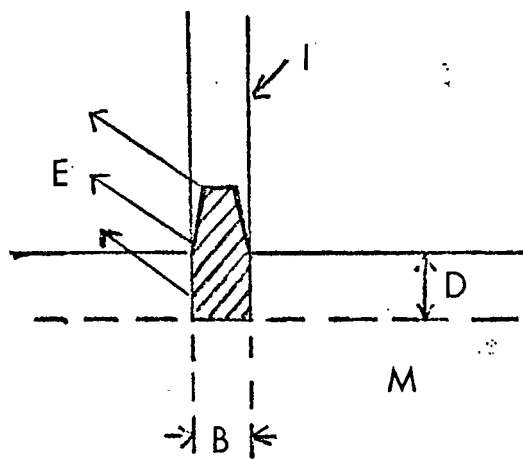
D - depth of penetration of secondary
electrons

E - secondary electrons

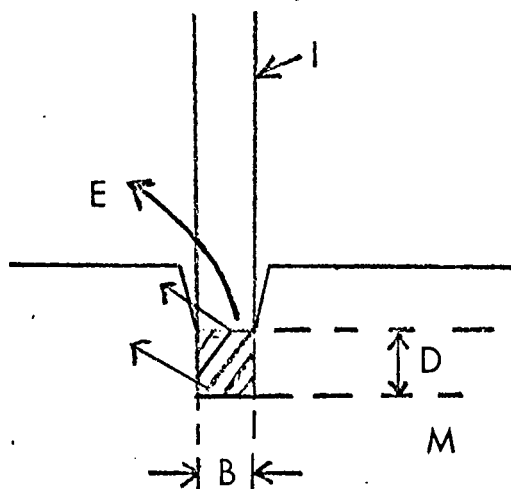
The shaded region indicates the volume from which
secondary electrons may escape from the material.



(a)



(b)



(c)

done by measuring the x-ray intensity as a function of wavelength, producing a spectrum which can be compared to the characteristic x-ray spectra of the elements. Usually, an energy dispersive detector is used, which gives spectra of low resolution, so that only elements of relatively high atomic number can be detected. Although wavelength dispersive detectors have a much better resolution, they are not commonly used because they are more complicated to use and more difficult to maintain.²³

Electron Spectroscopy for Chemical Analysis (ESCA)

Electron spectroscopy, in general, involves the examination of energy spectra of electrons emitted from atoms. The emission of electrons can be stimulated by bombardment of the sample with photons or with electrons. Another possible mechanism for causing electron emission is the Auger process, in which an excited ion decays into a lower energy state with the emission of another electron. The excited ions may be produced by photon or electron bombardment.

The type of electron spectroscopy dealing with electron emission due to x-ray photons is usually termed Electron Spectroscopy for Chemical Analysis. Since x-ray photons generally stimulate core electron emission and data on core electron energy levels can be used to identify the atoms in a sample, this terminology is appropriate. Ultraviolet photons, which are less energetic, can be used to cause photoejection of valence electrons, and these electron spectra can be used to study the bonding of atoms in a sample. This type of electron spectroscopy is termed Photoelectron Spectroscopy (PES). Electron beams are not generally used to stimulate electron emission, due to the large number of scattered electrons which causes a high level background at the detector.

In order to obtain accurate values for the energy levels of the photoejected electrons, the incident photon beam must be monochromatic, and the energy of the emitted electrons must be determined. This is done by passing the photoelectrons from the sample through a variable monochromator and into a detector. The electron intensity at the detector is measured as a function of the electron energy picked out by the monochromator. Due to incomplete knowledge of the work function of the sample, only differences between the electron energies at the detector are of significance, but this is not a serious problem, since Auger electrons (which have energies independent of the energy of the incident photons) can be used as a standard of reference. A more complete discussion of electron spectroscopy can be found in reference 24.

Particle Size Determination by X-Ray Diffraction

The breadth of the x-ray diffraction peaks from a powder sample depends on the size of the crystallites and on other factors. For very small particles, the dependence on particle size is dominant. For larger crystallites, a correction for other factors can be made by comparison to a standard diffraction peak from a large single crystal. The effective particle size L normal to the surface of the sample is given by:

$$L = \frac{\lambda}{\beta(2\theta) \cos \theta}$$

where λ is the x-ray wavelength, 2θ is the scattering angle, and $\beta(2\theta)$ is the full width of the peak at half maximum.²⁵

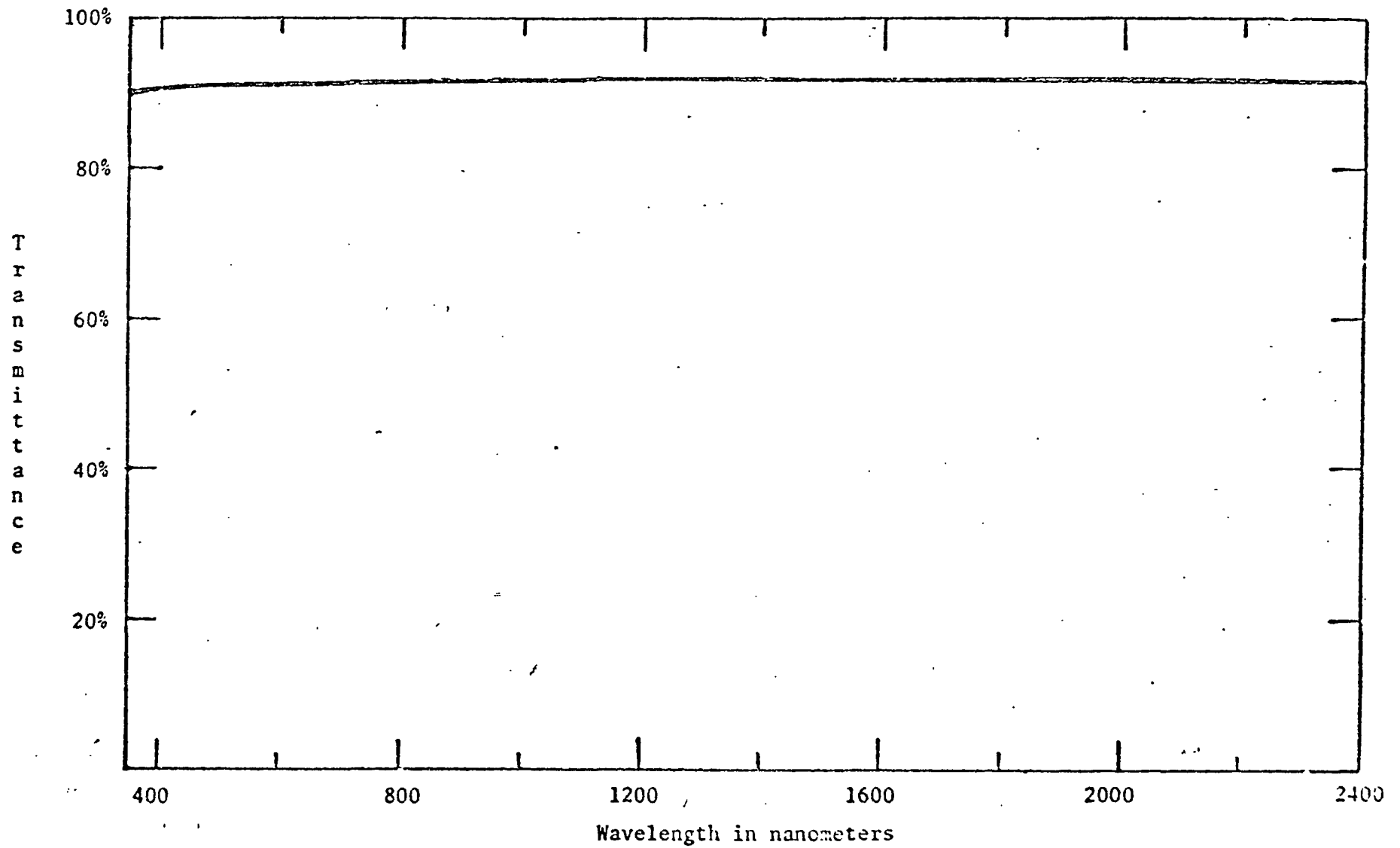
The x-ray particle size measurements were done on a diffractometer using Cu K α radiation with a Ni filter ($\lambda = 1.54 \text{ \AA}$). The (111) reflection of gold was used, with a diffraction angle of $2\theta = 38.26^\circ$. The full width of the standard peak was $.27^\circ$ and all sample peaks had widths of about 1.0° . No correction was applied for instrument broadening.

Appendix D

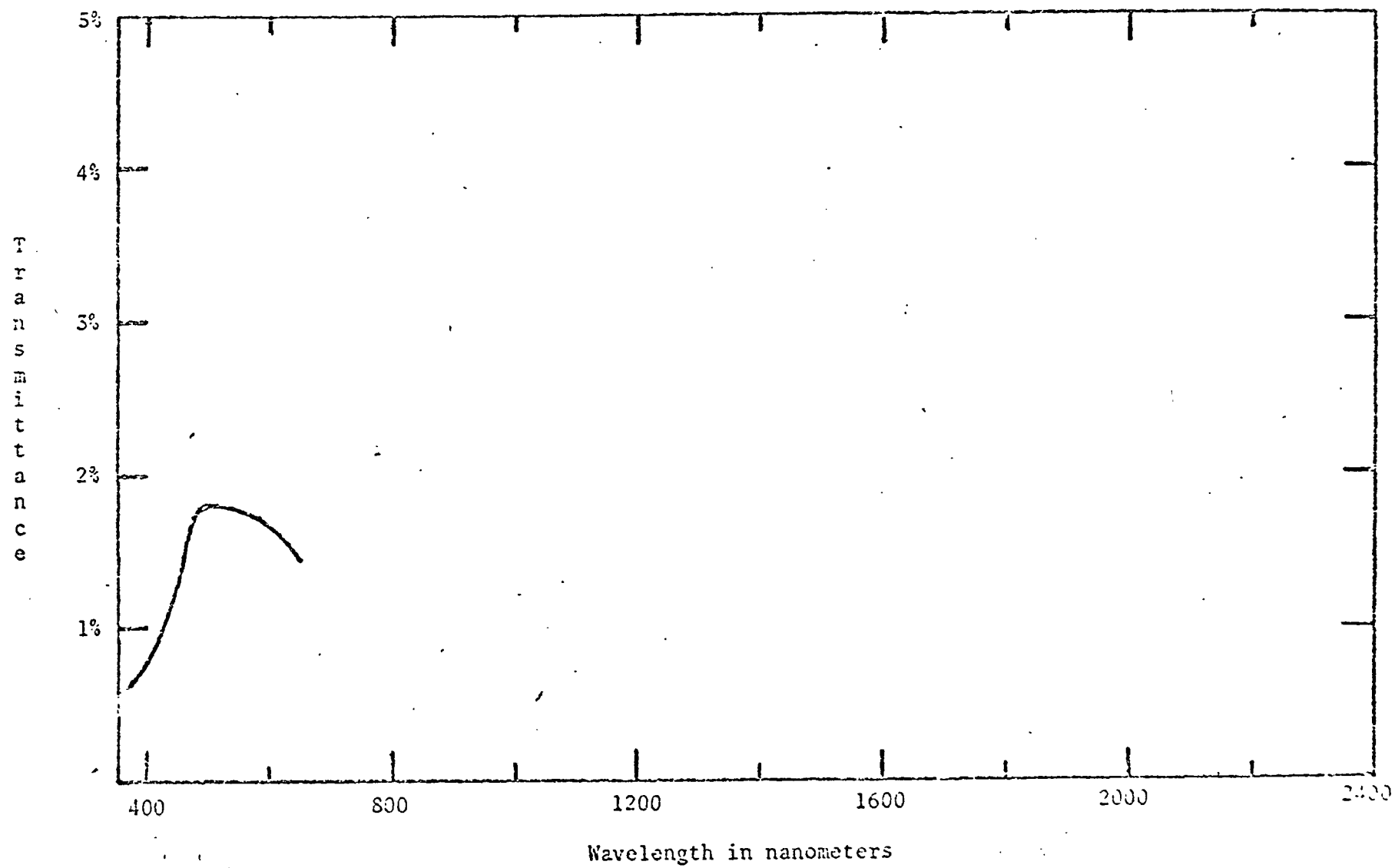
Data -- Optical Properties of Gold Blacks

The samples which we examined were prepared under the conditions listed in Table 3. Total (diffuse and specular) reflectance measurements of samples 9, 10, and 11 were made. In all cases, the reflectance was less than 1% for the spectral region of .35 to 2.4 μm . Direct transmittance curves of samples 9, 10, and 11 for the visible spectrum (.35 to .65 μm) are included in this appendix. Total transmittance measurements of the remaining samples, except for sample 8, were done for the spectral region of .35 to 2.4 μm , and the data are in this appendix. The sample transmittances have not been corrected for the reflectance from the glass substrates, but the transmittance curve for a blank glass substrate covering .35 to 2.4 μm is included.

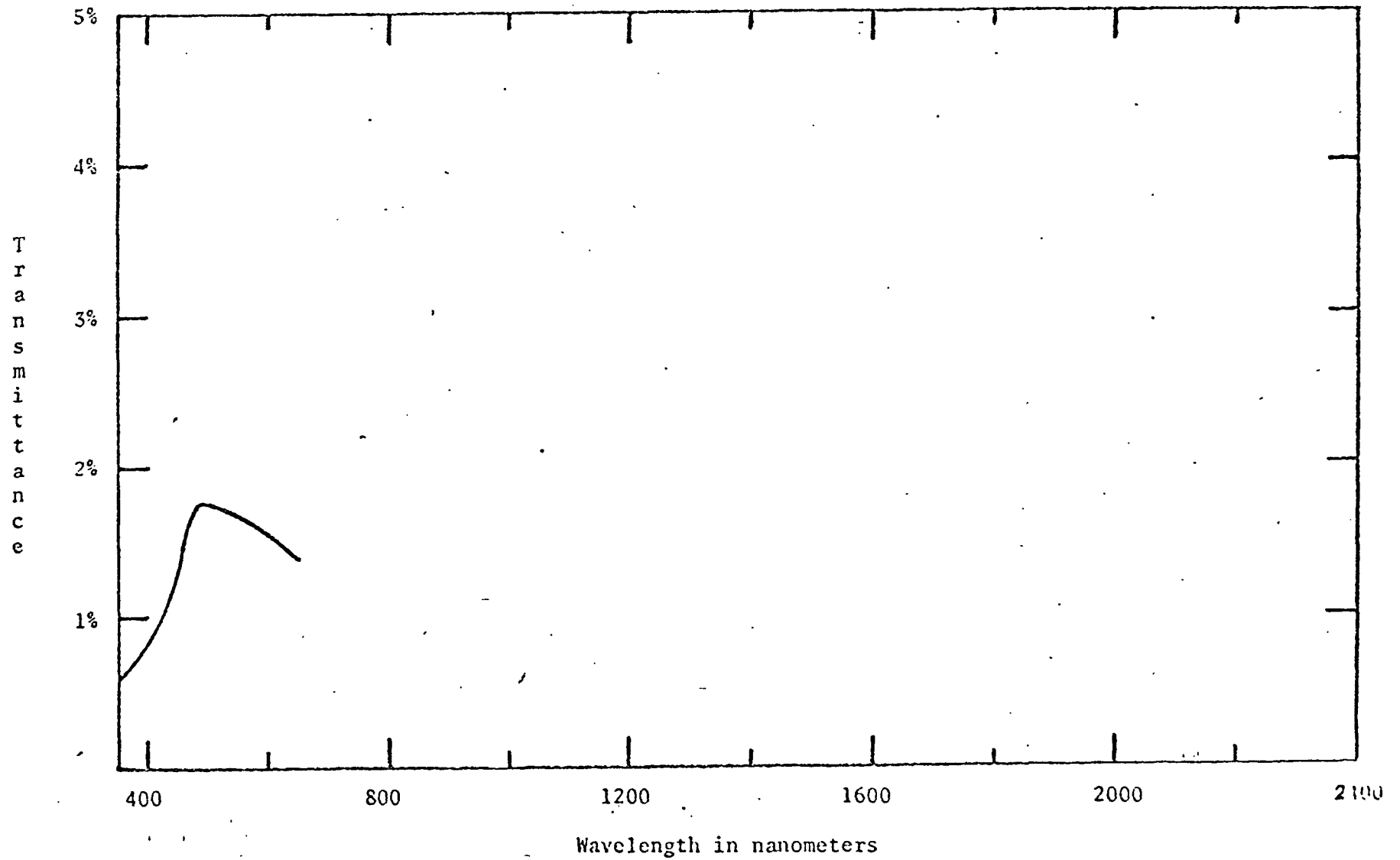
Glass Cover Slip



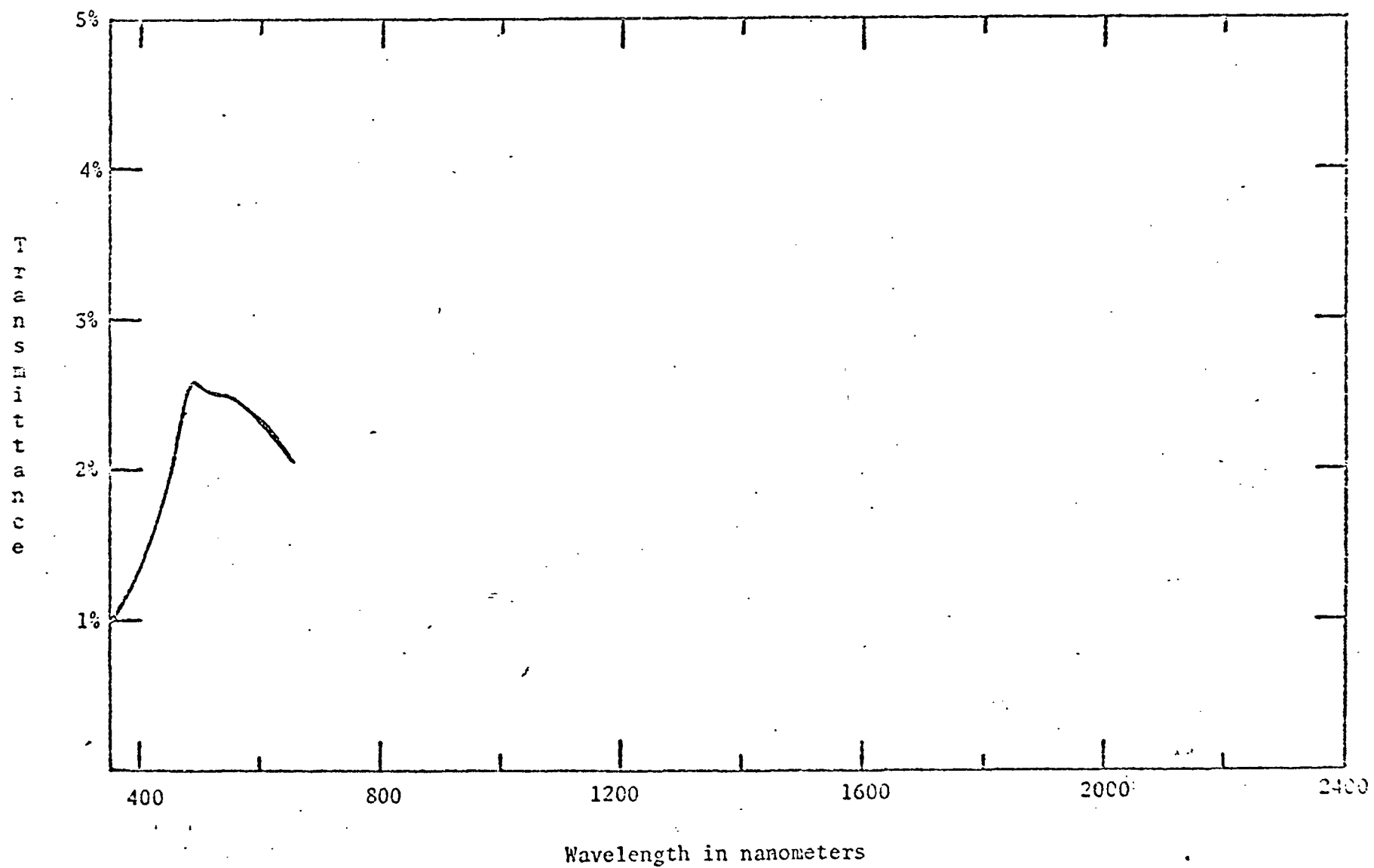
Sample # 9a



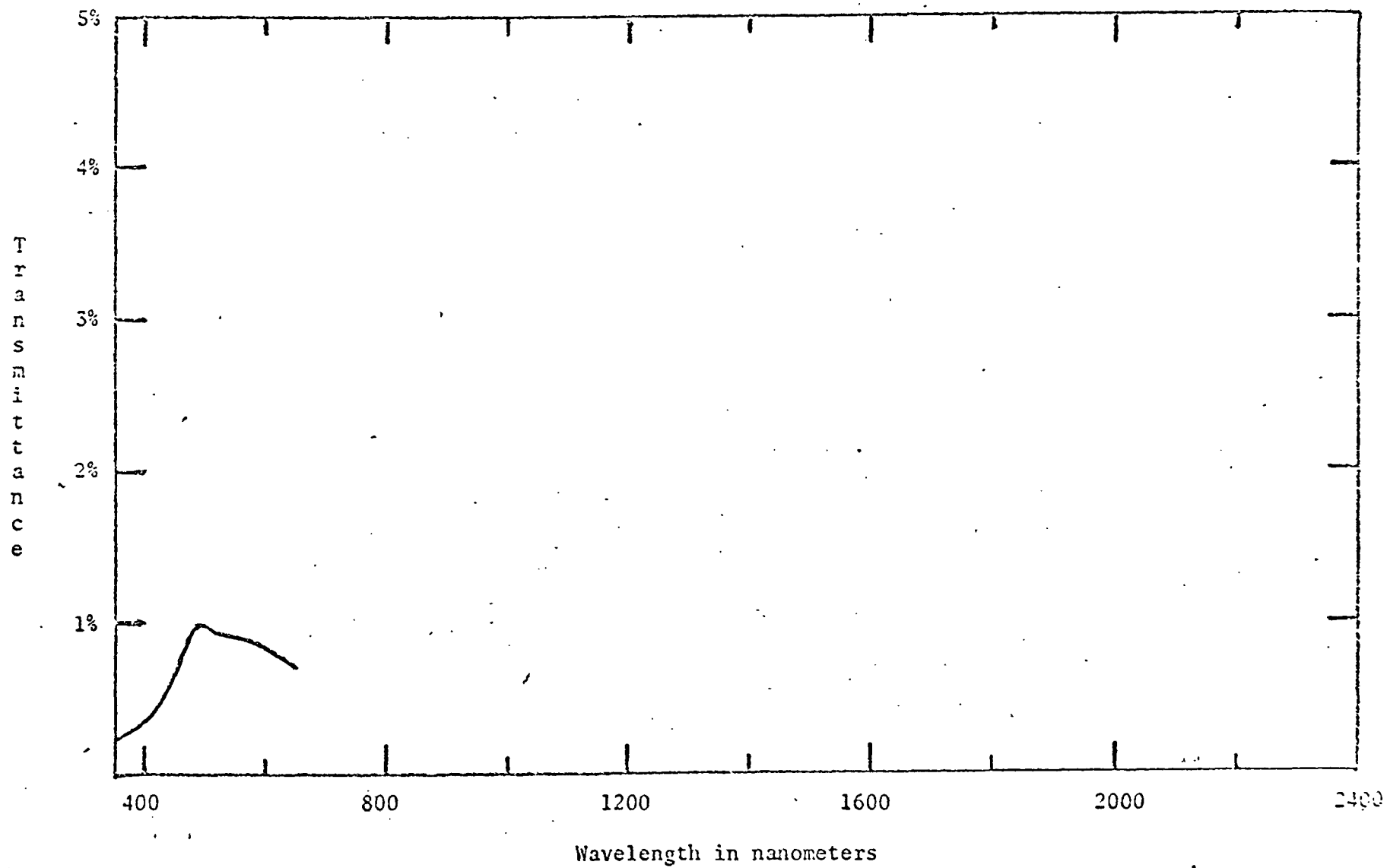
Sample # 10a



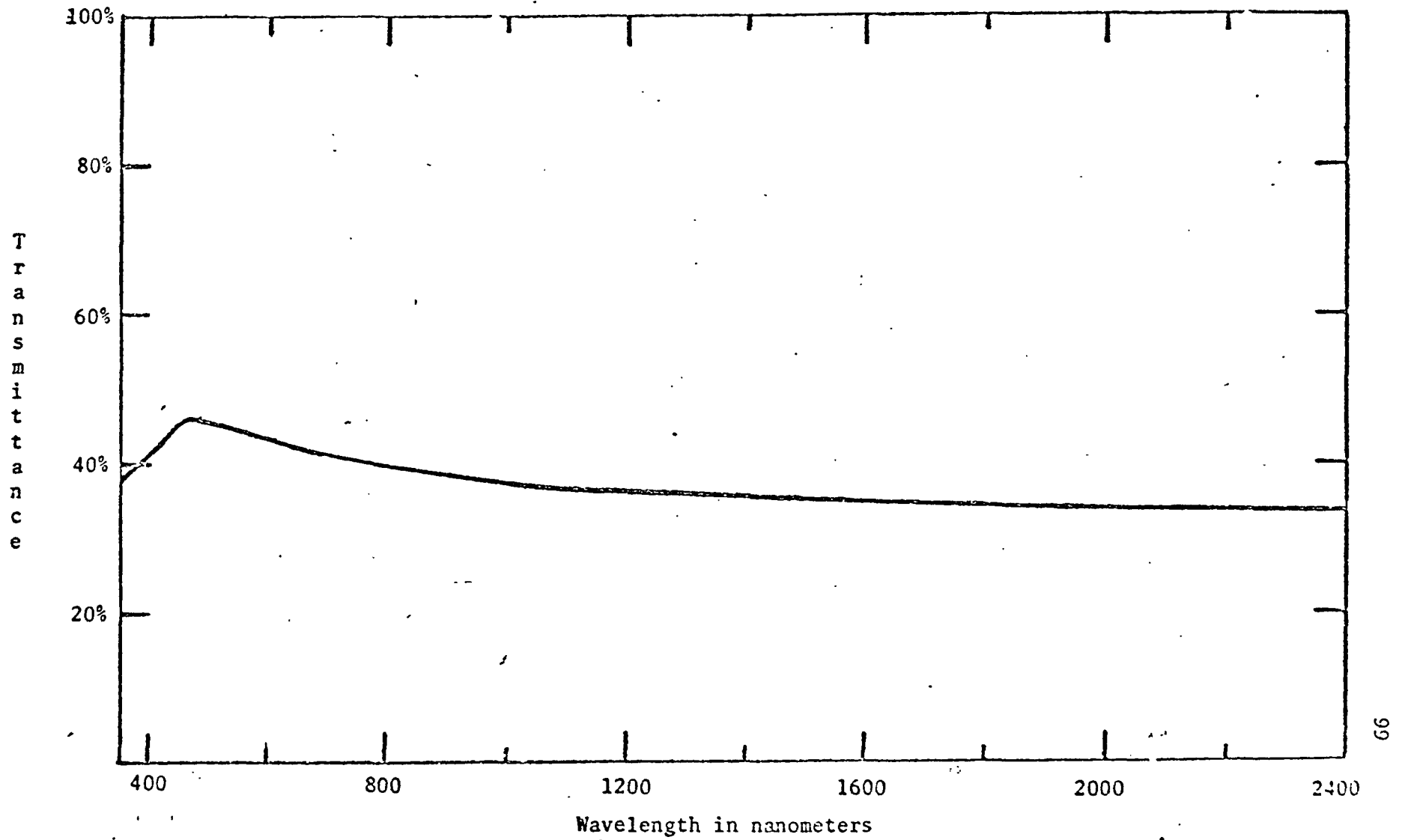
Sample # 11a



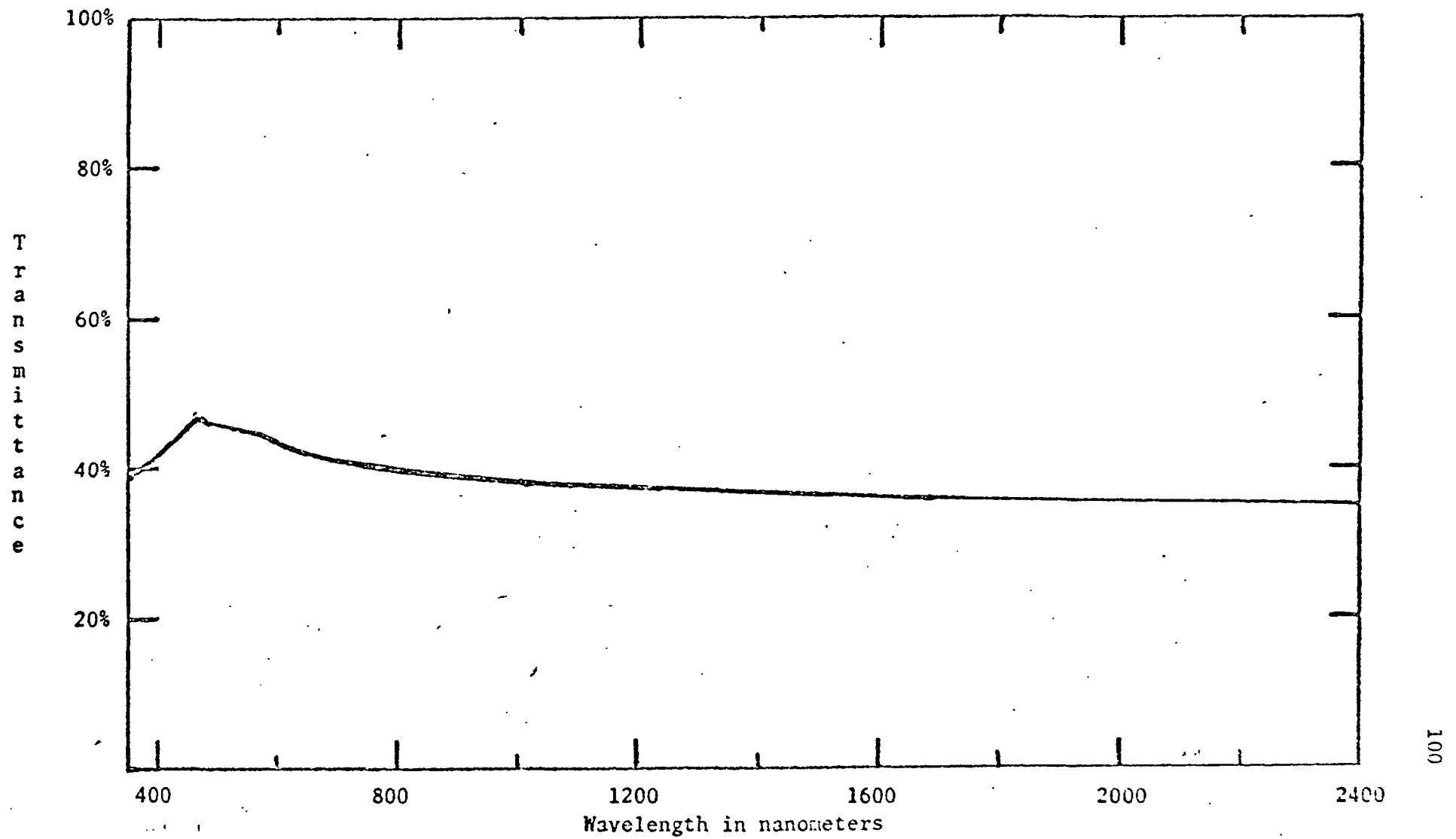
Sample # 11b



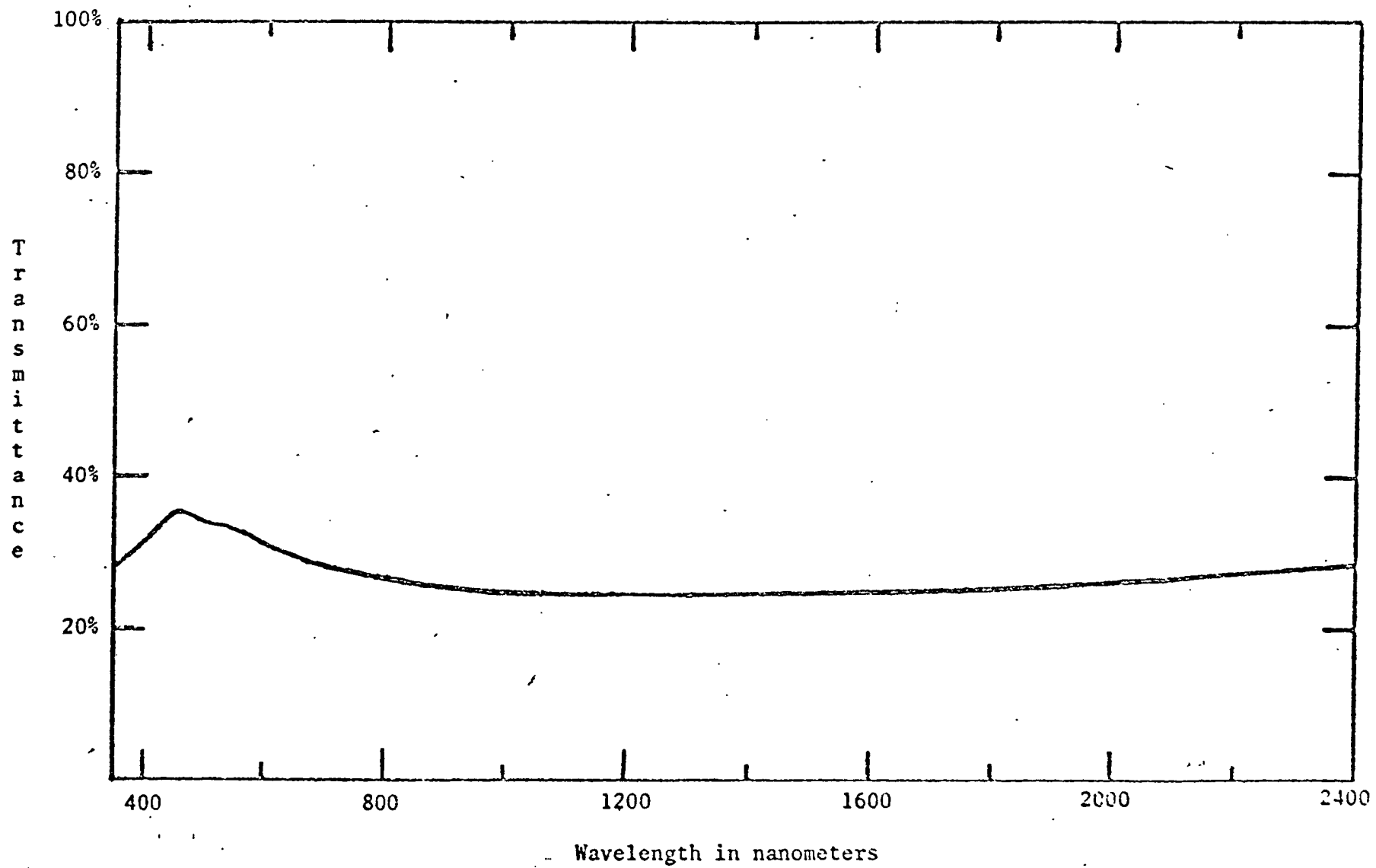
Sample # 14a



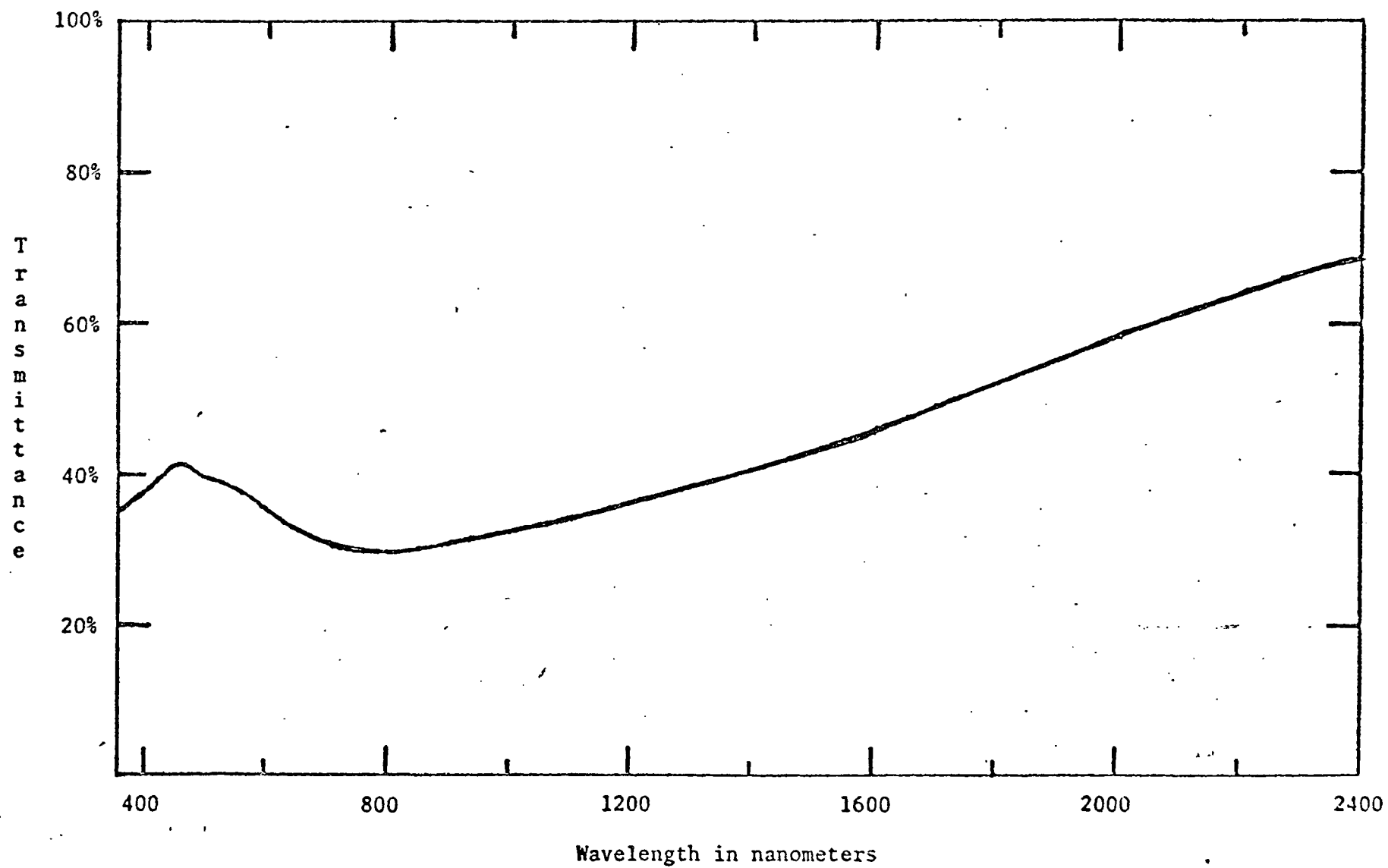
Sample # 14b



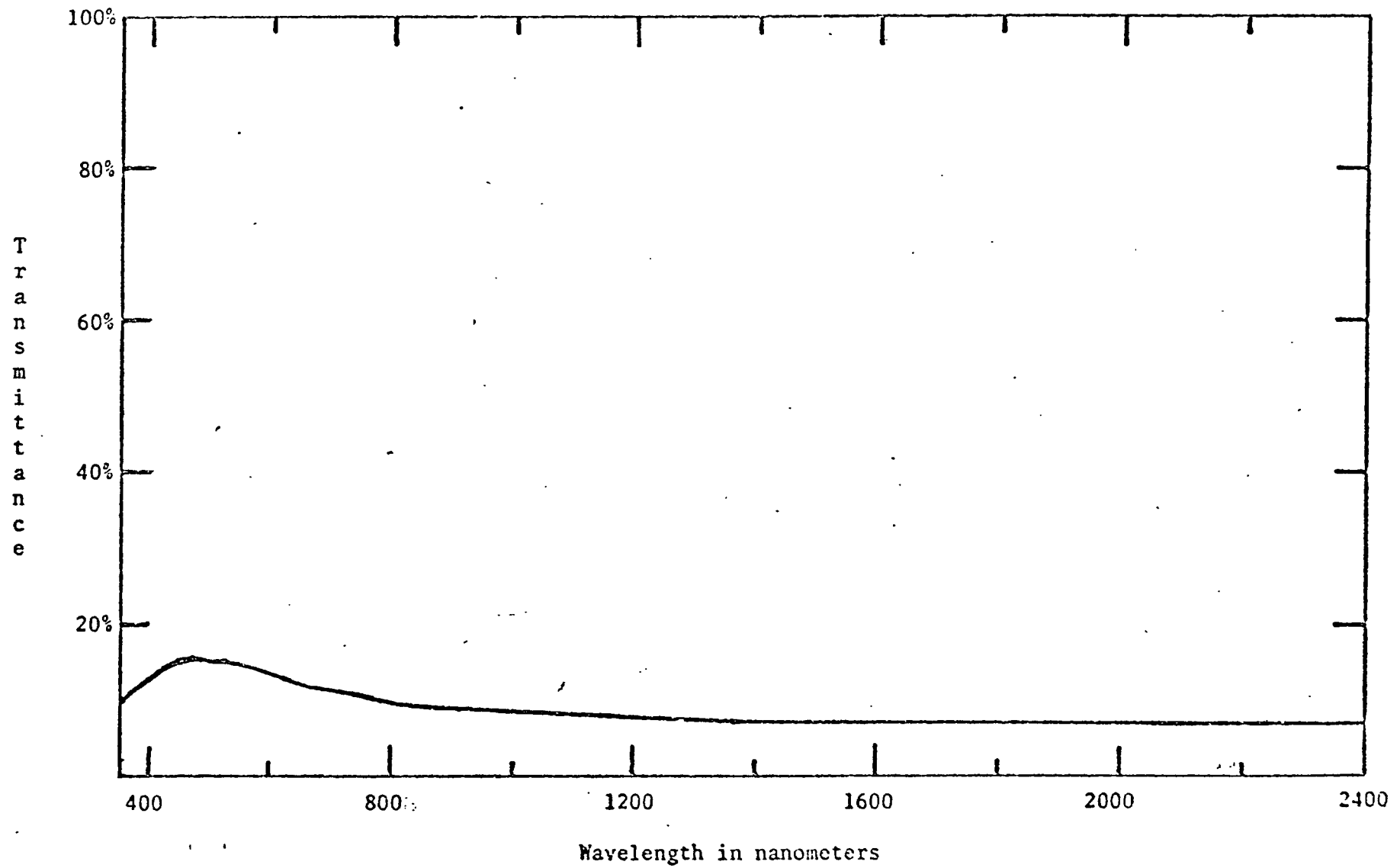
Sample # 15a



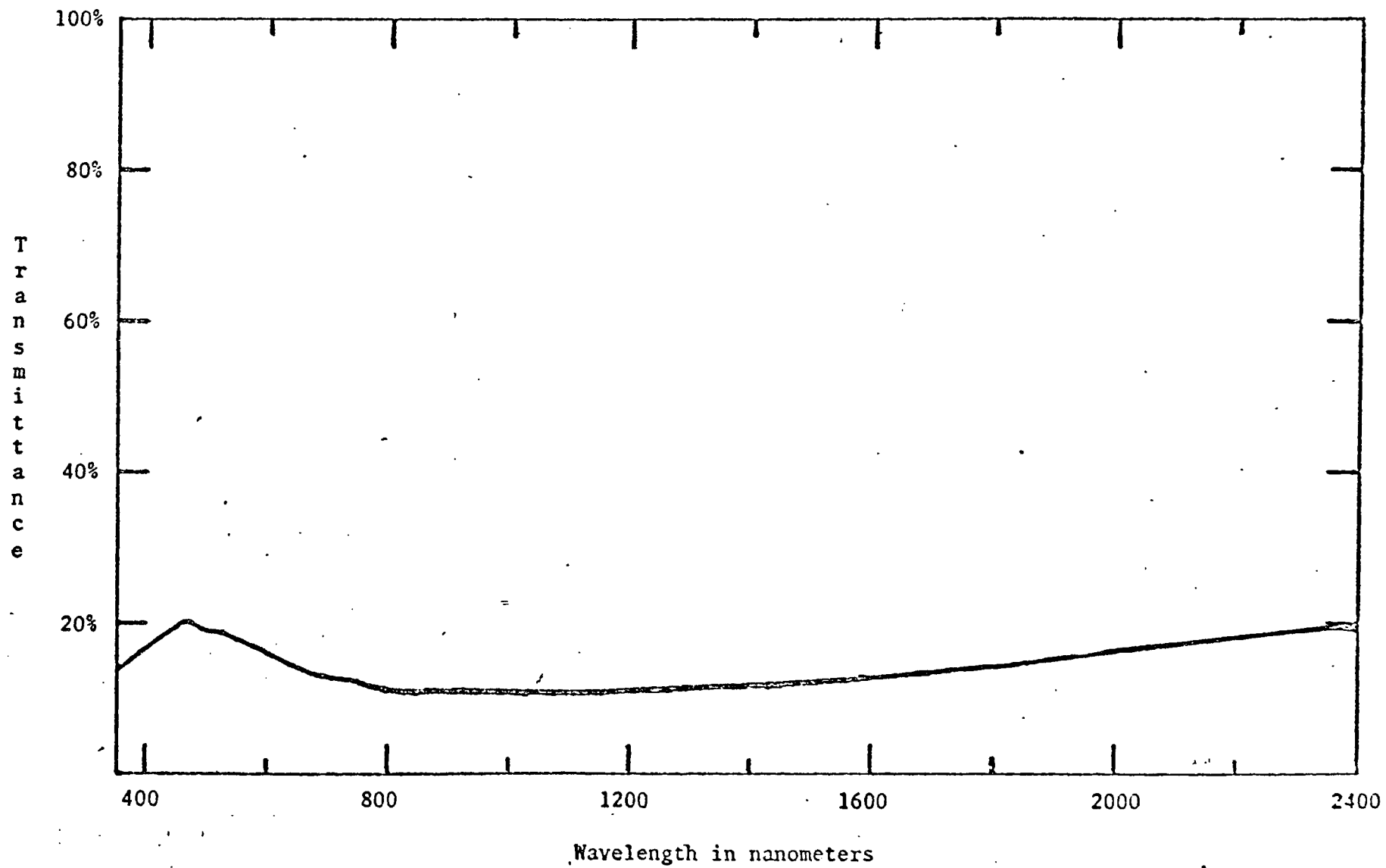
Sample # 15b



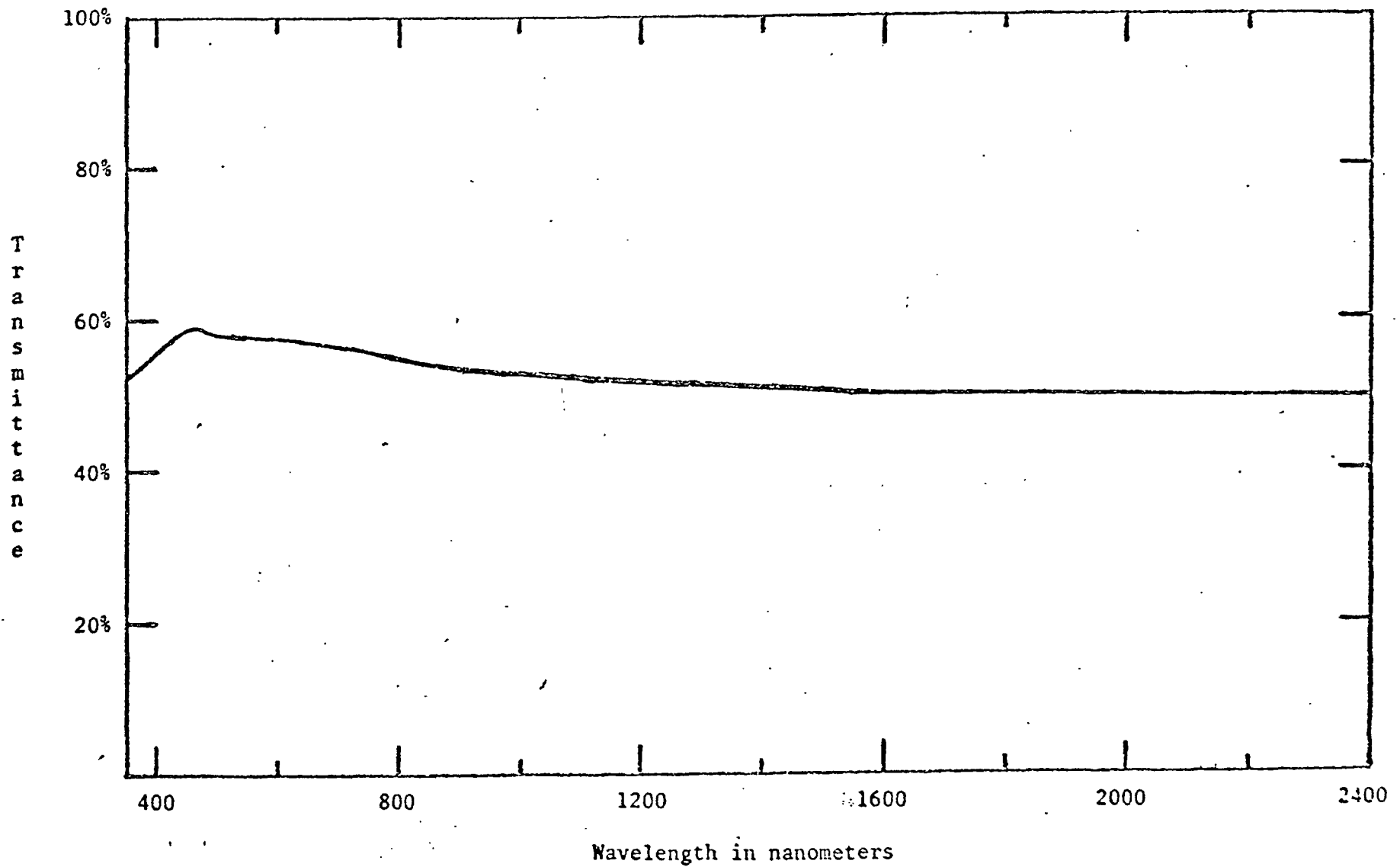
Sample # 16a



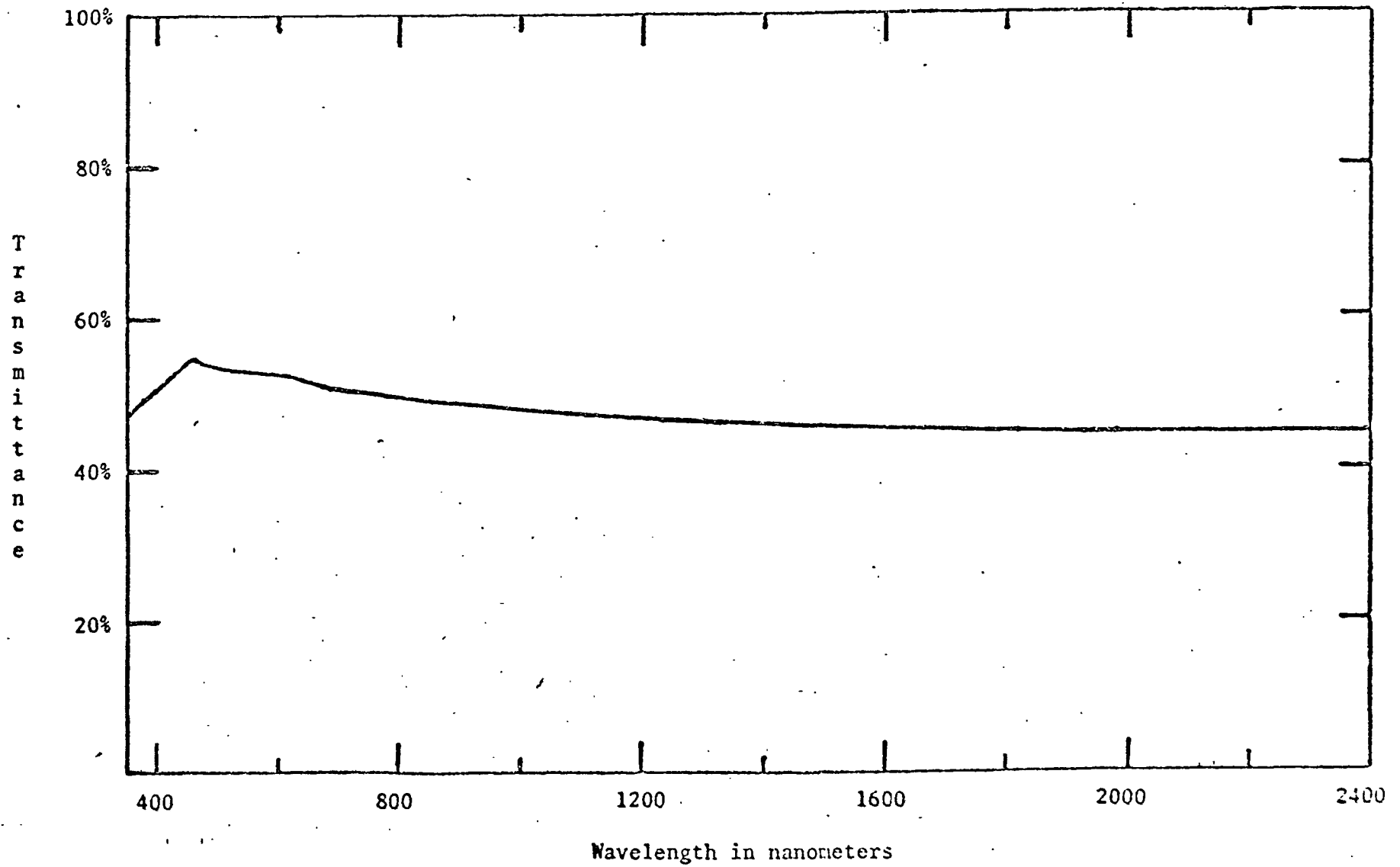
Sample # 16b



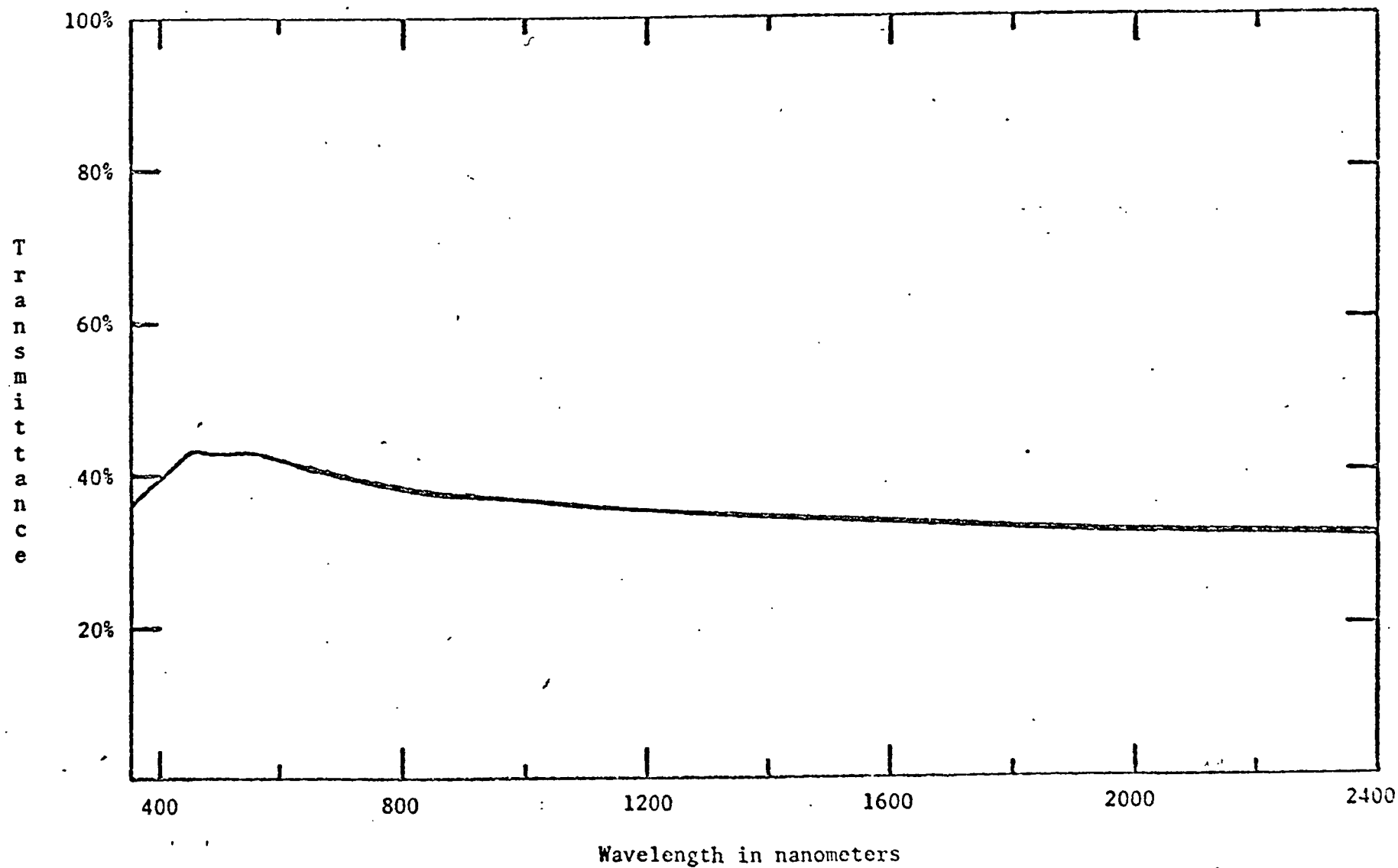
Sample # 17a



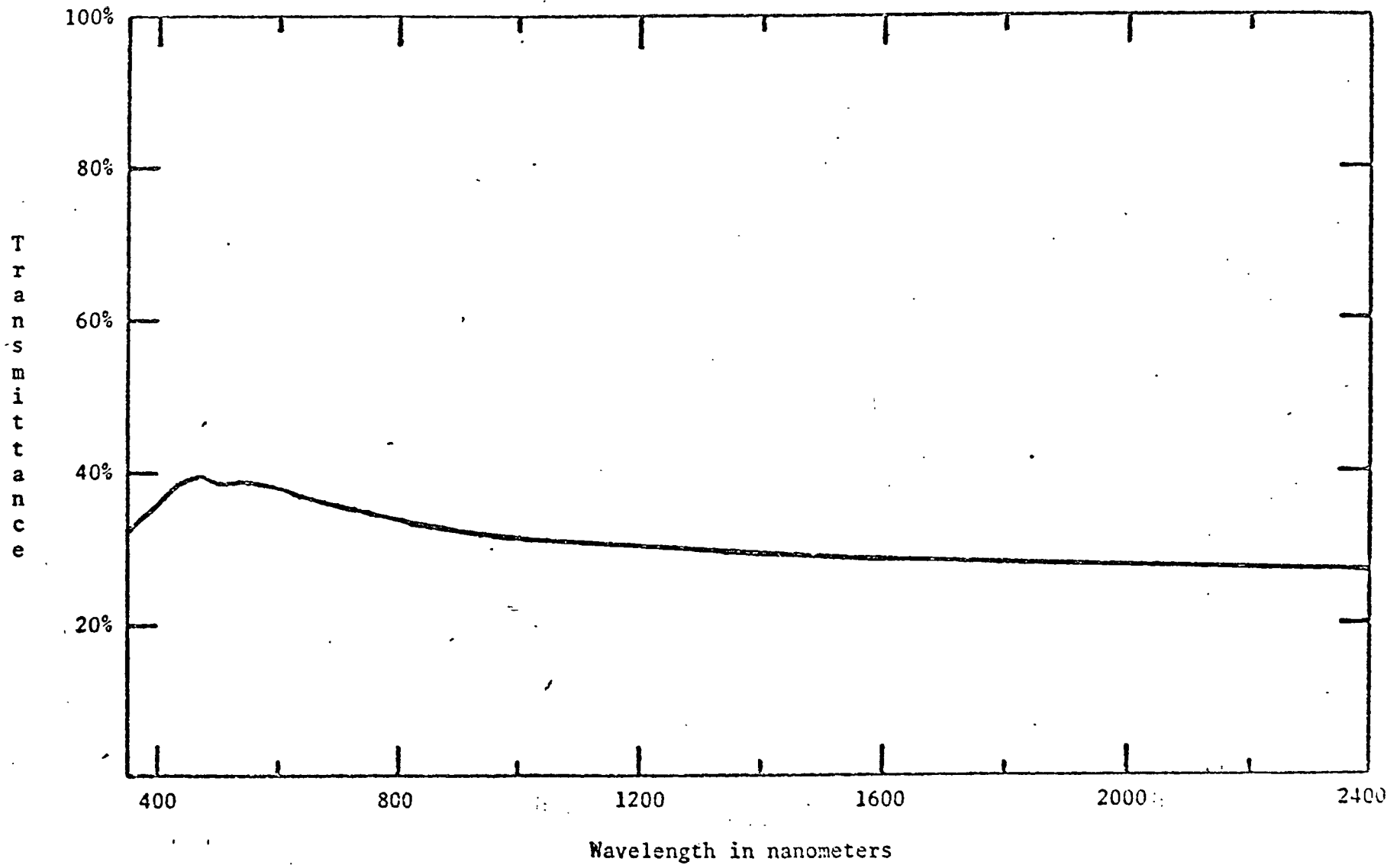
Sample # 17b



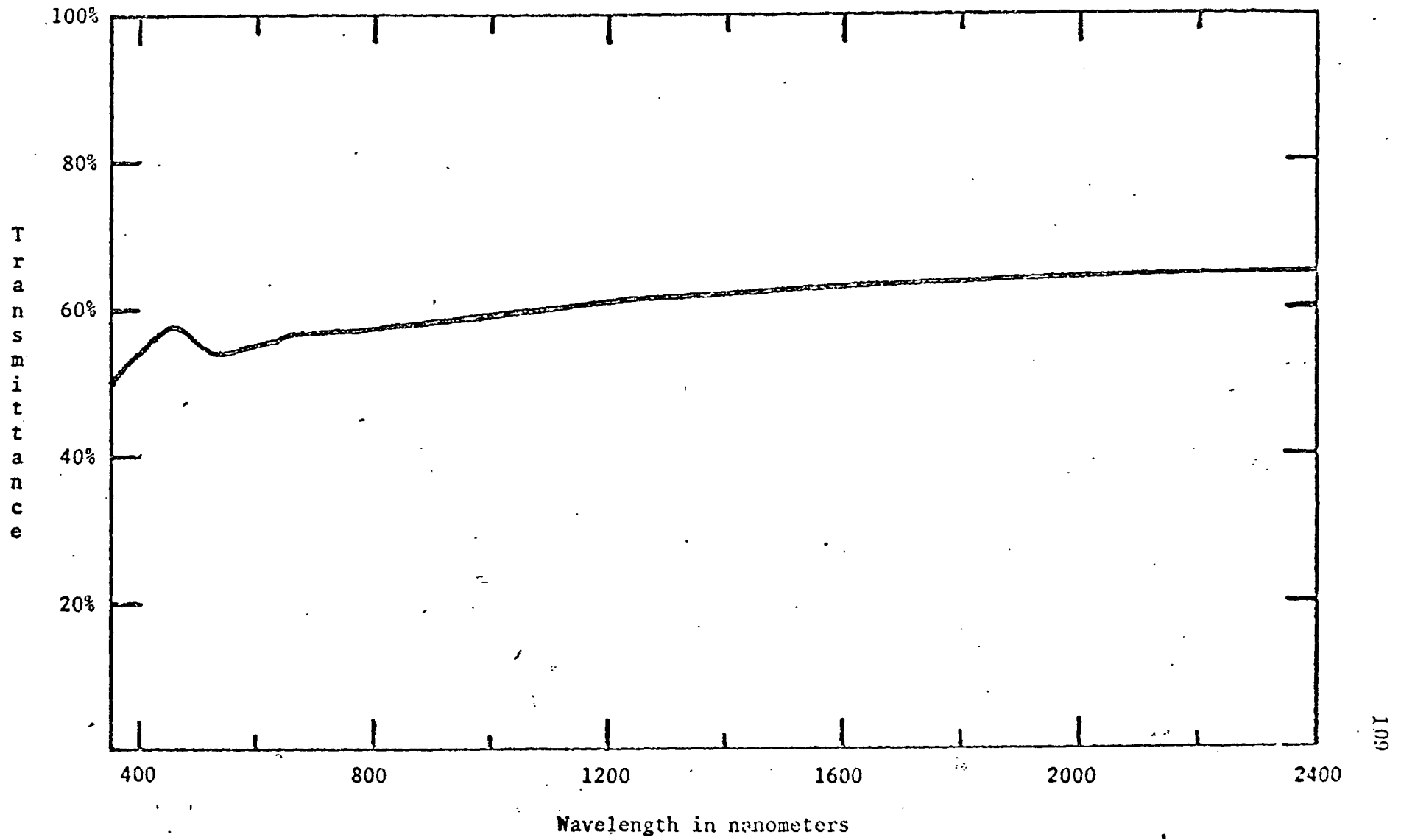
Sample # 18a



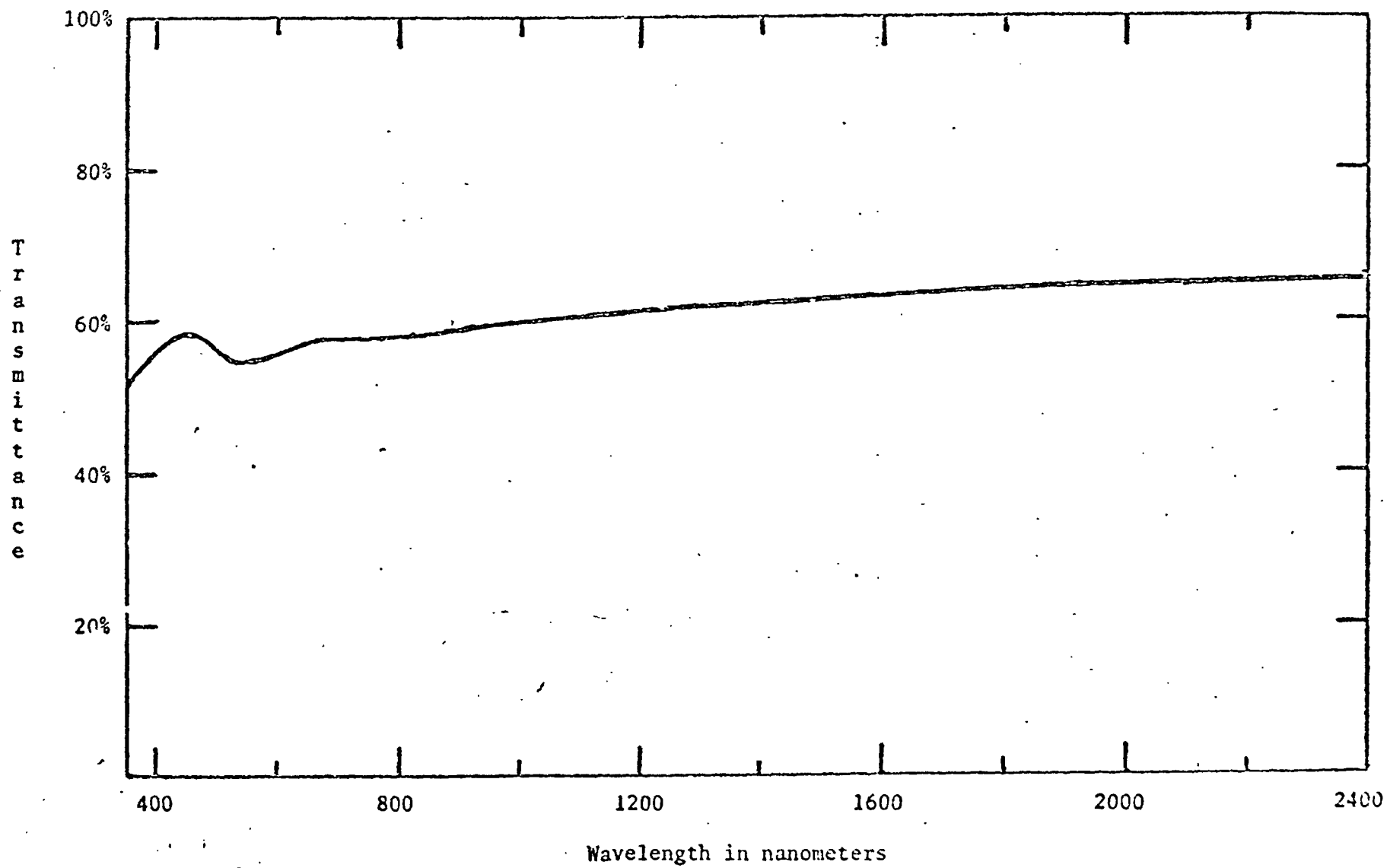
Sample # 18b



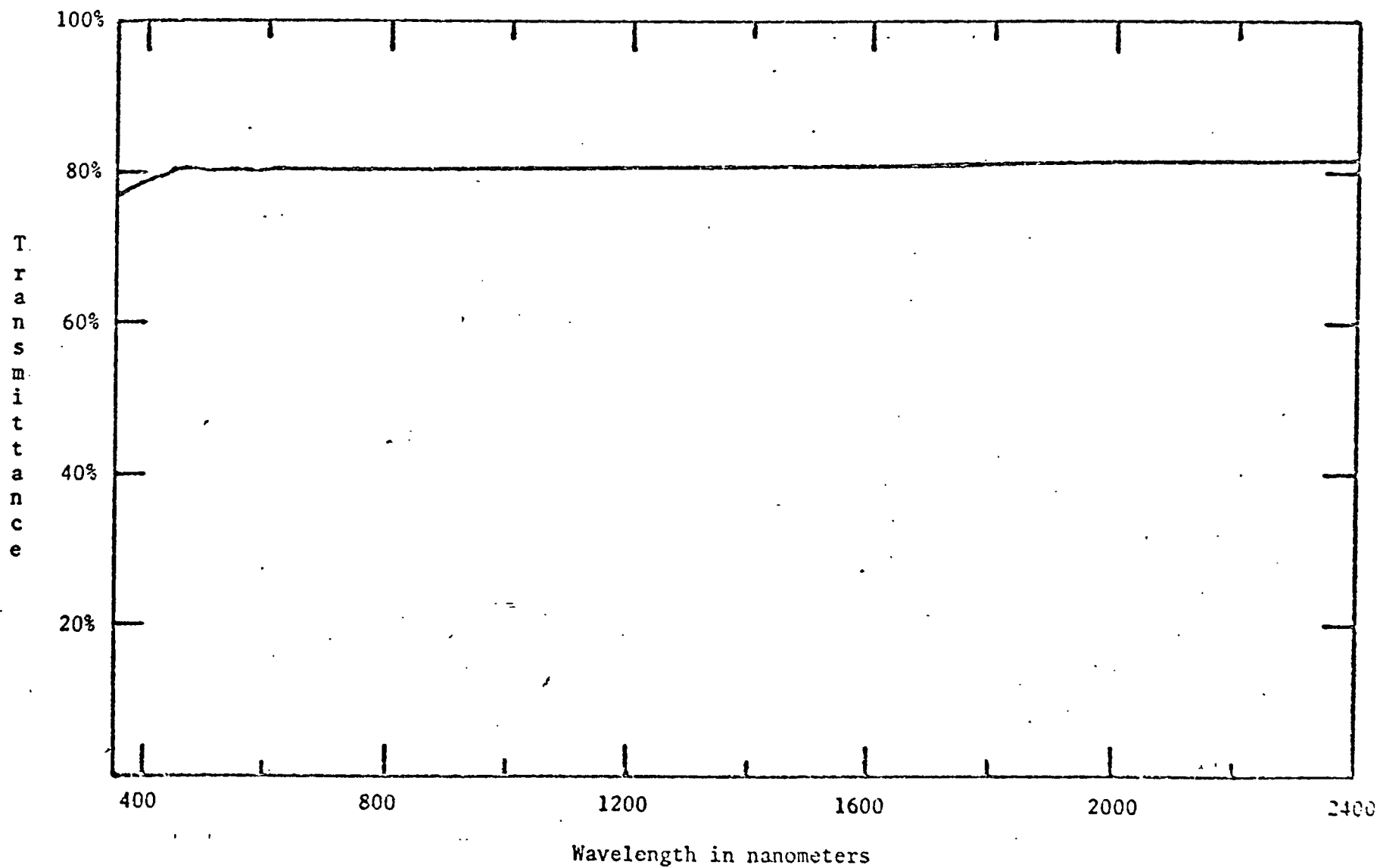
Sample # 19a



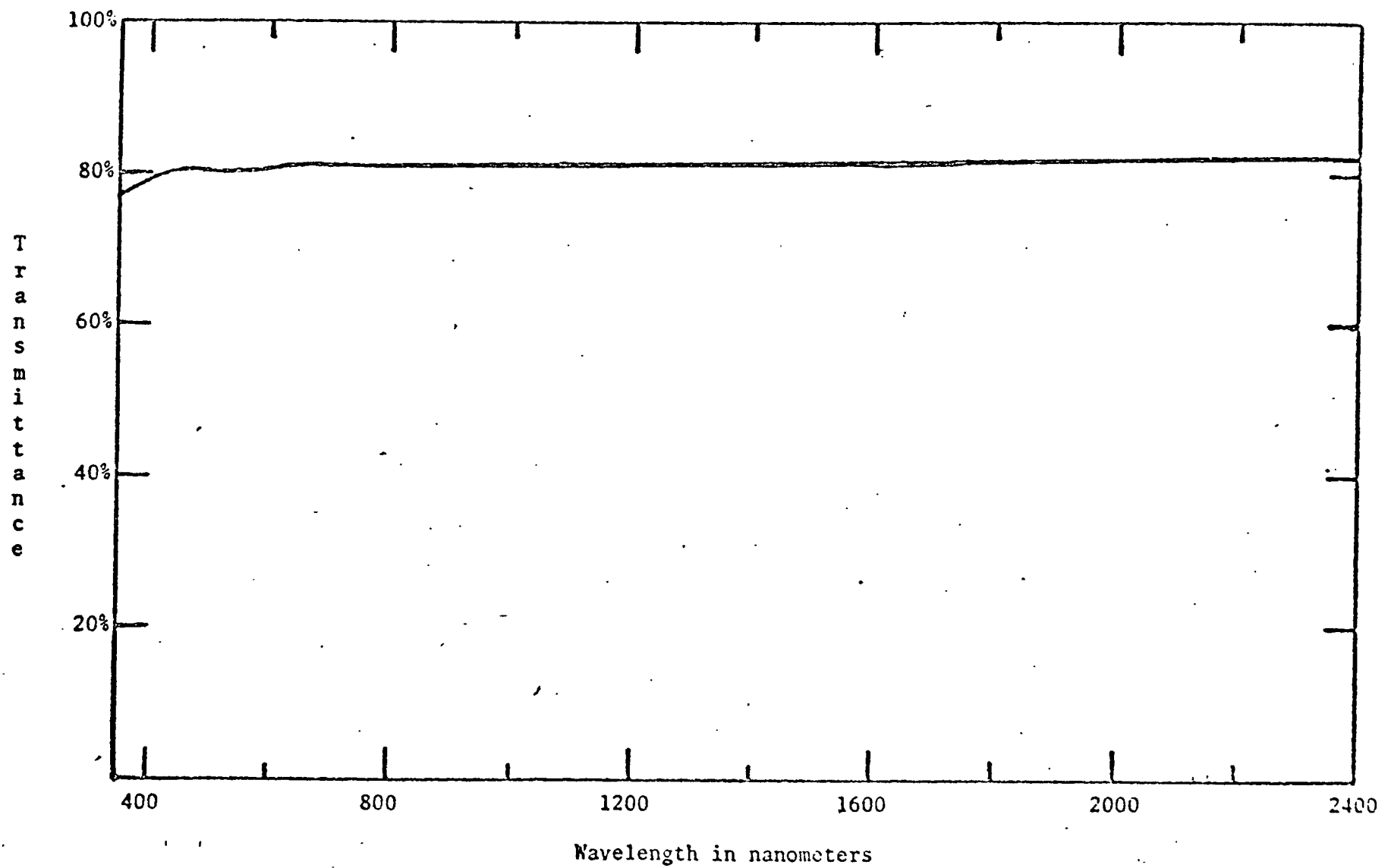
Sample # 19b



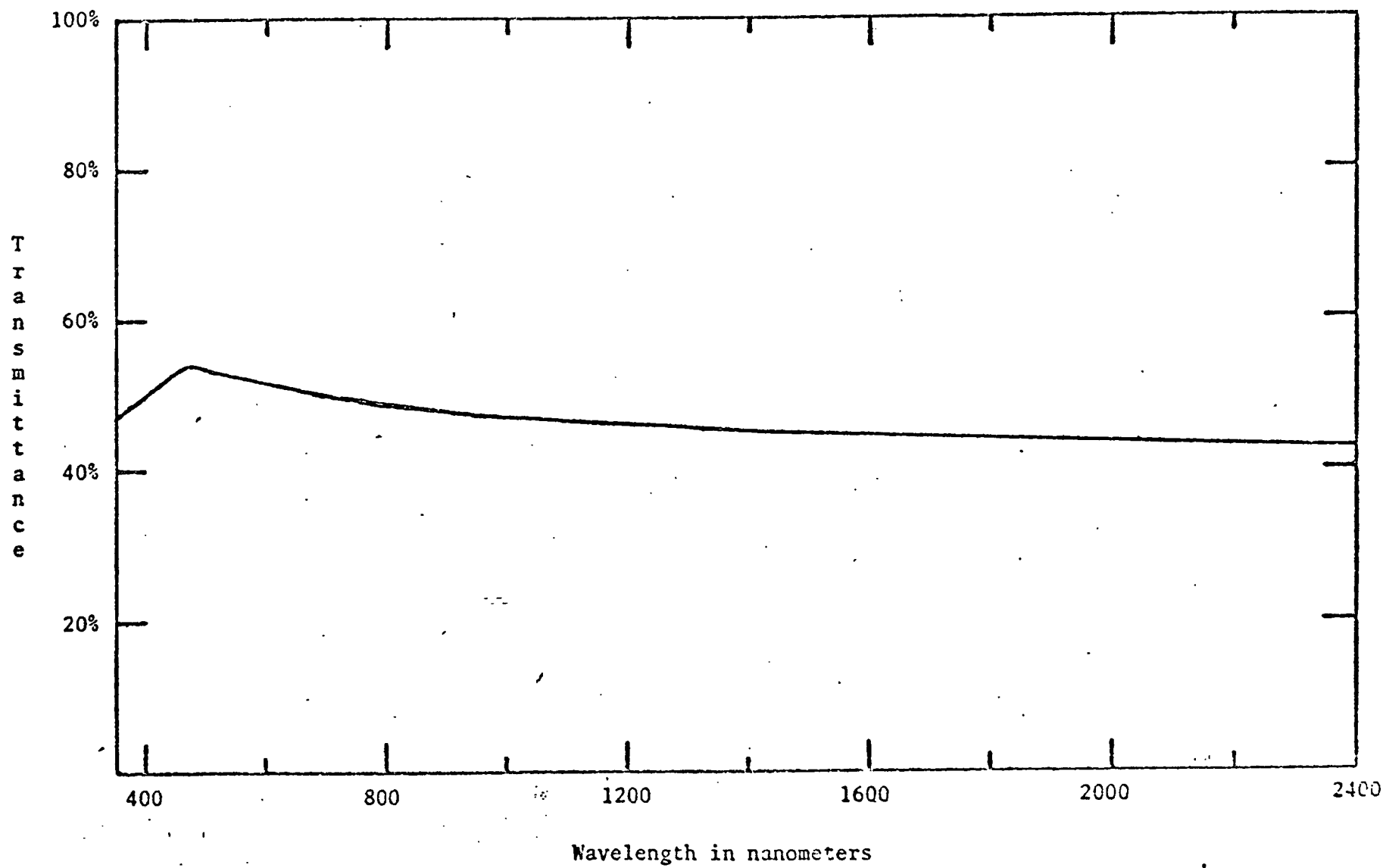
Sample # 21a



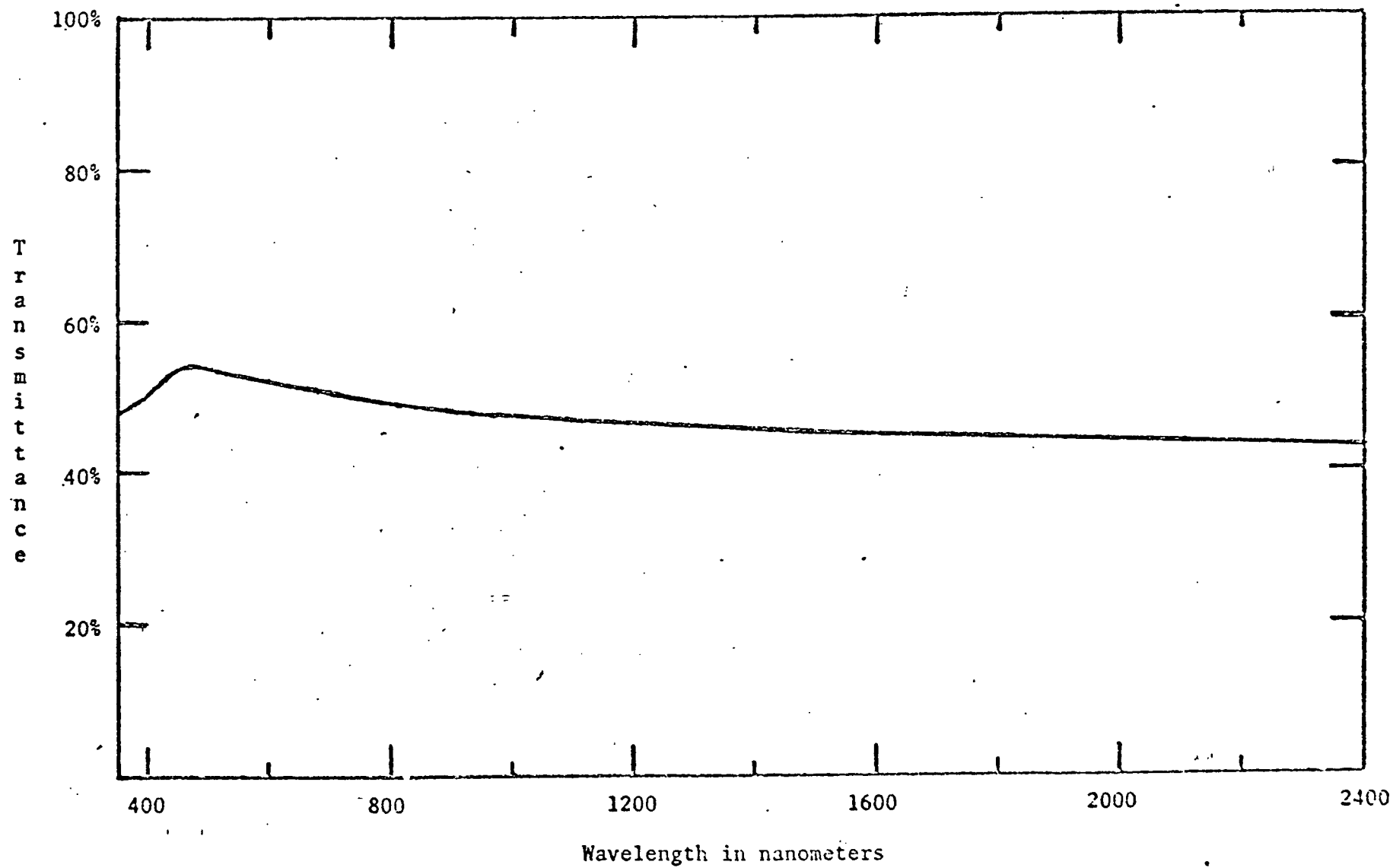
Sample # 21b



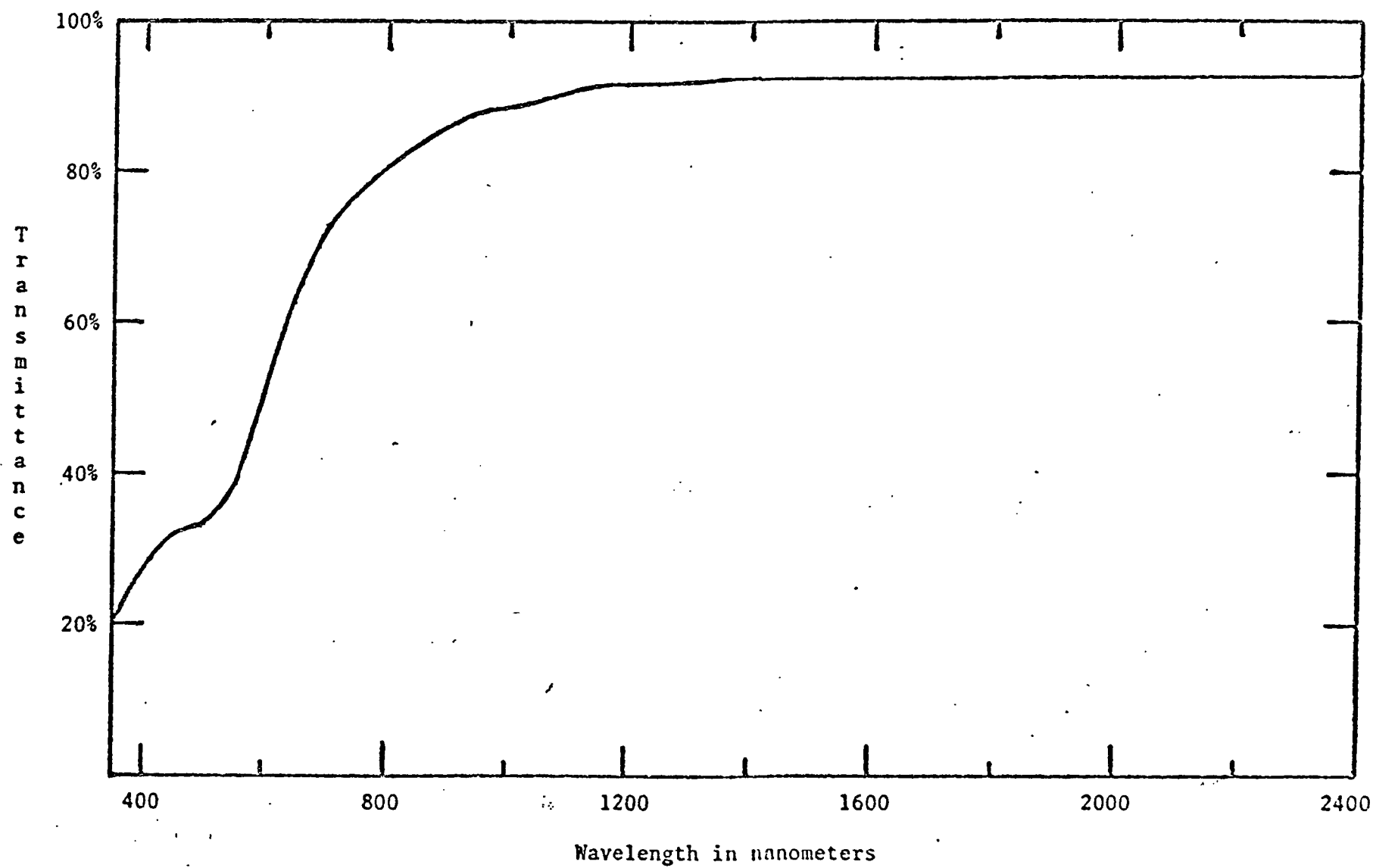
Sample # 22a



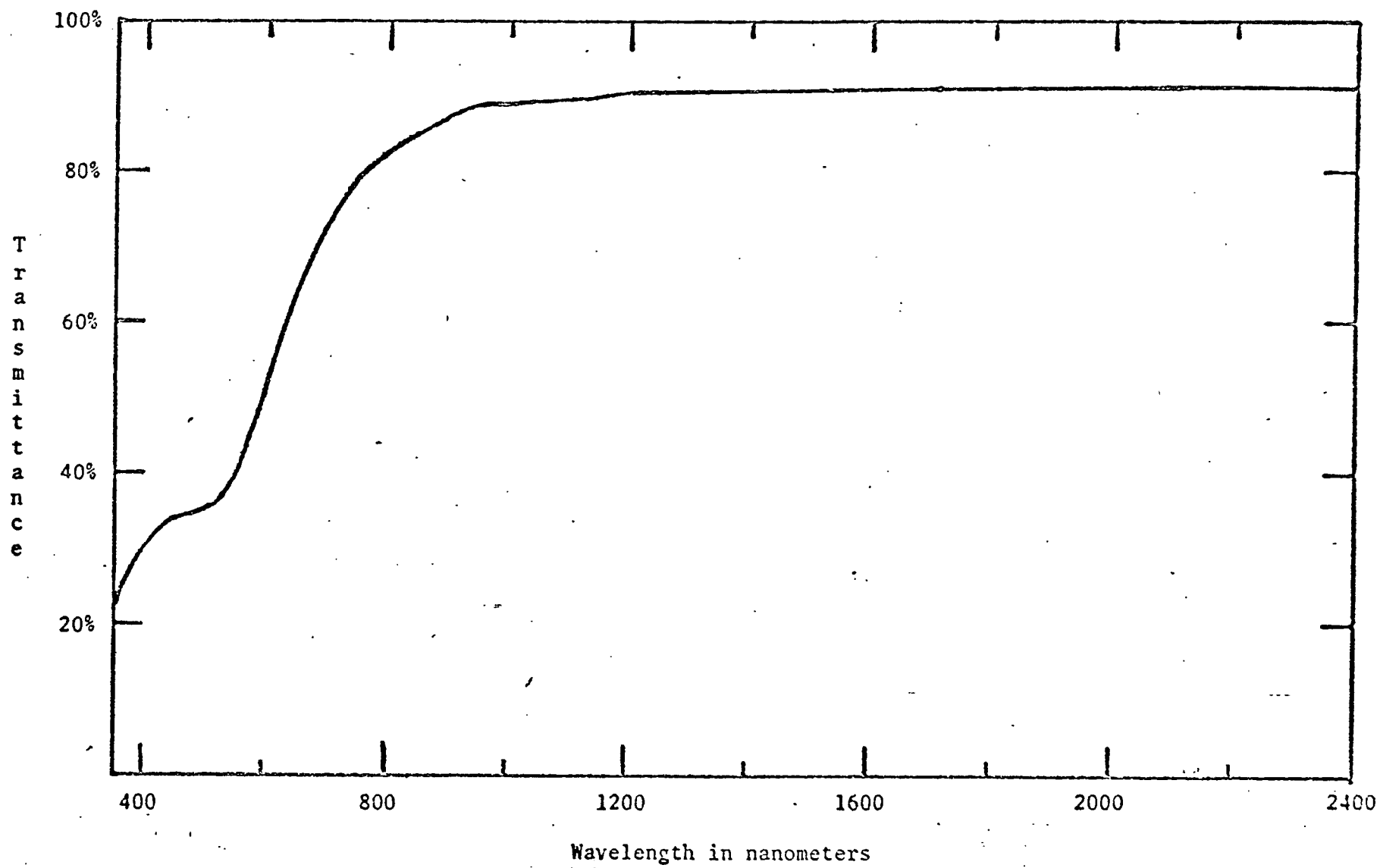
Sample # 22b



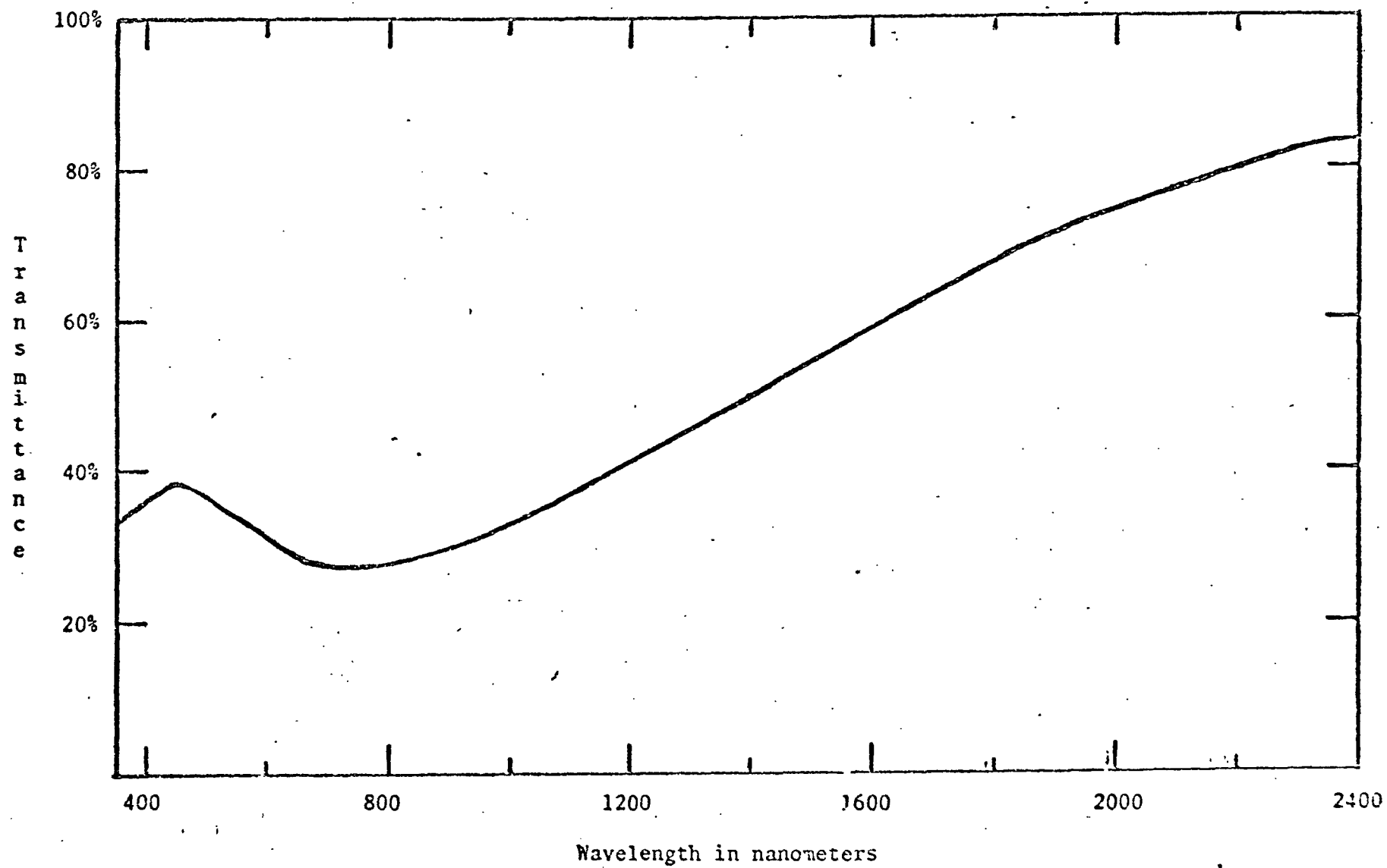
Sample # 26a



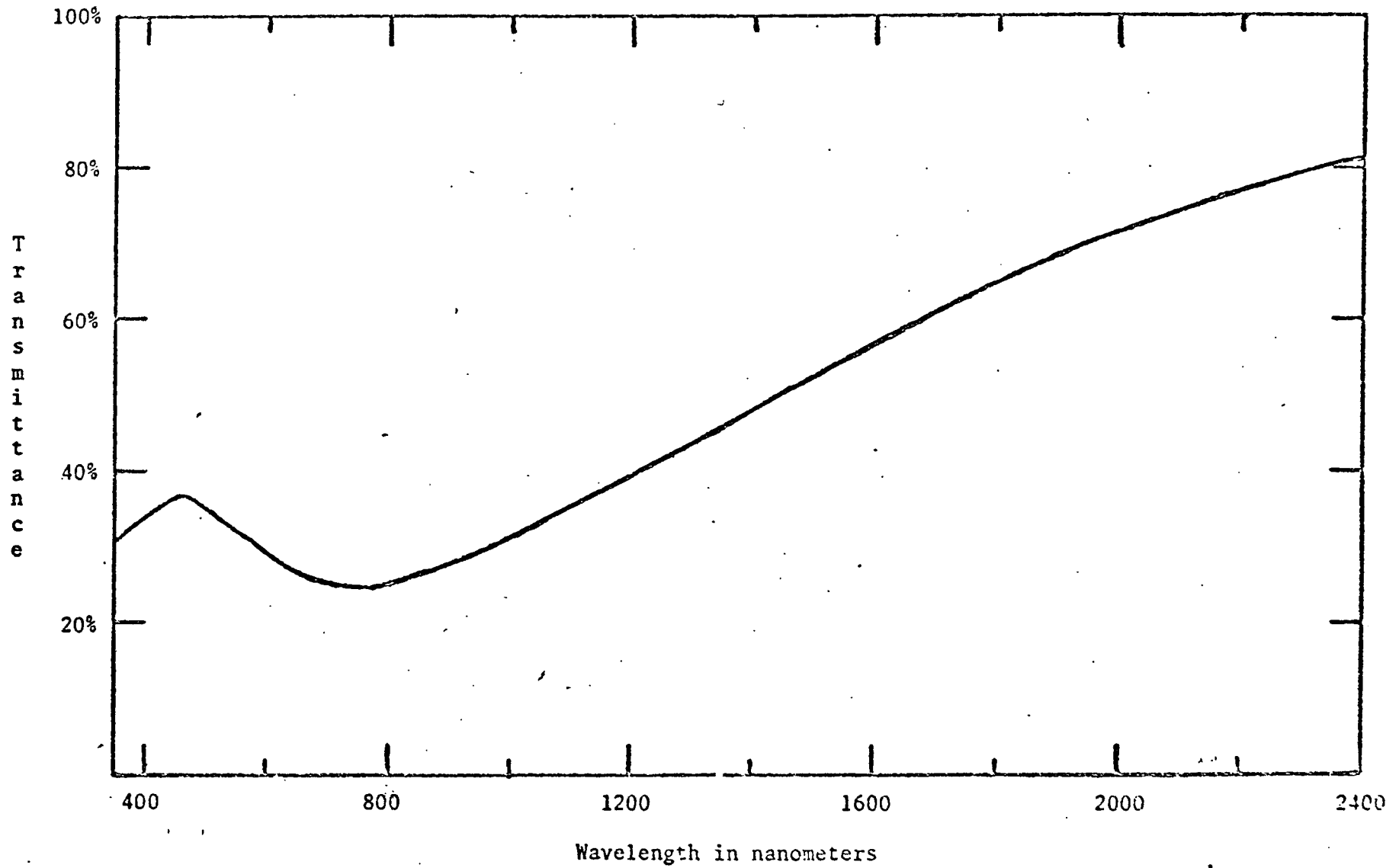
Sample # 26b



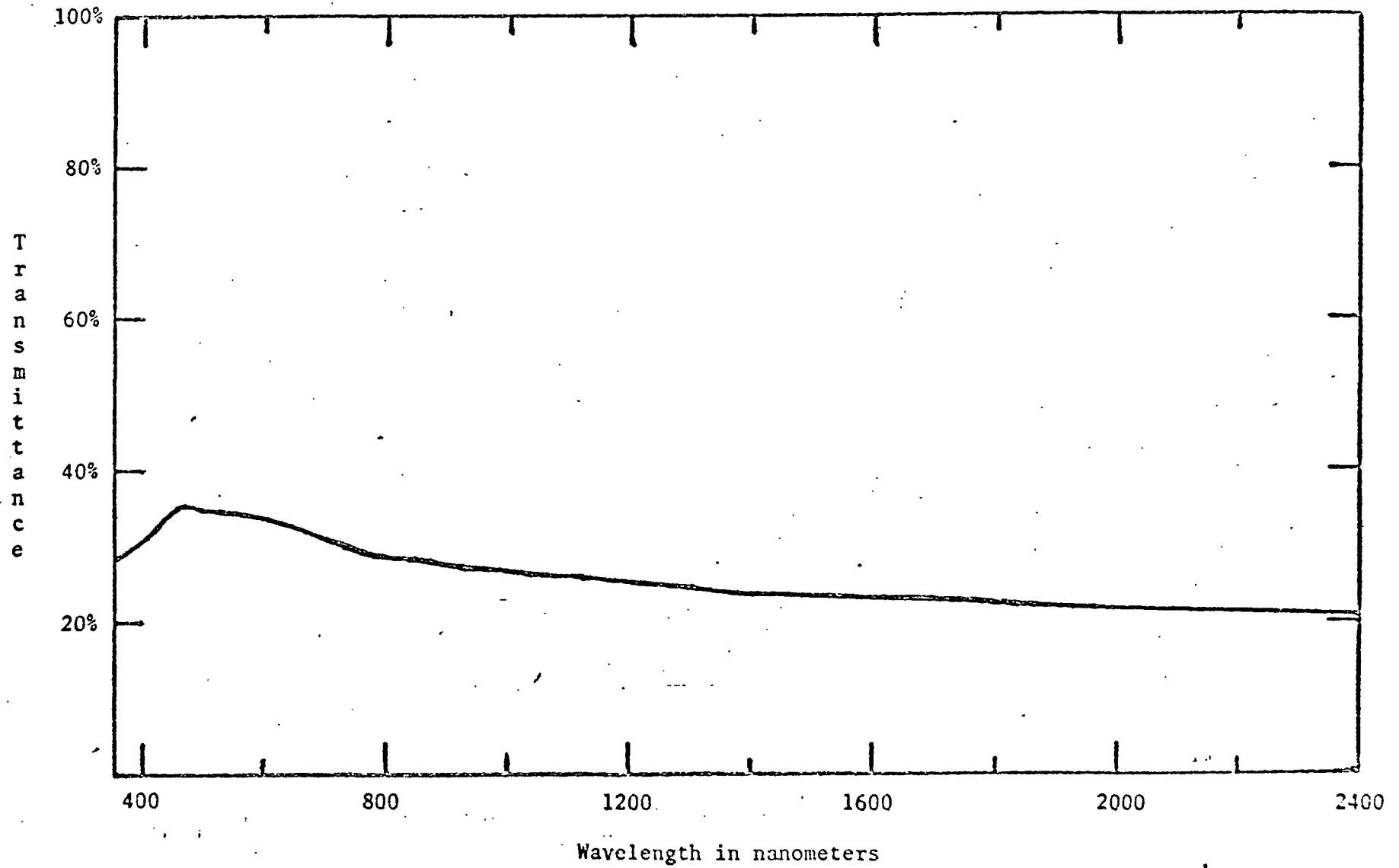
Sample # 27a



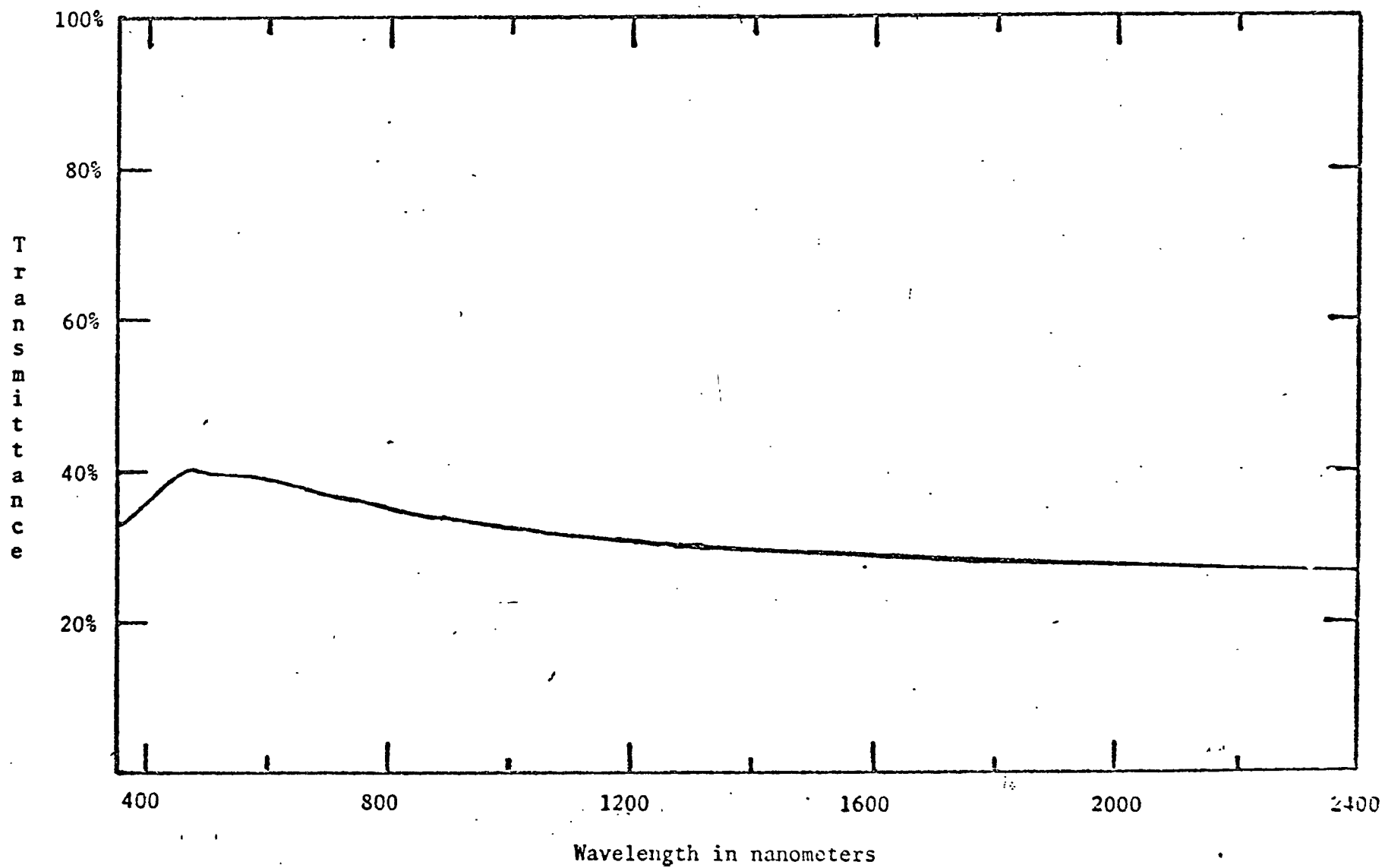
Sample # 27b



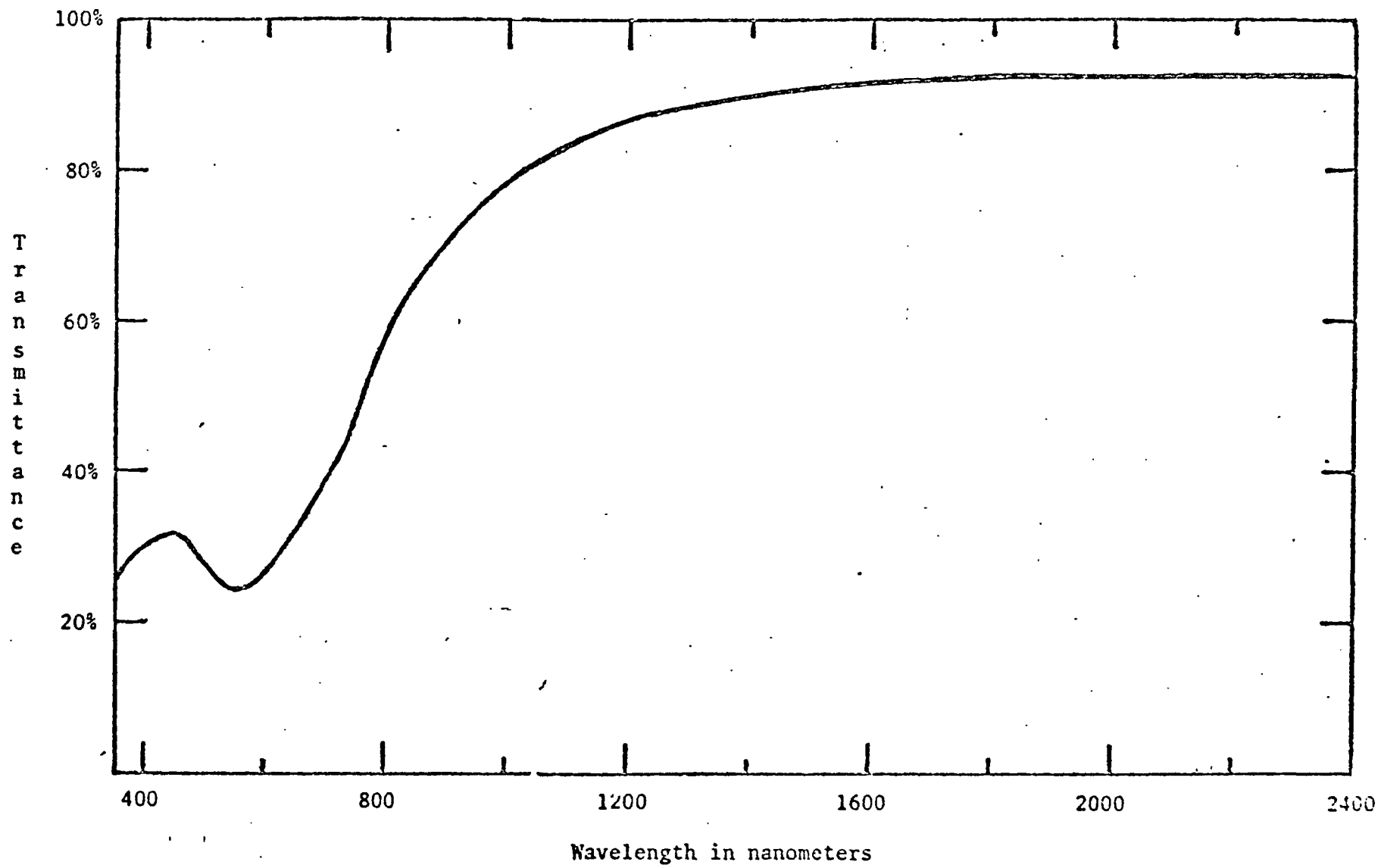
Sample # 28a



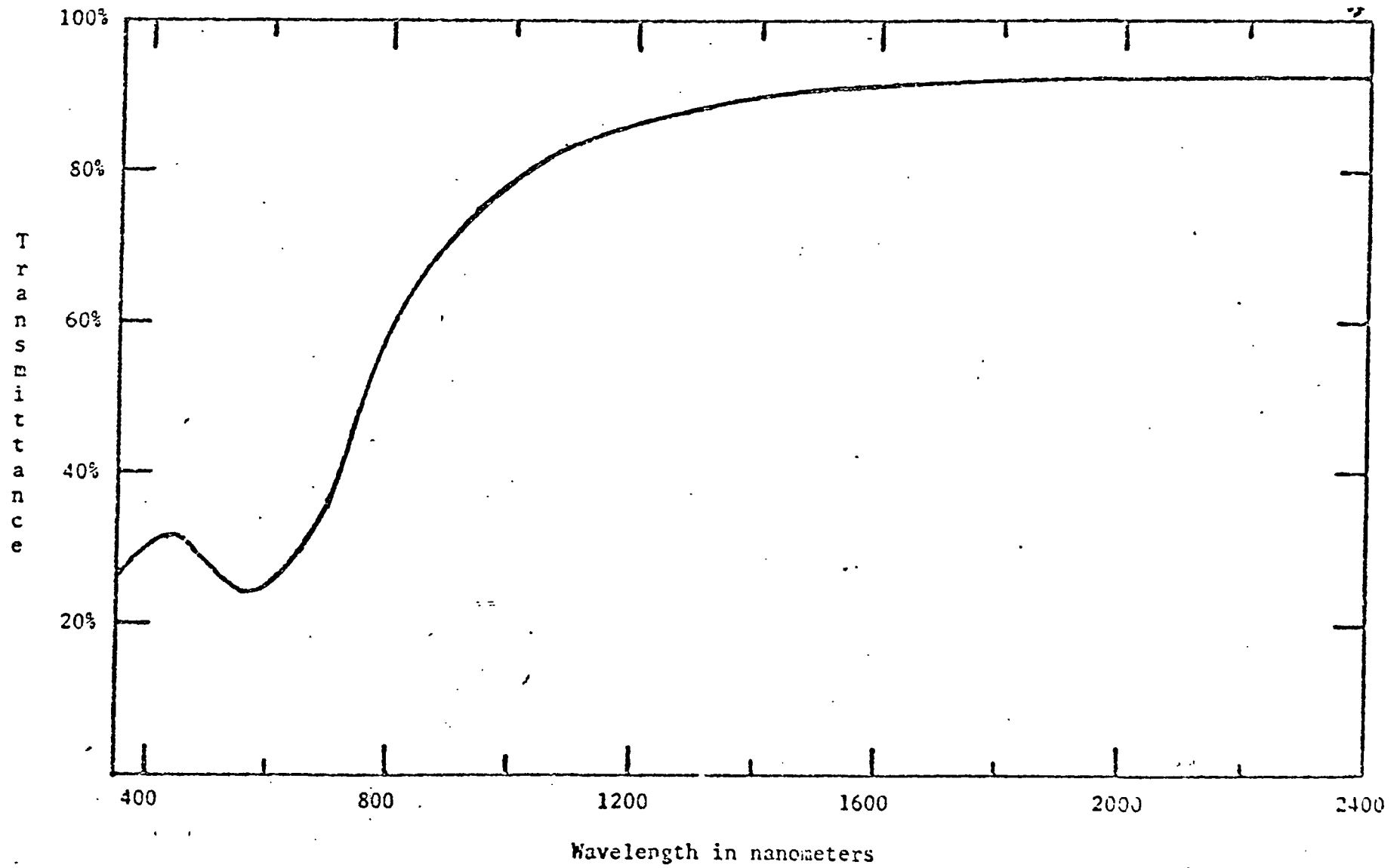
Sample # 28b



Sample # 29a



Sample # 29b



Appendix E

Useful Data for Gold

Density	$D = 19.32 \text{ g cm}^{-3}$
Resistivity	$\rho = 2.44 \times 10^{-6} \Omega \text{ cm}$
Conductivity	$\sigma = 4.05 \times 10^{17} \text{ sec}^{-1}$
Relaxation Time	$\tau = 2.40 \times 10^{-14} \text{ sec}$
Damping Coefficient (d. c.)	$\gamma_0 = 4.16 \times 10^{13} \text{ sec}^{-1}$
Damping Coefficient (optical)	$\gamma_0 = 7.07 \times 10^{13} \text{ sec}^{-1}$

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