STUDIES ON TRANSITION METAL PORPHINES AND PHTHALOCYANINES

Thesis by

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In Partial Fulfillment of the Requirements
For the Degree of
Master of Science

California Institute of Technology
Pasadena, California
1971

(Submitted May 19, 1971)

To my parents and to the memory of my grandfather, Mr. Frank E. Hunter, and my grandmother, Mrs. G. M. Strickland, for all the time they spent developing in me a desire to understand God's great world.

ACKNOWLEDGMENTS

This thesis could not have been done without the help of many people. Dr. Harry B. Gray has been a continuing source of encouragement and understanding. George Rossman and Jack Leonard have helped tremendously, both in aiding me with suggestions about experiments and in furthering my education. I am deeply grateful to these three people.

The data reduction could not have been accomplished in time without the aid of several members of Ruddock House. Bruce McLaughlin donated several days of his time. Kent Nakamoto, Debbie Dison, and Bob Murphree each spent several hours assisting me in the reduction of the data. Dave Wellman, Phil Massey, Carroll Boswell, Peter Kwok , John Kessides, Ian Kling, and Bob Coleman also helped for a few hours. Their aid has been invaluable, and I am very appreciative of their friendship.

Finally, I wish to thank the National Science Foundation which partially financed this research.

ABSTRACT

Model systems for heme were constructed using three different compounds. The tetrasulfophthalocyanine transition metal derivatives were studied and rejected due to problems with the purification procedure. Transition metal derivatives of tetrapyridyl porphine were studied and rejected due to problems in the synthesis and low concentrations of the chemical in solution. Finally, the transition metal derivatives of tetraphenyl porphine were studied and spectral data were obtained.

The spectral data indicate that Fe(II)TPP is stable in the presence of oxygen. A photochemical reaction does occur, however, which appears to change the Fe(II)TPP to Fe(III)TPP.

Other facts were also found. The ZnTPP is found to undergo a photochemical reaction similar to the one for Fe(II)TPP. The MnTPP appears to have already changed oxidation state upon synthesis.

The data suggest that TPP is a possible system for studying the interaction of heme and oxygen. The TPyP system might be even better if the problems with synthesis could be solved since its water solubility should solve the problem due to a low concentration.

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I. INTRODUCTION

Hemoglobin has the distinction of being the molecule responsible for much of the transport of gases in most higher animals. In particular, it carries oxygen from the lungs through the bloodstream to the cells, finally releasing the oxygen for use in the combustion of food in the cells. Similarly, the hemoglobin aids in the transport of carbon dioxide from the cells through the bloodstream to the lungs for exhalation into the atmosphere. The importance of these transport functions to the survival of the animal has brought much attention to the mechanisms of gas transport by hemoglobin. Hemoglobin was found to consist of four subunits--two α sections and two β sections.(1) Each section was found to consist of a protein chain and a porphyrin molecule, heme. The porphyrin was found to contain a single Fe(II) atom. The protein portion, globin, and the porphyrin portion, heme, were found to be separable based on pH. At low pH, hemoglobin in HCl and acetone would precipitate globin hydrochloride and leave ferroprotoporphyrin in solution.(2) At neutral pH values, the globin and ferroprotoporphyrin recombined to produce hemoglobin.

Further investigation revealed that the two functions of hemoglobin were separate. The transport of oxygen seemed to involve a different mechanism from the process of transport of carbon dioxide.(2, 3) It appeared that carbon dioxide transport is chiefly due to the globin while oxygen transport involved the porphyrin. It was found that, at the pH within the erythrocytes, the imidazole groups on the histidine residues of globin exhibit a marked buffering effect.

Thus, as the cells absorb oxygen from oxyhemoglobin and expel carbon dioxide into the blood plasma, the oxyhemoglobin is becoming hemoglobin. Oxyhemoglobin is a stronger acid than hemoglobin, so when oxyhemoglobin is deoxygenated to hemoglobin, acid must be added to the blood plasma to keep the pH constant. The imidazole group on the histidine residues donate their hydrogens (pK = 6.0) which protonate the carbon dioxide from the cells to make carbonic acid.(2, 4) The carbonic acid is then transported as a solute by the blood plasma. When the hemoglobin reaches the lungs, the oxygenation to oxyhemoglobin reverses these processes and produces carbon dioxide. A second interaction of hemoglobin with carbon dioxide is the formation of carbamino groups:

$$RNH_2 + CO_2 \rightleftharpoons RNCOO^- + H^+$$

This reaction is of minor importance in carbon dioxide transport and does not involve any portion of the hemoglobin molecule near the heme.

The oxygen transport has definitely been connected with the presence of the iron atom by X-ray structure determinations. Three different states exist. Hemoglobin is the molecule in the absence of all oxygen. On addition of oxygen under otherwise anaerobic conditions, oxyhemoglobin is formed. Hemoglobin in contact with air will produce methemoglobin. It appears from magnetic data and from spectral data that hemoglobin contains Fe(II) while methemoglobin contains Fe(III). Oxyhemoglobin is diamagnetic and has an electronic spectrum which closely resembles that of hemoglobin. The two spectra differ mainly in that hemoglobin has a broad band with a maximum at 552.5 nm while oxyhemoglobin has two sharper bands in this region with maxima at 541.5 and 576 nm. This close agreement of the two spectra has been known since 1938 and has led to much speculation that oxyhemoglobin contains Fe(II) though no exact mechanism for the attachment of the oxygen to the iron was proven.

One of the problems in studying the spectra of hemoglobin was the insolubility of heme. Hemoglobin itself could be studied, but for exact studies of the spectral properties of just the heme and its interaction with oxygen, the solubility properties of heme made it undesirable. Since heme is a porphyrin, however, it seemed reasonable that a similar porphyrin could serve as a model for heme. The present research was begun on a series of related compounds, the phthalocyanines. Further work has been done on two porphines. The purpose of the research was the investigation of the interaction of oxygen with various transition metals placed in the porphyrin environment. Some work on such a cobalt compound suggested that the reaction to a higher oxidation state was quite fast.(5) Thus, one would expect that an iron compound would go immediately to Fe(III). This research was also intended to test this premise.

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II. STUDIES OF DERIVATIVES OF TETRASULFOPHTHALOCYANIDES

The first compounds attempted were the water-soluble metal derivatives of terrasulfophthalocyanine (Figure 1). The compounds would be isolated as the tetrasodium salt of the tetrasulfophthalocyanine, and aqueous solutions would be used for the spectral measurements.

A. Experimental Section

The metal tetrasulfophthalocyanines (MSPc) were made as described in the literature by Weber and Busch.(1) The purification procedure was altered to an expanded one proposed by Helen Brooks and was slightly altered.(2)

The sodium salt of 4-sulfophthalic acid was made by neutralization of commercially available 4-sulfophthalic acid with sodium hydroxide. The water was evaporated and the resulting acid (0.162 mole, 43.2 g) was dissolved in 40 milliliters of nitrobenzene. The solution was heated to 180°C and a mixture of ammonium molybdate catalyst (0.68 g, 0.0006 mole), ammonium chloride buffer (4.7 g, 0.09 moles), urea (58 g, 0.97 mole), and a metal salt (0.048 mole of desired metal salt) were added slowly. The resulting heterogeneous mixture was heated for 6 to 10 hours at 180°C until the evolution of carbon dioxide had ceased. The mixture was then cooled to room temperature, the nitrobenzene was drained from the reaction flask, and the crude product was washed several times with methanol until the odor of nitrobenzene was removed. The solid was then placed in

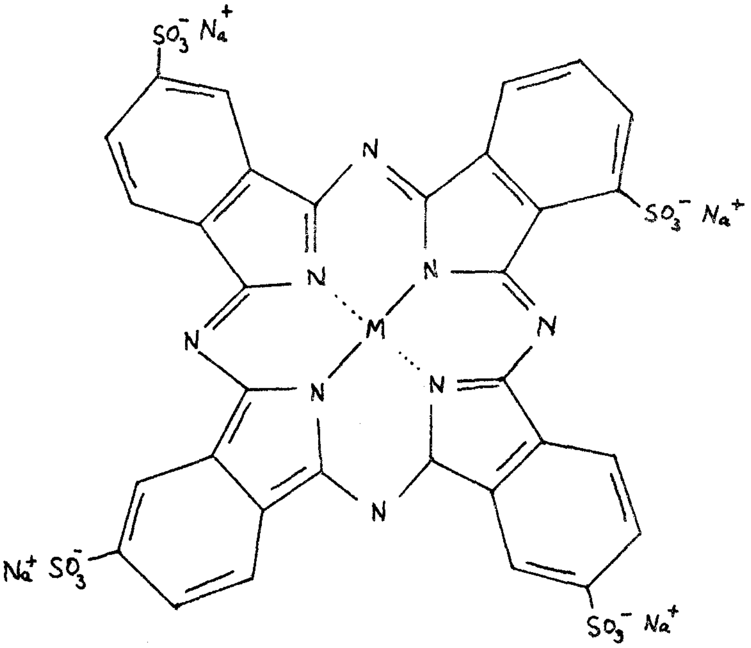

Figure 1

Tetrasulfophthalocyanine derivative

1100 milliliters of 1 M HCl, stirred for several minutes, and filtered. The product, MSPc, is insoluble in hydrochloric acid, but the transition metal chlorides should be soluble and should therefore be separated from the product at this stage. The remaining solid was then dissolved in 700 milliliters of 0.1 M sodium hydroxide and filtered to remove any insoluble impurities. Sodium chloride was added (about 300 g) until the MSPc precipitated from solution. This was filtered and washed with small amounts of 80% aqueous ethanol to remove excess sodium chloride. The product was redissolved in water and precipitated with acetone. This slurry was filtered and washed with ethanol. The solid was then redissolved in the smallest amount of water possible. It was found that two compounds seemed to be present. One was quite dark in color and was more soluble. The other was much lighter in color and relatively insoluble in water. By adding water slowly, the two compounds could be partially separated. Each resulting solution was precipitated with acetone and filtered until no further purification seemed possible. Attempts at using Dowex exchange resins failed due to the large charge of the MSPc (-4 after the four sodium cations have been ionized off) keeping the compound trapped on the column regardless of eluent. In this manner, the copper, zinc, cobalt, and nickel derivatives were made.

B. Analysis

The CuSPc, AnSPc, CoSPc, and NiSPc compounds were sent to Schwarzkopf Microanalytical Laboratory for analysis. Expected values were calculated for a molecular formula of $C_{32}H_{12}N_8S_4O_{12}Na_4M$ for each of the compounds. The CuSPc was a dark blue powder which had 2.34% copper as opposed to the calculated 6.46%. The ZnSPc was a dark green solid which was analyzed as 1.17% zinc instead of the expected 6.63%. The CoSPc had a light green powder which had been separated from a dark blue powder. The light green powder was below 0.96% cobalt while the blue powder was 2.15% cobalt. The calculated value for cobalt is 6.02%. The NiSPc was a dark blue solid with 6.69% nickel instead of the expected 5.99%. With the exception of the NiSPc, all the compounds were lower than the expected values, suggesting that some of the contaminating, lighter-colored compounds still remained. This is supported by the two values for the cobalt analyses. Both the dark blue CuSPc and the dark blue CoSPc were about 36% pure after similar steps of purification, and the lighter compound had a much smaller amount of cobalt in it.

Based on these results and the failure of the Dowex columns to purify the compounds, this system was abandoned.

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III. STUDIES OF α, β, γ, δ-TETRA-(f-PYRIDYL)-PORPHINE

Another water soluble model for heme was then investigated. Due to the four pyridyl groups which could be protonated in mild acid, studies began on α, β, γ, δ-tetra-(4-pyridyl)-porphine (see Figure 2). When the pyridyl groups are protonated, the compound should become soluble in water. Since aqueous solutions offer a better understood system for redox reactions than do organic solutions, this was a definite advantage.

A. Experimental Section

The literature synthesis for the tetrapyridyl porphine (TPyP) is due to Everly Fleischer.(1) The compound is made by first synthesizing the zinc derivative, ZnTPyP. All other derivatives can then be made from this by removing the zinc with 6 M hydrochloric acid, extracting the free base porphine into chloroform after neutralization of the acid, purifying the free base on a talc column (or purifying the original ZnTPyP on an alumina column), and finally refluxing the free base in glacial acetic acid with the acetate of the desired metal followed by neutralization and extraction into chloroform.

The synthesis of ZnTPyP is performed by placing 50 milliliters of pyridine, 15 grams of dried zinc acetate, 25 milliliters of pyrrole, and 35 milliliters of 4-pyridine carboxaldehyde (isonicotinaldehyde) in a 250 milliliter all-glass pressure bomb. The bomb is flushed with nitrogen, sealed, and heated at 110°C for 48 hours. A 10% yield of purple crystals of ZnTPyP is supposed to result. These crystals are

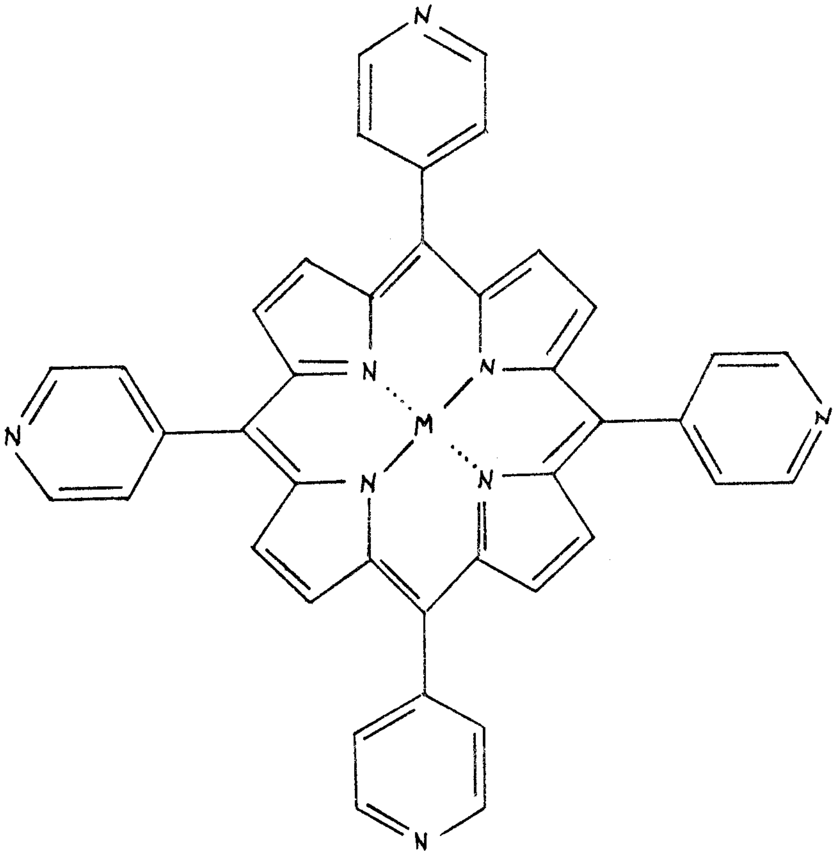

Figure 2

α, β, γ, δ-tetra-(4-pyridyl)-porphine derivative

(MTPyP)

filtered, washed with ethanol and with ether, and dried. TheZnTPyP can be purified on an alumina column using chloroform as the solvent and a 5% methanol-chloroform mixture as eluent. When this experiment was tried, no purple crystals were formed. The only change in procedure was the method of heating. Everly Fleischer used an oil bath at 110°C and presumably only partially immersed the bomb. In the present research, concern for safety caused the replacement of the oil bath by a small oven with thick walls. Presumably the total heating of the bomb rather than a partial heating in an oil bath which would cause the upper portions of the bomb to be cool is the cause of the fact that no purple crystals formed and merely a black tar was found. Many attempts were made to obtain some ZnTPyP from the black tar. One attempt included evaporating the pyridine from the tar, placing it and some chloroform in a Soxhlet extractor for several days, and finally passing it through several extractions from chloroform to acid and from neutralized acid back to chloroform. None of these attempts ever resulted in any product.

In one attempt at the synthesis, only one half of the literature quantity of isonicotinaldehyde was available. Thus, the quantities of each component used was cut in half, and the reaction was performed in the usual 250 milliliter bomb. At the end of 48 hours, a 3% yield of purple crystals was found in the bomb. These were purified as the literature suggests except that their solubility in chloroform was so low that purification on alumina would take too long. Thus, a sample was dissolved and passed through the column with no evidence of any contamination. The rest of the ZnTPyP was assumed to be pure. Later attempts with the full literature amount of reagents still gave a black tar while half of the literature amount gave crystals and one third the literature amount gave a black tar.

B. Spectra

The ZnTPyP was used to make Fe(II)TPyP in a small centrifuge tube fitted with a rubber serum cap and with nitrogen gas constantly flowing through the reaction vessel. The concentration of the Fe(II)TPyP was hard to estimate due to the small quantitites involved in making only 10 milliliters of solution. Solutions were made and spectral data taken, then the solutions were evaporated to half the original volume to get a second spectrum. This was done for both 10^{-5} M and 10^{-4} M Fe(II)TPyP. Oxygen was then bubbled through the 10^{-5} M solution of Fe(II)TPyP and this spectrum was taken. These spectra are presented in Figures 7 through 12.

Interpretation of the spectra is not very accurate due to the uncertainty in the concentration and the poor resolution of the features due to the low concentrations. It would appear that the Fe(II)TPyP does not follow Beer's Law as evidenced by the tremendous changes in the relative sizes of peaks at 600 nm, 563 nm, 530 nm, and 420 nm between Figures 7 and 9. It does appear, however, that oxygenation does change the spectrum. Comparing Figures 9 and 12 shows that oxidation of Fe(II)TPyP removed the Fe(II)TPyP band at 700 nm and added bands at 650 nm and possibly at 500 nm. The Soret band at 420 seems relatively unchanged.

In addition to these spectra, the polarization of the peaks in the Zn TPyP spectrum were determined by the use of liquid crystals. The polarizations of the peaks agreed with those reported by Sundbom as being typical of porphines.(2)

C. Interpretation

Not much can be said about the Fe(II)TPyP and its interaction with oxygen. The changes in the spectra could be due to an immediate oxidation of Fe(II) to Fe(III), but the data is not good enough to state this definitely. Much better data could possibly have been obtained if more of the compound had been made. This would have allowed the spectrum to be made in water rather than chloroform and would have allowed much higher concentrations.

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IV. STUDIES OF α, β, γ, δ-TETRAPHENYL PORPHINE

Due to the difficulties involved in obtaining large samples of pure ZnTPyP, it was decided to use the more easily synthesized tetraphenyl porphine (Figure 3) even though the water solubility would have to be sacrificed. The tetraphenyl porphines could at least suggest whether further study of the tetrapyridyl porphine was reasonable.

A. Experimental Procedure

A new process for the synthesis of tetraphenyl porphine (TPP) did away with the necessity for a bomb reaction.(1,2) In the new process, 56 milliliters of freshly distilled pyrrole, 80 milliliters of reagent benzaldehyde, and 3000 milliliters of reagent propionic acid are refluxed for thirty minutes. The mixture is cooled to room temperature and filtered. The blue solid collected by this filtration is washed with methanol and then with hot water. The resultant solid is air dried to remove volatile substances and then in a vacuum to remove acid. The solid is dissolved in chloroform and purified on an alumina column. This is the free base porphine. Further purification is possible using recrystallization from chloroform.

The metal derivatives were then made from the purified free base porphine. The free base porphine is placed in glacial acetic acid. The acetate of the desired metal is added (or, in the case of Fe(III) where the acetate was not available, the sulfate of the desired metal and five times as much sodium acetate). The solution is refluxed

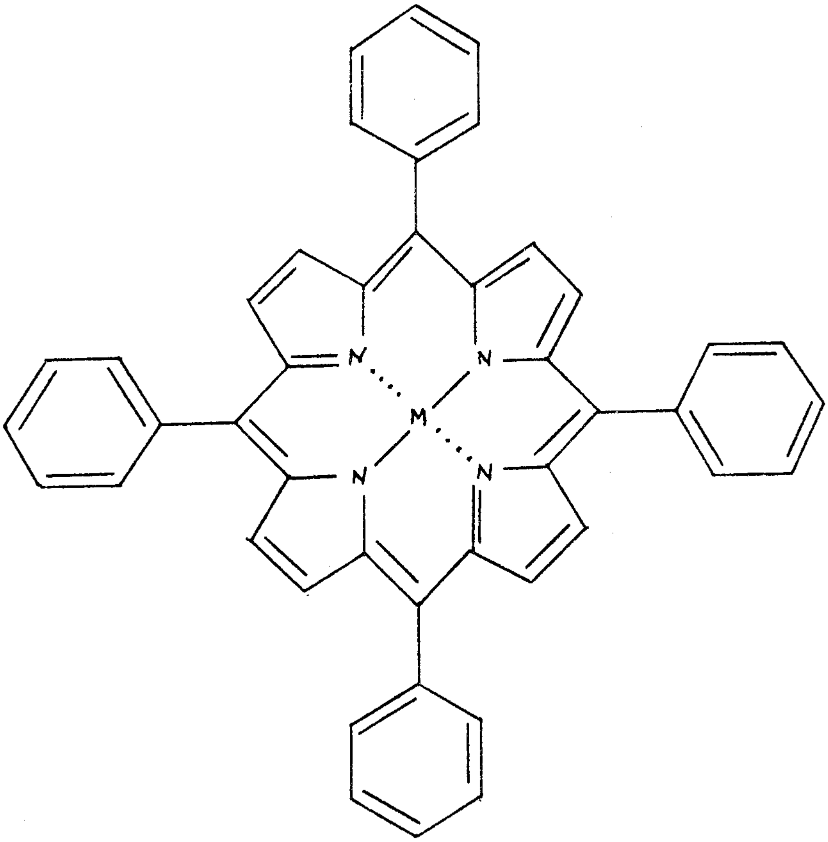


Figure 3

α, β, γ, δ-Tetraphenyl porphine derivative

(MTPP)

for five or ten minutes to prepare the metal derivatives. The glacial acetic acid was diluted with about three times its volume of water, and the metal porphines were then extracted into chloroform. The chloroform solutions were diluted in volumetric flasks to make precisely known concentrations. This process was used to make 50 milliliter volumes of 0.000115 M iron(III) tetraphenyl porphine acetate, 0.000106 M manganese tetraphenyl porphine, and 0.000106 M zinc tetraphenyl porphine. The last two solutions were protected from the light by wrapping aluminum foil around all the containers used in synthesis and storage of the compounds.

Since the iron(II) tetraphenyl porphine was expected to be air sensitive, its synthesis was slightly modified. Free base porphine and elemental iron were added to glacial acetic acid in a centrifuge tube fitted with a serum cap. Nitrogen was passed through the tube for ten minutes before the solution was heated. The nitrogen was continued while the refluxing was done turning the emerald green solution of H_2TPP into a pink solution of Fe(II)TPP. This solution was then diluted with three times the volume of water which had been bubbled with nitrogen for ten minutes. The Fe(II)TPP was then extracted into deoxygenated chloroform. This was transferred with a syringe to a 100 milliliter volumetric flask and diluted to make 100 milliliters of 0.000104 M Fe(II)TPP which was stored briefly in the dark until spectra could be made. A second FeTPP sample was made by the same procedure except that no precautions were taken to exclude air from the solutions. This was diluted to 50 milliliters of an 0.000112M FeTPP solution. Electronic spectra of these solutions were taken. Following the spectra, the remaining portions of the solutions were concentrated by evaporating the chloroform. The solutions were brought to a total volume of 8.20 milliliters, and magnetic susceptibility measurements were taken on a Gouy balance. It was doubtful that the magnetic data would be meaningful since one normally attempts to have about a 30% concentration of solute for such measurements while the most concentrated of the porphine solutions was only 0.06% solute. Reduction of the data confirmed this pessimism by revealing nothing other than the chloroform diamagnetic correction. Thus, only spectral data have been obtained.

B. Molecular Orbital Diagrams

Interpretation of the spectra presents a problem. The numerous porphine bands must first be located and explained. This task has been done by Sundbom with a satisfactory agreement between calculated and measured band positions.(3) Several spectral studies have been reported in literature.(4,5) Little analysis of the spectra in terms of molecular orbital diagrams has been done. One reason for this is the lack of applicability of Tanabe-Sugano diagrams. These diagrams are applicable to octahedral and tetrahedral systems.(6) The tetraphenyl porphines, however, are in either the D_{4h} or C_{4v} point groups making the use of Tanabe-Sugano diagrams questionable. Simplified molecular orbital diagrams are included in Tables 1 and 2 and in Figures 4, 5, and 6 for several possible configurations of the MTPP. The exact ordering of the molecular orbital energy levels has not

Table 1. Orbital Symmetries for MN_4X_2

Orbital	I	$2C_4(z)$	$C_2''(z)$	$2C_2(x)$	$2C_2'$	σ_h	$2\sigma_v$	$2\sigma_d$	$2S_4$	i	Symmetry
Metal s	1	1	1	1	1	1	1	1	1	1	a_{1g}
Metal p_z	1	1	1	-1	-1	-1	1	1	-1	-1	a_{2u}
Metal p_x, p_y	2	0	-2	0	0	2	0	0	0	-2	e_u
Metal $d_{x^2-y^2}$	1	-1	1	1	-1	1	1	-1	-1	1	b_{1g}
Metal d_{z^2}	1	1	1	1	1	1	1	1	1	1	a_{1g}
Metal d_{xy}	1	-1	1	-1	1	1	-1	1	-1	1	b_{2g}
Metal d_{xz}, d_{yz}	2	0	-2	0	0	-2	0	0	0	2	e_g
N s	4	0	0	2	0	4	2	0	0	0	a_{1g}, b_{1g}, e_u
N p_z	4	0	0	2	0	4	2	0	0	0	a_{1g}, b_{1g}, e_u
N p_x, p_y	8	0	0	-4	0	0	0	0	0	0	a_{2g}, a_{2u} b_{2g}, b_{2u} e_g, e_u
X s	2	2	2	0	0	0	2	2	0	0	a_{1g}, a_{2u}
X p_z	2	2	2	0	0	0	2	2	0	0	a_{1g}, a_{2u}
X p_x, p_y	4	0	-4	0	0	0	0	0	0	0	e_g, e_u

Table 2. Orbital Symmetries for MN_4XY

Orbital	I	$2C_4(z)$	C_2''	$2\sigma_v$	$2\sigma_d$	Symmetry
Metal s	1	1	1	1	1	a_1
Metal p_z	1	1	1	1	1	a_1
Metal p_x, p_y	2	0	-2	0	0	e
Metal $d_{x^2-y^2}$	1	-1	1	1	-1	b_1
Metal d_{z^2}	1	1	1	1	1	a_1
Metal d_{xy}	1	-1	1	-1	1	b_2
Metal d_{xz}, d_{yz}	2	0	-2	0	0	e
N s	4	0	0	2	0	a_1, b_1, e
N p_z	4	0	0	2	0	a_1, b_1, e
N p_x, p_y	8	0	0	0	0	a_1, a_2, b_1, b_2, e, e
X s	1	1	1	1	1	a_1
X p_z	1	1	1	1	1	a_1
X p_x, p_y	2	0	-2	0	0	e
Y s	1	1	1	1	1	a_1
Y p_z	1	1	1	1	1	a_1
Y p_x, p_y	2	0	-2	0	0	e

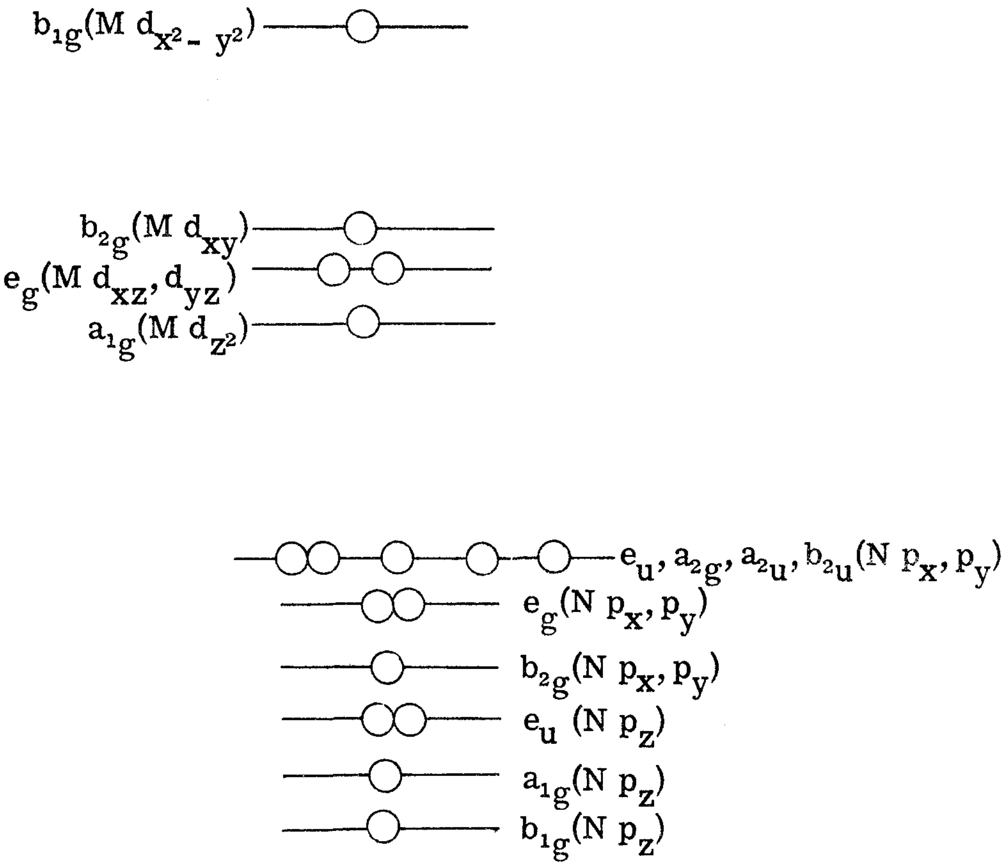


Figure 4

Molecular orbital diagram for square planar MN_4

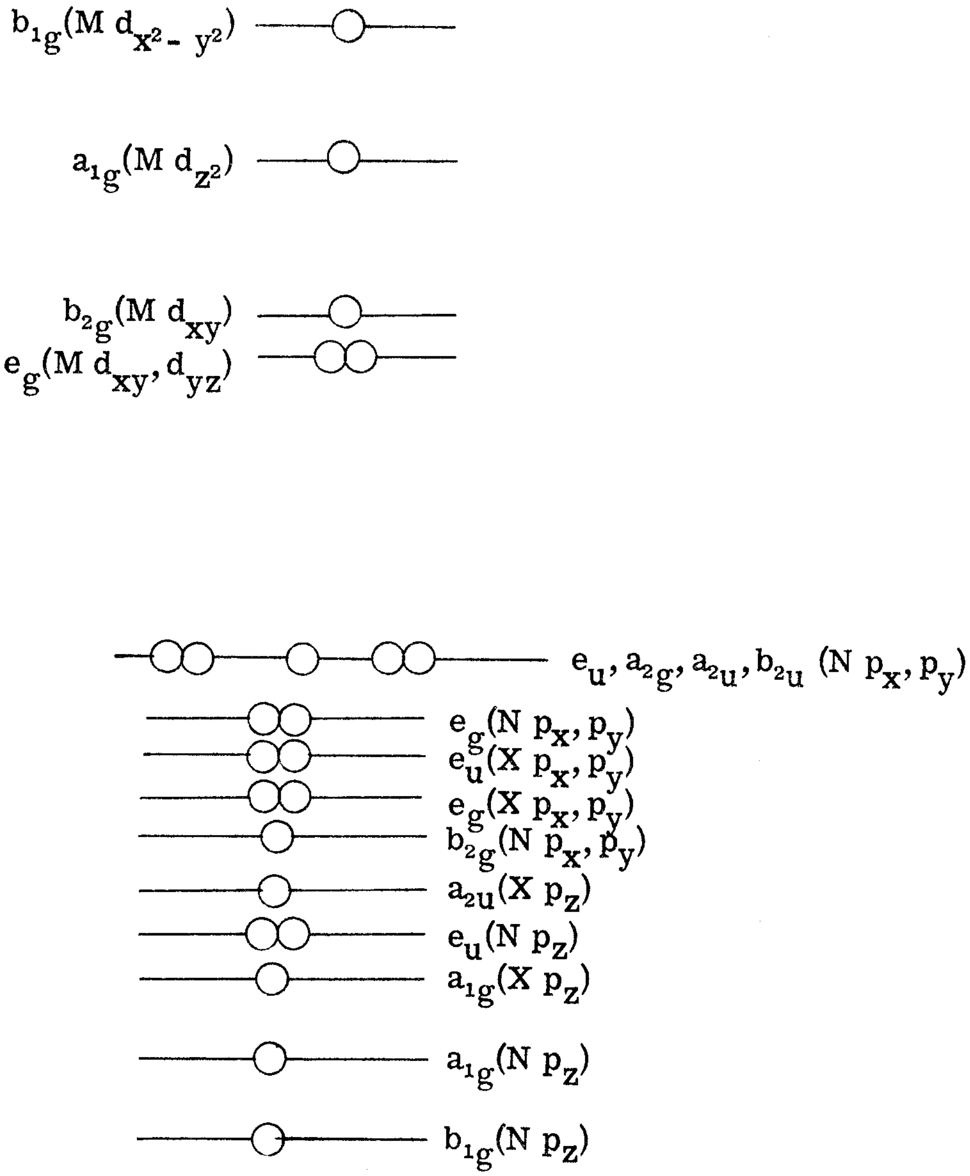


Figure 5

Molecular orbital diagram for MN_4X_2

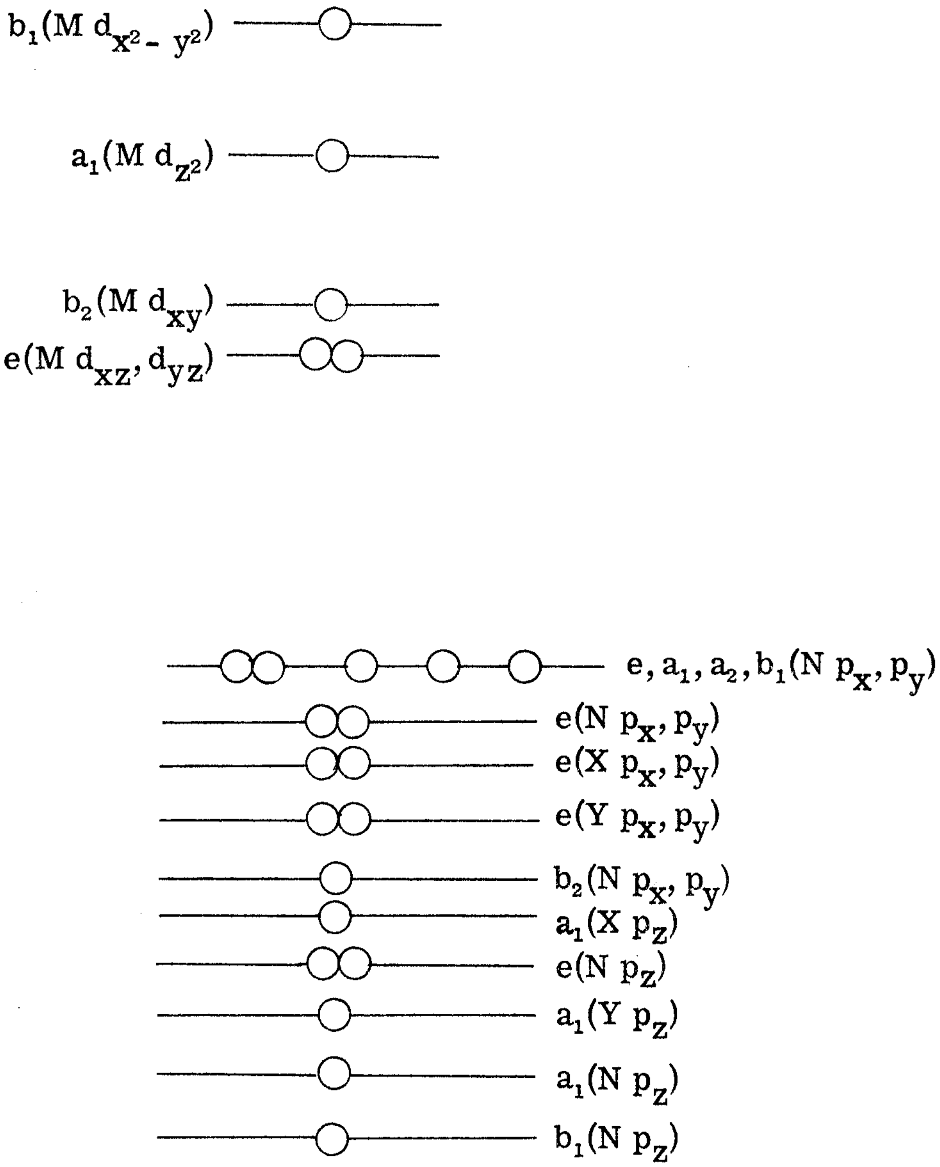


Figure 6

Molecular orbital diagram for MN_4XY

been calculated. The order presented is based on a qualitative argument from the physical situation.(7, 8, 9) Thus, in Figure 4, the square planar diagram has the b_{1g} level from $d_{x^2-y^2}$ most destabilized due to its being directed at the four nitrogen atoms. The b_{2g} from d_{xy} is the next most destabilized since this d orbital is still in the plane with the ligands. Lower in energy is the e_g level from d_{xz} and d_{yz} which are out of the plane of the ligands. Finally, lowest in energy would be the a_{1g} from the d_{z^2} orbital which is perpendicular to the plane of the ligands. Thus, for Fe(II) the ground state would be $(a_{1g})^2(e_g)^4$ or ${}^1A_{1g}$. The first excited state would be $(a_{1g})^2(e_g)^3(b_{2g})^1$ which is ${}^3E_g$ and ${}^1E_g$ making an xz or yz polarized transition. The second and third excited states will be $(a_{1g})^1(e_g)^4(b_{2g})^1$ which is ${}^3B_{2g}$ and ${}^1B_{2g}$ and $(a_{1g})^2(e_g)^3(b_{1g})^1$ which is ${}^3E_g$ and ${}^1E_g$. The exact ordering would depend on the ligand field splitting. For Fe(III), the ground state would be $(a_{1g})^2(e_g)^3$ which is ${}^2E_g$. The first excited state would be $(a_{1g})^2(e_g)^2(b_{2g})^1$ which gives the terms ${}^4A_{1g}$, ${}^4A_{2g}$, ${}^4B_{1g}$, ${}^4B_{2g}$, ${}^2A_{1g}$, ${}^2A_{2g}$, ${}^2B_{1g}$, and ${}^2B_{2g}$. The ordering of these levels can be calculated by a method similar to that of Ciampolini.(10) The doublets would all be allowed and would be xz and yz polarized. The second and third excited states are again variable in ordering. One is $(a_{1g})^1(e_g)^3(b_{2g})^1$ which gives ${}^4E_g$ and ${}^2E_g$ and is z^2 polarized. The other is $(a_{1g})^2(e_g)^2(b_{1g})^1$ which gives the same terms and polarizations as the first excited states.

Figure 5 presents the molecular orbital diagram for a D_{4h} arrangement for MN_4X_2. With the addition of the two ligands in the fifth and sixth positions, the a_{1g} from the d_{z^2} orbital is destabilized while the e_g from d_{xz} and d_{yz} and the b_{2g} from d_{xy} are not as affected. If the X ligand had the same effect as the nitrogens, the system would become octahedral making the b_{1g} and a_{1g} degenerate and the e_g and b_{2g} degenerate giving the familiar t_{2g} and e_g of the octahedral symmetry. Since, however, the fifth and sixth positions of the metal are not bound as tightly and are generally not nitrogen, these degeneracies should not be assumed. Thus, for Fe(II) the ground state becomes $(e_g)^4(b_{2g})^2$ or $^1A_{1g}$ with a first excited state of $(e_g)^4(b_{2g})^1(a_{1g})^1$ or $^3B_{2g}$ and $^1B_{2g}$ which is allowed and xy polarized. The second and third excited states would be $(e_g)^3(b_{2g})^1(a_{1g})^1$ or ^4E_g and ^1E_g which is xz and yz polarized and $(e_g)^4(b_{1g})^1$ or $^2B_{1g}$ which is orbitally forbidden.

Figure 6 shows the molecular orbital diagram for the C_{4v} molecule MN_4XY. The ordering is the same as that for MN_4X_2 since the same phenomena are occurring. Thus, for Fe(II) the ground state is $^1A_1$ while the first excited state is $^3B_2$ and $^1B_2$ requiring xy polarization. The second and third excited states would be $^3A_2$ and $^1A_2$ for one which is forbidden orbitally and ^3E and ^1E for the other which is allowed and polarized like x or y. The Fe(III) has a ground state of $^2B_2$ with a first excited state of $^2A_1$ requiring an xy polarized transition. The second and third transitions would be to $^2B_1$ which is $x^2 - y^2$ polarized and to ^4E and ^2E which is allowed and polarized along the x or y axes.

C. Spectra

The spectra are given in Figures 13 through 46. The IR 2 source on the Cary 14 produces a large amount of visible and ultraviolet light. It was found that this IR 2 source would cause the pink ZnTPP to photochemically react to give an orange compound (see Figures 13 through 18). The MnTPP was made to serve as another reference which, like ZnTPP, would have no d-d spectrum. The MnTPP was green when it was synthesized and remained green. Its spectrum (see Figures 19 through 22) suggests that it was formed as a different kind of compound. The H_2TPP spectrum agrees with literature spectra, so the sample was pure H_2TPP (see Figures 23 through 25). The Fe(III)TPP acetate (Figures 27 through 30), Fe(II)TPP (Figures 31 through 39), and the FeTPP prepared in air (Figures 40 through 46) allow a comparison of the different iron compounds. One notes that Fe(III) has peaks which Fe(II) does not by comparing Figure 29 with Figure 31. The extra peaks are at 865 nm, 700 nm, and 480 nm. Figure 41 reveals that these same peaks appear on the FeTPP made in air, and they are not removed by sodium dithionite. When the Fe(II)TPP was irradiated with the IR 2 source, the same peaks appeared. Bubbling with oxygen could not change the spectrum and more irradiation after the oxygen seemed fairly ineffective. Two conclusions could be reached. The Fe(II)TPP could be photosynsensitive and could have been changed merely by the light. Another possibility would be that some oxygen was dissolved in the chloroform solution but was not reacting with the Fe(II).

Irradiation by strong ultraviolet light provided enough energy to cause the redox reaction and produce Fe(III). Unfortunately, sodium dithionite was not added to test the reversibility of the reaction under reducing conditions. The second possibility is quite likely in view of the great probability that crude syringe techniques could not totally exclude oxygen. This suggests that Fe(II)TPP is stable in the presence of small amounts of oxygen. Better techniques of synthesis could probably produce information about the binding of oxygen to heme. The study of the photochemical reaction of ZnTPP and its relationship to that of Fe(II)TPP might also be fruitful.

Figure 7

Fe(II)TPyP in $CHCl_3$ at about 10^{-5} M.

Figure 7

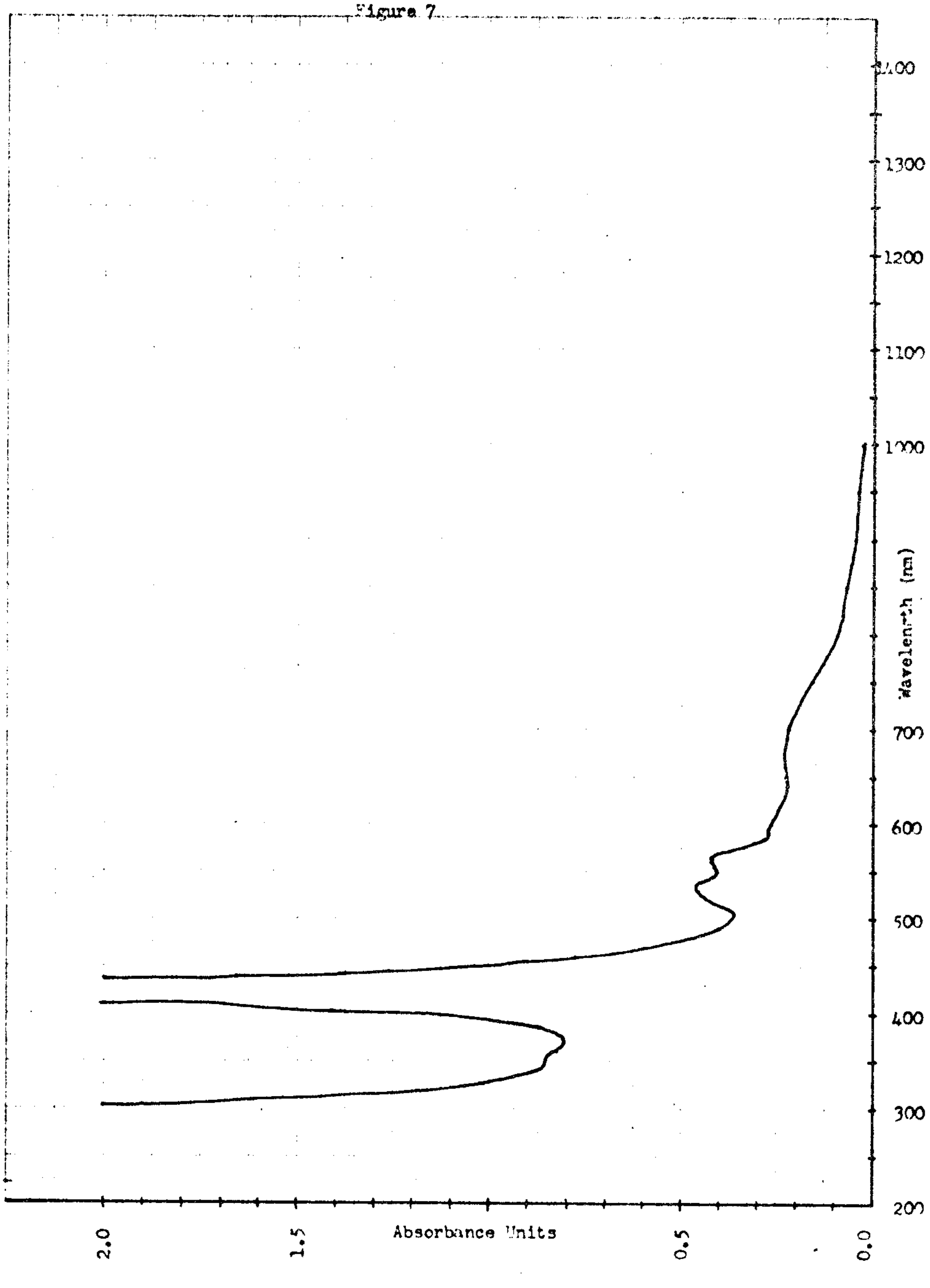

1400
1300
1200
1100
1000
Wavelength (nm)
700
600
500
400
300
200
Absorbance Units
2.0
1.5
0.5
0.0

Figure 8

Fe(II)TPyP in $CHCl_3$ at about 2×10^{-5} M.

Figure 8

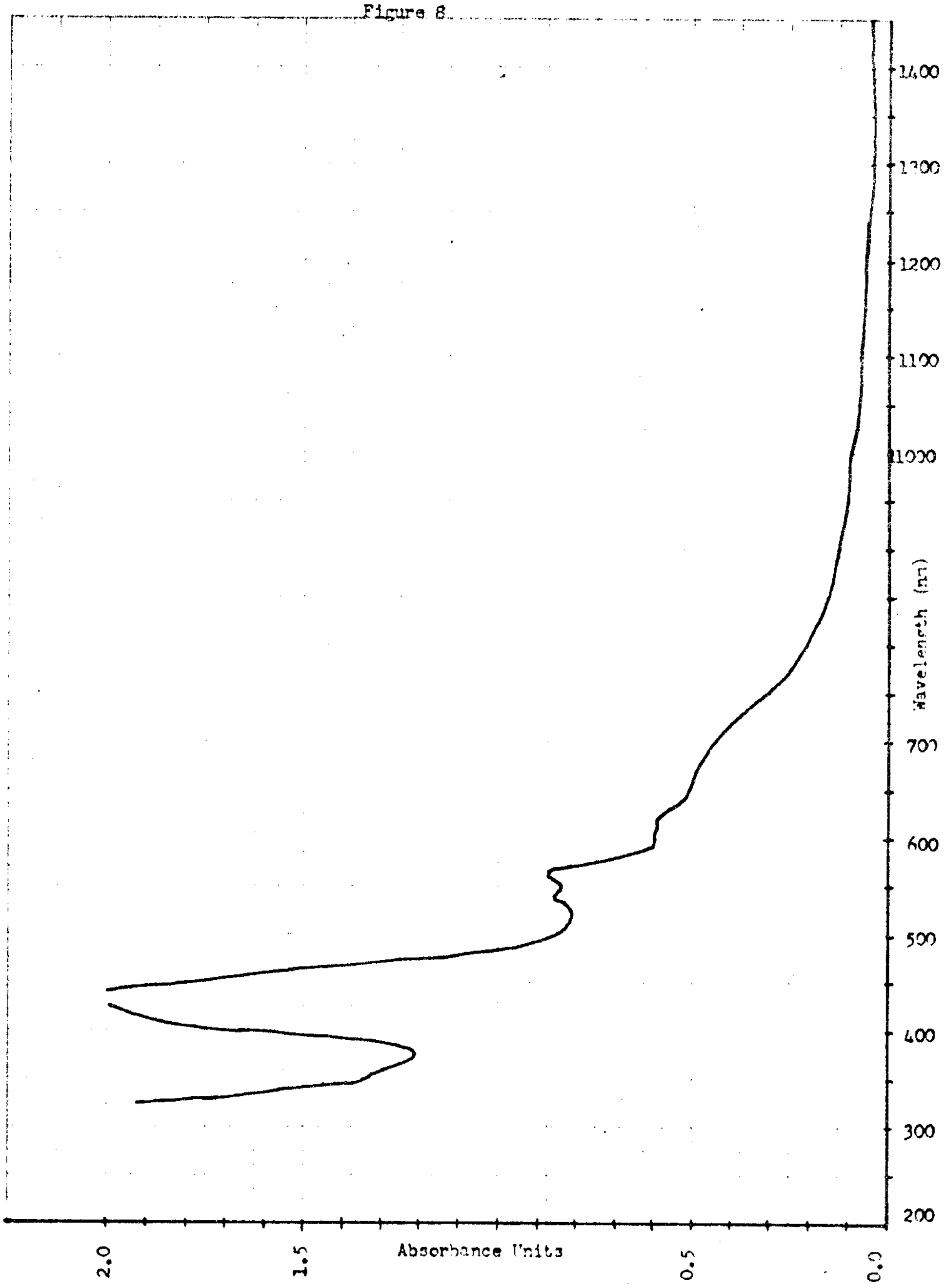

Absorbance Units
2.0
1.5
0.5
0.0
Wavelength (nm)
200
300
400
500
600
700
1000
1100
1200
1300
1400

Figure 9

Fe(II)TPyP in $CHCl_3$ at about 10^{-4} M.

Figure 9

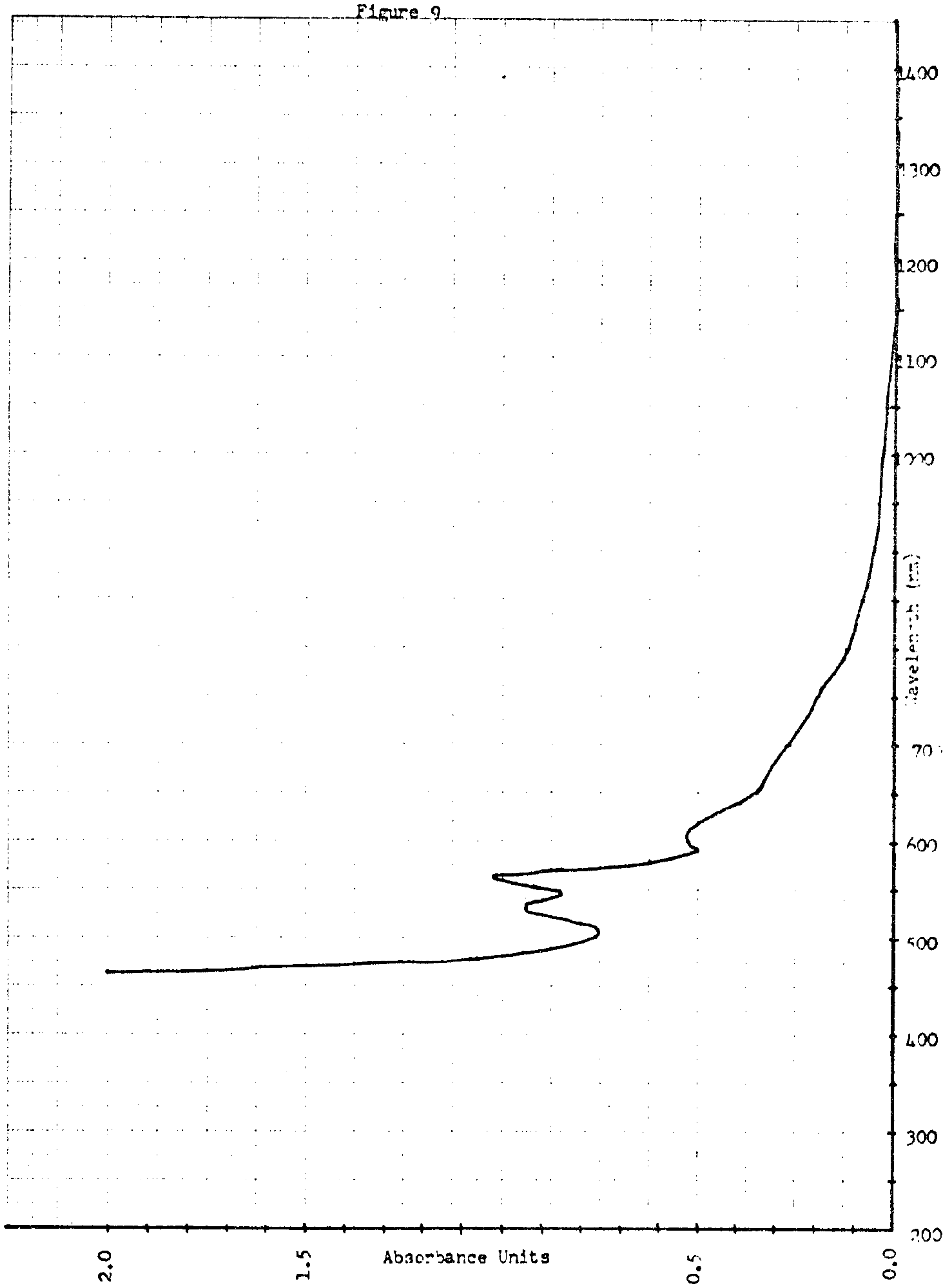

1400
1300
1200
1100
1000
Wavelength (nm)
700
600
500
400
300
200
2.0
1.5
Absorbance Units
0.5
0.0

Figure 10

Fe(II)TPyP in $CHCl_3$ at about 2×10^{-4} M.

Figure 10

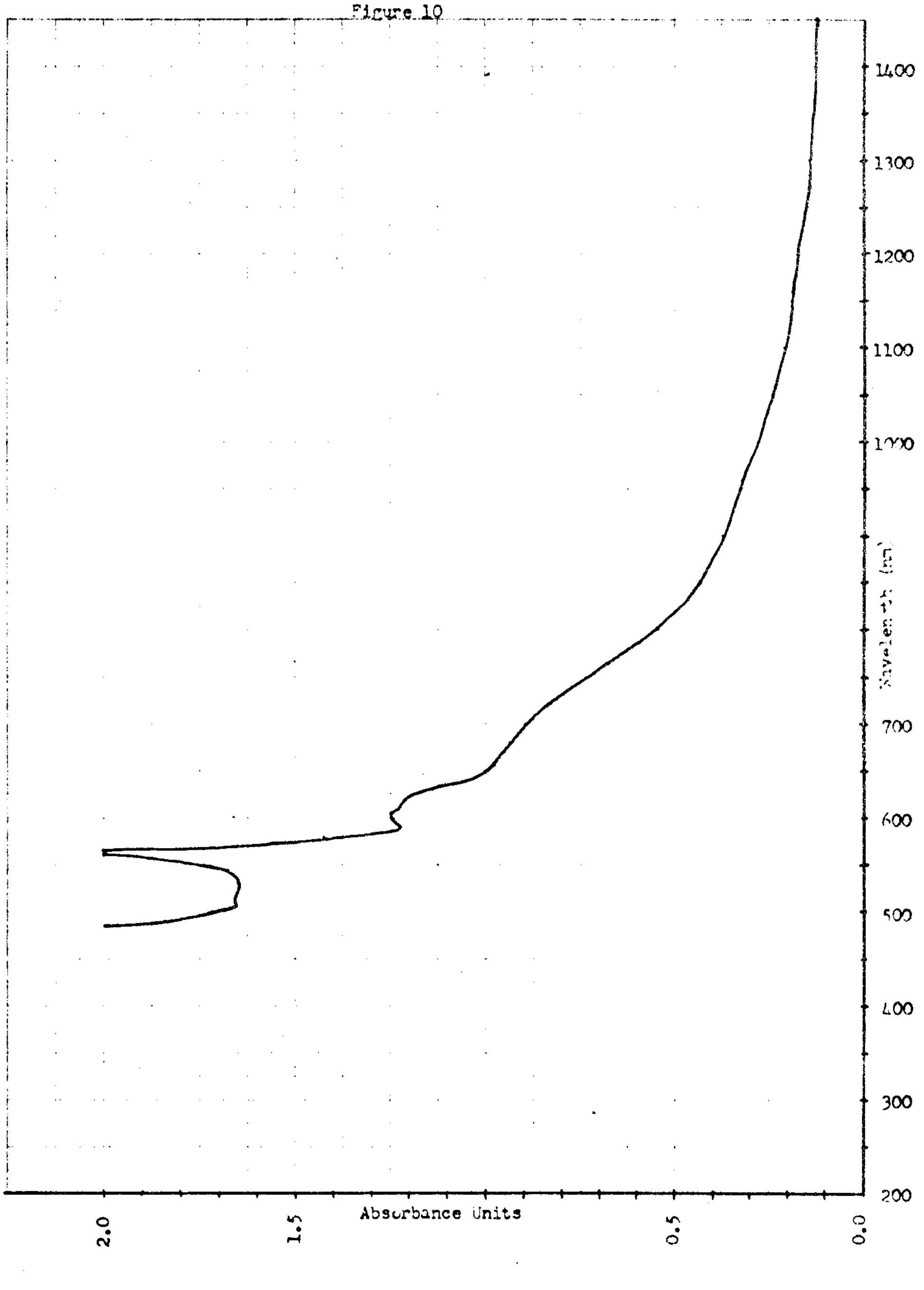

Absorbance Units
2.0
1.5
0.5
0.0
Wavelength (nm)
200
300
400
500
600
700
1000
1100
1200
1300
1400

Figure 11

Fe(II)TPyP in $CHCl_3$ after bubbling with O_2.
Concentration about 10^{-5} M.

Figure 11

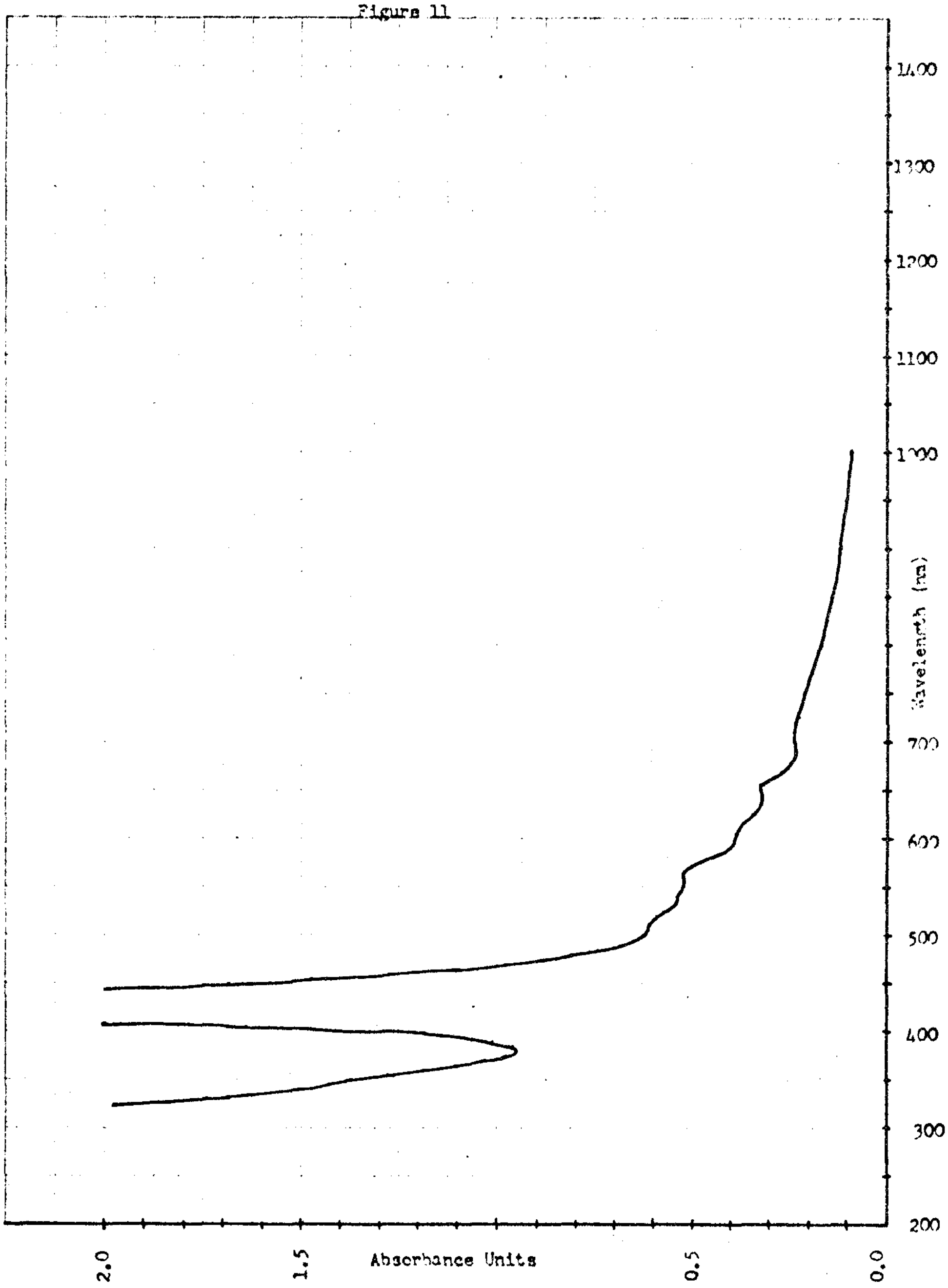

1400
1300
1200
1100
1000
700
600
500
400
300
200
Wavelength (nm)
2.0
1.5
Absorbance Units
0.5
0.0

Figure 12

Fe(II)TPyP in $CHCl_3$ after bubbling with O_2.
Concentration about 2×10^{-5} M.

Figure 12

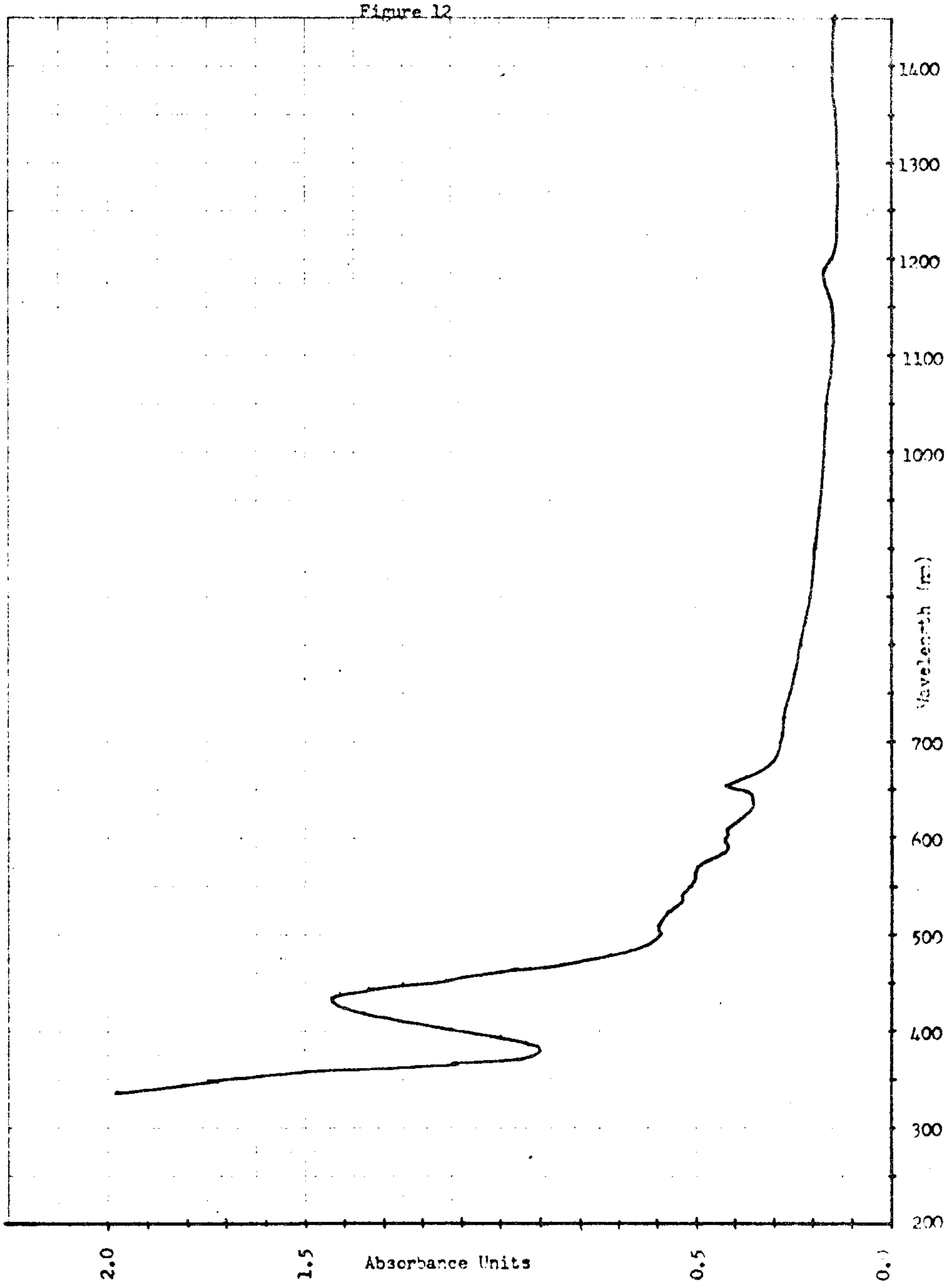

1400
1300
1200
1100
1000
Wavelength (nm)
700
600
500
400
300
200
2.0
1.5
Absorbance Units
0.5
0.0

Figure 13

ZnTPP at 1.06 × 10^{-4} M. The solution is pink and has not been irradiated with the IR 2 source.

Figure 13

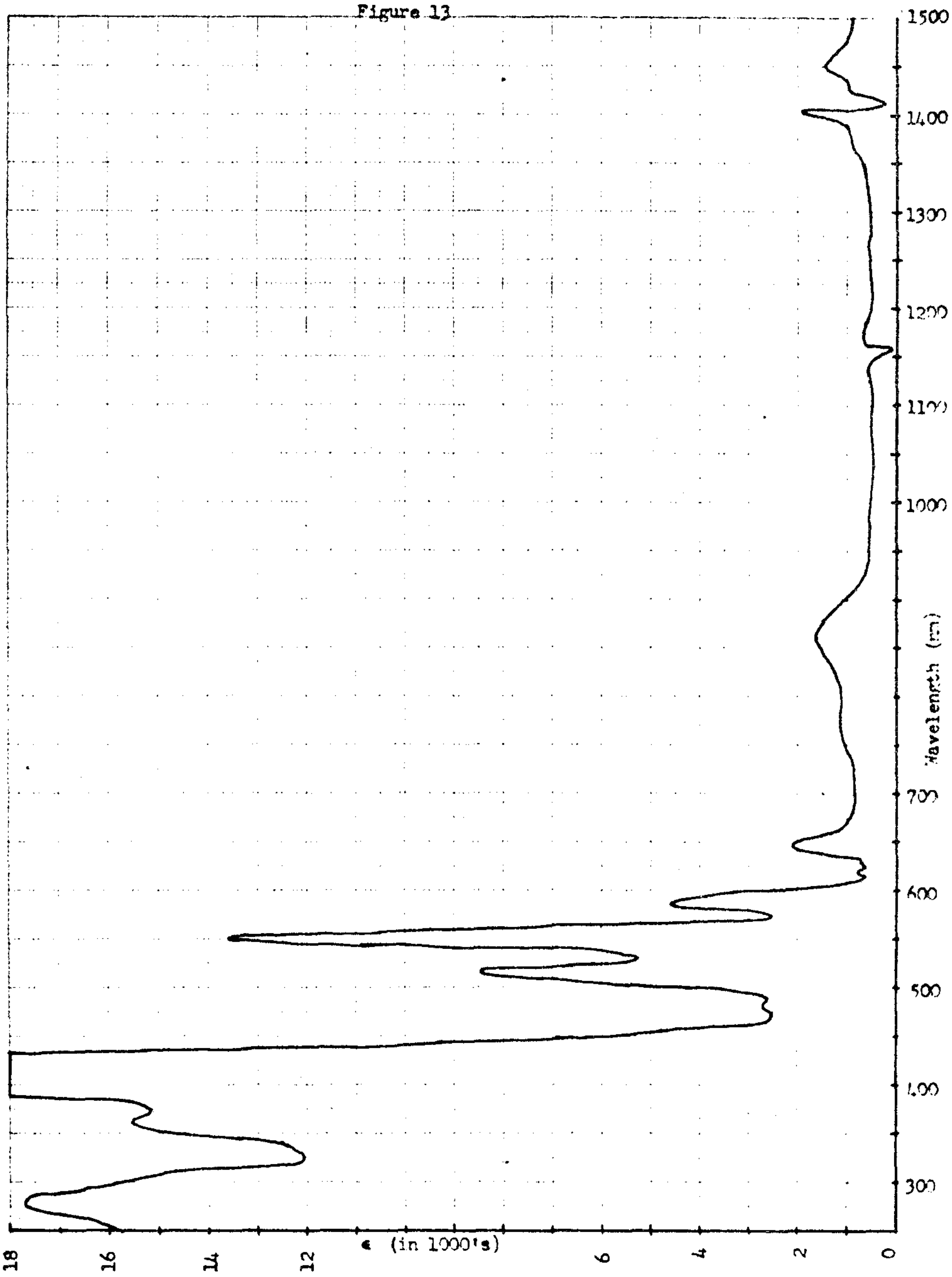

ε (in 1000's)
18
16
14
12
6
4
2
0
Wavelength (nm)
300
400
500
600
700
1000
1100
1200
1300
1400
1500

Figure 14

ZnTPP at 1.06×10^{-4} M using 1 mm cell to see the Soret band. The solution is pink and has not been irradiated with the IR 2 source.

Figure 14

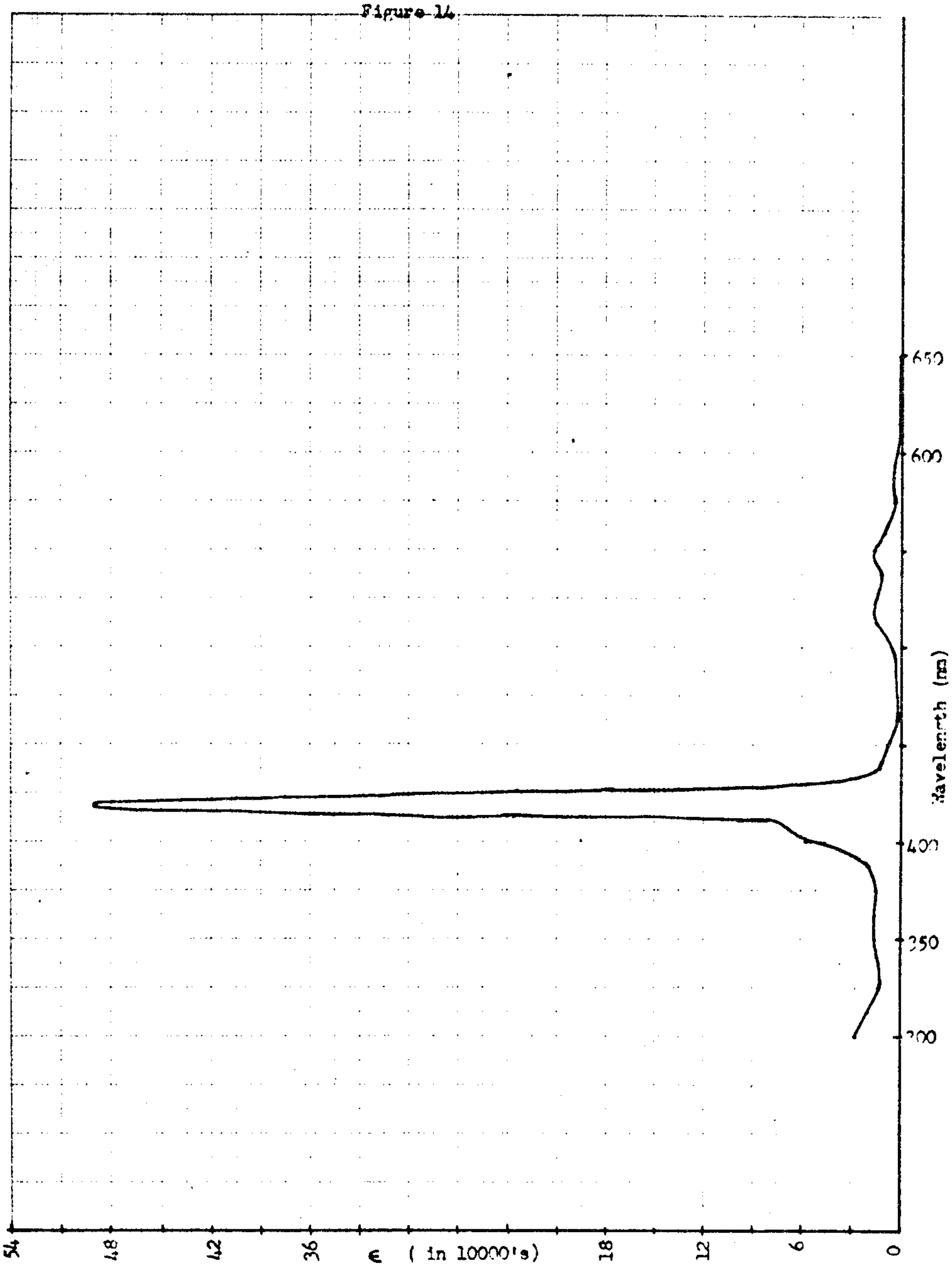

650
600
400
350
300
Wavelength (nm)
54
48
42
36
ε (in 10000's)
18
12
6
0

Figure 15

ZnTPP at 1.06×10^{-4} M showing the peak at 1900 nm before the use of the IR 2 source. The solution is pink.

Figure 15

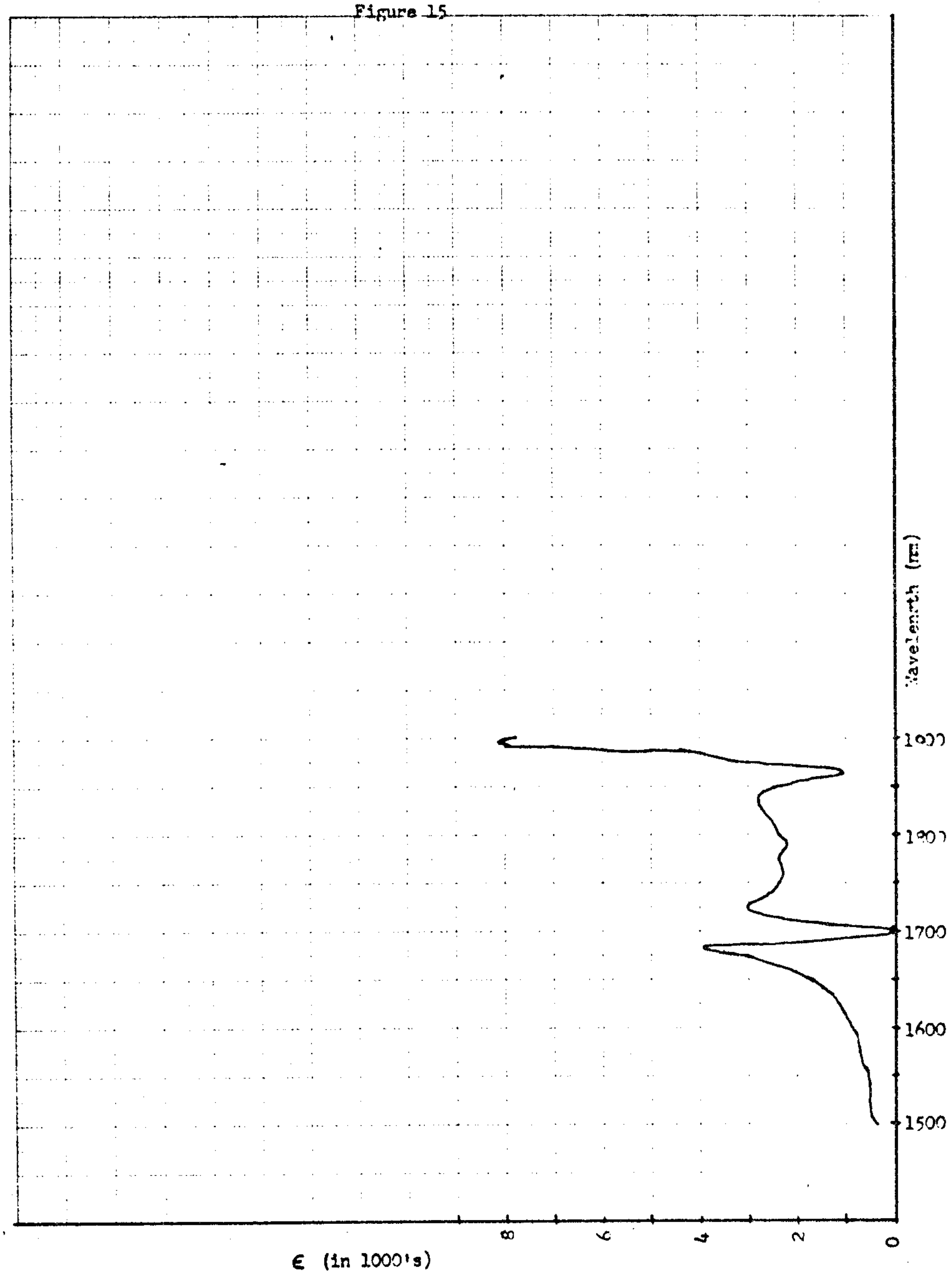


Figure 16

ZnTPP at 1.06 × 10^{-4} M using the IR 2 source. The solution is brown-orange.

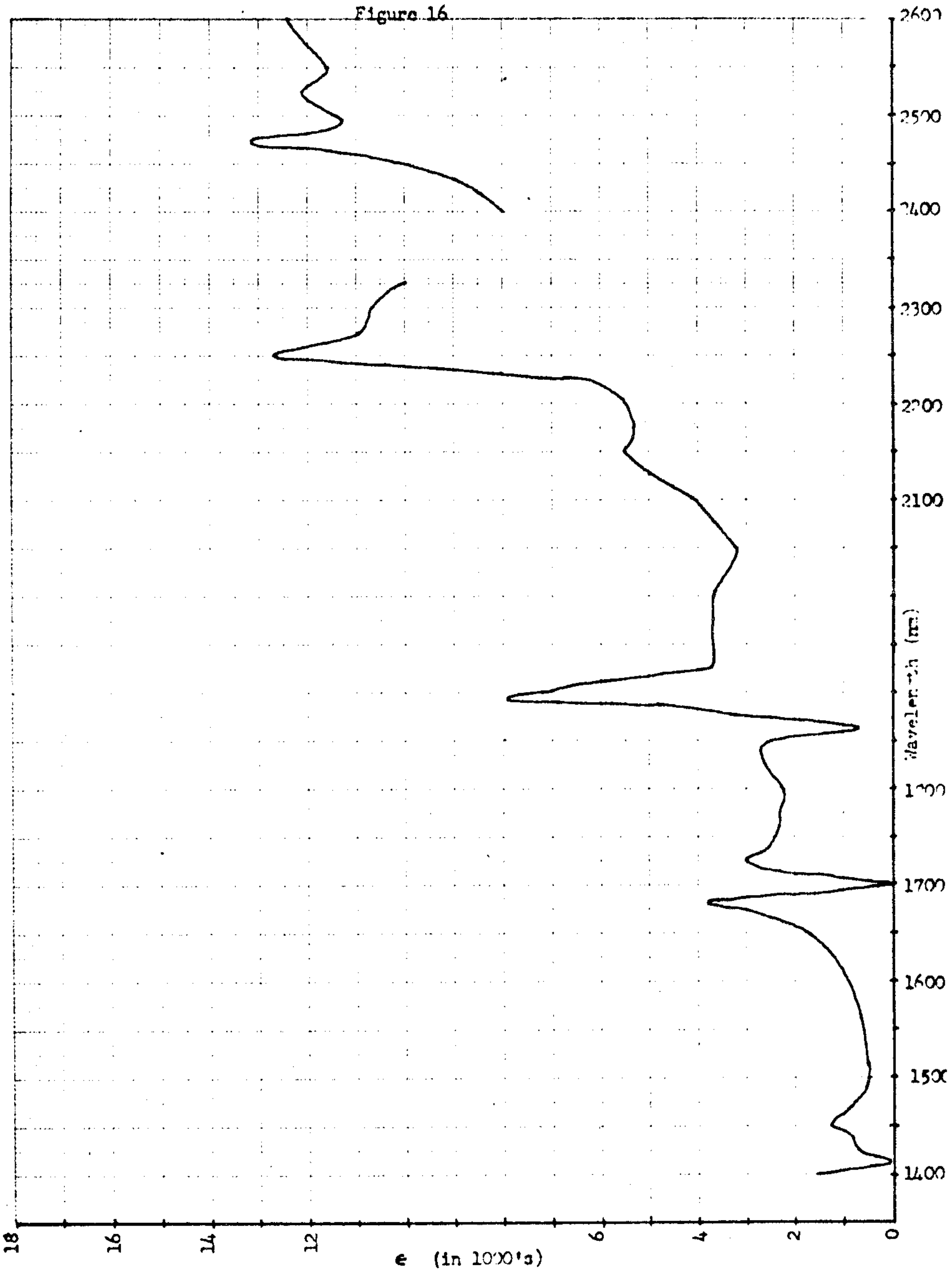


Figure 16

2600
2500
2400
2300
2200
2100
1900
1700
1600
1500
1400
Wavelength (m)
18
16
14
12
6
4
2
0
ϵ (in 1000's)

Figure 17

ZnTPP at 1.06×10^{-4} M after using the IR 2 source so that the solution is orange. This decomposition spectrum should be compared to Figure 13.

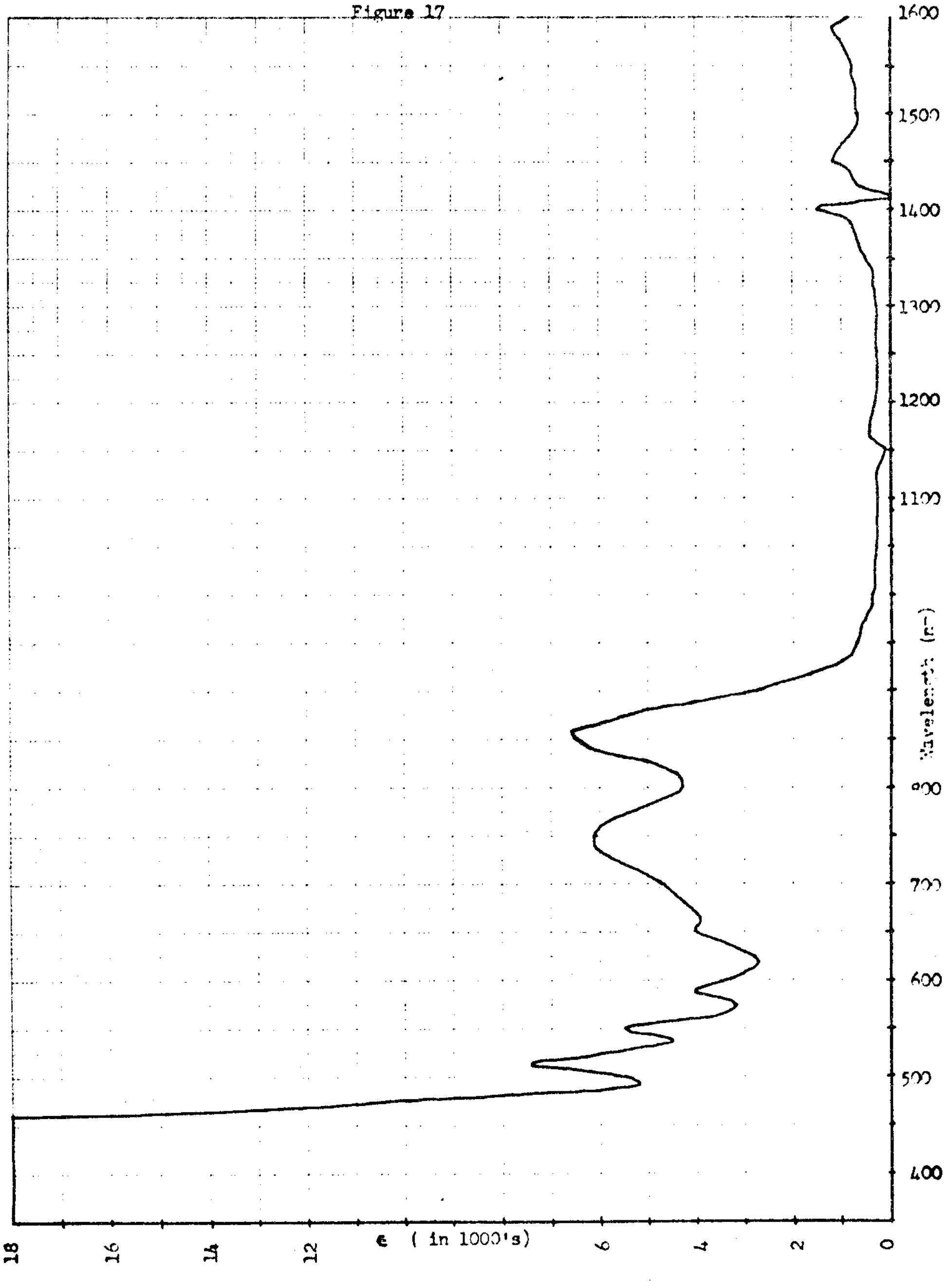

400
500
600
700
800
1100
1200
1300
1400
1500
1600
Wavelength (mμ)
0
2
4
6
ε (in 1000's)
12
14
16
18

Figure 17

Figure 18

ZnTPP at 1.06×10^{-4} M after using the IR 2 source. The solution is orange is in the 1 mm cells to show the Soret band.

Figure 18

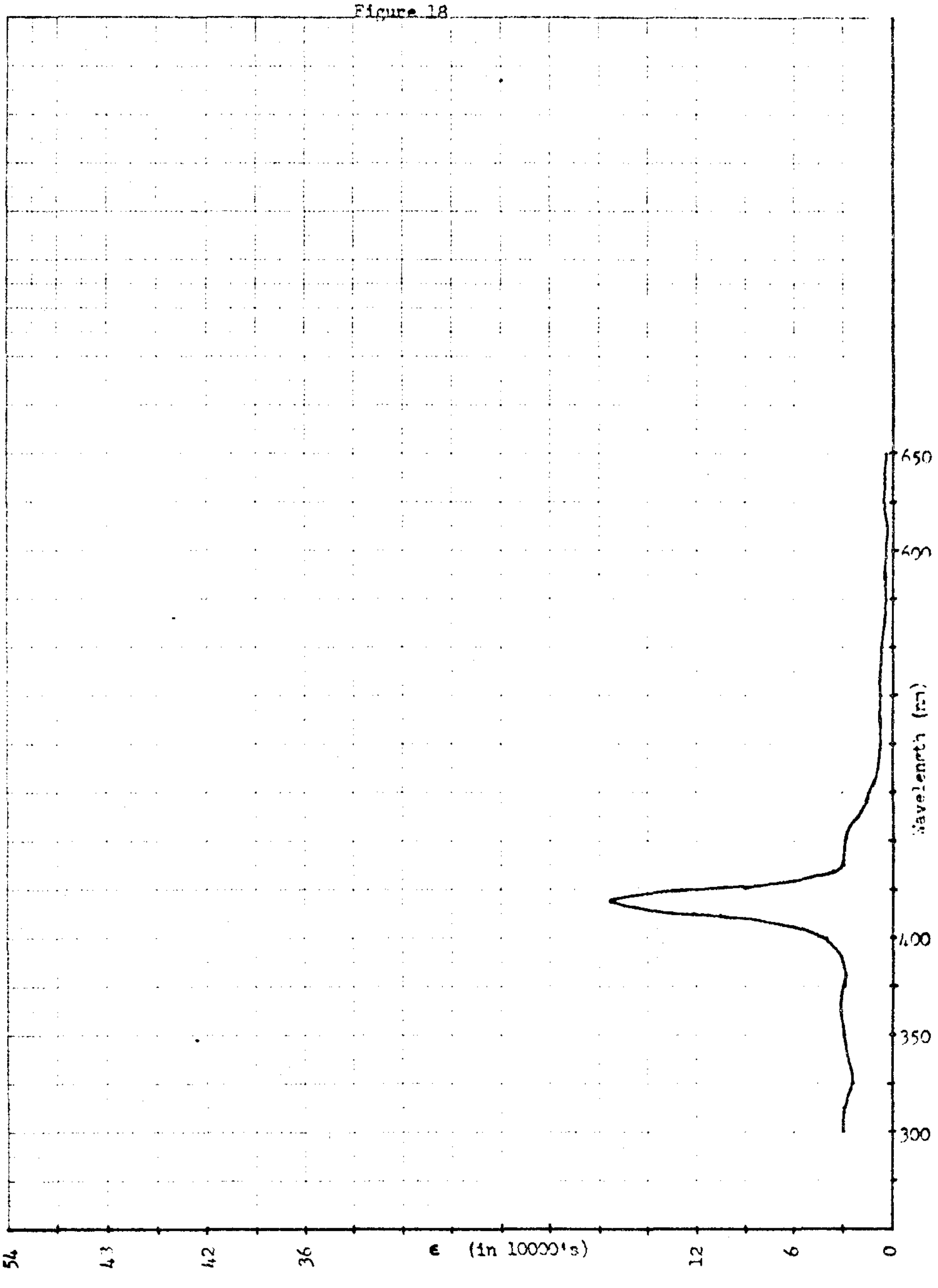


Figure 19

MnTPP at 1.06×10^{-4} M using the IR 2 source. The solution is green before and after the spectrum.

Figure 19

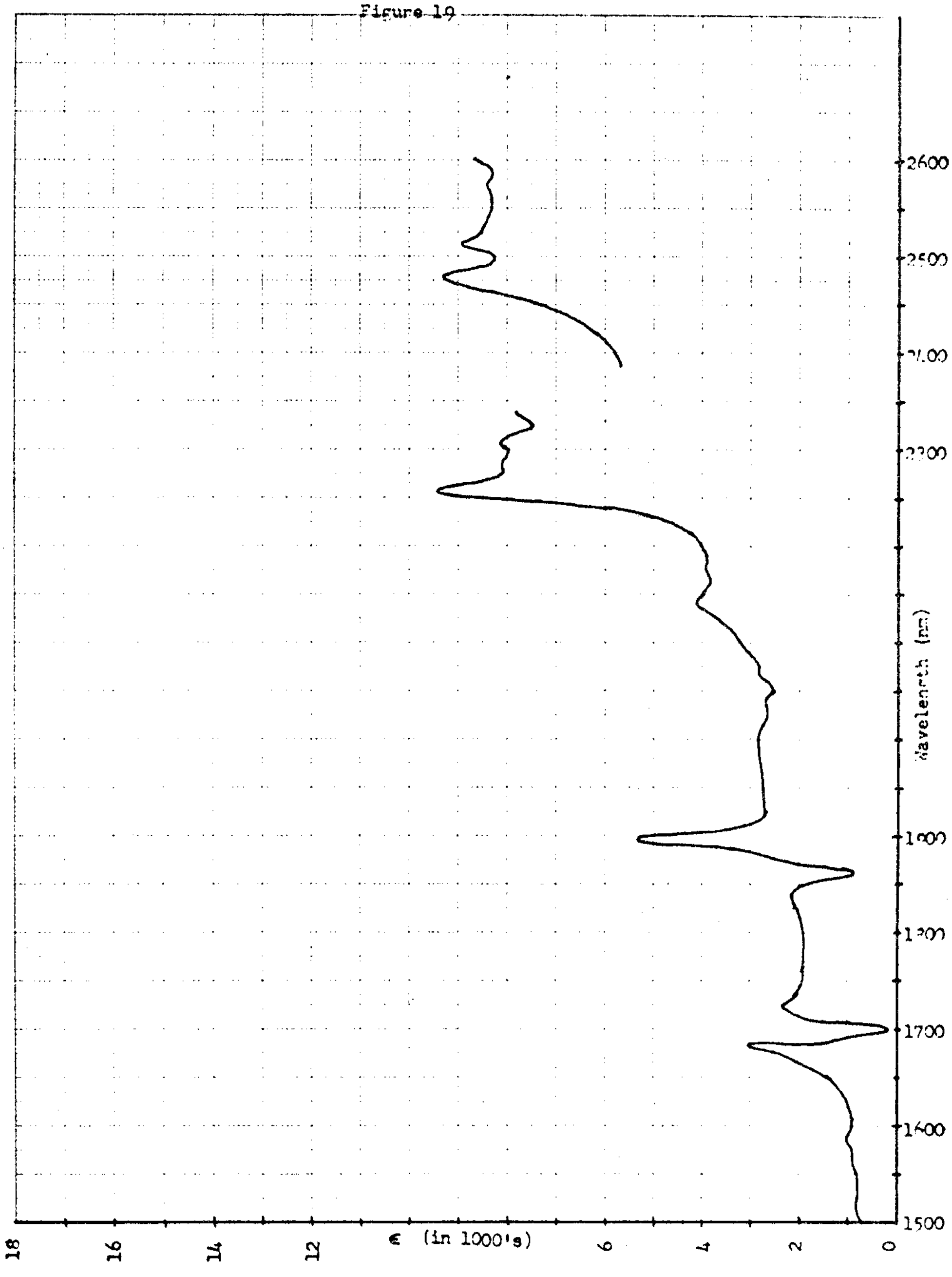

ε (in 1000's)
0
2
4
6
12
14
16
18
Wavelength (nm)
1500
1600
1700
1800
1900
2300
2400
2500
2600

Figure 20

MnTPP at 1.06×10^{-4} M after the IR 2 source. The solution is green.

Figure 20

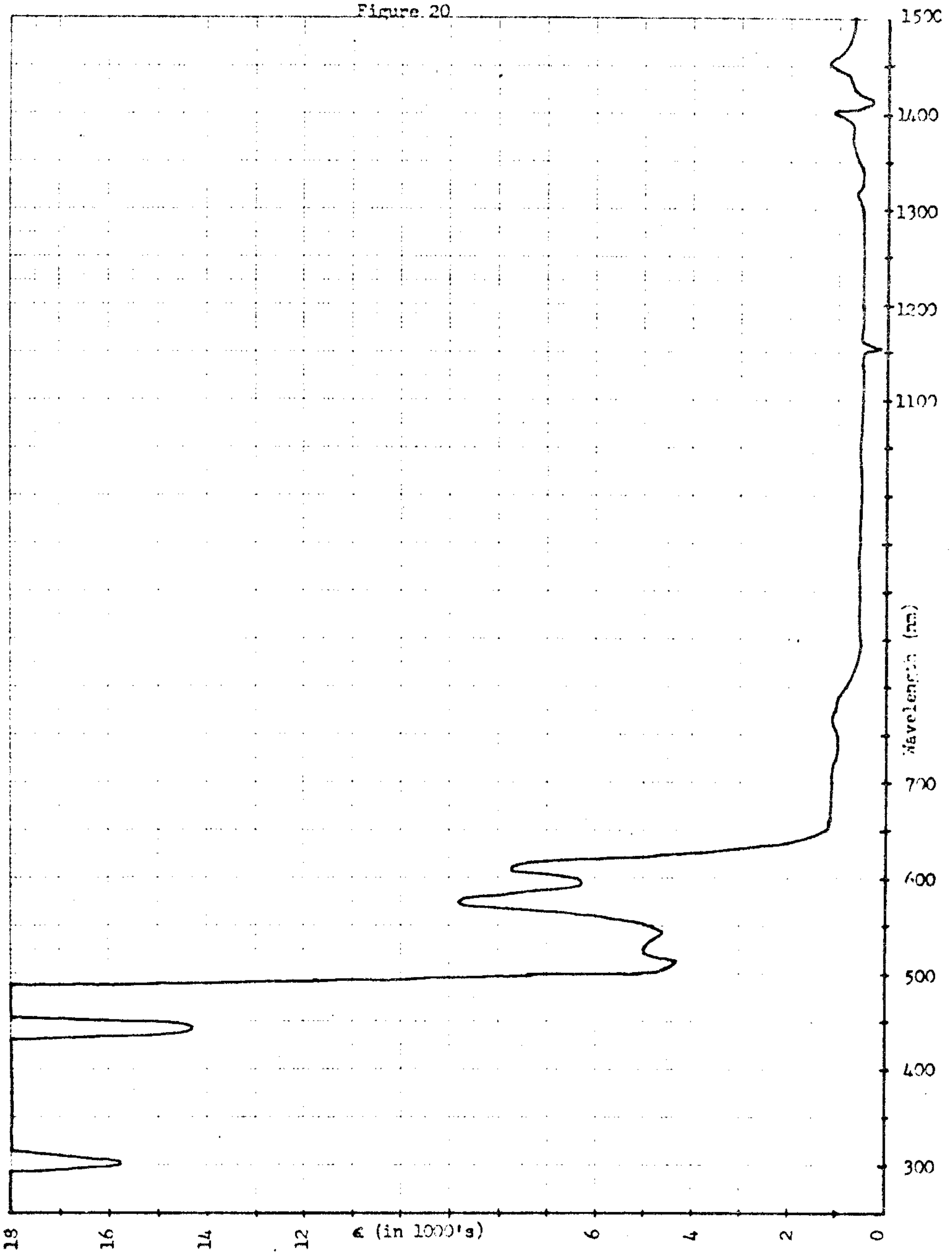

Wavelength (nm)
1500
1400
1300
1200
1100
700
600
500
400
300
ε (in 1000's)
18
16
14
12
6
4
2
0

Figure 21

MnTPP at 1.06×10^{-4} M after the IR 2 source. The solution is in the 1mm cells. Note the extremely small peak in place of the Soret band.

Figure 21

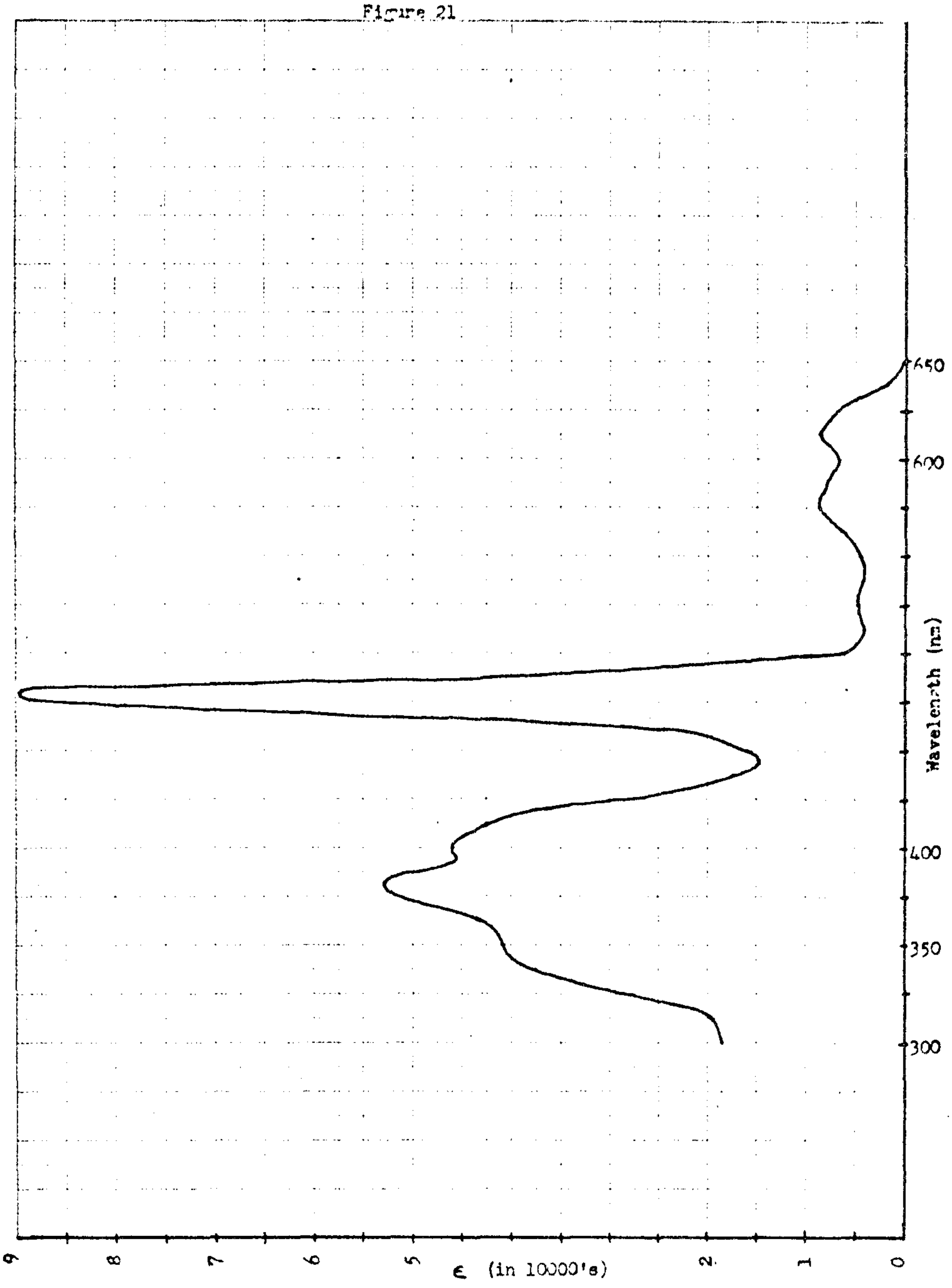


Figure 22

MnTPP at 5.30×10^{-5} M after the IR 2 source. Beer's Law appears to hold fairly well.

Figure 22

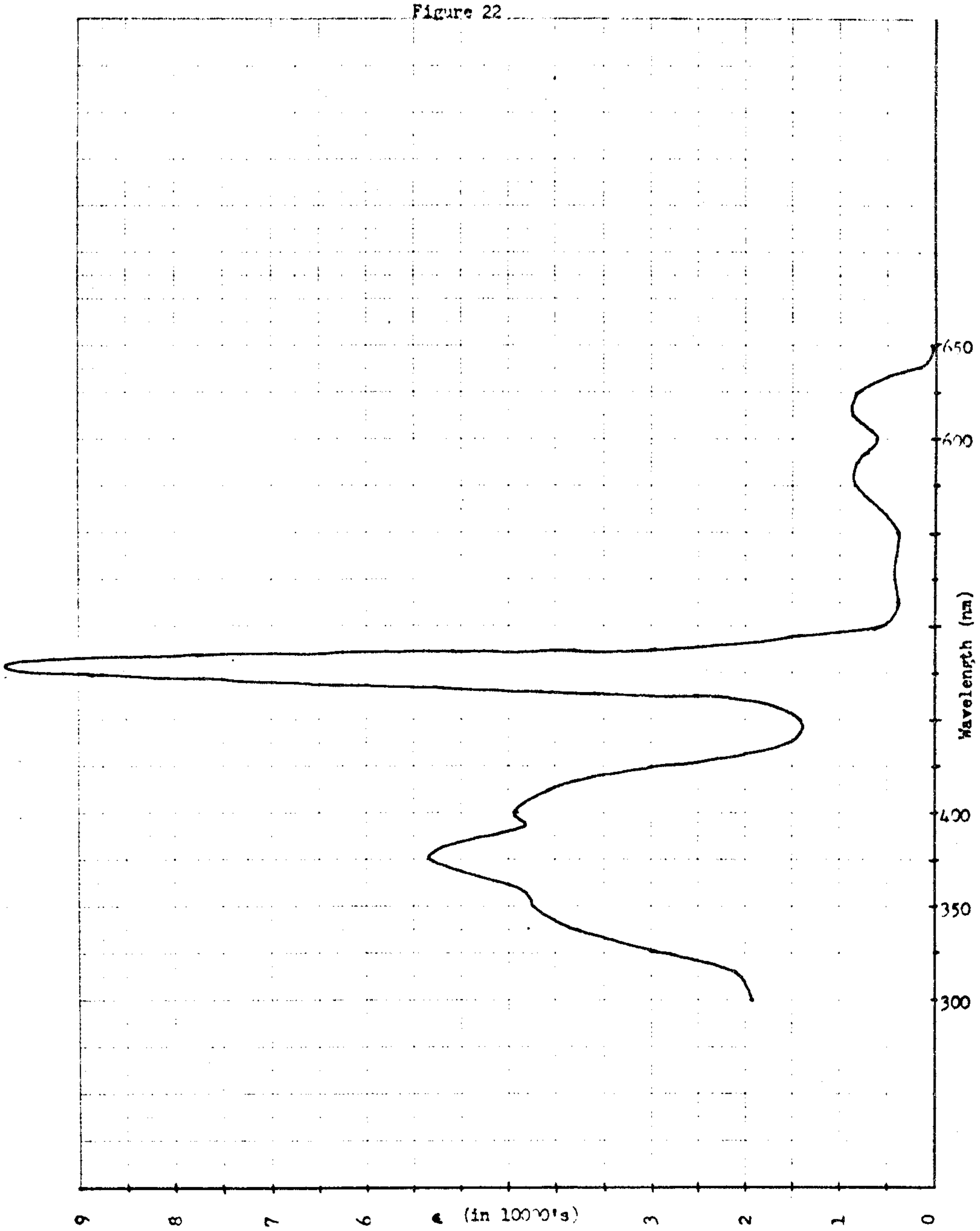


Figure 23

H_2TPP at 1.00×10^{-4} M using the IR 2 source.

Figure 23

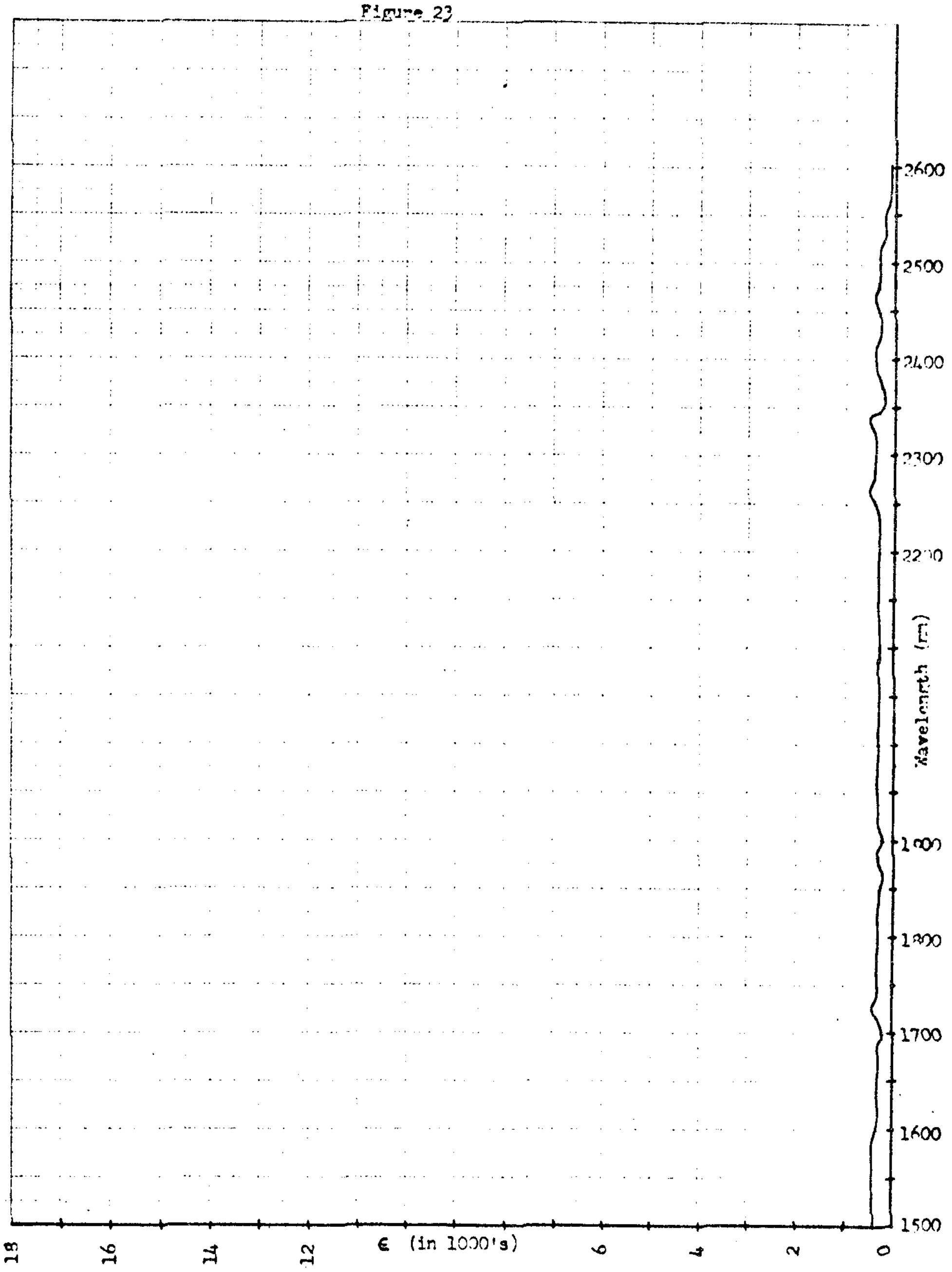

2600
2500
2400
2300
2200
Wavelength (nm)
1900
1800
1700
1600
1500
18
16
14
12
ε (in 1000's)
6
4
2
0

Figure 24

H_2TPP at 1.00×10^{-4} M after the IR 2 source.

Figure 24

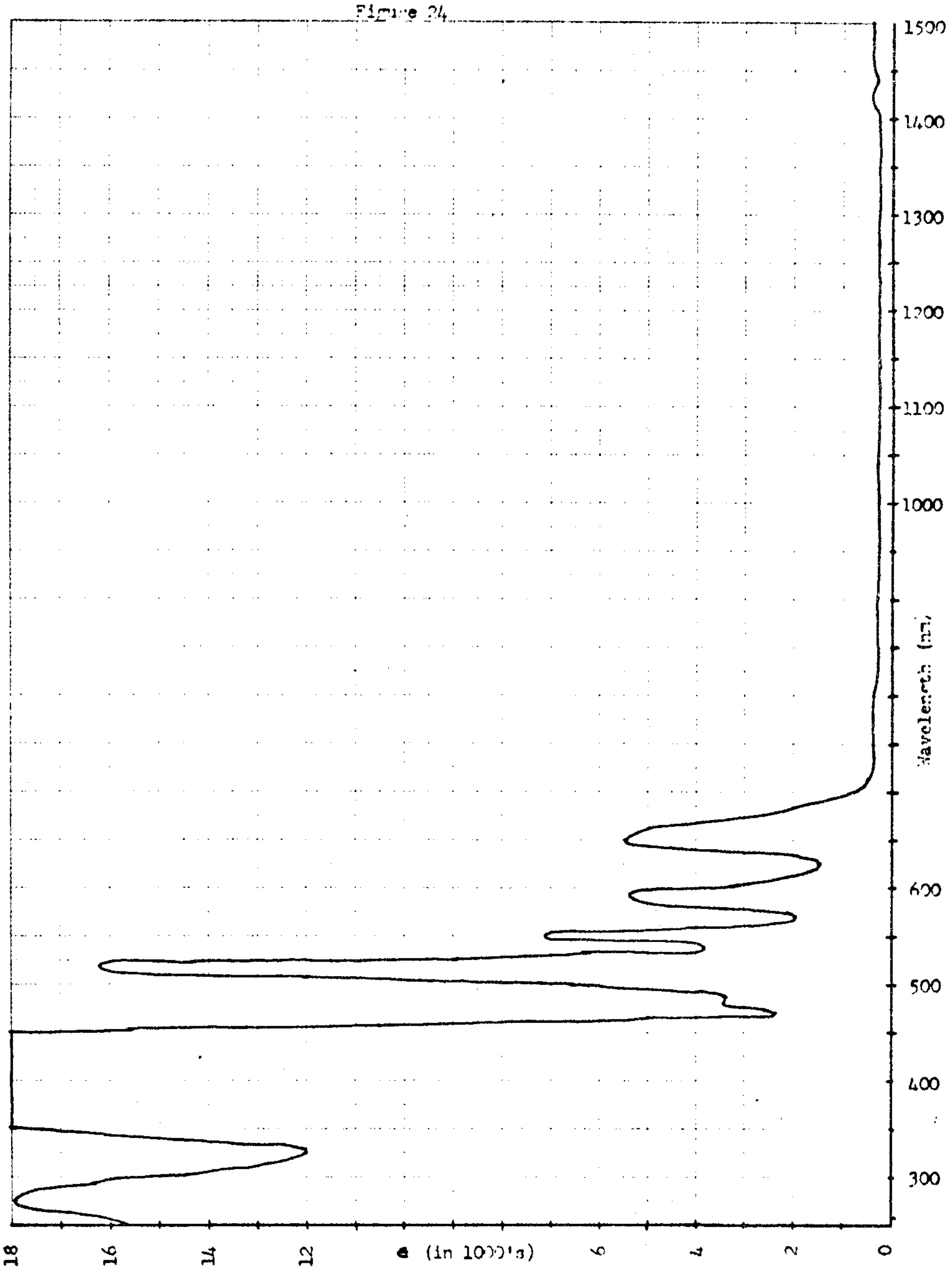

1500
1400
1300
1200
1100
1000
Wavelength (nm)
600
500
400
300
18
16
14
12
ε (in 1000's)
6
4
2
0

Figure 25

H_2TPP at 1.00×10^{-4} M after the IR 2 source. This uses the 1mm cells to observe the Soret band.

Figure 25

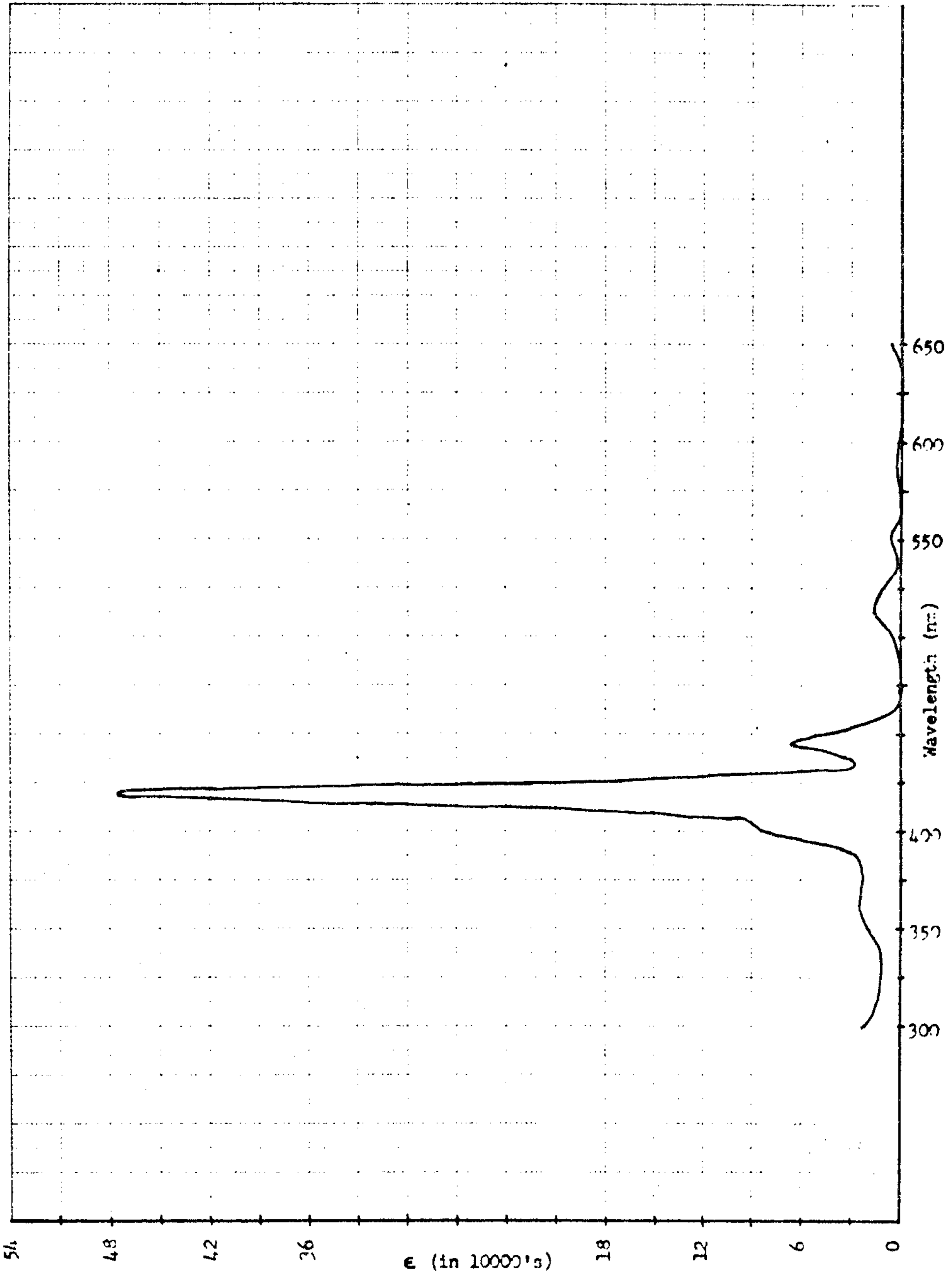

650
600
550
400
350
300
Wavelength (nm)
54
48
42
36
18
12
6
0
ε (in 10000's)

Figure 26

Fe(III)TPPOAc at 1.15×10^{-4} M before using the IR 2 source. The solution is orange.

Figure 26

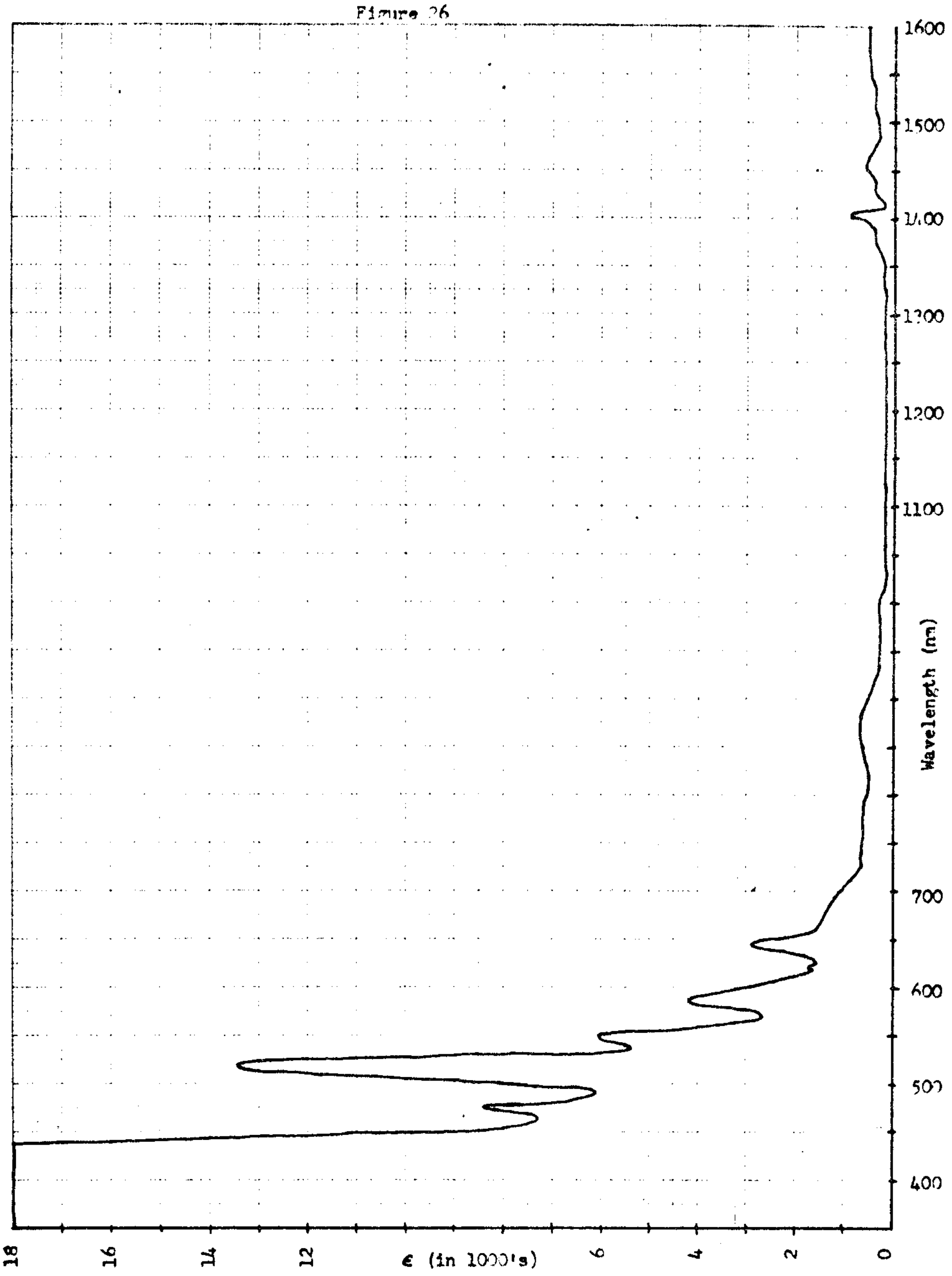

1600
1500
1400
1300
1200
1100
700
600
500
400
Wavelength (nm)
18
16
14
12
ε (in 1000's)
6
4
2
0

Figure 27

Fe(III)TPPOAc at 1.15×10^{-4} M before using the IR 2 source. This uses the 1 mm cells to observe the Soret band.

Figure 27

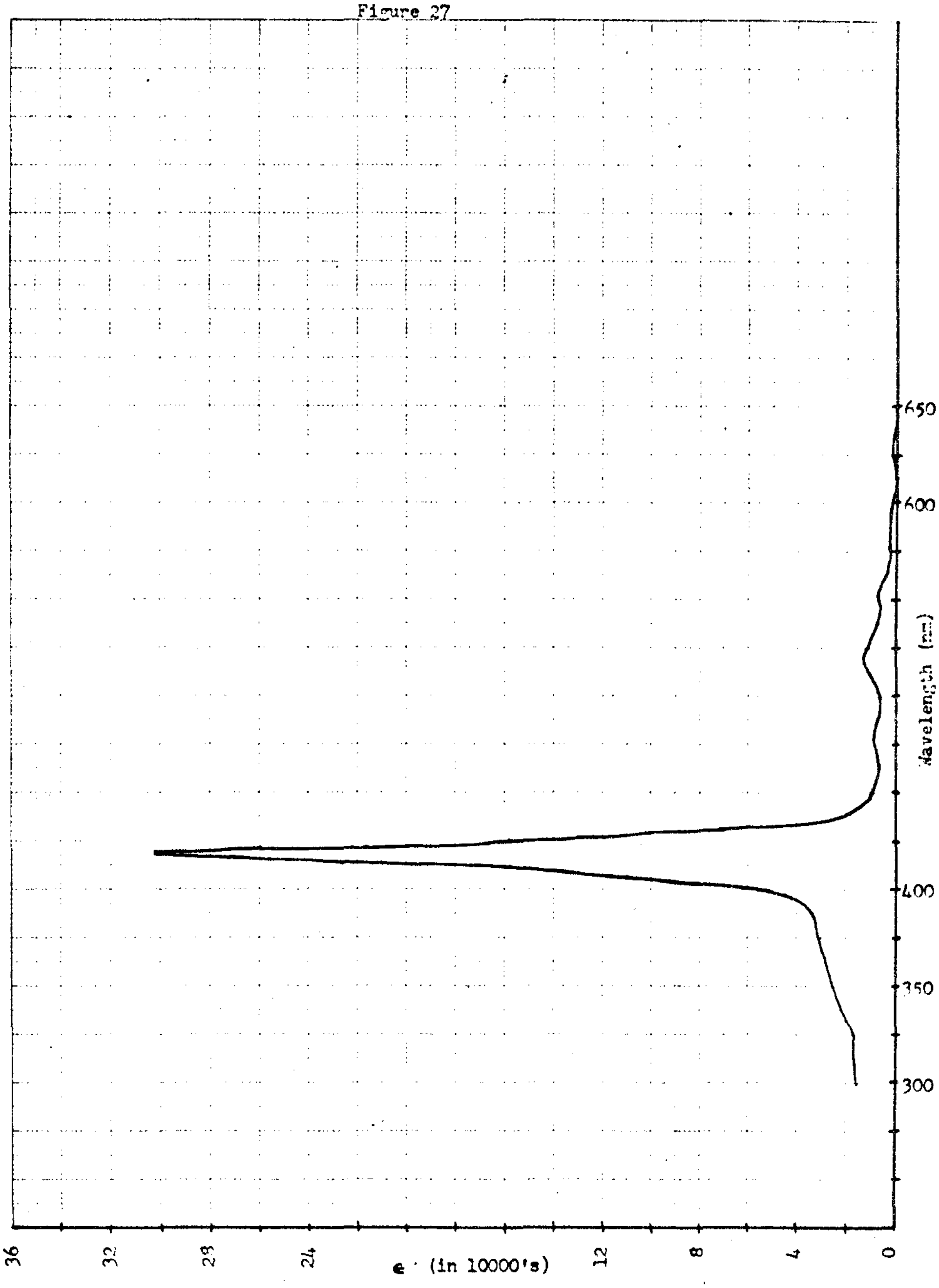


Figure 28

Fe(III)TPPOAc at 1.15×10^{-4}M using the IR 2 source.

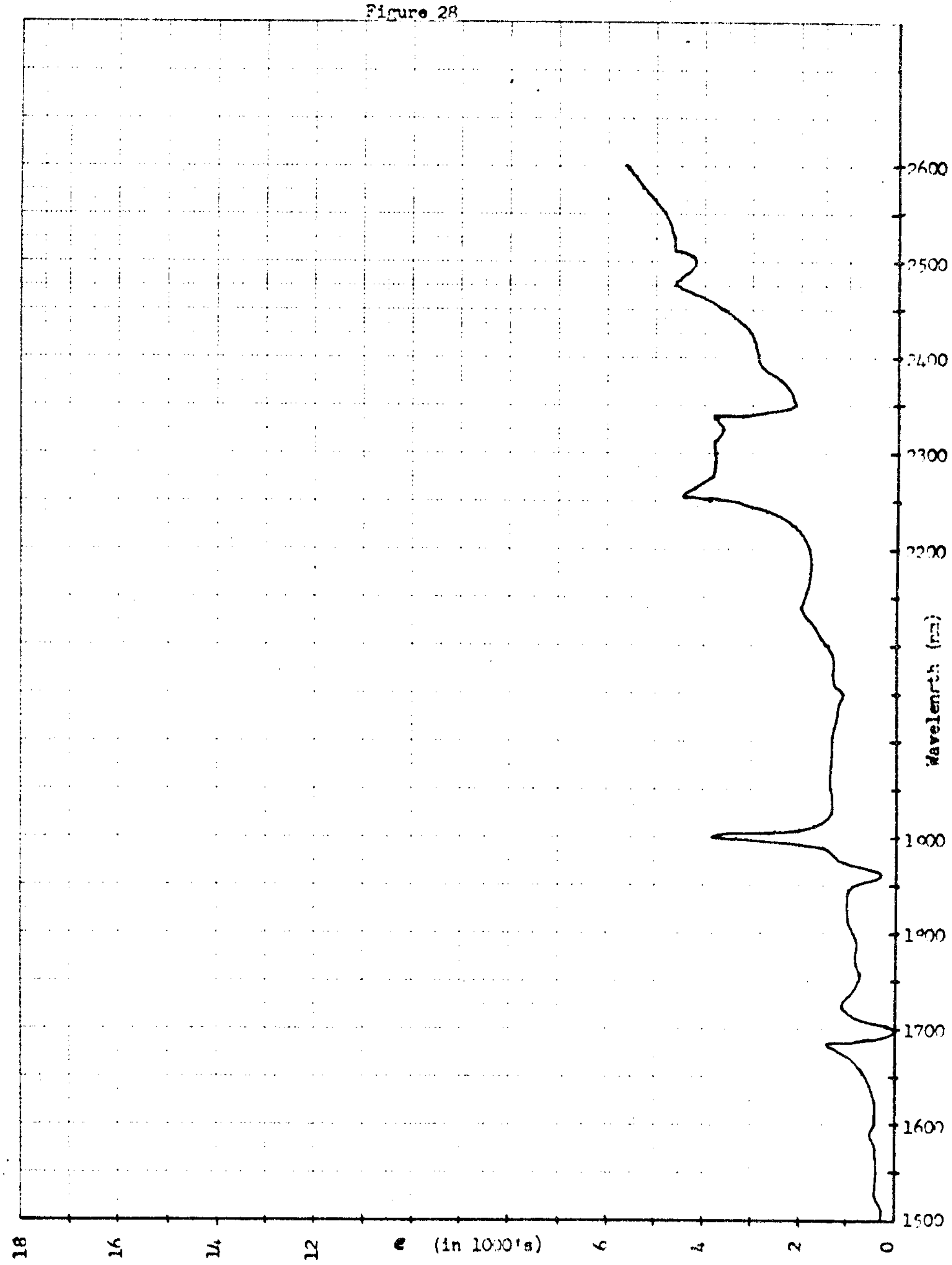


Figure 28

2600
2500
2400
2300
2200
Wavelength (nm)
2000
1800
1700
1600
1500
18
16
14
12
ε (in 1000's)
6
4
2
0

Figure 29

Fe(III)TPPOAc at 1.15×10^{-4} M after the IR 2 source. No changes from Figure 26 have occurred.

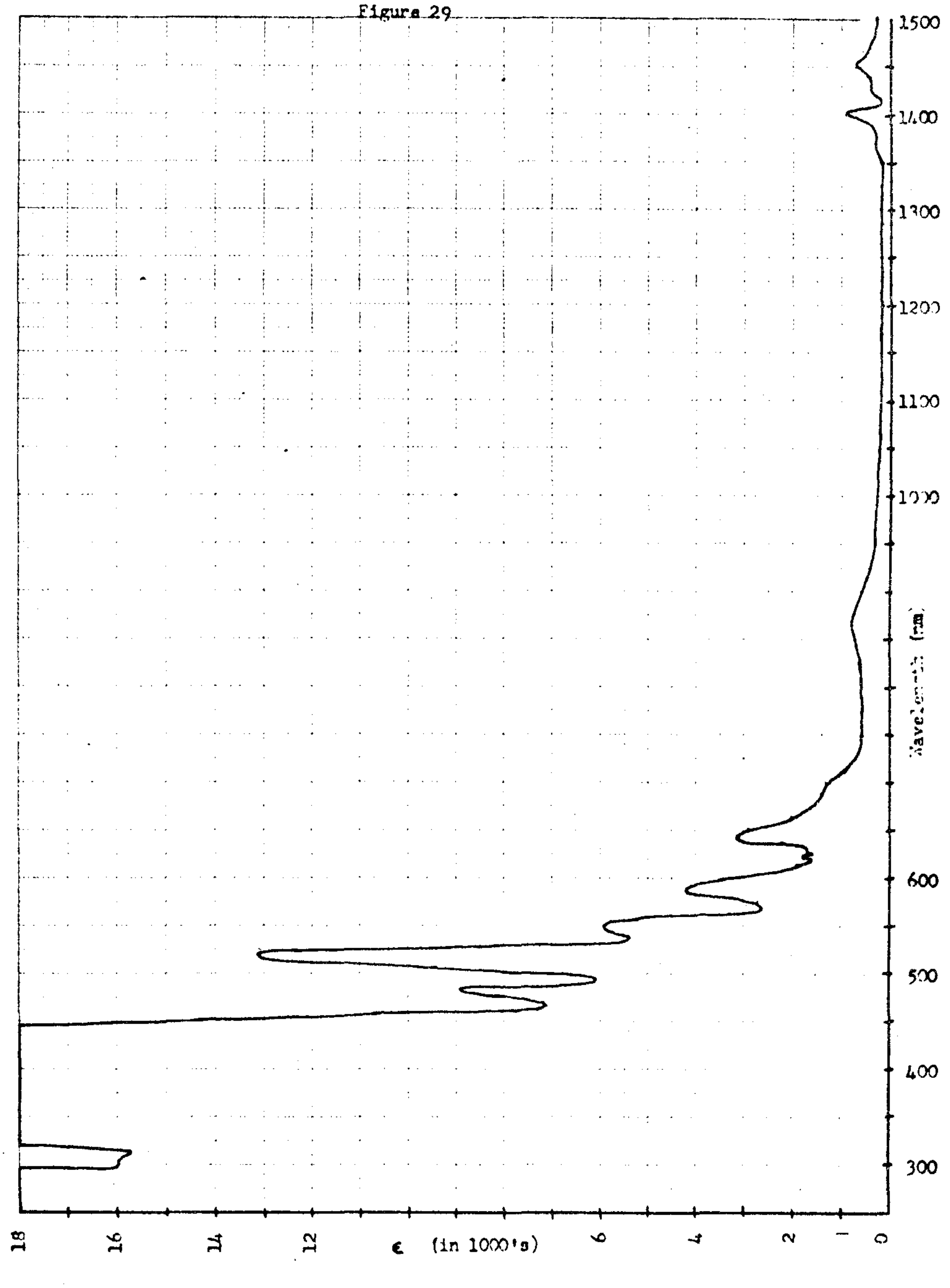


Figure 29

1500
1400
1300
1200
1100
1000
600
500
400
300
Wavelength (nm)
18
16
14
12
ε (in 1000's)
6
4
2
1
0

Figure 30

Fe(III)TPPOAc at 1.15×10^{-4} M after the IR 2 source. This uses the 1 mm cell and shows no changes from Figure 27.

Figure 30

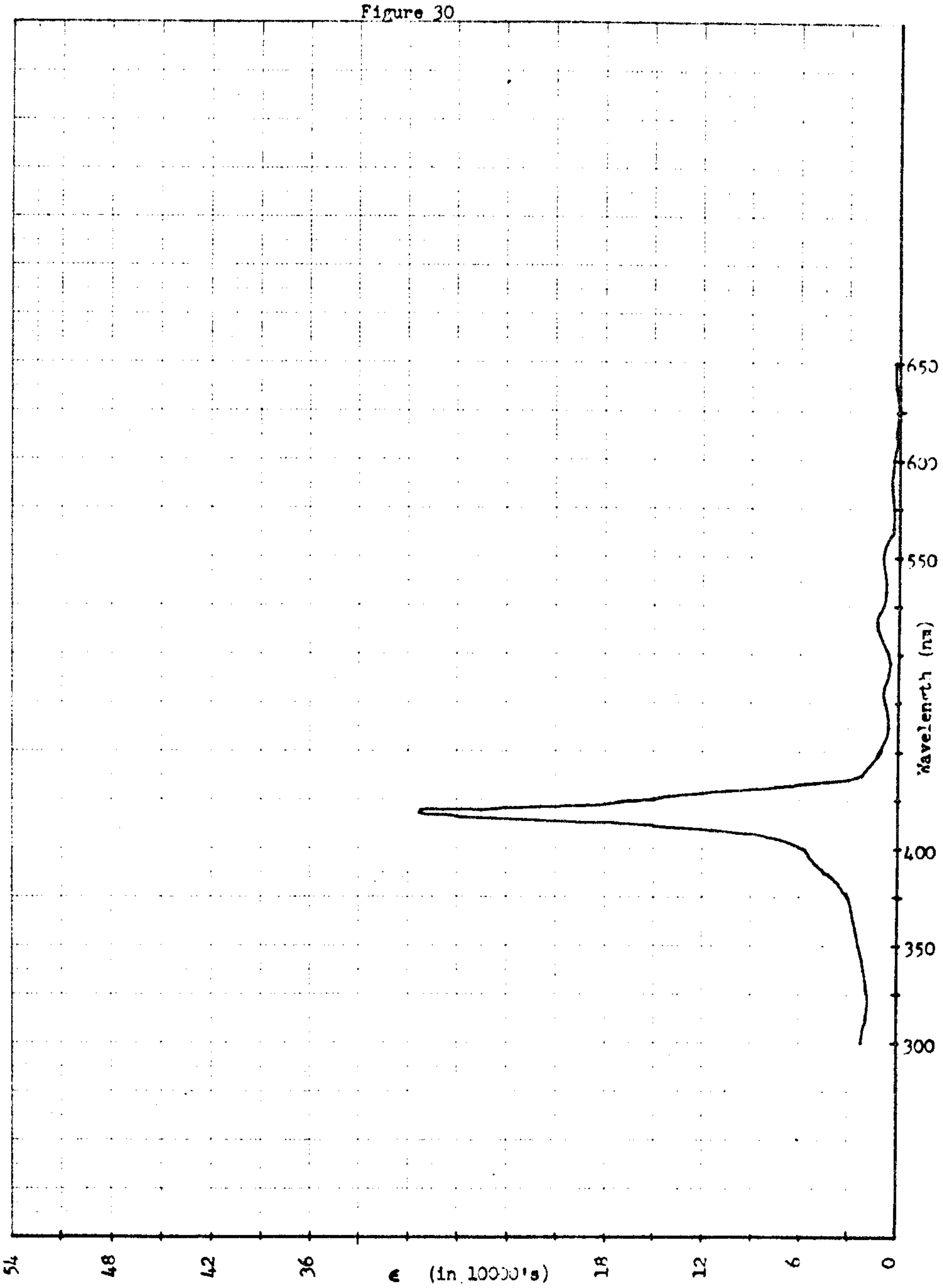

650
600
550
Wavelength (nm)
400
350
300
54
48
42
36
ε (in 10000's)
18
12
6
0

Figure 31

Fe(II)TPP at 1.04 × 10^{-4} M. Pink solution found before use of IR 2 source.

Figure 31

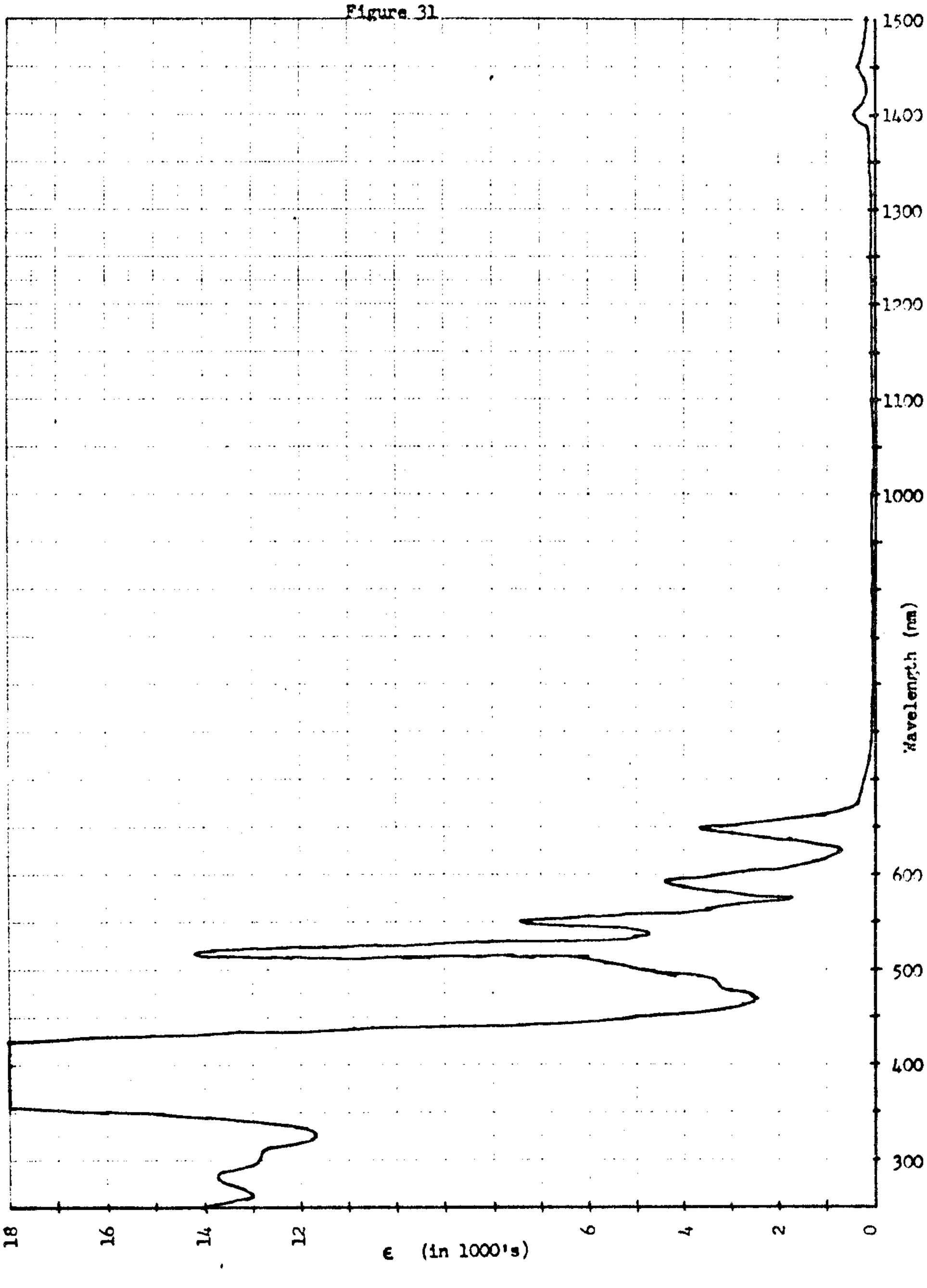

1500
1400
1300
1200
1100
1000
Wavelength (nm)
600
500
400
300
18
16
14
12
ε (in 1000's)
6
4
2
0

Figure 32

Fe(II)TPP at 1.04×10^{-4} M in the 1 mm cells. IR 2 has not been used and solution is still pink.

Figure 32

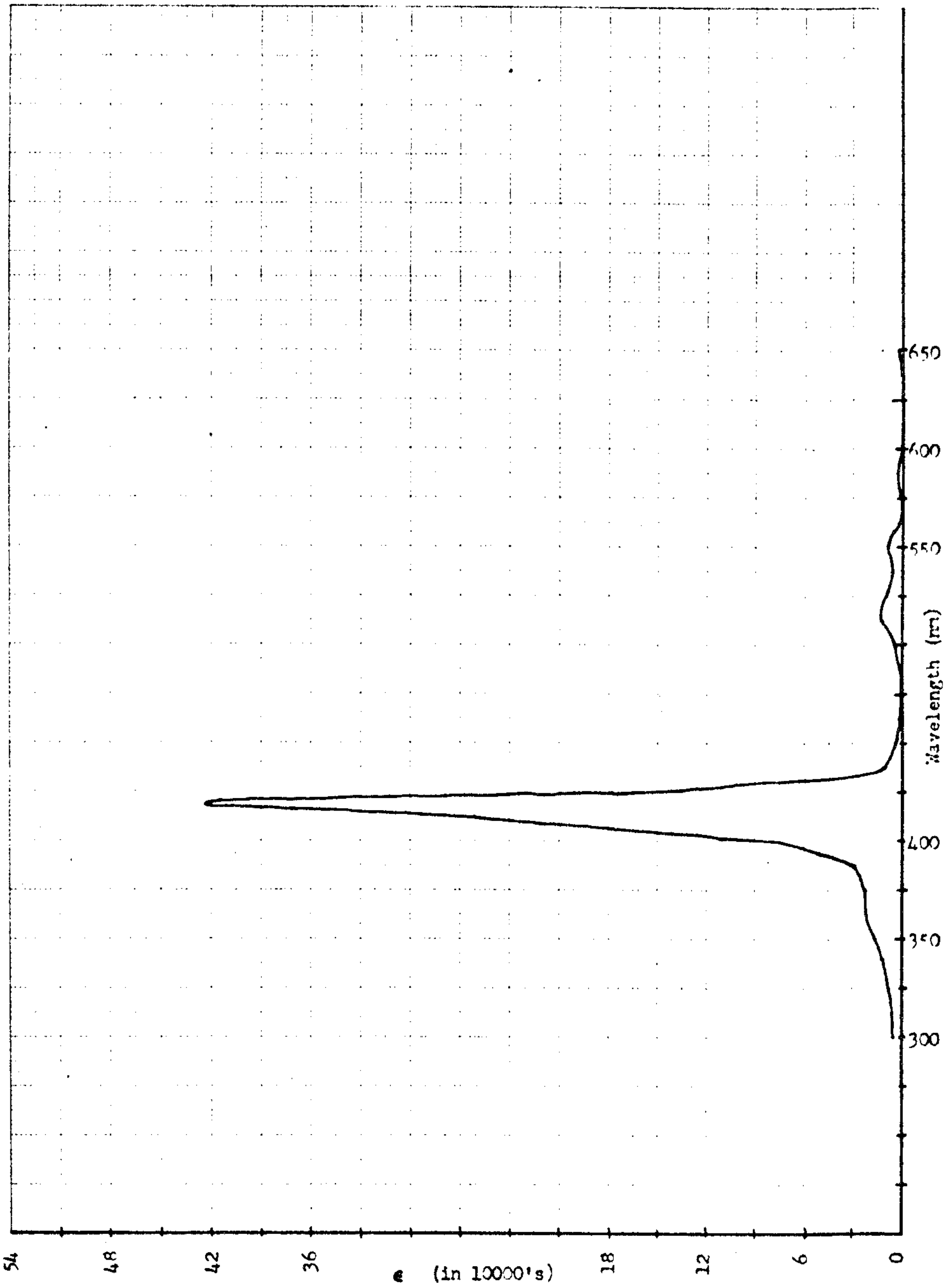

650
600
550
400
350
300
Wavelength (nm)
54
48
42
36
ε (in 10000's)
18
12
6
0

Figure 33

Fe(II)TPP at 1.04×10^{-4} M using the IR 2 source.

Figure 33

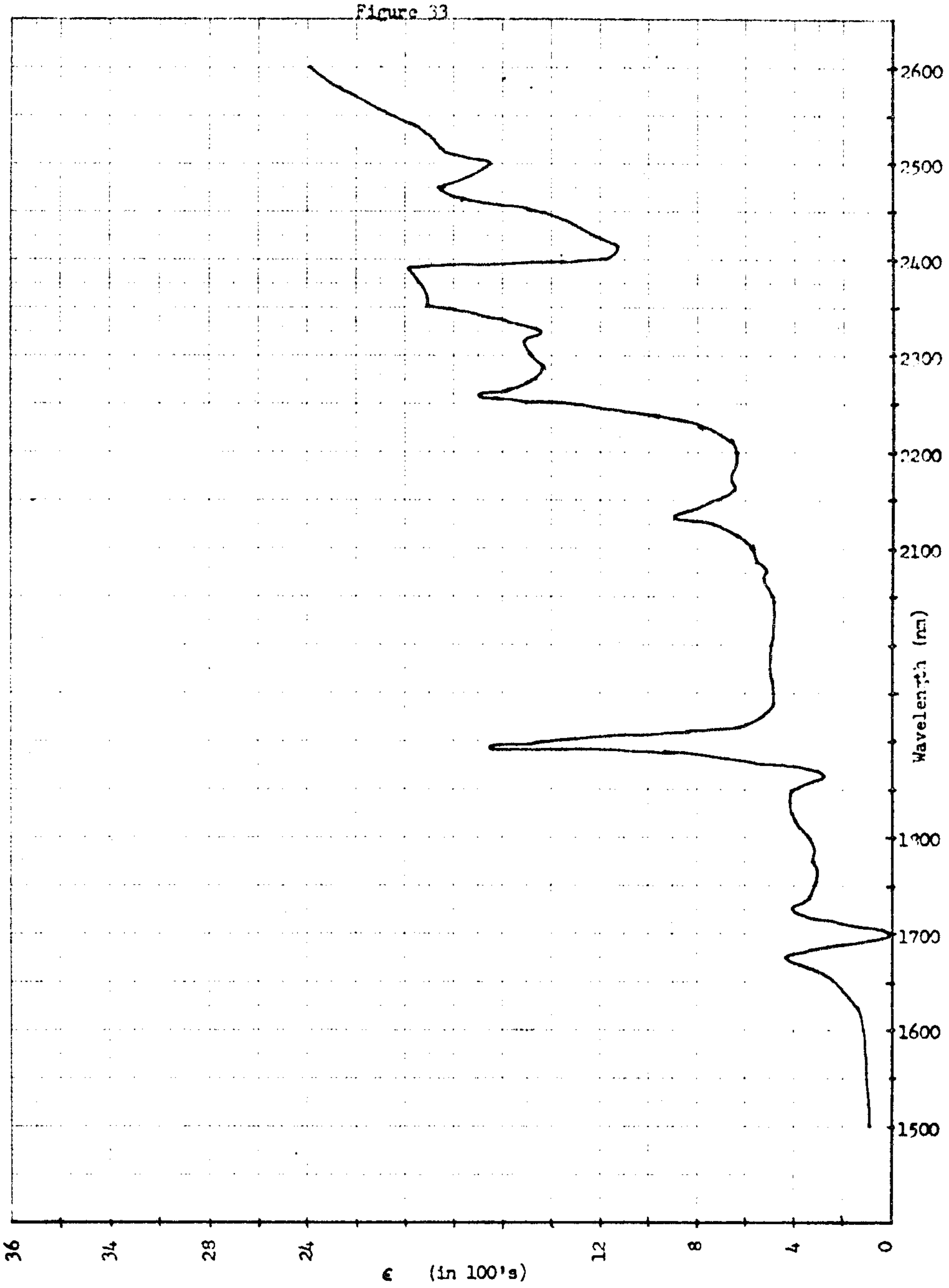

2600
2500
2400
2300
2200
2100
Wavelength (nm)
1900
1700
1600
1500
36
34
28
24
12
8
4
0
ε (in 100's)

Figure 34

Fe(II)TPP at 1.04×10^{-4} M after the IR 2 source. Changes have occurred from Figure 31 though the solution is still pink.

Figure 34

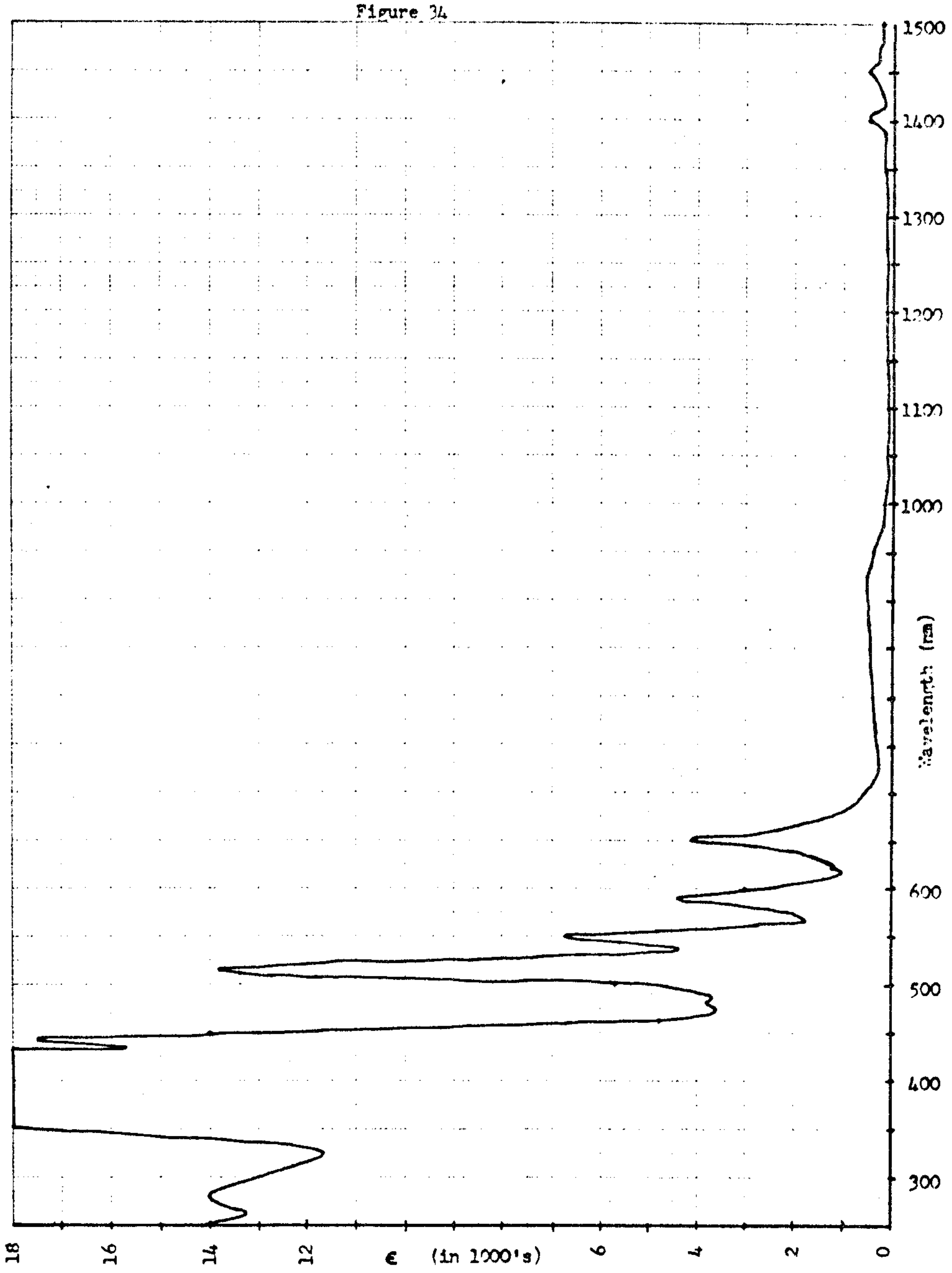

ε (in 1000's)
0
2
4
6
12
14
16
18
Wavelength (nm)
300
400
500
600
1000
1100
1200
1300
1400
1500

Figure 35

Fe(II)TPP at 1.04 × 10^{-4} M after first using the IR 2 source and then bubbling O_2 through the solution.

Figure 35

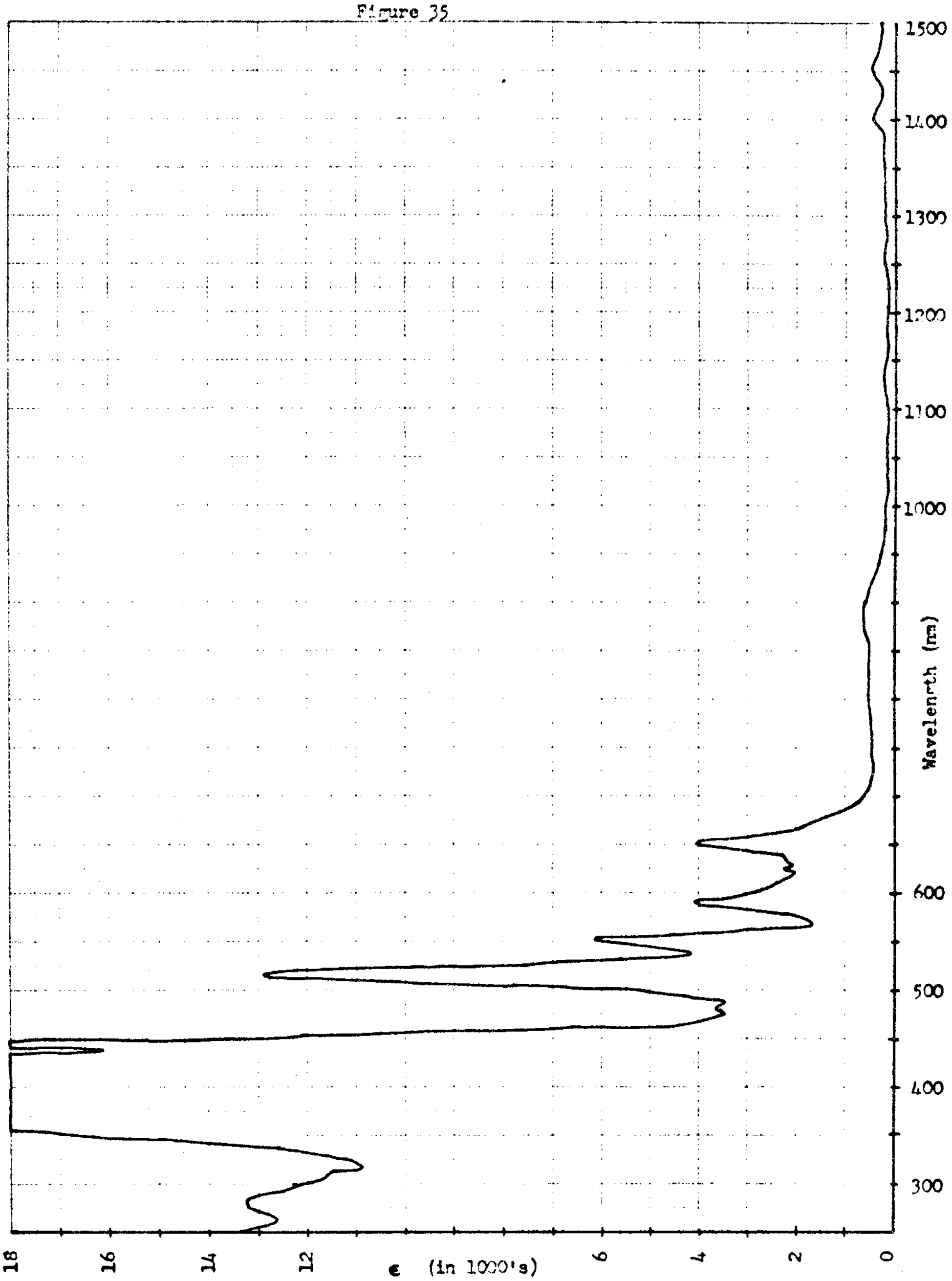

1500
1400
1300
1200
1100
1000
600
500
400
300
Wavelength (nm)
18
16
14
12
ε (in 1000's)
6
4
2
0

Figure 36

Fe(II)TPP at 1.04×10^{-4} M after first using the IR 2 source and then bubbling O_2 through the solution. The Soret band is shown with the 1 mm cells.

Figure 36

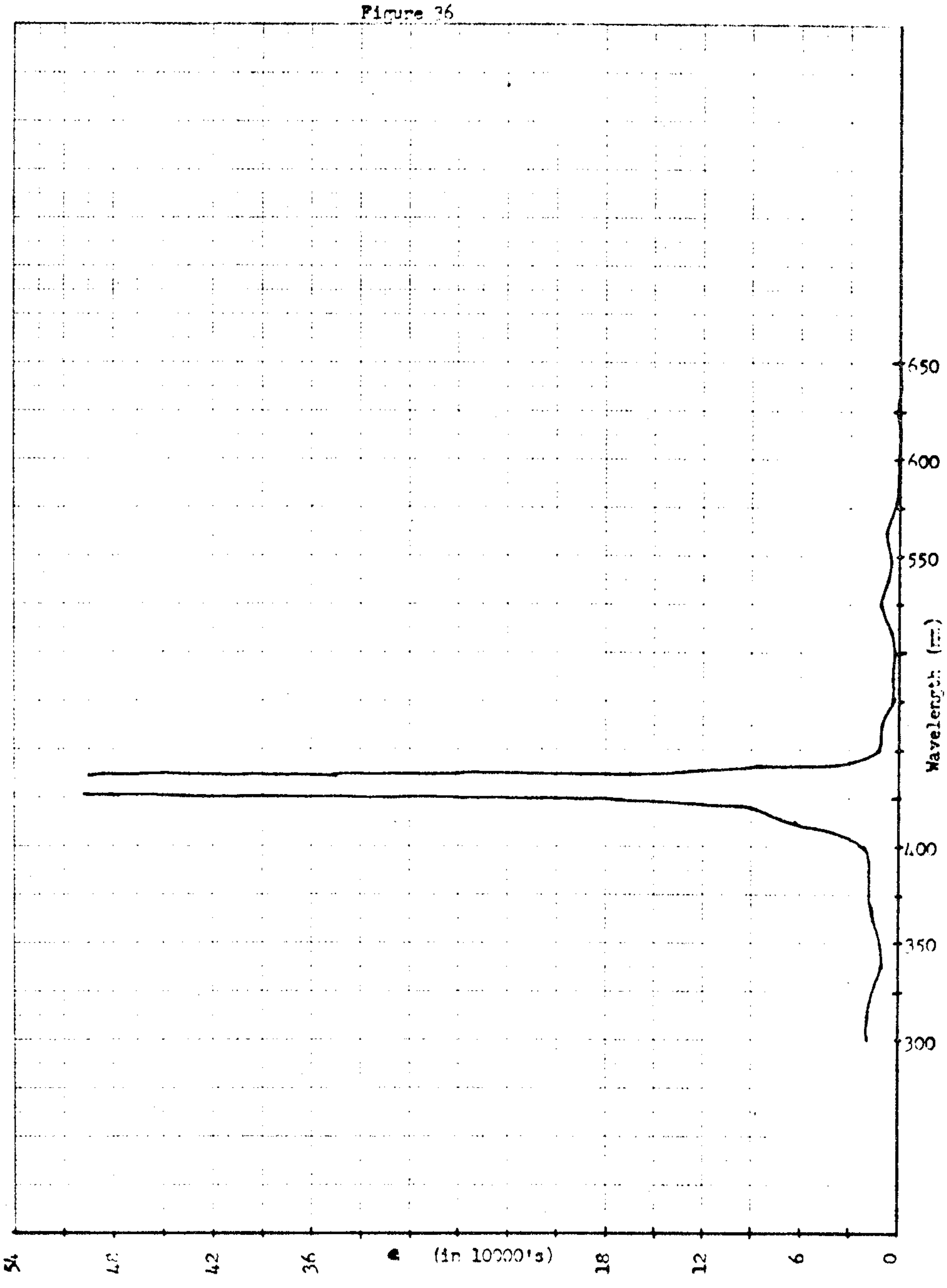

650
600
550
400
350
300
Wavelength (mμ)
54
48
42
36
ε (in 10000's)
18
12
6
0

Figure 37

Fe(II)TPP at 1.04 × 10^{-4} M after first using the IR 2 source, then bubbling O_2 through the solution, and finally shaking it with water saturated with air to determine if the changed dielectric constant affected oxygen uptake.

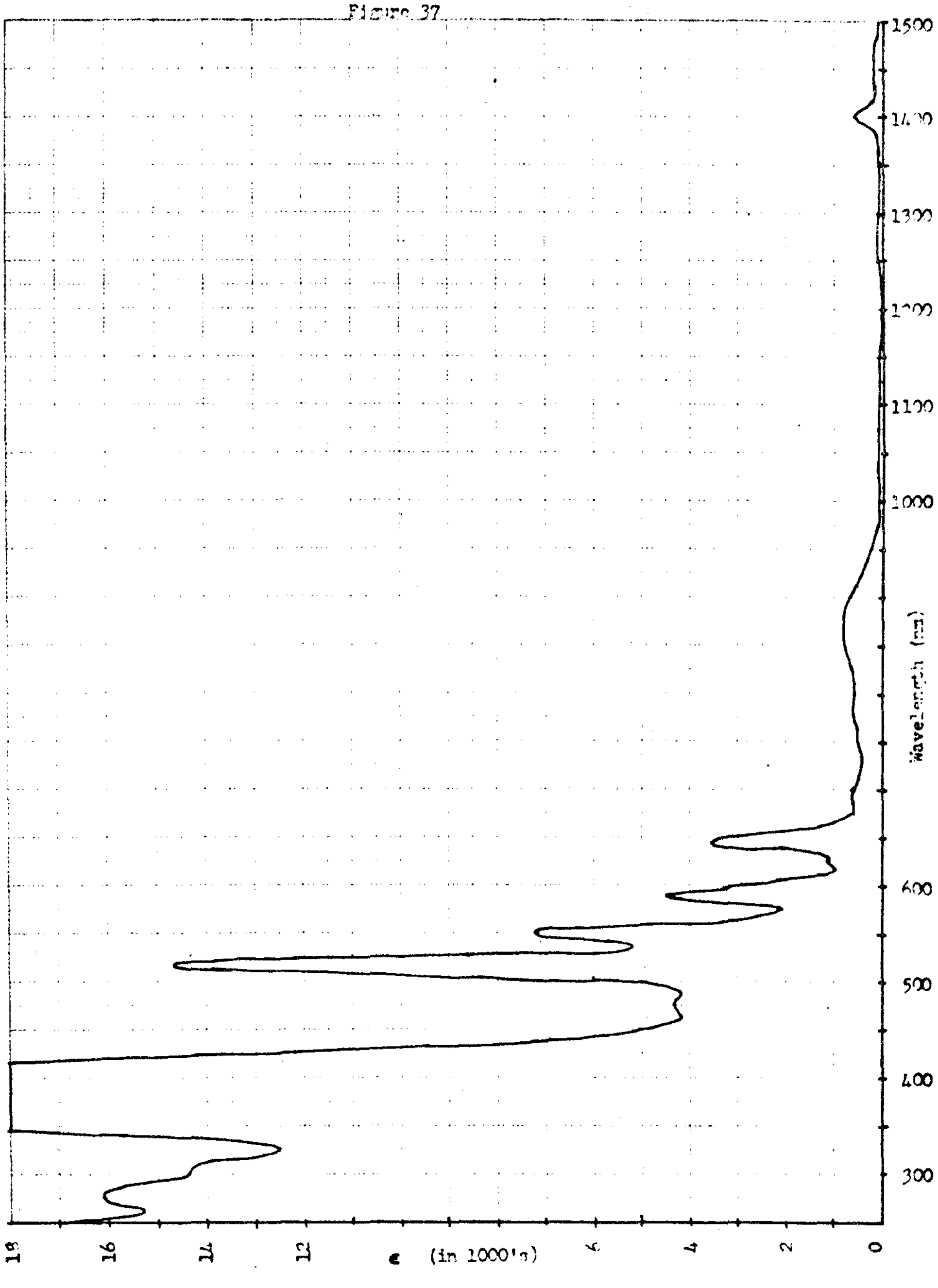


Figure 37

1500
1400
1300
1200
1100
1000
600
500
400
300
Wavelength (nm)
18
16
14
12
ε (in 1000's)
6
4
2
0

Figure 38

Fe(II)TPP at 1.04 × 10^{-4} M after first using the IR 2 source, bubbling O_2 through the solution, and shaking with air-saturated water. The IR 2 source is being used.

Figure 28

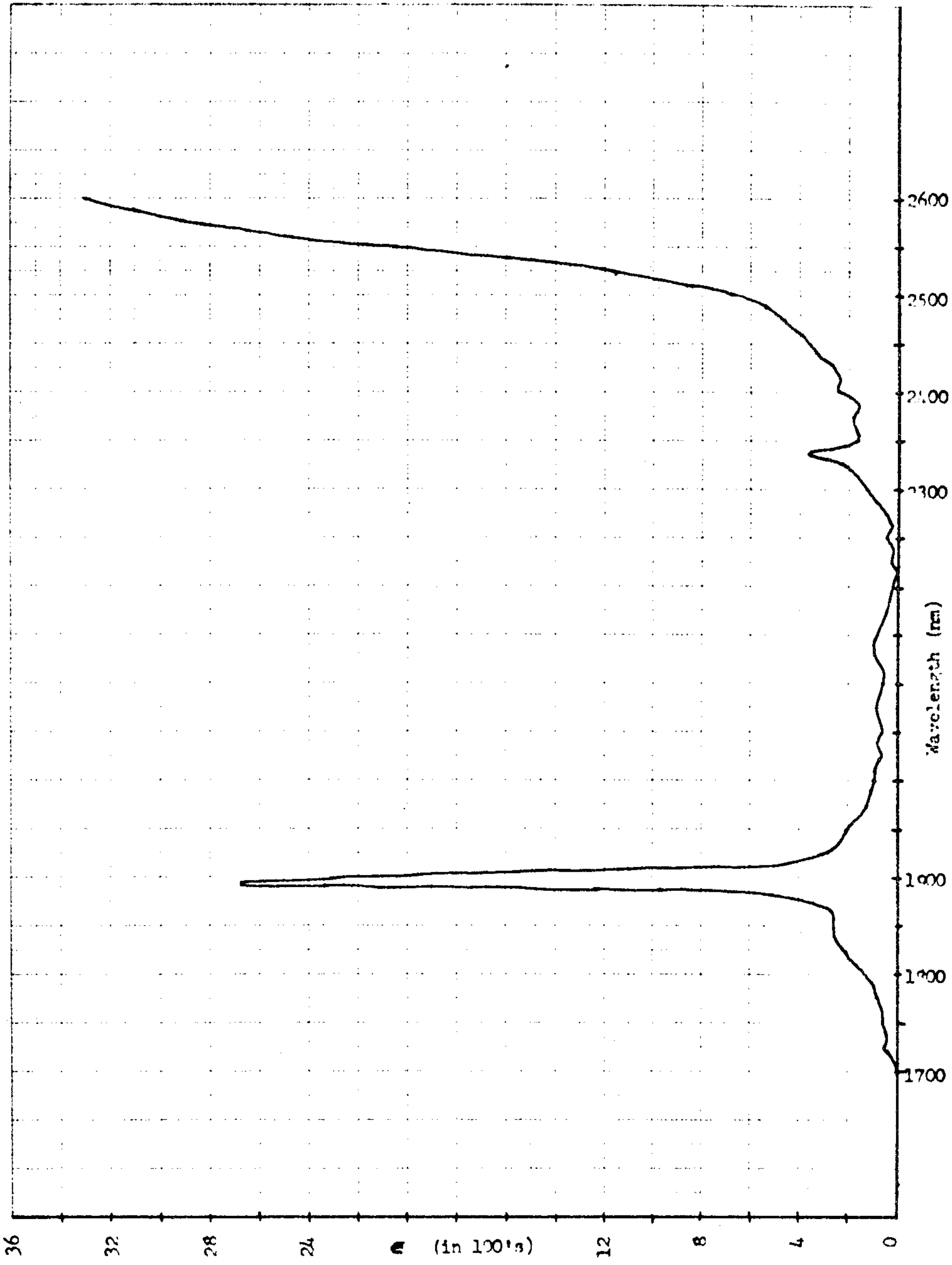

2600
2500
2400
2300
Wavelength (nm)
1900
1800
1700
36
32
28
24
ε (in 100's)
12
8
4
0

Figure 39

Fe(II) at 1.04×10^{-4} M after first using the IR 2 source, bubbling O_2 through the solution, shaking with air-saturated water, and using the IR 2 source.

Figure 39

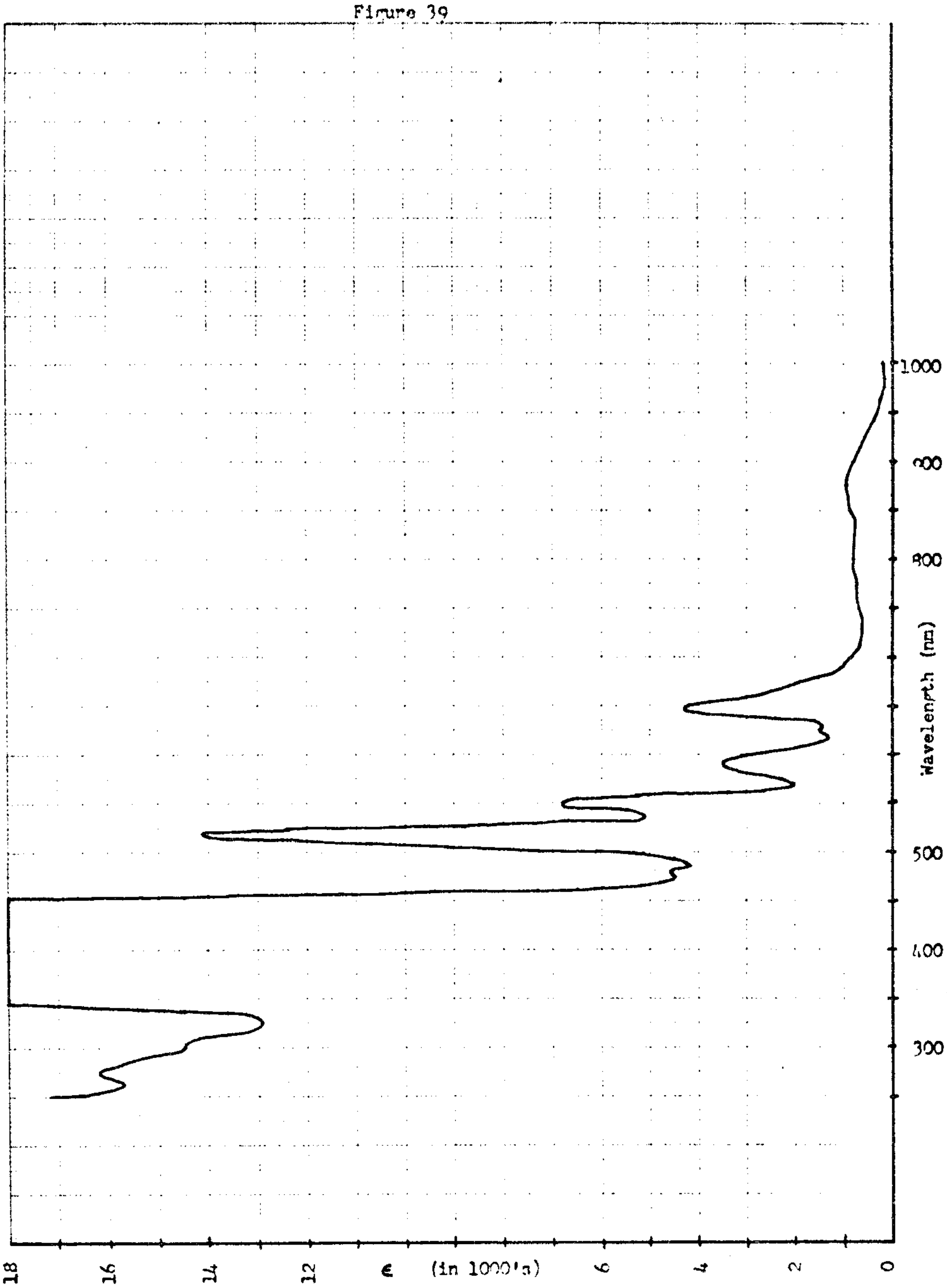

1000
900
800
500
400
300
Wavelength (nm)
18
16
14
12
ε (in 1000's)
6
4
2
0

Figure 40

FeTPP at 1.00×10^{-4} M made in air. Using IR 2 source.

Figure 40

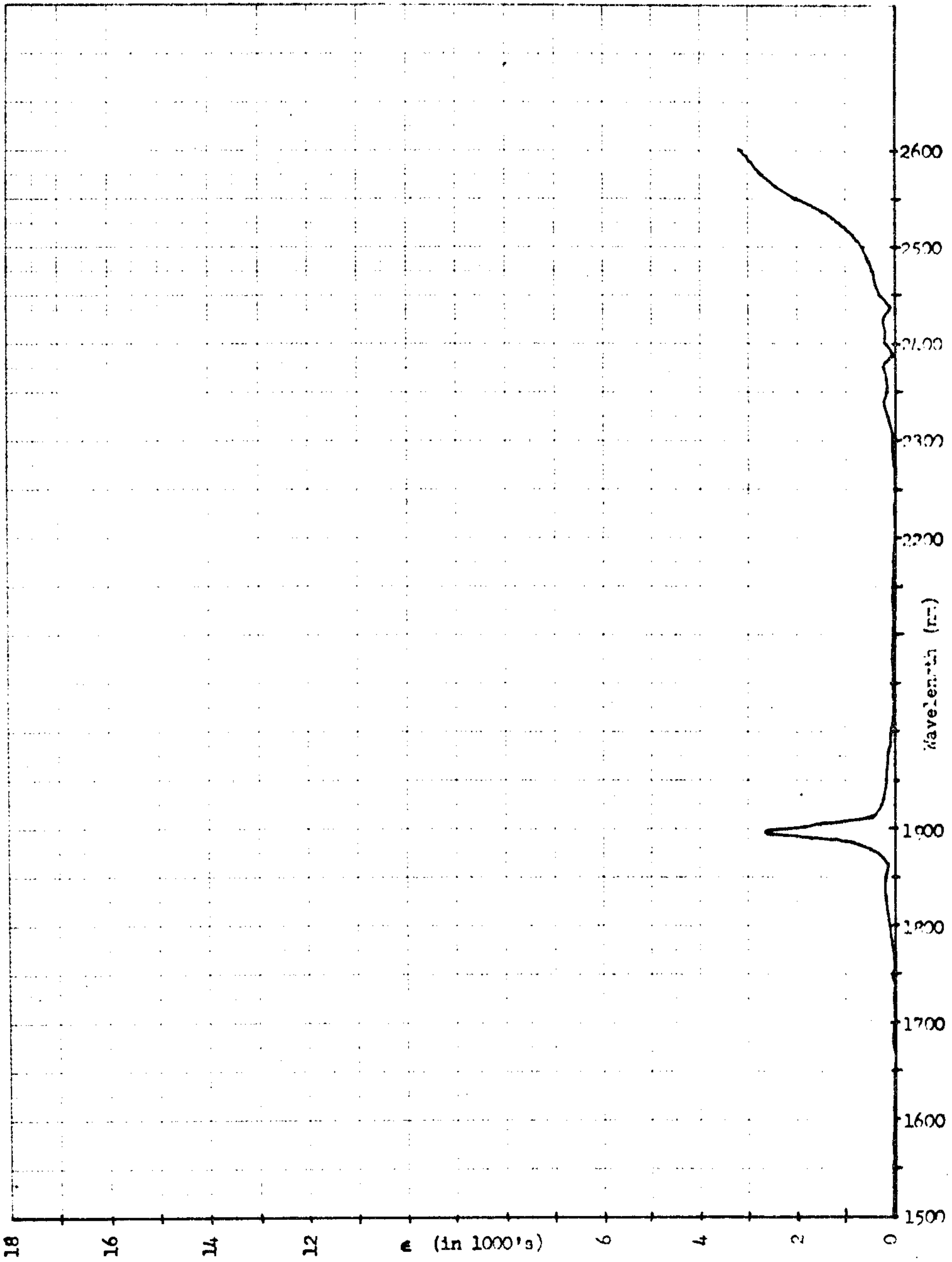

2600
2500
2400
2300
2200
1900
1800
1700
1600
1500
Wavelength (nm)
18
16
14
12
ε (in 1000's)
6
4
2
0

Figure 41

FeTPP at 1.00×10^{-4} M made in air and irradiated with IR 2 source.

Figure 41

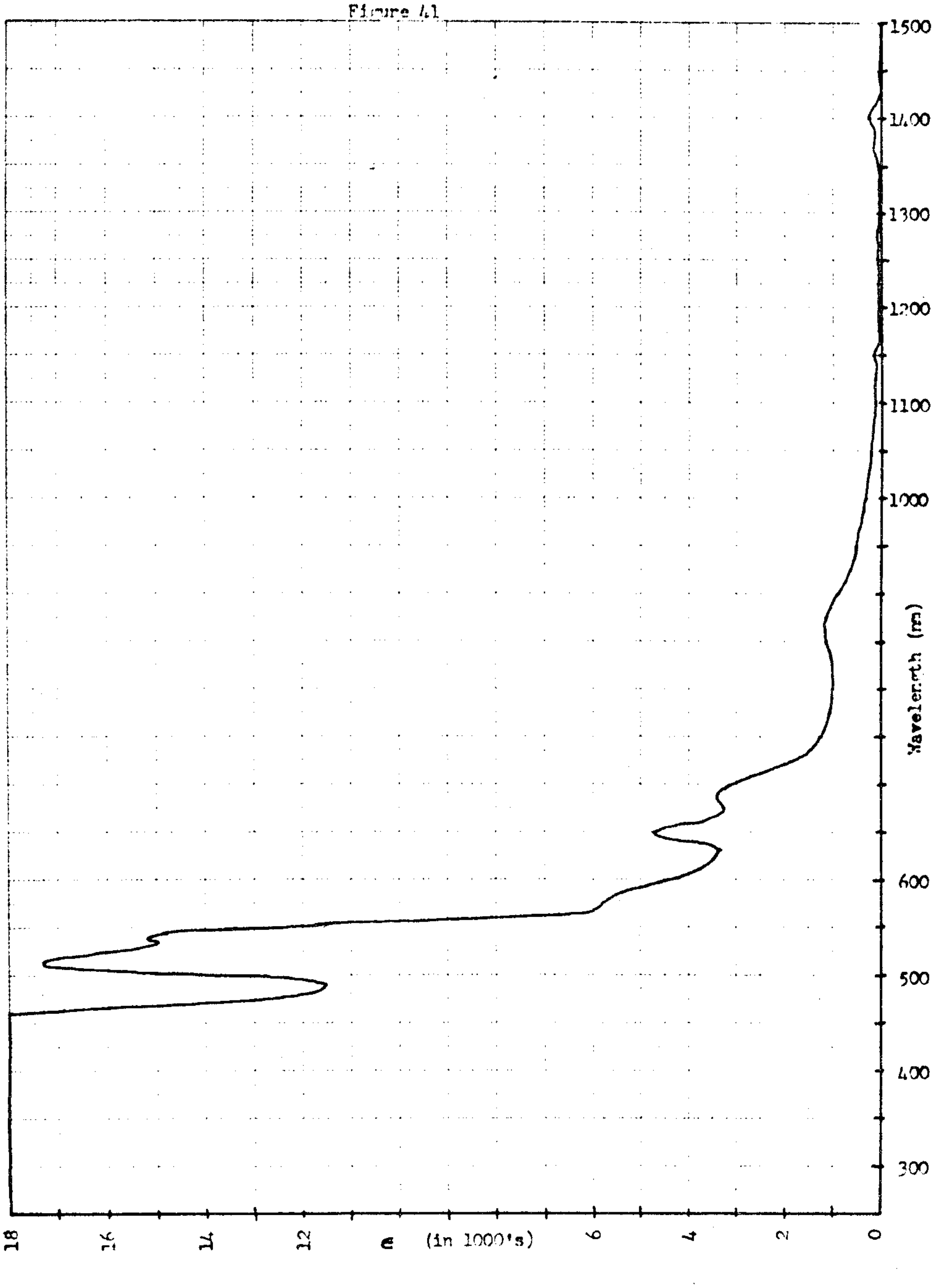

1500
1400
1300
1200
1100
1000
600
500
400
300
Wavelength (nm)
18
16
14
12
ε (in 1000's)
6
4
2
0

Figure 42

FeTPP at 1.00×10^{-4} M made in air and irradiated with IR 2 source. The 1 mm cells are being used.

Figure 42

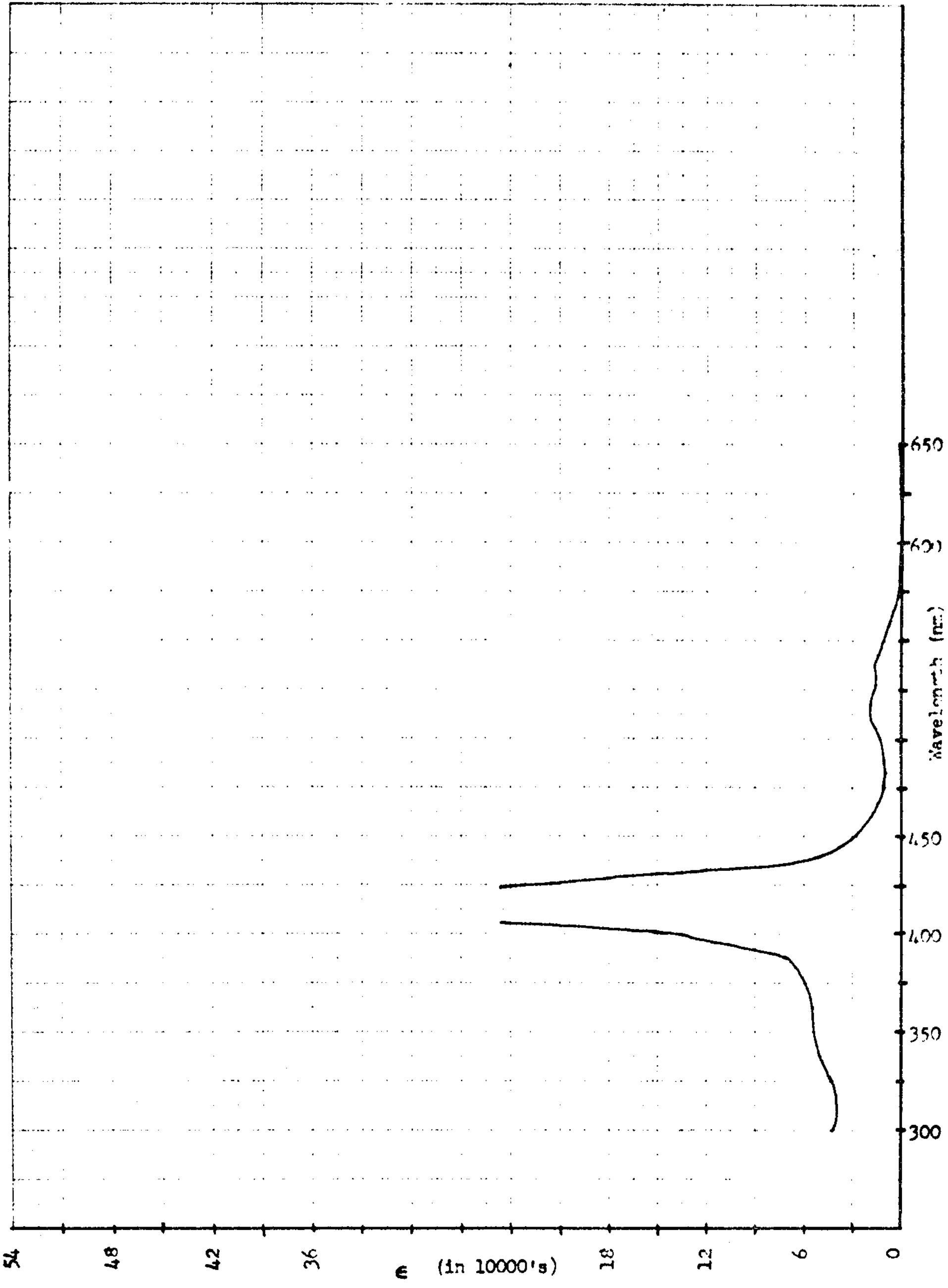

650
600
450
400
350
300
Wavelength (nm)
54
48
42
36
ε (in 10000's)
18
12
6
0

Figure 43

FeTPP at 5.00×10^{-5} M made in air and irradiated with IR 2 source. The 1mm cells are being used.

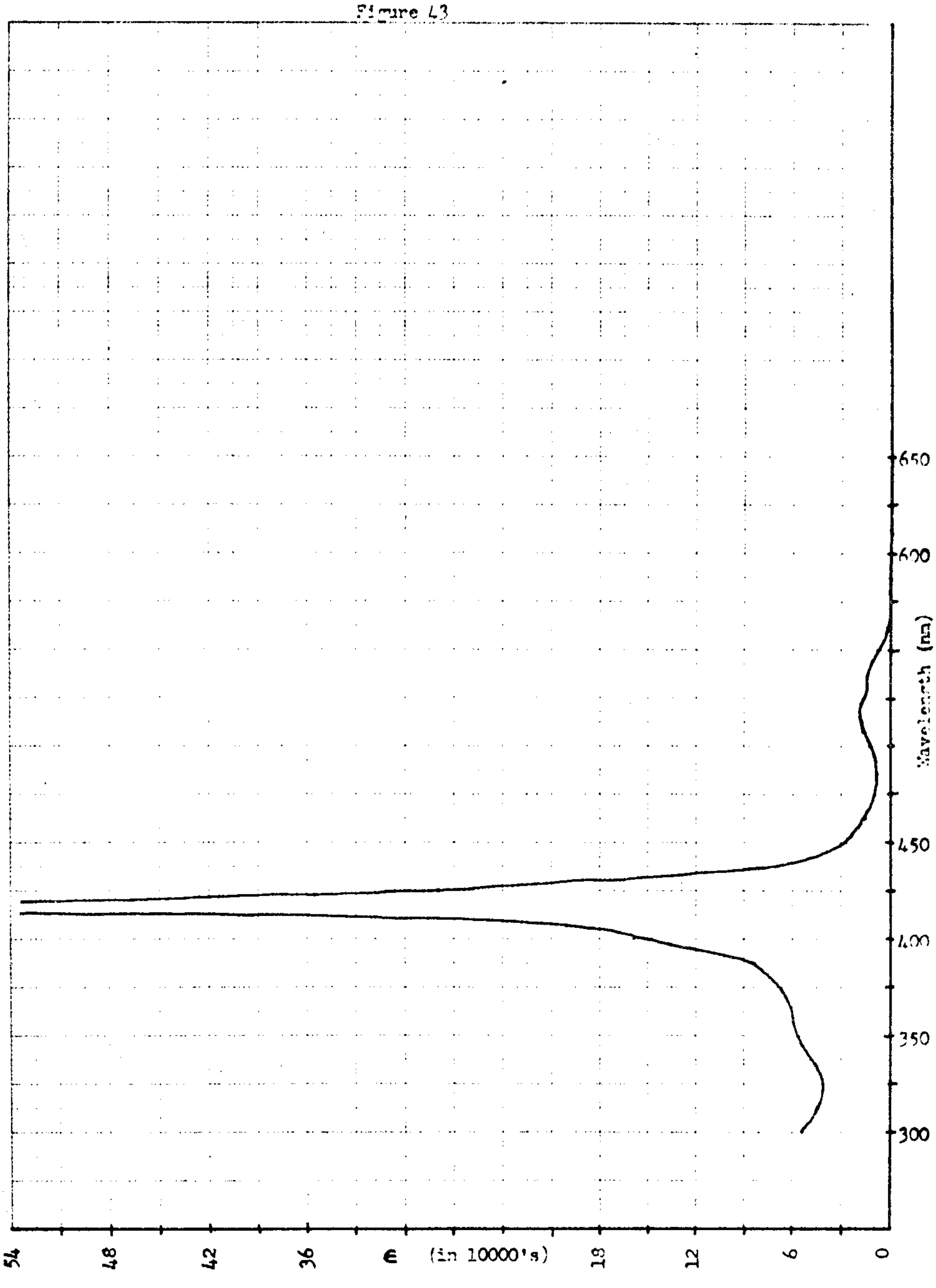


Figure 43

54
48
42
36
ε (in 10000's)
18
12
6
0
Wavelength (nm)
650
600
450
400
350
300

Figure 44

FeTPP at 2.50×10^{-5} M made in air and irradiated with IR 2 source. The 1mm cells are being used. Beer's Law is valid.

Figure 44

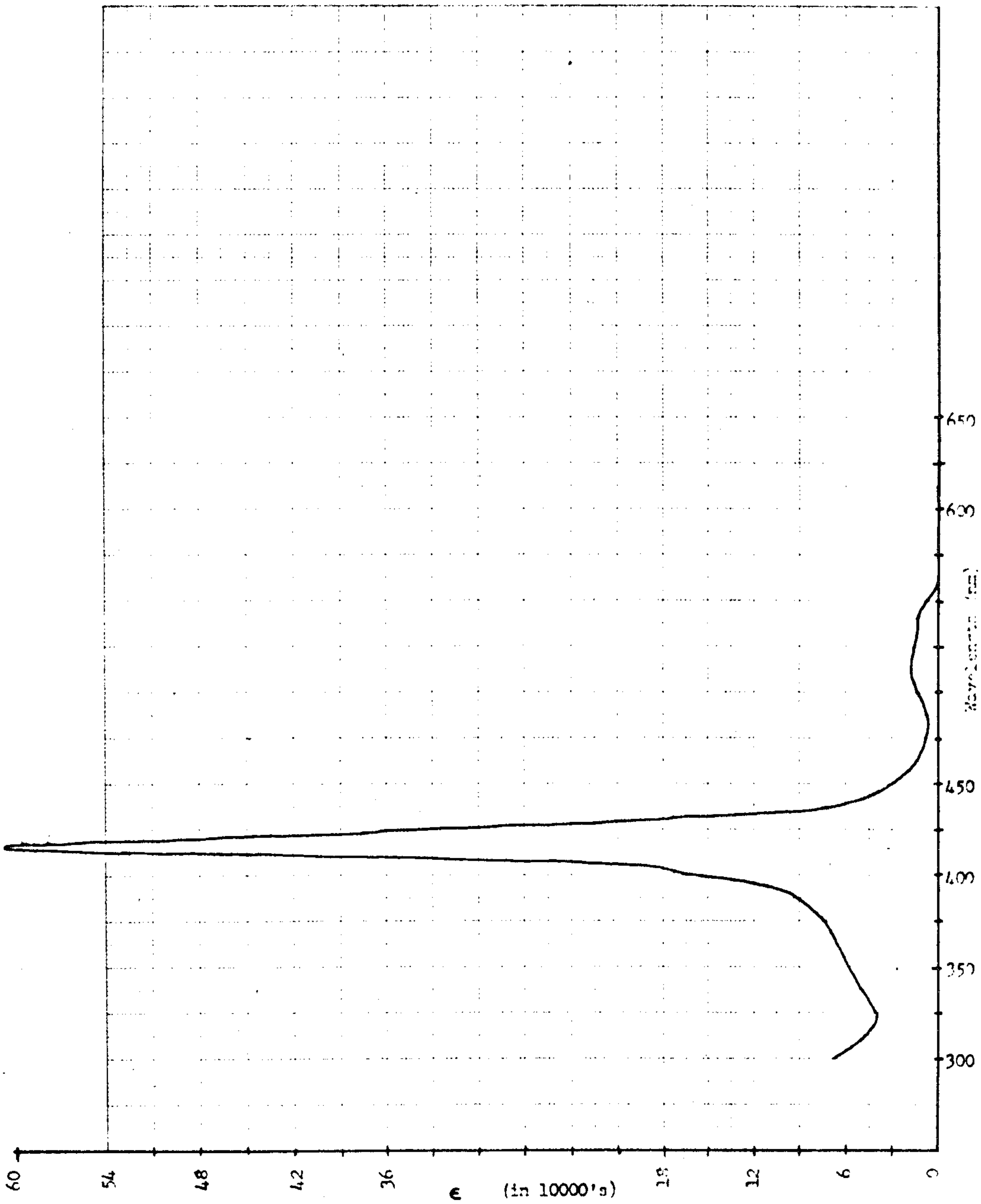

650
600
450
400
350
300
Wavelength (nm)
60
54
48
42
36
ε (in 10000's)
18
12
6
0

Figure 45

FeTPP at 1.00×10^{-4} M made in air, irradiated with IR 2 source, and reduced with sodium dithionite. The IR 2 source is being used.

Figure 45

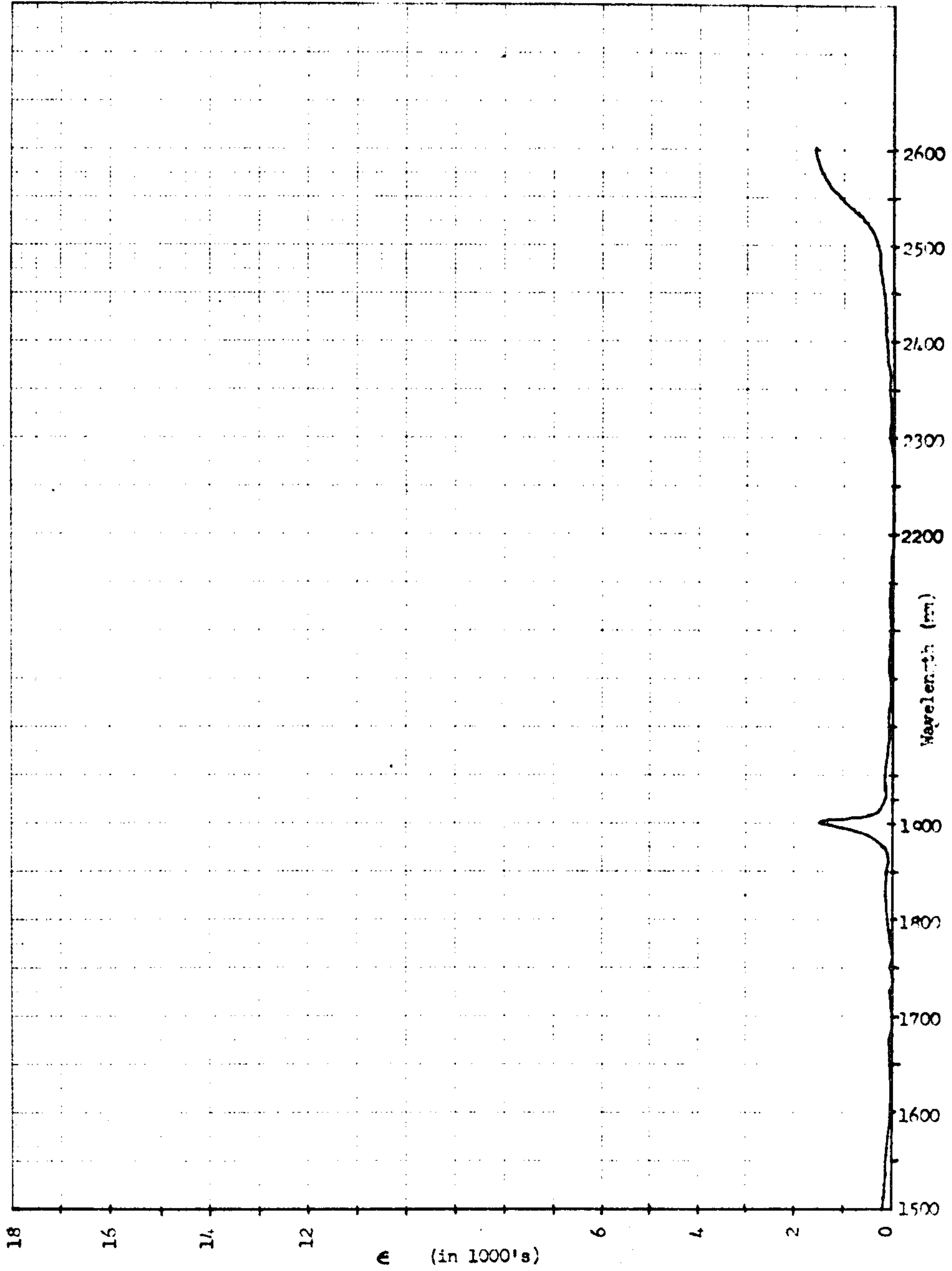
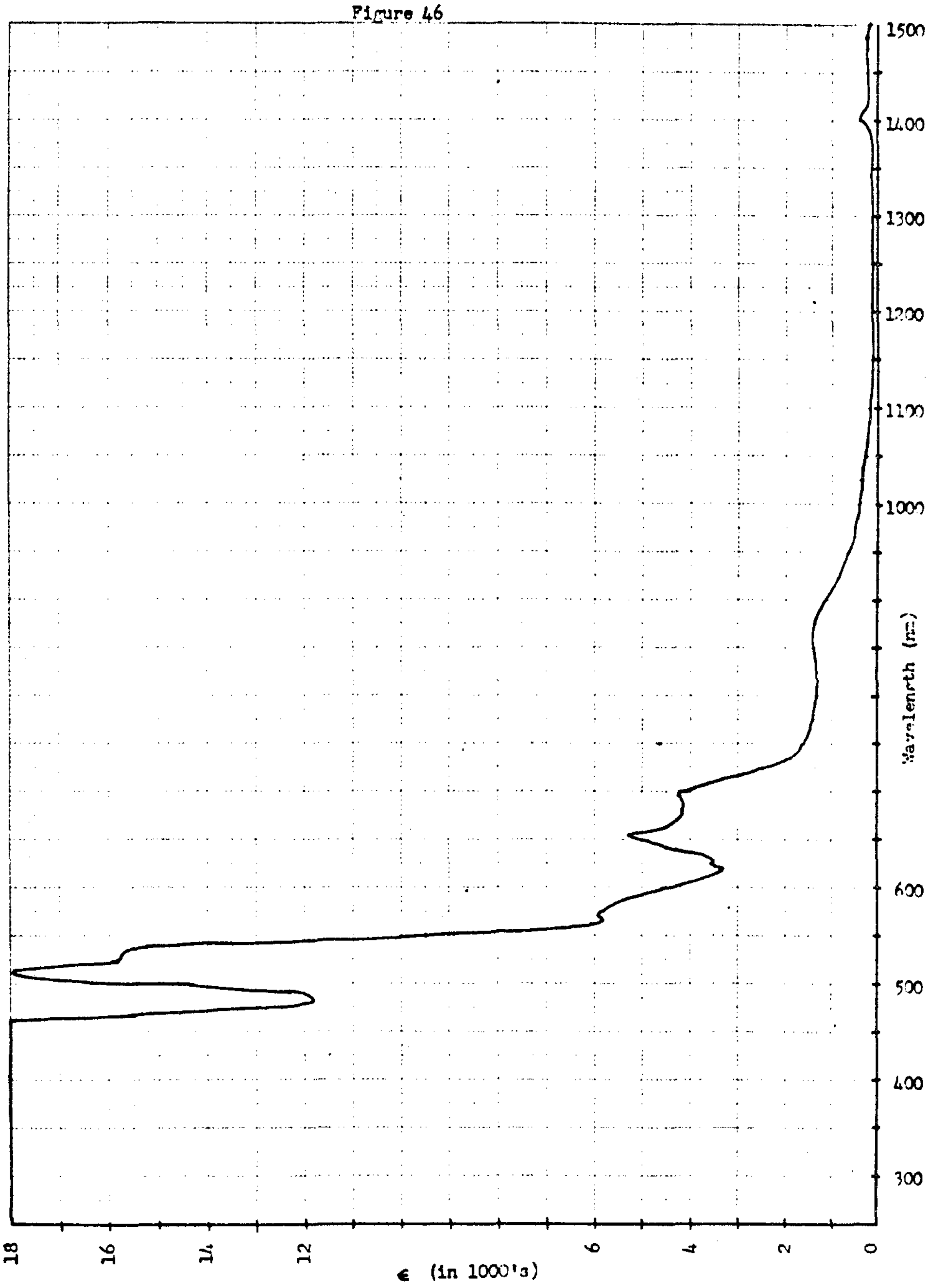

2600
2500
2400
2300
2200
1900
1800
1700
1600
1500
Wavelength (mμ)
18
16
14
12
6
4
2
0
ε (in 1000's)

Figure 46

FeTPP at 1.00×10^{-4} M made in air, irradiated with IR 2 source, reduced with sodium dithionite, and irradiated with IR 2 source. Very minor changes from Figure 41 suggest that reduction either has not occurred or does not affect spectrum.

Figure 46


1500
1400
1300
1200
1100
1000
600
500
400
300
Wavelength (nm)
18
16
14
12
6
4
2
0
ε (in 1000's)

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