Summer 1963

THE GAMMA RADIOLYSIS OF AQUEOUS AND ALCOHOLIC SOLUTIONS OF ORANGE IV

ALLEN ALBERT DENIO

Recommended Citation

DENIO, ALLEN ALBERT, "THE GAMMA RADIOLYSIS OF AQUEOUS AND ALCOHOLIC SOLUTIONS OF ORANGE IV" (1963). *Doctoral Dissertations*. 783.
https://scholars.unh.edu/dissertation/783

63–4767

DENIO, Allen Albert, 1934–
THE GAMMA RADIOLYSIS OF AQUEOUS AND ALCOHOLIC SOLUTIONS OF ORANGE IV.

University of New Hampshire, Ph.D., 1963
Chemistry, organic

University Microfilms, Inc., Ann Arbor, Michigan

THE GAMMA RADIOLYSIS
OF
AQUEOUS AND ALCOHOLIC SOLUTIONS OF ORANGE IV

BY

ALLEN ALBERT DENIO

B. S., Lowell Technological Institute, 1956
M. S., Lowell Technological Institute, 1957
M. S., University of New Hampshire, 1961

A THESIS

Submitted to the University of New Hampshire
In Partial Fulfillment of
The Requirements for the Degree of
Doctor of Philosophy

Graduate School
Department of Chemistry
August, 1962

This thesis has been examined and approved.

Charles M. Whitney Jr

Frank L. Pilar

Alexander R. Cinil

August 20, 1952
Date

ACKNOWLEDGMENT

The author of this thesis wishes to express his sincere appreciation to his research adviser, Professor Alexander R. Amell, for the encouragement and the numerous valuable suggestions provided during the course of this study. The author is indebted to the Atomic Energy Commission which provided the Cobalt-60 radiation source used in this research and financial assistance. The dye Orange I was donated by the National Aniline Division of the Allied Chemical Corporation.

Alden A. Denio

TABLE OF CONTENTS

LIST OF TABLES

Number | Page

LIST OF ILLUSTRATIONS

INTRODUCTION

In previous work performed in these laboratories,[1] the gamma ray induced decolorization of aqueous, methanolic and ethanolic solutions of Orange IV was reported. The decolorization reaction was attributed to free radical attacks upon the dye molecules. The free radicals are produced by interaction of the gamma radiation with the solvent molecules, or by interaction of the initial solvent free radicals with other solvent molecules or secondary products.

The spectra of irradiated aqueous solutions gave no indication of the structures of any of the products. The spectra of irradiated methanolic solutions, however, indicated the presence of the sodium salt of sulfanilic acid and p-aminodiphenylamine. These are the products expected from the reduction of the azo linkage of the dye by hydrogen atoms. The reaction in ethanolic solutions appeared to be identical with that in methanol from the data available.

The decolorization reaction proceeded immediately when aqueous solutions were exposed to gamma radiation. However, the decolorization was preceded by an induction period when alcoholic solutions were irradiated, indicating the presence of a radical scavenger.

Post-irradiation reactions were observed in aqueous and methanolic solutions. The decolorization was observed to continue after aqueous solutions were removed from the source.

However, the decolorization reaction was partially reversed upon discontinuing the irradiation of methanolic solutions. The aqueous phenomenon was attributed to the decolorization by hydrogen peroxide formed during irradiation. The reversal in the methanol was attributed to the instability of the decolorization product in the irradiated methanol.

The most widely studied dye in radiation chemistry is methylene blue.[2] In deaerated aqueous solutions the "G"-value (molecules decolorized/100 e.v. absorbed) was found to be 1.5. The decolorization reaction is attributed to the addition of hydrogen atoms (reduction) and hydroxyl radicals (oxidation) to the unsaturated ring system. The exact nature of the decolorized molecule is not known. It is believed that in the reduction process, the addition of two hydrogen atoms results in the decolorized leuco-base. This product can be converted back to the original dye by the addition of oxygen. The oxidation product formed by the addition of hydroxyl radicals is stable, and thus this reaction is irreversible. When deaerated aqueous solutions are irradiated, 85 to 95% of the decolorization can be reversed by the addition of O_2.

If the solution containing oxygen is irradiated, however, the decolorization is irreversible. The spectrum of the product solution is the same as that obtained from the attack of hydroxyl radicals in the photolysis of hydrogen peroxide in an aqueous methylene blue solution. The hydrogen atoms are scavenged by the oxygen in solution so that only oxidation of the dye results. The "G"-value for methylene blue solutions containing oxygen was found to be about 0.7.

A dosimeter has been reported[3] in which methylene blue, as well as other dyes, are destroyed by gamma radiation when they are absorbed from solution by a very porous glass (28% void space). No explanation was presented for the destruction of the dyes in the solid state.

Aqueous solutions of indigocarmine containing oxygen exhibit an irreversible oxidation. When exposed to gamma radiation, a radical process occurs in which the central carbon-carbon bond is broken to yield two molecules of isatin-5-sulfonate.[4]

The kinetics of the decolorization of aqueous solutions of chlorphenol red by 120 Kev X-radiation has been investigated.[5] The molecule resulting from the initial decolorization has a reactivity for further reaction approximately equal to that of the dye molecule. The relatively low yield for decolorization (G=0.81) indicates that the reactiom of the dye with a radical does not necessarily result in decolorization according to the authors.

An early study by Seitz with X-rays proposed that the radiation interacted with the solvent to produce solvent ions and free electrons.[6] It was postulated that the dye molecules could undergo electron capture, followed by attraction of a hydrogen ion from the solvent ion. This was the mechanism suggested for the conversion of methylene blue to the leucobase.

Aqueous solutions of methyl orange, similar in structure to Orange IV, have been exposed to gamma radiation.[7] Five products were reportedly separated by paper chromatography. However, they were not identified and no mechanism was proposed for the reaction.

The photochemistry of azobenzene and 4-amino-4'nitroazobenzene solutions in isopropyl alcohol and isooctane has been studied.[8] The fading process was attributed to the addition of hydrogen atoms abstracted from the solvent to the azo linkage to form substituted hydrazines, and eventually substituted aniline derivatives. These results seem parallel to the work reported in the initial phase of this study.

The radiation chemistry of the solvents has been extensively studied by other workers. The agreement of data has not always been as good as desired. However, recent studies seem to have eliminated much of the variation. There still is considerable difference in theory concerning the fundamental processes. However, we are concerned mainly with the secondary reactions upon which there is more agreement.

The radiolysis of water and aqueous solutions is probably the most widely investigated system in this field.[9] The initial interaction of water and gamma radiation is still subject to much speculation. However, the net result of the primary reaction is believed to be as follows:

$$H_2O \xrightarrow{\gamma} H,\ OH,\ H_2,\ H_2O_2 \qquad (1)$$

Some reactions found for aqueous solutions can not be explained with only these products present. Therefore, it has been necessary to postulate other intermediates such as the solvated electron (H_2O^-), the hydroperoxyl radical ($HO_2\cdot$) and the hydrogen molecule ion (H_2^+).

The decomposition of methanol by gamma radiation has been studied extensively by measuring product yields, scavenger studies, and more recently by electron spin resonance.[10] The observed products are hydrogen, ethylene glycol, formaldehyde, methane, and carbon monoxide. The yields of hydrogen atoms, methyl radicals and $\cdot CH_2OH$ radicals have been determined. There is little agreement on the primary reaction. Actually it appears that there may be three different primary processes occurring simultaneously. Again, however, we shall be concerned with the reactions of the radicals formed.

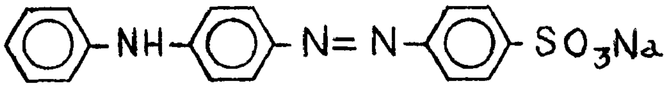
The influence of gamma radiation on ethanol has been reported by measuring product yields and by scavenger studies.[11] The products observed are hydrogen, butane-2,3-diol, acetaldehyde, methane and carbon monoxide, with trace amounts of ethane, ethylene and acetylene. The yields of hydrogen atoms and methyl radicals have been determined. The major bond rupture seems to be at the alpha carbon-hydrogen bond, although some carbon-carbon bond rupture also occurs.

The purpose of this thesis is to discuss the results of further investigations of the decolorization of Orange IV solutions when exposed to gamma radiation. It is hoped that this work will greatly elucidate the observations made in the preliminary study.

EXPERIMENTAL

A. DYESTUFFS

Structure No. 1:



Chemical Name: Sodium salt of p—(p—anilinophenylazo)—benzenesulfonic acid.

Commercial Name: Orange IV

Color Index Number: 143

Manufacturer: Eastman Kodak Company

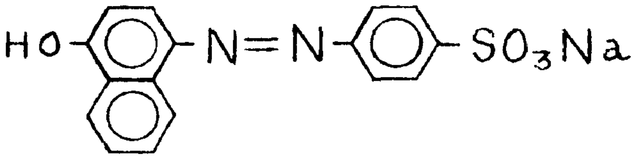
Purification: The commercial sample was known to contain uncoupled dye components and possibly other impurities. These were removed in the following manner.

A chromatographic column was prepared by lining the base of a Buchner funnel with filter paper, followed by adding a suspension of basic Alumina in 95% ethanol slowly until a one inch layer was obtained. Approximately 500 ml. of a 95% ethanol solution of Orange IV was allowed to drip slowly over the entire surface of the column. This was followed by the addition of 900 ml. of 95% ethanol in the same slow, uniform manner. The impurities were observed in the various solvent fractions emerging from the column. The dye was adsorbed near the surface of the Alumina column.

The dye was first removed from the Alumina by shaking with distilled water. These solutions were filtered after standing and the water slowly boiled off. The final portion was allowed to dry at room temperature.

The dye was redissolved in about 16 liters of 95% ethanol. After standing, the solution was filtered through a very fine fritted glass funnel. The solvent was boiled off slowly from an evaporating dish. The final portion was allowed to evaporate at room temperature.

Structure No. 2:



Chemical Name: Sodium salt of p-(4-hydroxy-1-naphthylazo)-benzenesulfonic acid.

Commercial Name: Orange I

Color Index Number: 150

Manufacturer: National Aniline Division, Allied Chemical Corporation.

Purity: This dye sample was the grade sold for drug and cosmetic use. Such applications require a high degree of purity to meet the government standards. This sample was used without further purification.

B. SOLVENTS

1. Water: Distilled and deionized water was obtained from the Sprague Electric Company.
2. Methanol: Fisher Certified (Catalog No. A-412), Fisher Scientific Co.
3. Ethanol: Absolute (200 Proof) of Commercial Solvents Corporation.

C. OTHER CHEMICALS

1. p-Aminodiphenylamine: Matheson, Coleman & Bell (Catalog No. PX880), Matheson Co., Inc.
2. Ferrous sulfate heptahydrate: C. P. grade of J. T. Baker Chemical Co.
3. Hydrogen peroxide: 30% Solution, Reagent chemical of Fisher Scientific Co.
4. Nitrogen: Extra Dry, The Matheson Co., Inc.
5. Oxygen: U. S. P., Linde Co., Union Carbide Corp.
6. Sodium chloride: Certified reagent grade of Fisher Scientific Co.
7. Sulfanilic acid monohydrate: A. R. grade of Mallinckrodt Chemical Works.
8. Sulfuric acid: A.R. grade of Mallinckrodt Chemical Works.

D. SOLUTIONS

In the normal method for deaerating solutions prior to analysis, about 125 ml. of solution was placed in a 125 ml. Erlenmeyer flask. A two-hole stopper with a glass tube nearly reaching the flask bottom was placed in the neck of the flask. Dry nitrogen was bubbled through the solution for 30 minutes. The flask was stoppered tightly while the nitrogen was passed through the irradiation vessel via a small tube inserted through one opening. A 100 ml. pipet with a large suction bulb was used to quickly transfer 100 ml. of the solution from the flask to the vessel. The nitrogen was bubbled through the solution for an additional 15 minutes. The vessel was stoppered tightly. This method proved effective in eliminating the induction period due to oxygen dissolved in alcohol solutions. The initial concentration of the dye solution was determined from the solution remaining in the flask. The evaporation loss during the final stage in the vessel was negligible.

The calibration curves were obtained for Orange IV (Batch 1) using the "Spectronic 20" at 440 mμ for aqueous solutions, 420 mμ for methanolic solutions and 425 mμ for ethanolic solutions. These are shown in Figures 1, 2, and 3. The extinction coefficients for Orange IV are 24,000, 30,000 and 32,000 liter-mole^{-1}-cm^{-1}, respectively, at these wavelengths and at approximately 25° C.

A calibration curve was prepared for Orange IV (Batch 1) using the "Spectracord" at 271 mμ for methanolic solutions. This is shown in Figure 4. The extinction coefficient for Orange IV at 271 mμ is 13,300 liter-mole^{-1}-cm^{-1} at approximately 25° C.

A calibration curve was prepared for the sodium salt of sulfanilic acid using the "Spectracord" at 252 mμ for methanolic solutions. This is shown in Figure 5. The extinction coefficient at 252 mμ is 14,300 liter-mole^{-1}-cm^{-1} at approximately 25° C. Likewise, the calibration curve for p-aminodiphenylamine at 285 mμ is given in Figure 6. The extinction coefficient is 18,400 liter-mole^{-1}-cm^{-1} at approximately 25° C.

E. INSTRUMENTATION

1. Bausch & Lomb "Spectronic 20": This colorimeter was used to measure the optical density of the dye solutions.
2. Perkin-Elmer Model 4000 "Spectracord": This recording spectrophotometer provided the plotted spectra of the solutions in the visible region (350–750 mμ) and the ultraviolet region (225–370 mμ).
3. Beckman Model DU: This spectrophotometer was used to determine the concentration of ferric ions in the Fricke Dosimeter solution used to calibrate the source.

F. RADIATION SOURCE

The gamma radiation source used in this work was 148 Curies of Cobalt-60 obtained under a grant from the Atomic Energy Commission. A description of the source is included in reference 1.

G. SAMPLE EXPOSURE

The solutions were exposed to the source in the "rabbit-eared" container described in reference 1. This double walled vessel permitted excellent duplication of the exposures. The samples were irradiated in the dark source chamber so that changes observed should be due only to the gamma radiation.

H. CALIBRATION OF SOURCE

The activity of the source was measured using the Fricke dosimeter.[1] The dose rate calculated on December 8, 1961 was 1.11×10^{17} e.v./gm.-min. The dose rate at other times was calculated from the known rate of decay of Cobalt-60.

RESULTS

A. WATER SOLUTIONS

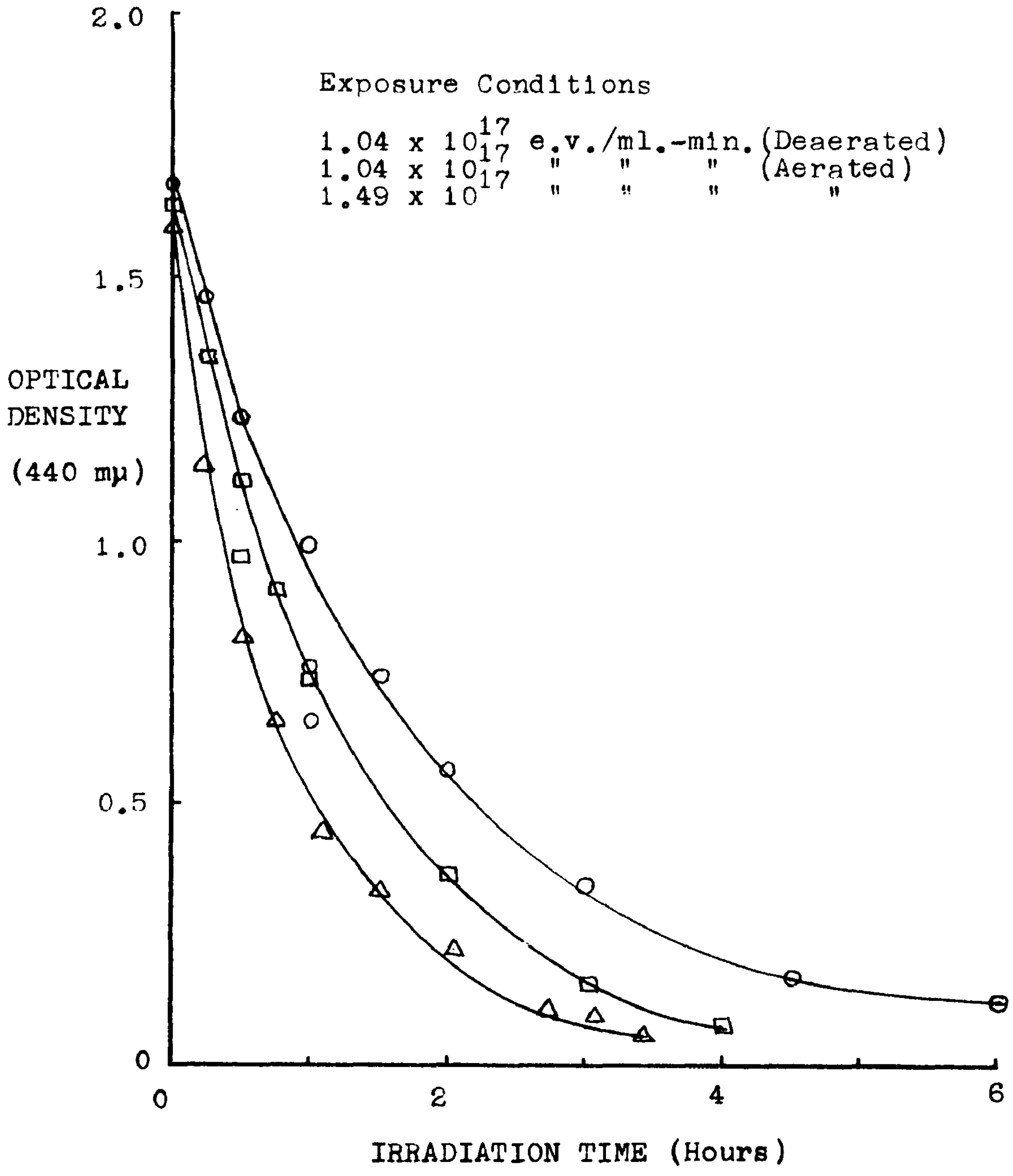
1. Rate of Decolorization: A liter of Orange IV solution was prepared having a concentration of 0.0255 gram/liter. 100 ml. samples were placed in the irradiation vessels with no attempt to exclude air. After each exposure the samples were removed from the source, opened, and the optical density measured immediately with the "Spectronic 20". Dilution of the samples was necessary to assure maximum sensitivity for exposures of less than two hours. The optical density as a function of irradiation time is given in Figure 7, at two different dose rates.

A liter of Orange IV solution was prepared having a concentration of 0.0261 gram/liter. 100 ml. samples, deaerated as described earlier, were irradiated and the optical density measured immediately. The results are also given in Figure 7. It should be mentioned that two of the three points taken at one hour fell in the region of the aerated solution, although they had been carefully deaerated. These are discussed in Section 4.

A note of caution must be added regarding the optical densities given in this figure. They were obtained at 440 mμ, the wavelength of maximum absorption of the dye in water. However, it is apparent from the spectra of some of these solutions given in Figure 8 that some of the products formed

FIGURE 7

Rate of Decolorization in Aqueous Solution



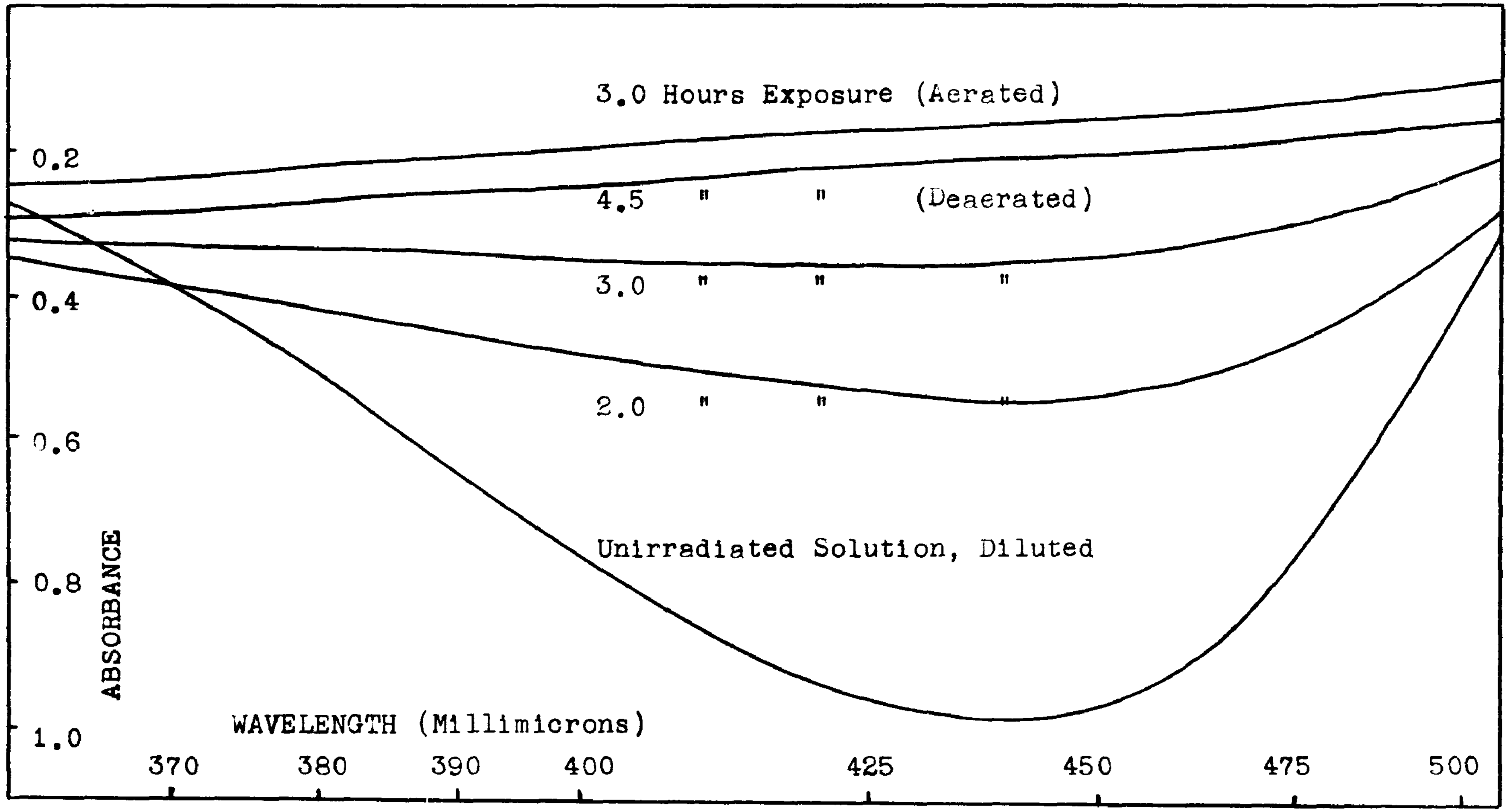


FIGURE 8: Visible Spectra of Irradiated Aqueous Solutions

also absorb light in this region. This was observed both with and without oxygen in solution. Since the intensity of product absorption at 440 mμ is small, the error resulting for exposures of less than one hour is negligible. At longer exposure times, the optical densities due to the dye should be less than the points given.

2. Calculation of G(–Dye): The G–value represents the number of dye molecules destroyed per 100 e.v. absorbed by the solution. This is obtained from the initial slope of the decolorization curve in Figure 7. The initial linear portion of the curve is extrapolated to the one hour point and the loss in dye concentration is determined. A sample calculation is given in Table I.

The solutions containing oxygen had $G \mp -0.43$ at a dose rate of 1.04×10^{17} e.v./ml.–min. and $G \mp -0.53$ at 1.49×10^{17} e.v./ml.–min. In the deaerated solutions, $G = -0.37$ at 1.04×10^{17} e.v./ml.–min.

3. Post–irradiation Effect: It was observed previously[1] that a solution containing dissolved oxygen undergoes further changes after removal from the source. A sample (C = 0.0248 gram/liter) irradiated for forty minutes reached equilibrium after about one week. The dye concentration decreased about 16% during this time. This phenomonenon was observed in the present work also.

In deaerated solutions this effect was not observed. Deaerated samples (C = 0.0260 gram/liter) irradiated for up

TABLE I

Calculation of G(–Dye) for Aerated Aqueous Orange IV Solution

Change in dye concentration: 0.0168 gram/liter in one hour

Dose–rate: 1.05×10^{17} e.v./gram–minute for Fricke dosimeter

Molecular weight of Orange IV: 375

Density of Fricke dosimeter solution: 1.027 gram/liter at 25°C.

Density of dye solution (taken as density of water): 0.997 gram/ml. at 25°C.

Dose–rate for dosimeter: $(1.05 \times 10^{17}$ e.v./gram–min.) (1.027 gram/ml.) = 1.08×10^{17} e.v./ml.–min.

Dose–rate for dye solution: $(1.08 \times 10^{17}$ e.v./ml.–min.) x

$$\frac{0.997}{1.027} = 1.04 \times 10^{17} \text{ e.v./ml.–min.}$$

$$G(\text{–Dye}) = \frac{0.0168 \text{ gram}}{1 \text{ liter – hr.}} \times \frac{1 \text{ mole}}{375 \text{ grams}} \times \frac{6.02 \times 10^{23} \text{ mol.}}{1 \text{ mole}} \times$$

$$\frac{1 \text{ hr.}}{60 \text{ min.}} \times \frac{1 \text{ liter}}{10^{3} \text{ ml.}} \times \frac{1 \text{ ml.–min.}}{1.04 \times 10^{17} \text{ e.v.}} \times 100$$

$$G(\text{–Dye}) = 0.43$$

to two or three hours were stable after removal from the source. However, samples exposed for longer periods were not stable, but changed in a reverse manner from oxygen containing solutions. A sample exposed for six hours underwent a 45% increase in optical density over a five-day period.

4. Product Formation: The characteristic absorption spectrum of the dye in the visible and ultraviolet regions was destroyed when aqueous solutions containing oxygen were irradiated. There was no evidence of the products formed, except for a gradually increasing absorption as one proceeds to lower wavelengths. The changes in the ultraviolet spectra are given Figure 9.

The changes in spectra of deaerated solutions are also difficult to interpret. They are similar in some respects to the spectra observed with oxygen present and are shown in Figure 10.

In Figure 7, two of the three points for deaerated solutions exposed for one hour fell in the region of the curve for the decolorization of solutions containing oxygen. However, these two samples had been carefully deaerated in the normal manner. It should be noted also that their ultraviolet spectra are not similar to those obtained for one hour samples containing oxygen. Rather, they both exhibit peaks at about 250 $m\mu$, as shown in Figure 11. Slight evidence can also be observed for absorption in this region in the 1.5 and 2.0 hour exposures of the deaerated solutions, especially after standing.

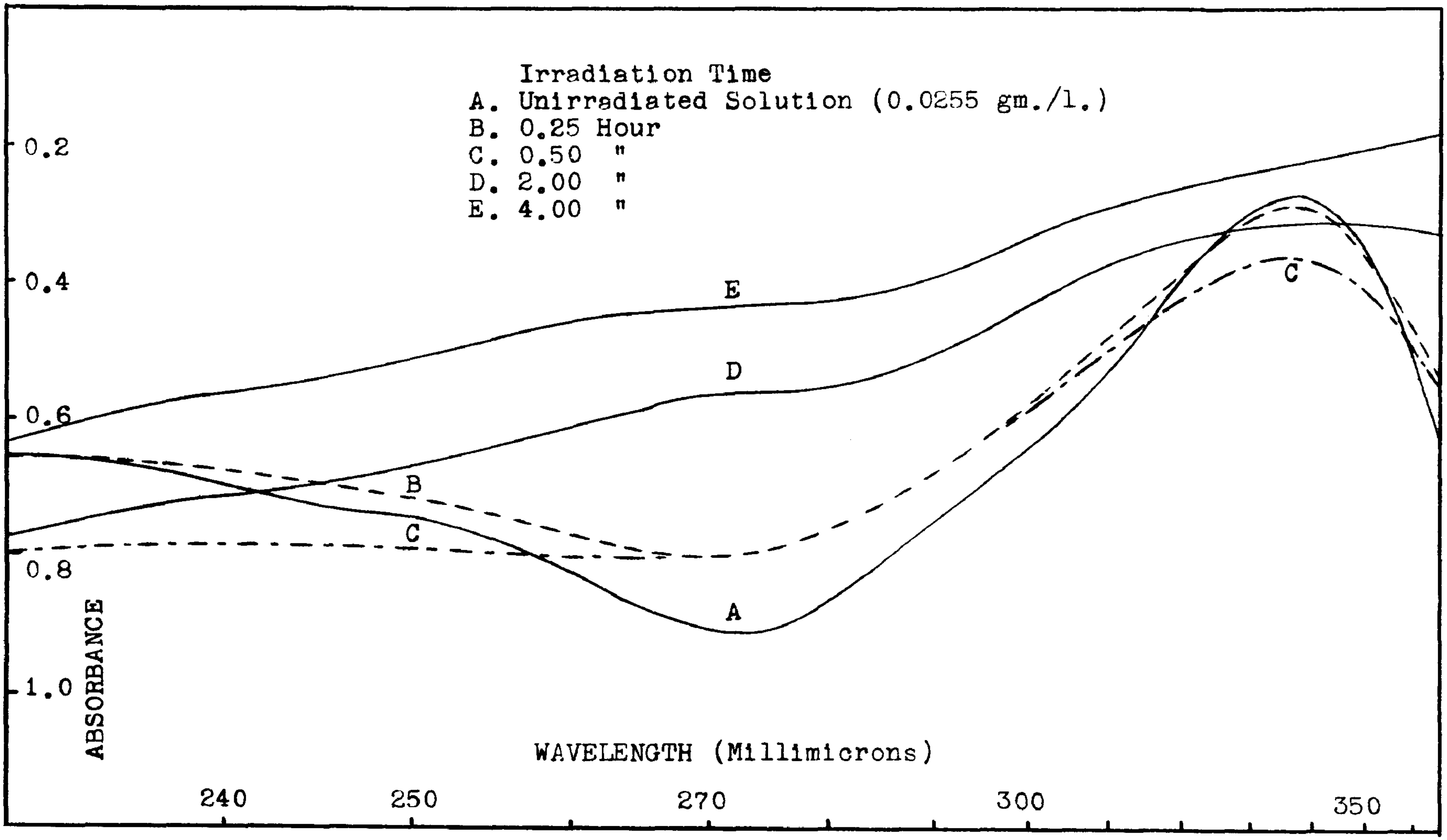


FIGURE 9: Ultraviolet Spectra of Irradiated Aqueous Solutions, Aerated

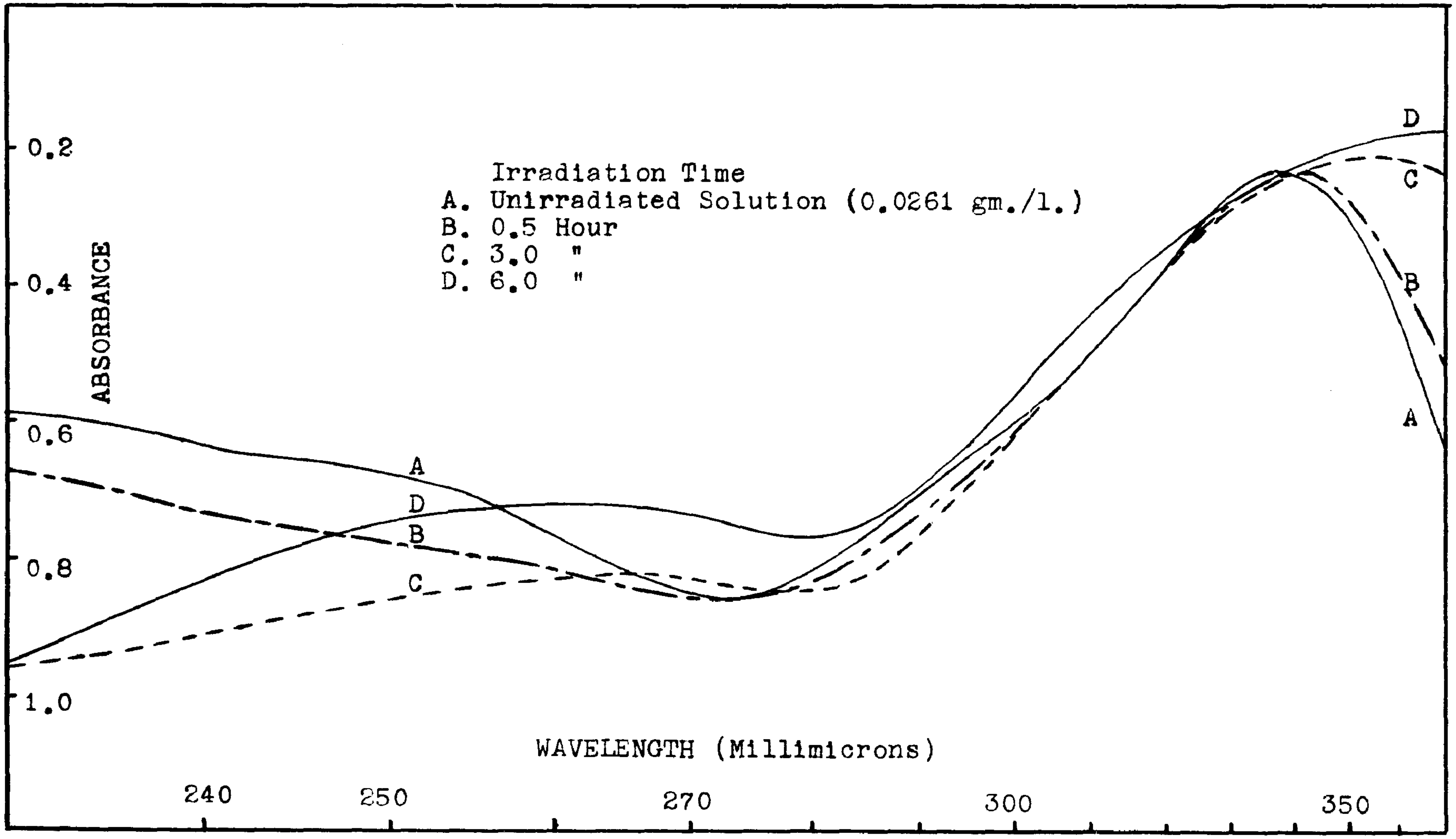


FIGURE 10: Ultraviolet Spectra of Irradiated Aqueous Solutions, Deaerated

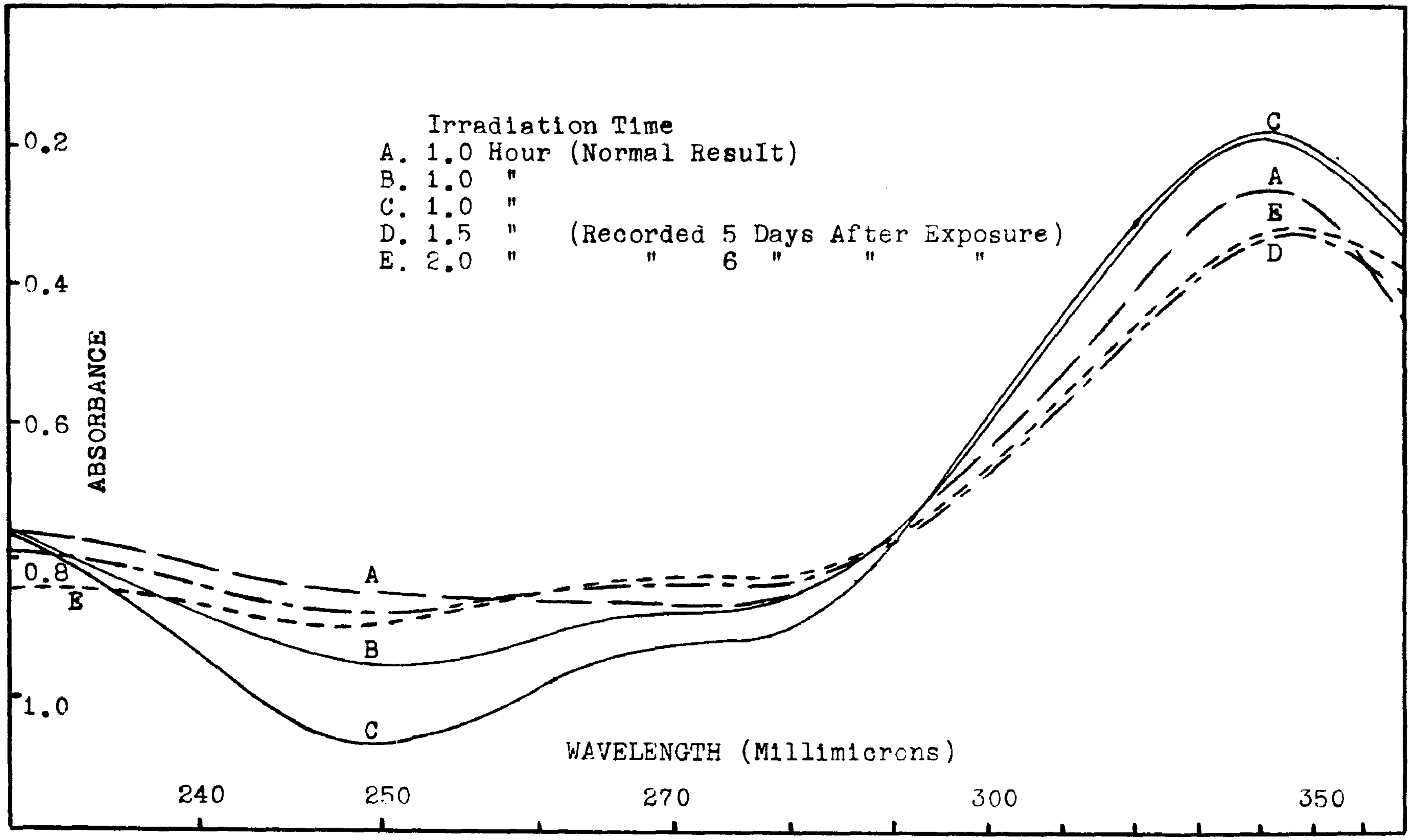


FIGURE 11:Ultraviolet Spectra of Irradiated (1 Hour) Aqueous Solutions, Deaerated

B. METHANOLIC SOLUTIONS

1. Rate of Decolorization: A stock solution of Orange IV was prepared containing 0.0264 gram/liter. This solution was exposed to the source in 100 ml. portions with no attempt to exclude air. The samples were diluted and the optical densities measured with the "Spectronic 20" immediately after removal from the source. The change in dye concentration with irradiation time at two different dose rates is given in Figure 12. The initial decolorization process is very slow. After a long induction period in which only a small fraction of the decolorization occurs, there is an abrupt change in the rate. The complete decolorization then occurs very rapidly. The induction period for the first experiment was 5.6 hours, and for the second experiment, 7.0 hours.

A stock solution of Orange IV was prepared containing 0.0227 gram/liter. After being deaerated as described earlier by purging with nitrogen, 100 ml. samples were irradiated. The concentrations were immediately measured as mentioned above. The change in dye concentration with irradiation time is given in Figure 13. There is no evidence of an induction period for the deaerated solutions. A linear relationship is observed for much of the change.

This experiment was repeated with a stock solution of Orange IV containing 0.0136 gram/liter. The data is included in the same figure. Again a linear relationship is observed, although the initial slope was 25% less than that obtained with

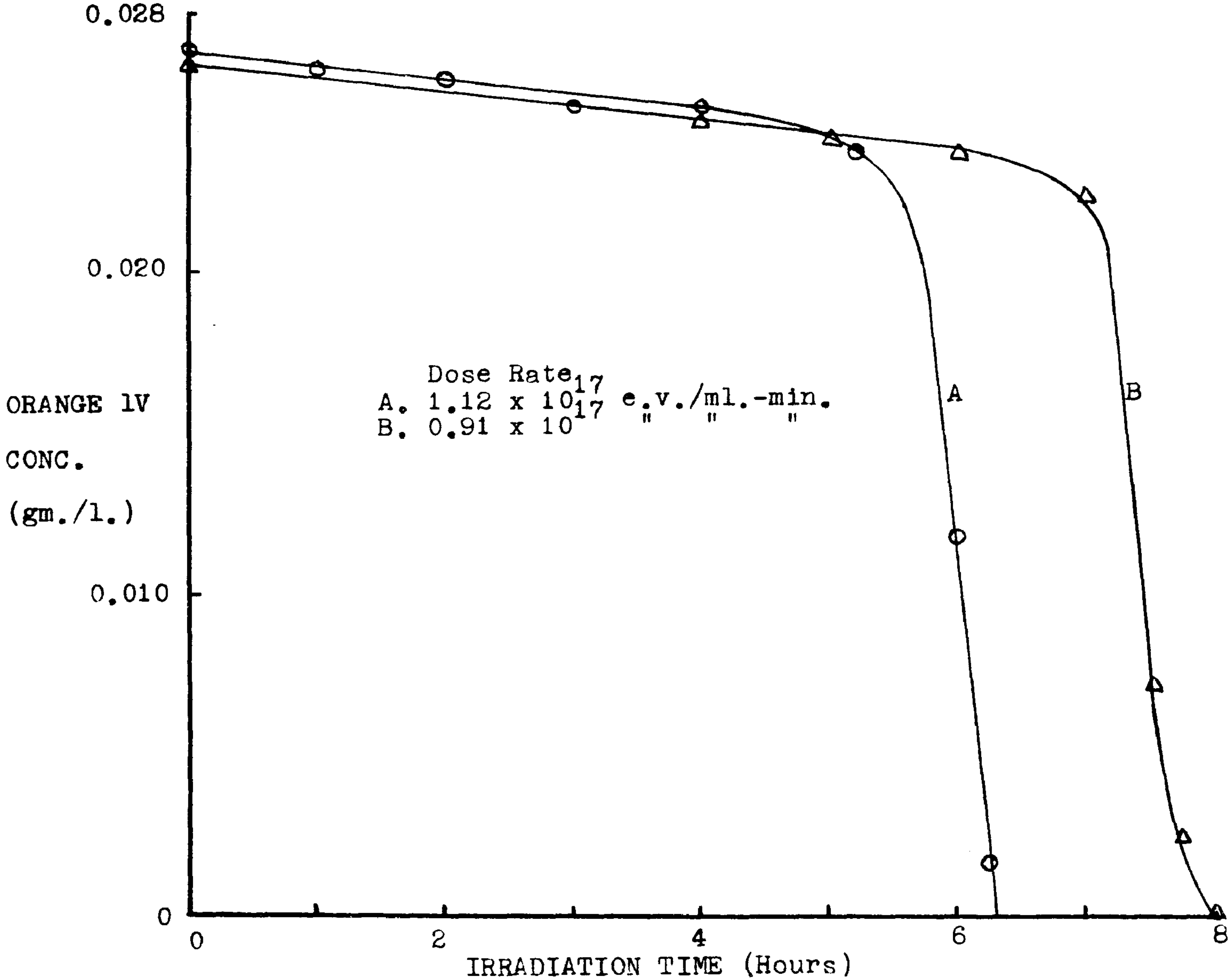
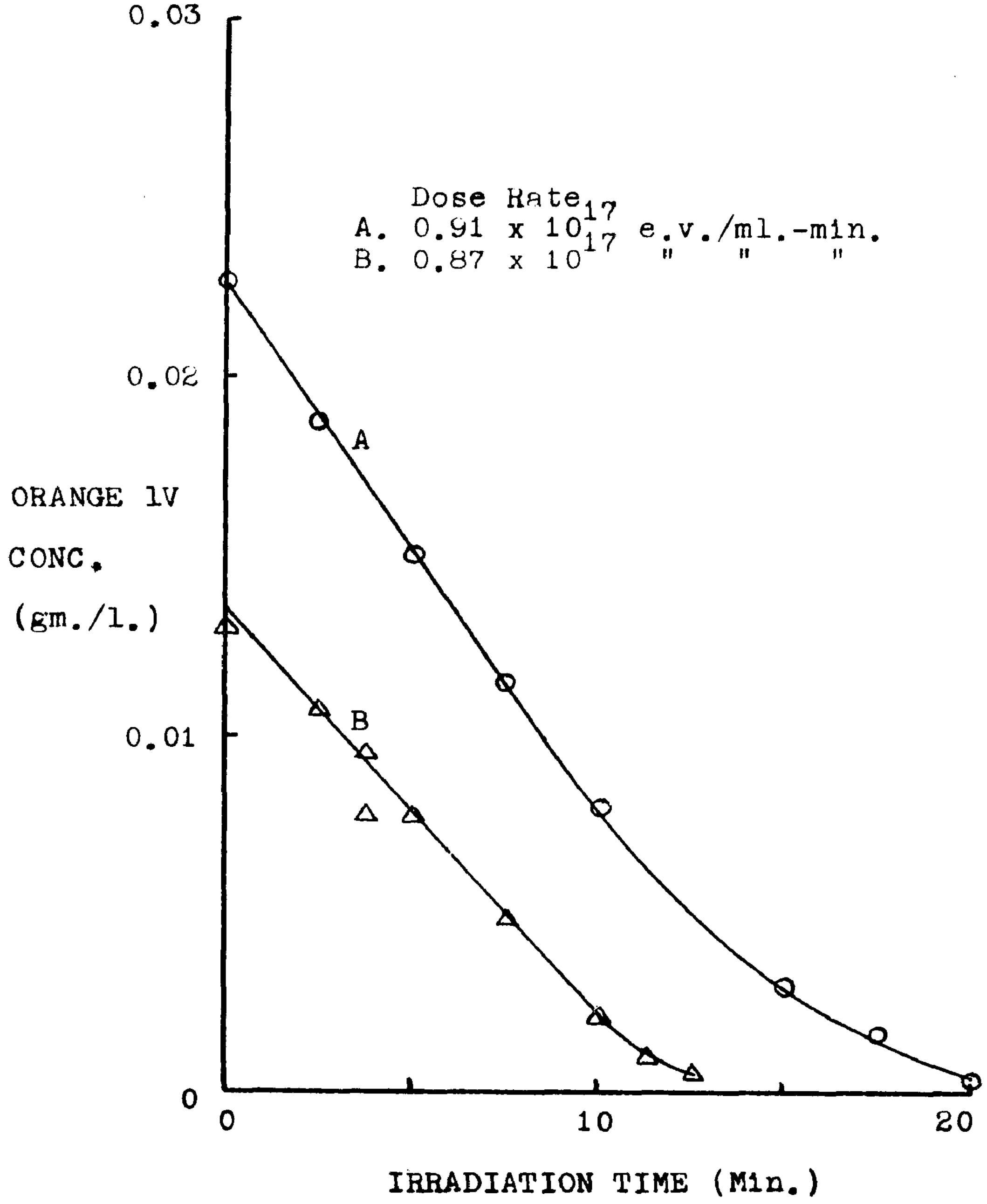


FIGURE 12: Rate of Decoloration in Methanolic Solution, Aerated

FIGURE 13

Rate of Decolorization in Methanolic Solution, Deaerated.



the higher initial concentration. Since the dose rate was 5% less in the second case due to radioactive decay, the corrected initial slope is 20% less.

The visible absorption spectra of these irradiated solutions were recorded. It appears that the dye reaction products are colorless in methanolic solutions, both with and without oxygen present. The spectra of almost completely decolorized solutions seemed to be only that of Orange IV. Therefore, the optical density of these irradiated solutions is an accurate measure of the dye concentration.

2. Calculation of G(-Dye): The G-value for the methanolic solutions containing oxygen was taken from the linear portion of the slope (Figure 12) during the rapid decolorization process rather than during the induction period. The G-values for deaerated methanolic solutions were taken from the initial slopes of the two decolorization curves in Figure 13. The calculation for the aerated solution is given in Table II.

It was found that $G = -1.28$ for aerated methanolic solutions. No dependence upon the dose rate was apparent from the data available.

The G-values in deaerated methanolic solutions were found to depend upon the initial dye concentration. With an initial concentration of 0.0227 gram/liter, $G = -2.67$ and at 0.0136 gram/liter, $G = -2.10$.

3. Post-irradiation Effect: Previous studies[1] in this laboratory have shown that methanolic solutions containing

TABLE II

Calculation of G(-Dye) for Aerated Methanolic Orange IV Solution

Change in dye concentration: 0.725×10^{-3} gram/liter-min.

Dose-rate: 1.12×10^{17} e.v./gram-min. for Fricke dosimeter

Density of Fricke dosimeter solution: 1.027 gram/ml. at 25° C.

Dose-rate: $(1.12 \times 10^{17}$ e.v./gram-min.$)$ $(1.027$ gram/ml.$) = 1.15 \times 10^{17}$ e.v./ml.-min.

Dose-rate for methanol:[10g] $(1.15 \times 10^{17}$ e.v./ml.-min.$)$ $(0.790) = 0.908 \times 10^{17}$ e.v./ml.-min.

Assumption: density of methanol = density of methanolic dye solution

$$G(-\text{Dye}) = \frac{0.725 \times 10^{-3}\ \text{gram}}{1\ \text{liter} - \text{min.}} \times \frac{1\ \text{mole}}{375\ \text{grams}} \times \frac{6.02 \times 10^{23}\ \text{mol.}}{1\ \text{mole}} \times \frac{1\ \text{liter}}{10^{3}\ \text{ml.}} \times \frac{1\ \text{ml.-min.}}{0.908 \times 10^{17}\ \text{e.v.}} \times 100$$

$$G(-\text{Dye}) = 1.28$$

oxygen are not stable after removal from the source. The optical density at 440 mμ of the solution which was decolorized in 6.25 hours increased from 0.04 to 0.14 in about three hours. A similar observation was made in the present work. The solution containing oxygen that was irradiated for 7.75 hours was recorded in the visible region 25 minutes after removal from the source, and again 11 days later. These spectra are shown in Figure 14. It should be noted that the increased absorption obtained on standing is apparently not due to an increase in the dye concentration, but rather to some other product formed which can absorb light in this wavelength region.

It has been observed that the time lapse between removal from the source and opening of the vessel can be important. Two samples of the same stock solution were irradiated for eight hours. They were opened and their visible spectra recorded at 16 minutes and 68 minutes after exposure. These spectra are shown in Figure 15, together with the spectra of these solutions a week later. About 10% of the initial dye concentration has been restored by allowing the irradiated solution to stand in the sealed vessel for an additional 52 minutes. A further change occurred in this solution after it had been opened, although again this slow increase in the absorption spectrum appears to be due to a substance other than the dye.

It has also been found that deaerated methanolic solutions are not stable after removal from the source. A

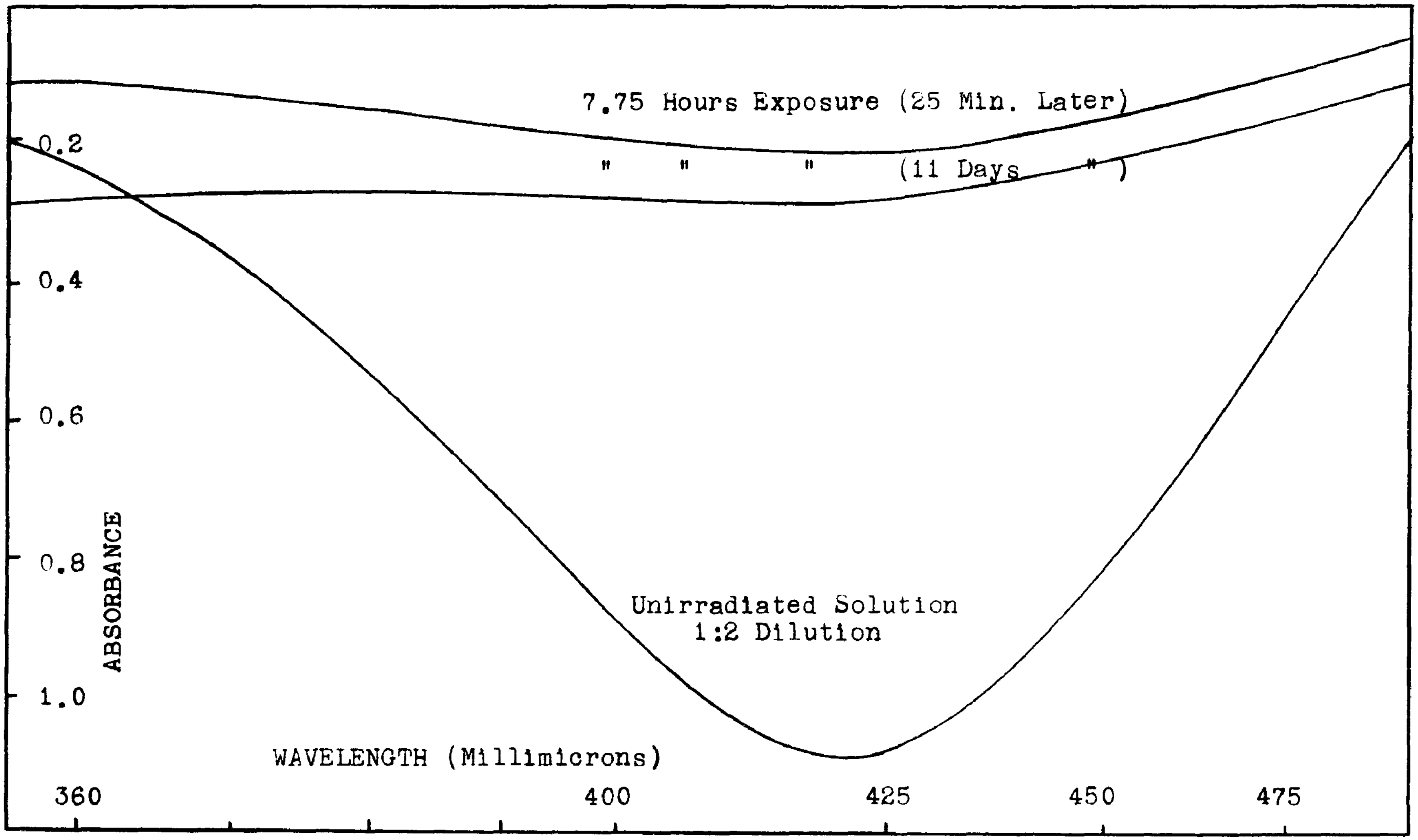


FIGURE 14: Visible Spectra of Irradiated Methanolic Solution,Aerated

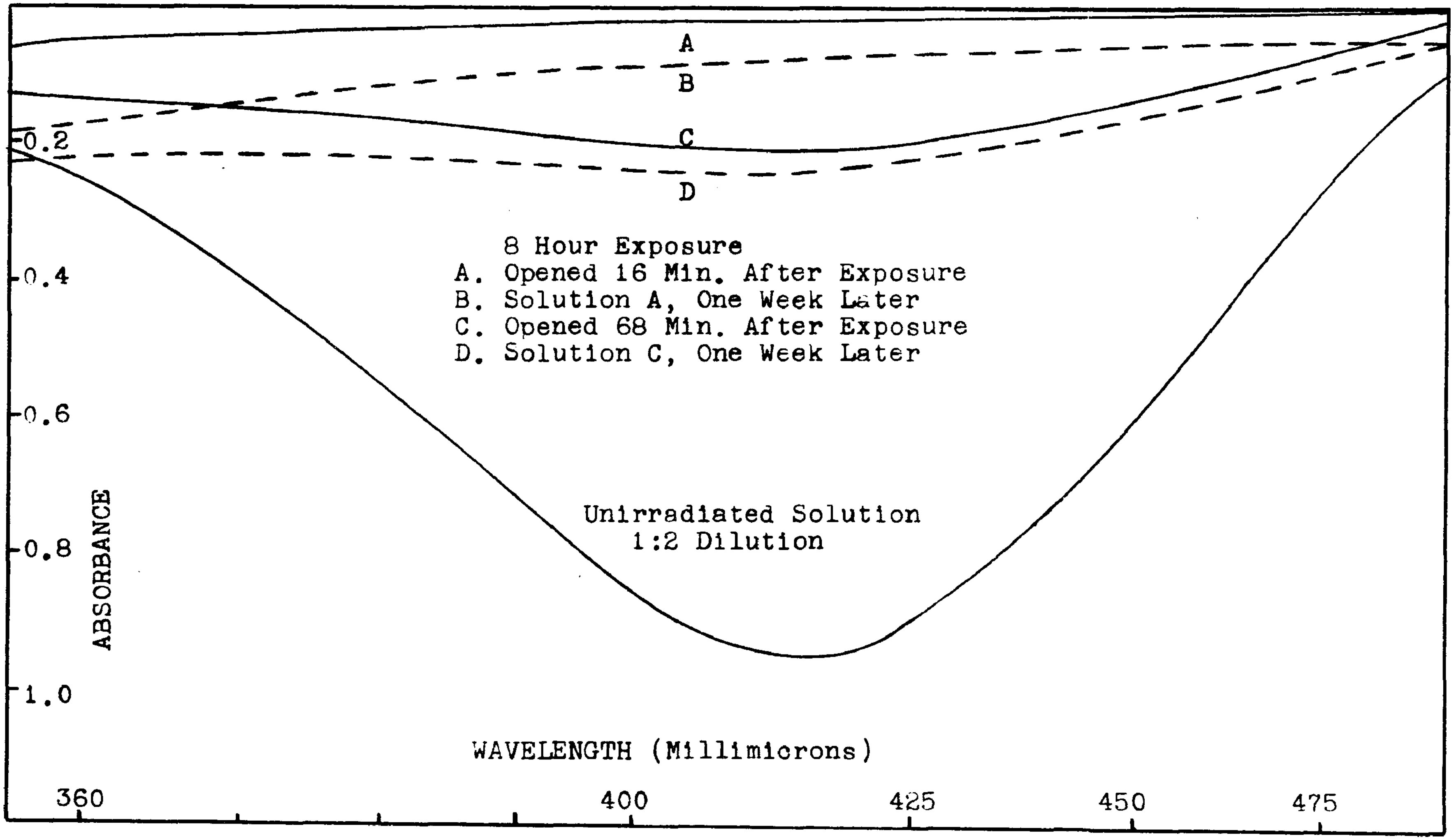


FIGURE 15: Change in Visible Spectra in Methanolic Solutions, Aerated

deaerated solution that was irradiated for 20 minutes had its visible absorption spectrum recorded 40 minutes after removal from the source and again 10 days later. These spectra are shown in Figure 16. The absorption spectrum in each case appears to be mainly that of Orange IV. Thus, the decolorization reaction is largely reversed upon standing.

The extent to which the decolorization can be reversed is indicated in Figure 17. This includes one of the decolorization curves of Figure 13, together with points indicating the changes in the dye concentration of the irradiated solutions after storage in a dark closet for various periods. The first series of points were obtained about one week after exposure, the second about two months after exposure. It should be noted that neither of these two sets of points extrapolate back to the initial dye concentration of 0.0227 gram/liter. This is attributed to evaporation of some solvent from the corked flasks.

The rate at which this reverse reaction proceeds was observed in the following manner. A deaerated methanolic solution of Orange IV (0.0136 gram/liter) was irradiated for 12.5 minutes. The sample was removed from the source, opened and a portion was poured directly into a colorimeter tube. The optical density of this solution was determined on the "Spectronic 20" 3 minutes after exposure, and again 18.5 minutes after exposure.

The irradiation vessel was stoppered after this first portion was removed. A second portion was placed in a

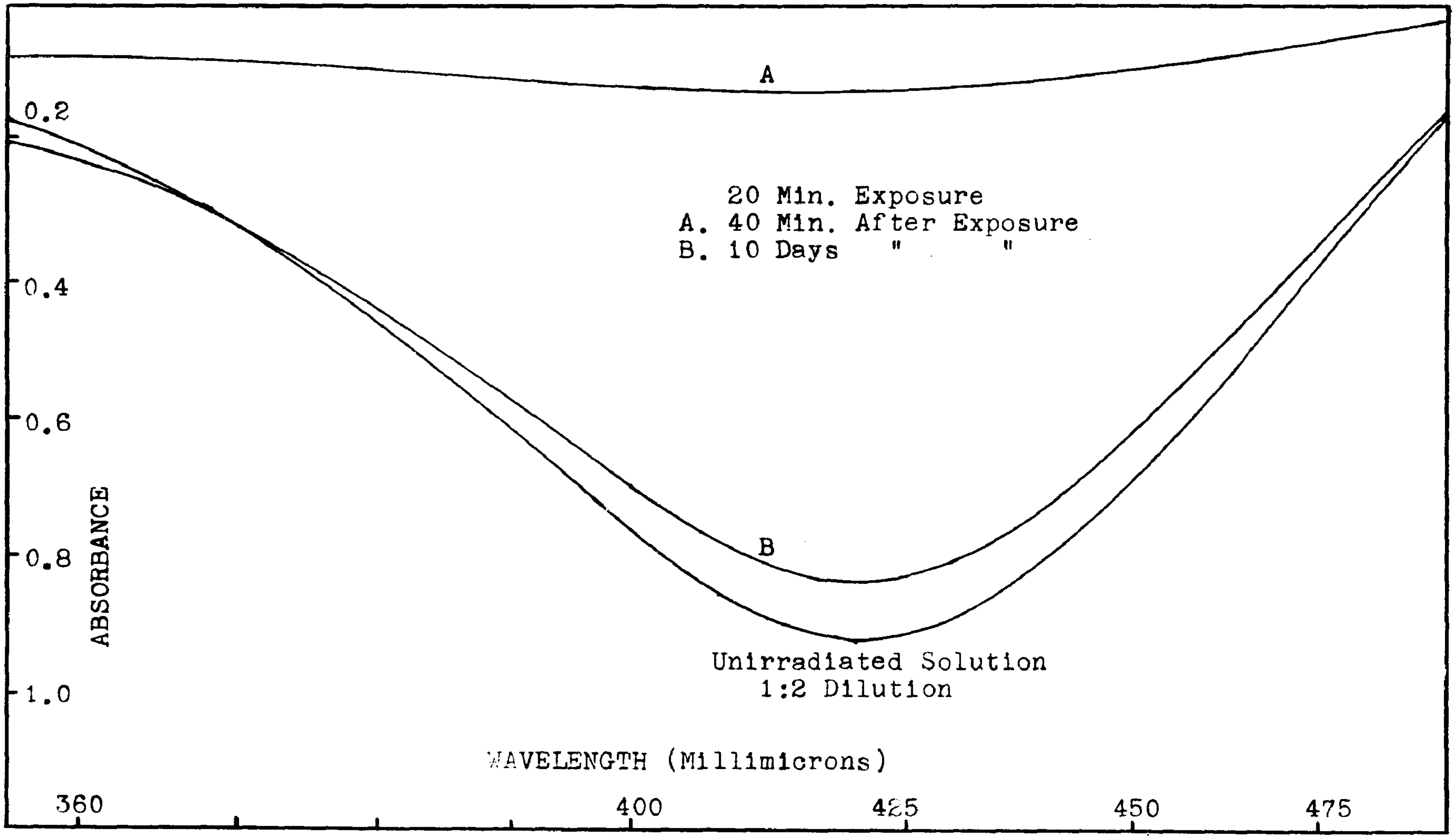
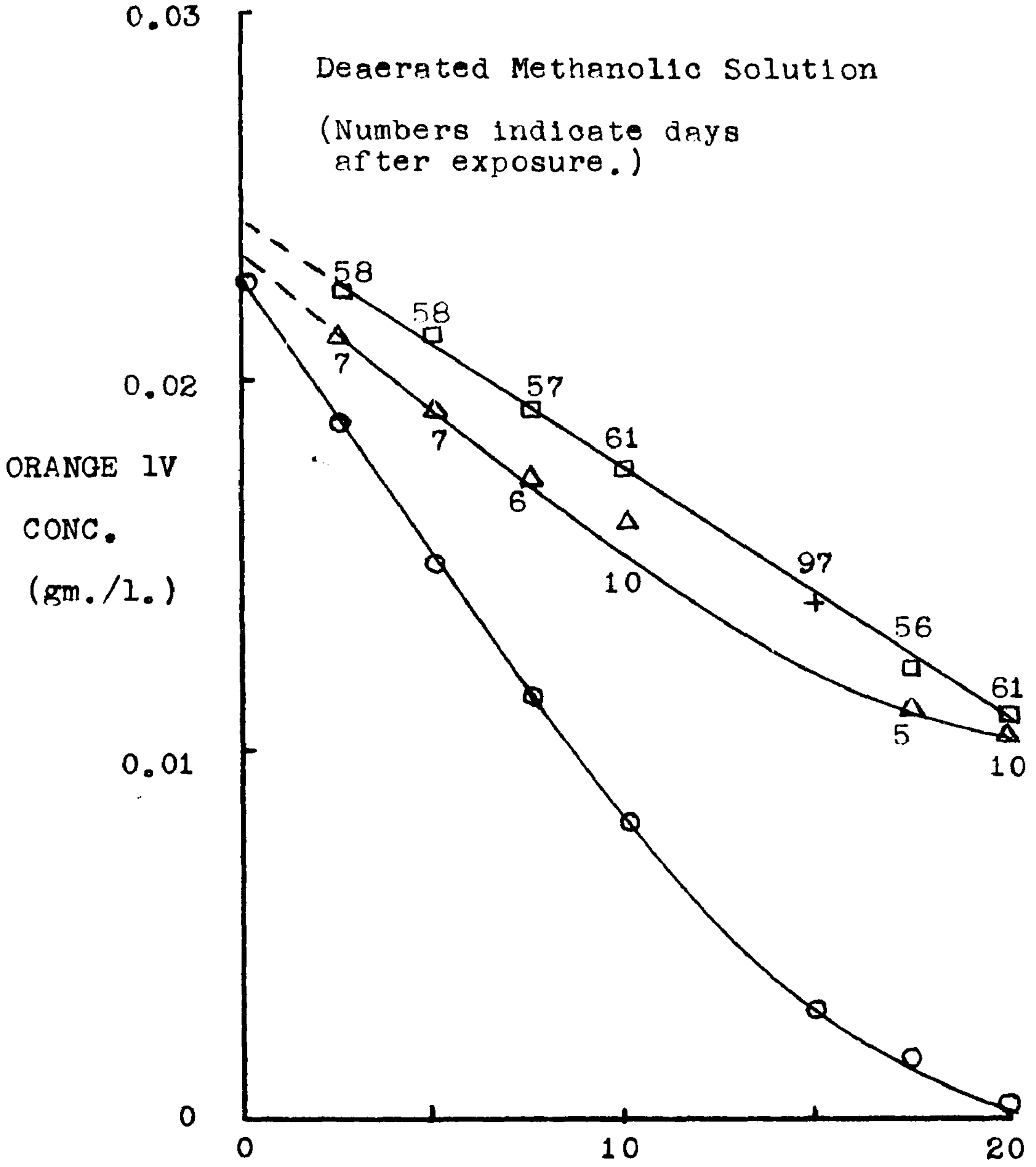


FIGURE 16: Visible Spectra of Irradiated Methanolic Solution, Deaerated

FIGURE 17

Change in Decolorization Curve With Time

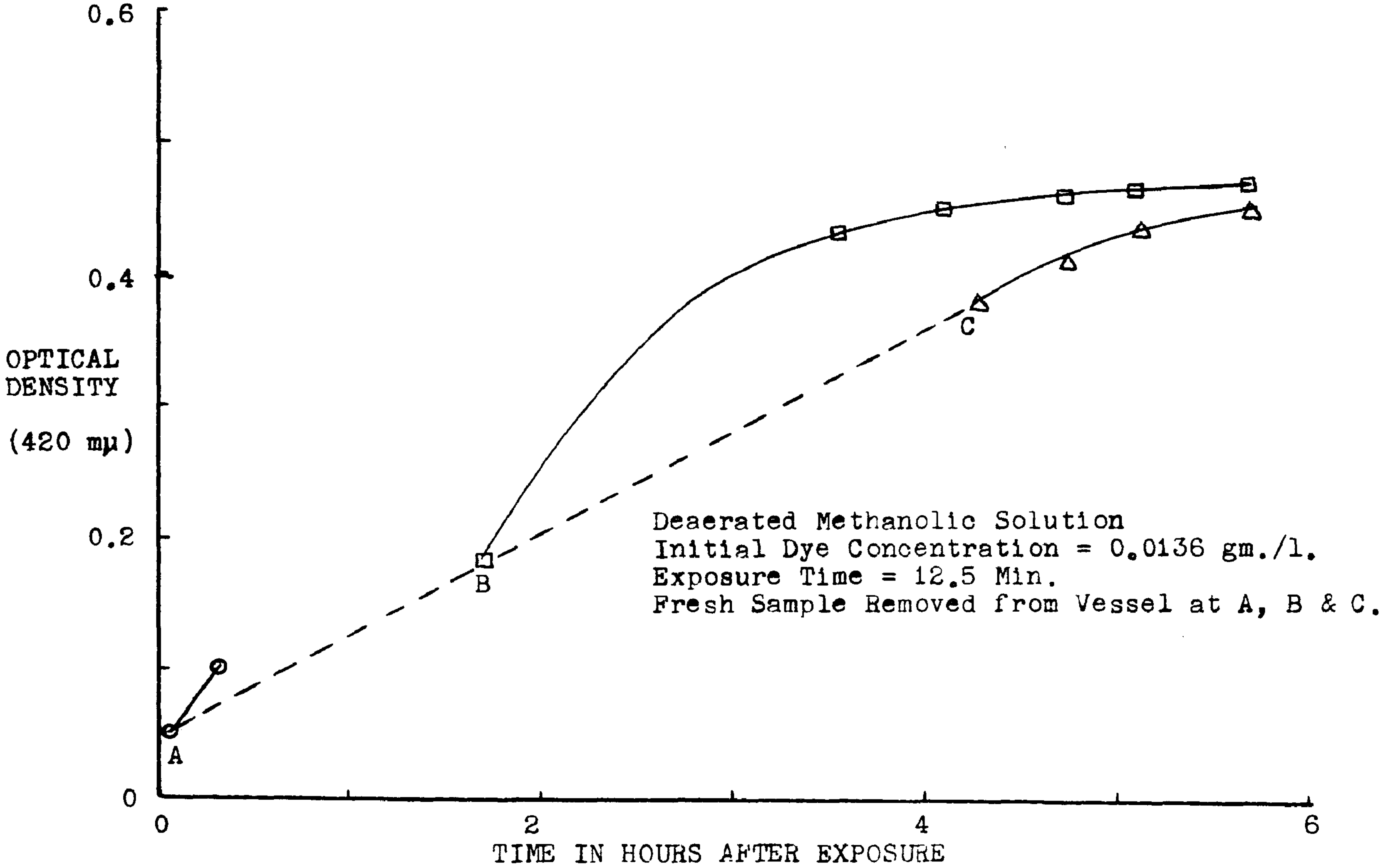


colorimeter tube and the optical density determined 1.70 hours after exposure, and again at regular time intervals. A third portion was transferred from the irradiation vessel and its optical density measured 4.27 hours after exposure, and again at regular time intervals. These colorimeter tubes were all stoppered between readings.

The changes in optical density with time after irradiation are shown in Figure 18. A dotted line is drawn through the three points for the optical density immediately after the sample was removed from the irradiation vessel. Thus, a linear increase in dye concentration with time after exposure is obtained for the solution in the irradiation vessel. However, the increase is much more rapid once the solution is exposed to the air.

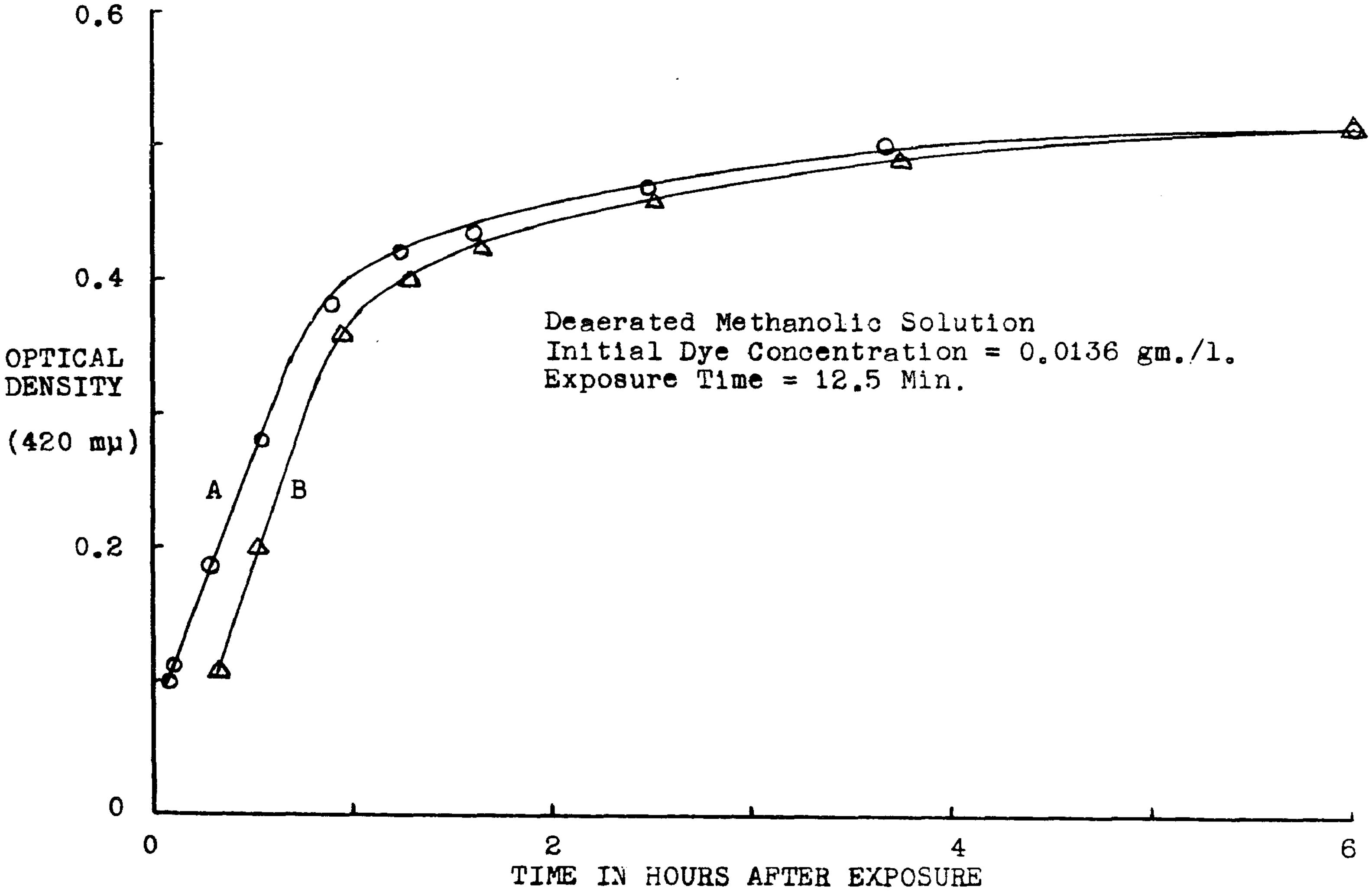
This increase in dye concentration was then followed continuously. A sample of the same Orange IV stock solution was deaerated and again irradiated for 12.5 minutes. Sample A was removed from the vessel and its optical density determined 3.5 minutes after exposure, and at intervals up to 11 hours. Sample B was removed from the vessel and its optical density determined 19.5 minutes after exposure, and also at intervals up to 11 hours. The results are shown in Figure 19. The dye concentration increases rapidly for the first hour after the irradiated solution was exposed to the air. The rate of reformation of Orange IV then became quite low after a few hours. The optical density of both samples was 0.52 when measured 6 hours after exposure.

It appeared that air exposure was responsible for the



Deaerated Methanolic Solution
Initial Dye Concentration = 0.0136 gm./l.
Exposure Time = 12.5 Min.
Fresh Sample Removed from Vessel at A, B & C.

FIGURE 18: Intermittent Changes in Optical Density With Time After Exposure



Deaerated Methanolic Solution
Initial Dye Concentration = 0.0136 gm./l.
Exposure Time = 12.5 Min.

FIGURE 19: Continuous Changes in Optical Density With Time After Exposure

rapid increase in dye concentration. Thus, the reverse reaction rate should be increased by bubbling oxygen through an irradiated solution.

A methanolic solution containing 0.0134 gram/liter was deaerated in the normal manner and irradiated for ten minutes. The vessel was opened 18 minutes after exposure and two samples were placed in colorimeter tubes. The optical density was measured with the "Spectronic 20". Oxygen was bubbled through sample A for 13 minutes and the optical densities of both solutions A and B were recorded over a period of time. After measuring the optical density of the oxygenated sample, methanol was added to correct for the evaporation loss and the optical density again recorded. This latter value was used in the curve given in Figure 20.

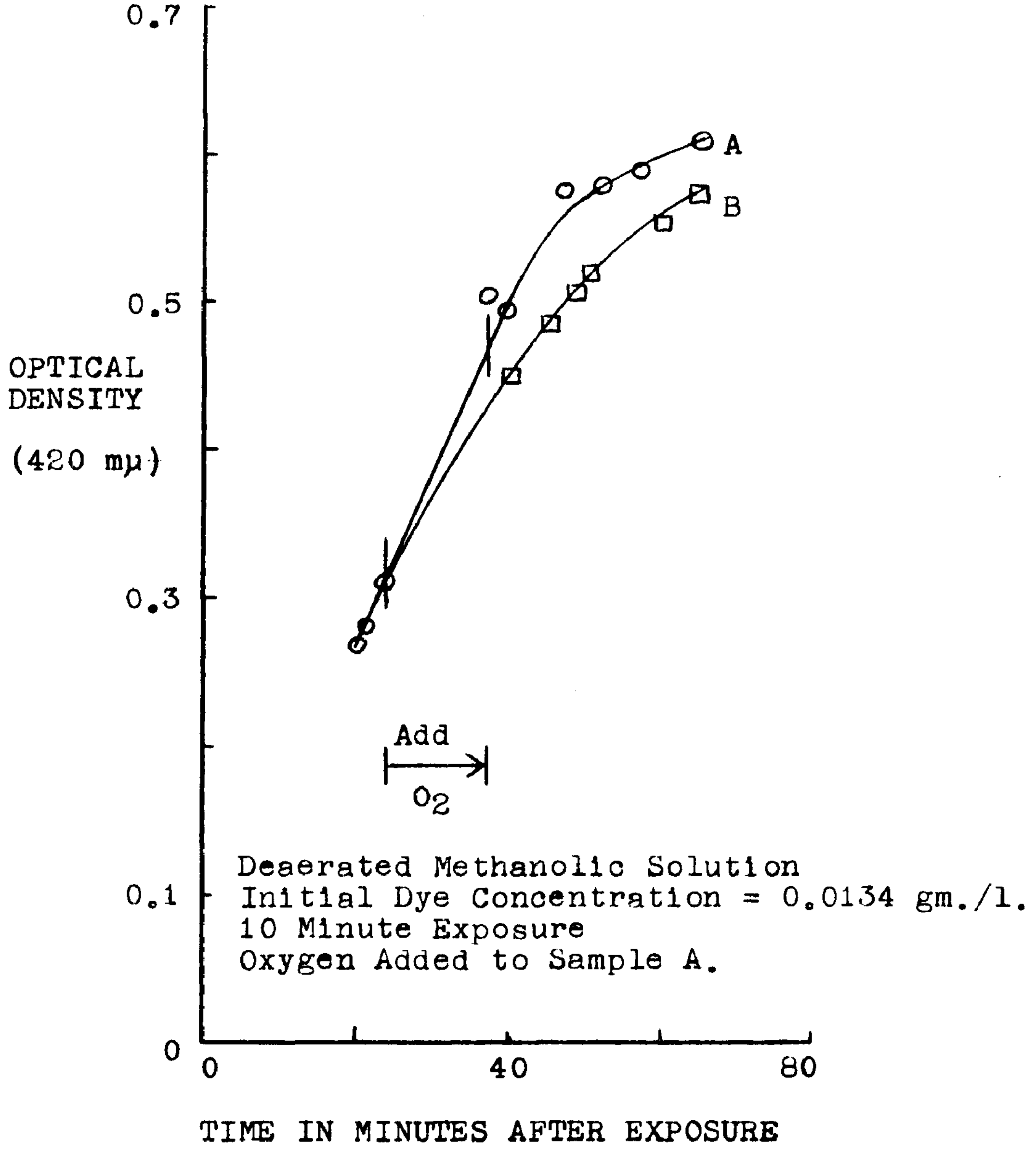
A sample of the same Orange IV solution used above was also deaerated and exposed for ten minutes. The vessel was opened 24 minutes after exposure and a sample transferred to a colorimeter tube. The optical density of sample A was measured immediately and then over a period of time during which the sample was not stoppered.

A second portion of the solution was placed in a ten milliliter graduated cylinder and oxygen was bubbled through this solution B for 10 minutes. A few drops of methanol were added to correct for the evaporation loss. The solution was transferred to a colorimeter tube and the optical density measured immediately and then over a period of time during which the sample was not stoppered.

A third portion of solution was removed from the

FIGURE 20

Addition of Oxygen to
Irradiated Solution I



covered irradiation vessel 42 minutes after exposure and the optical density measured immediately and then over a period of time during which sample C was stoppered. The data from this experiment is given in Figure 21.

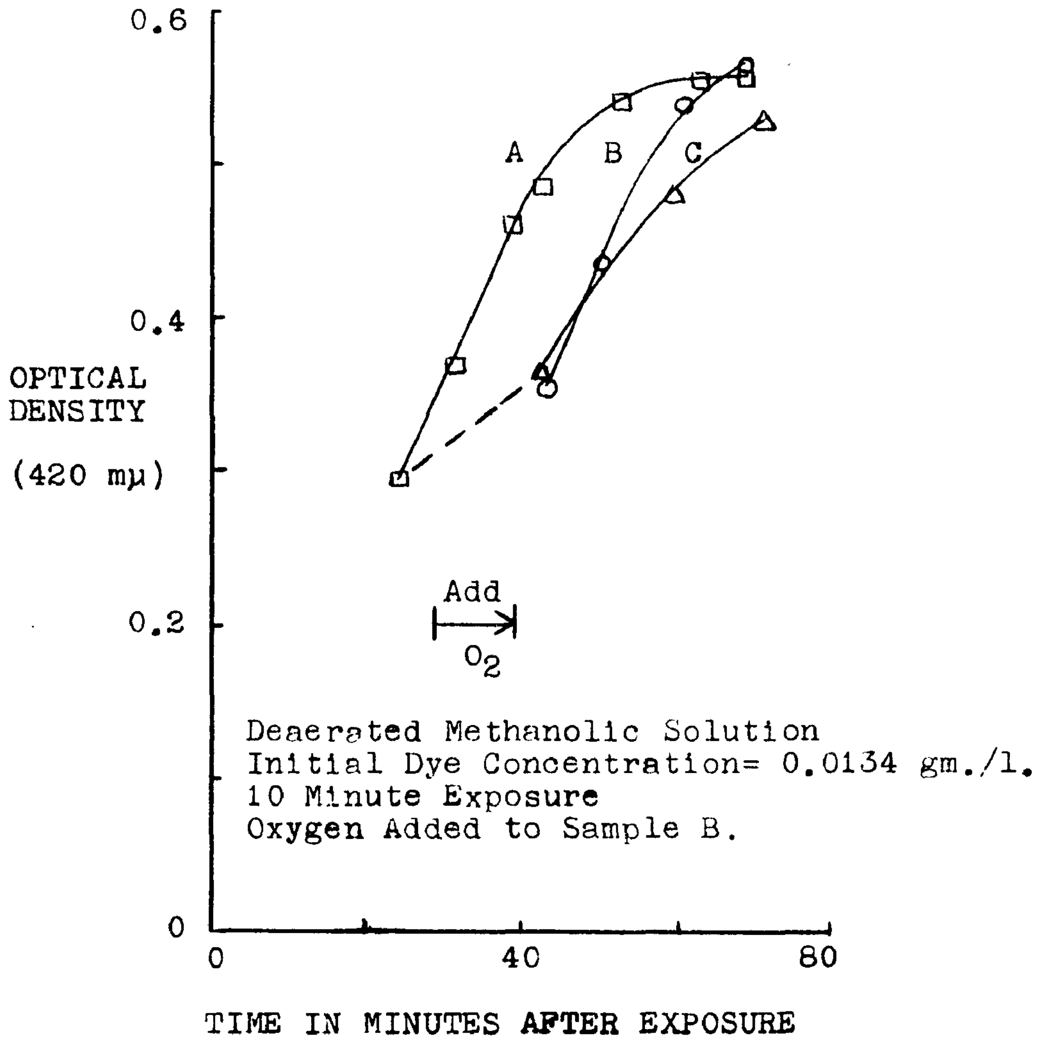
The post-irradiation behavior described previously is typical of deaerated methanolic Orange IV solutions. However, the sample exposed for 15 minutes (C = 0.0227 gram/liter), Figure 13, behaved strangely. The concentration increased at an abnormal rate, and 60 days after exposure seemed to exceed the initial dye concentration. These changes are shown in Figure 22. The dye concentrations were obtained from the recorded visible spectra via the calibration curve. The final observation made 97 days after exposure indicates a dye concentration in the region expected based on the final equilibrium concentrations of the other solutions in this series.

This strange behavior observed in the visible absorption spectrum is accompanied by different results in the ultraviolet spectrum also. These ultraviolet spectra are shown in Figure 23, where again the final observation after 97 days is typical of that expected based on the final equilibrium reached by the other solutions in this series. Attempts to reproduce these strange results have failed.

4. Product Formation: The methanolic solutions yield considerably more information than the aqueous solutions. The changes in the ultraviolet spectra of the irradiated methanolic solution containing oxygen can be seen in Figure 24. The spectrum of the dye is altered only slightly for the first

FIGURE 21

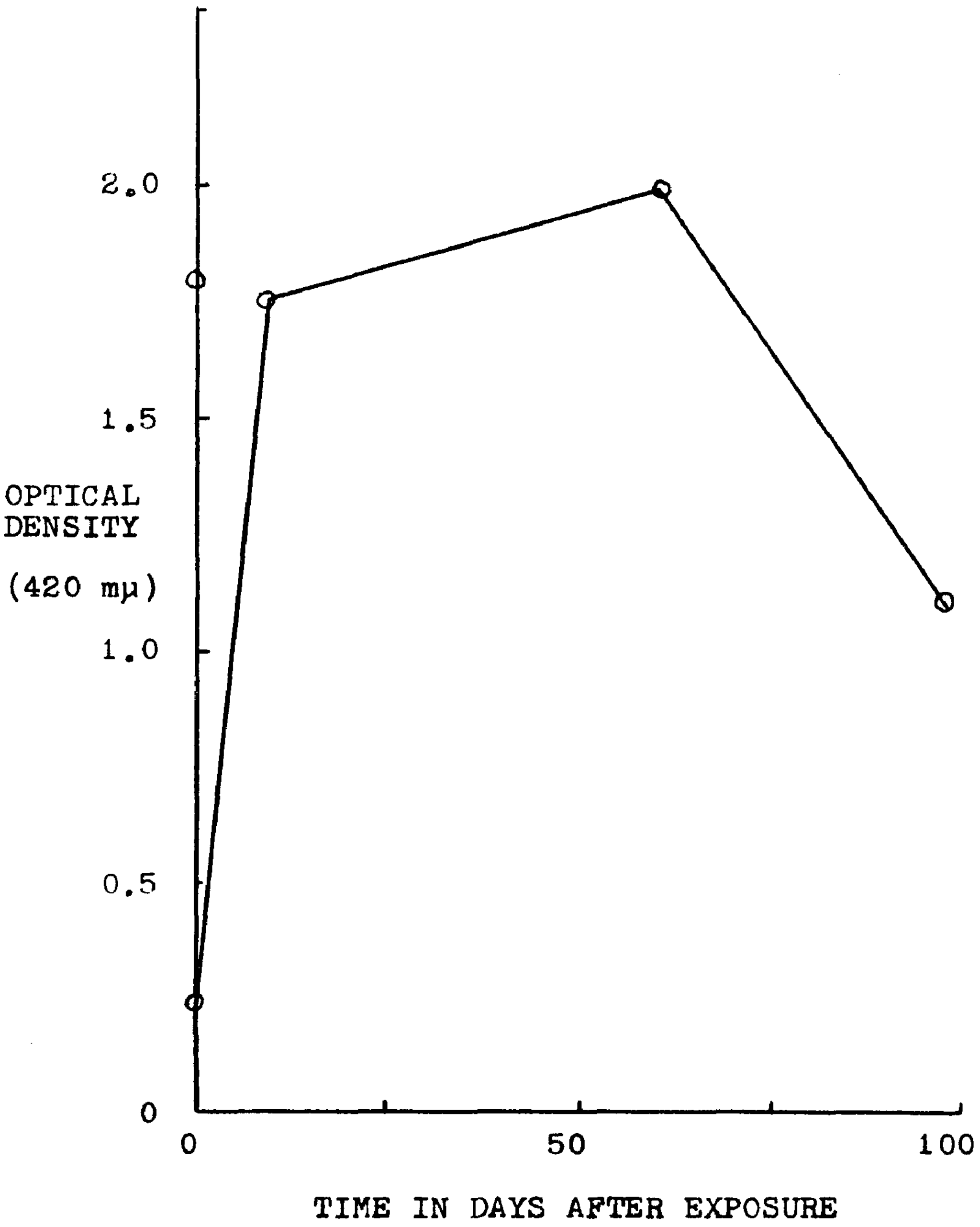
Addition of Oxygen to
Irradiated Solution II



Deaerated Methanolic Solution
Initial Dye Concentration= 0.0134 gm./l.
10 Minute Exposure
Oxygen Added to Sample B.

FIGURE 22

Abnormal Change in Optical Density
of Deaerated Methanolic Solution



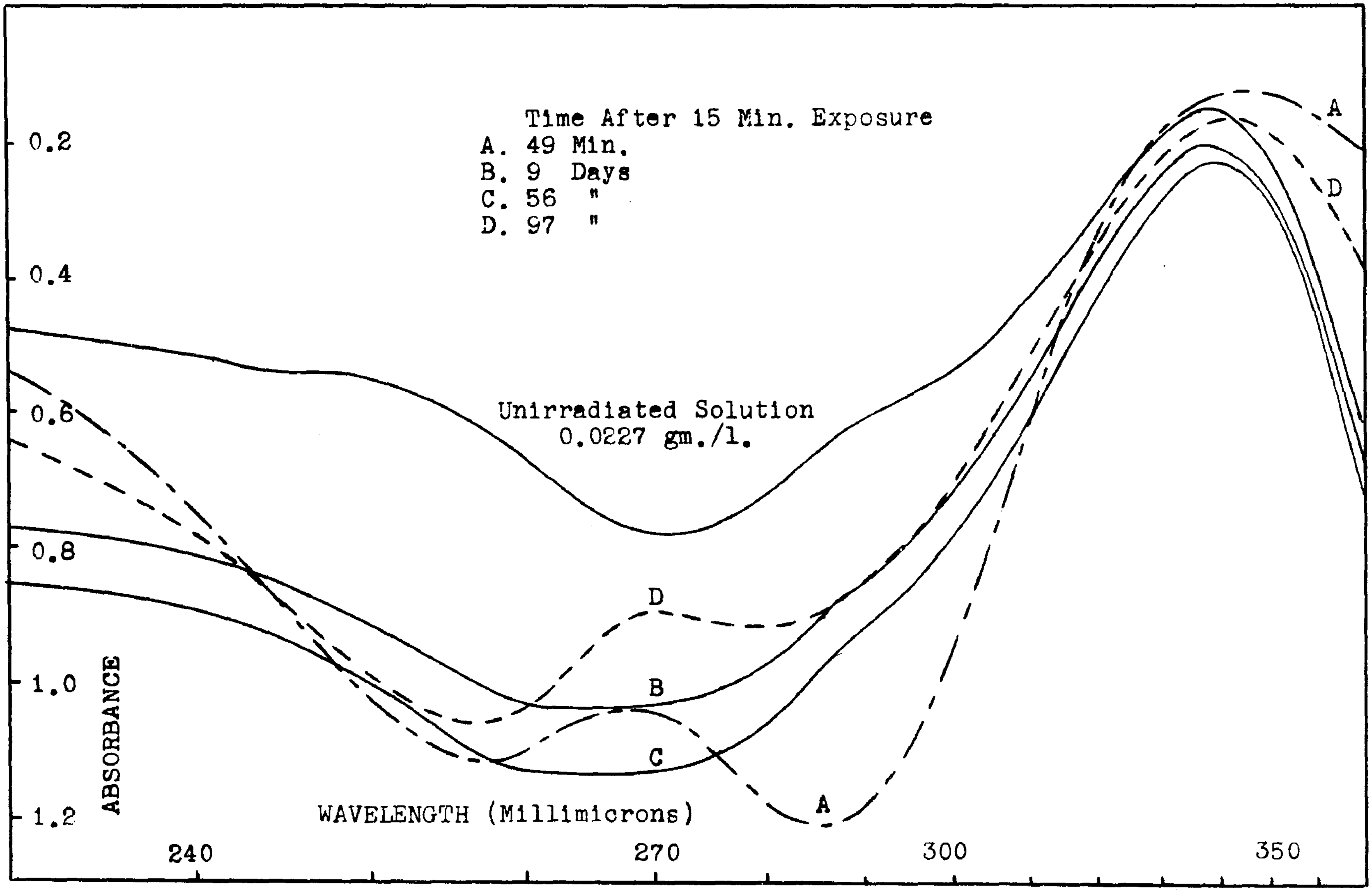


FIGURE 23: Abnormal Change in Ultraviolet Spectra of Deaerated Methanolic Solution

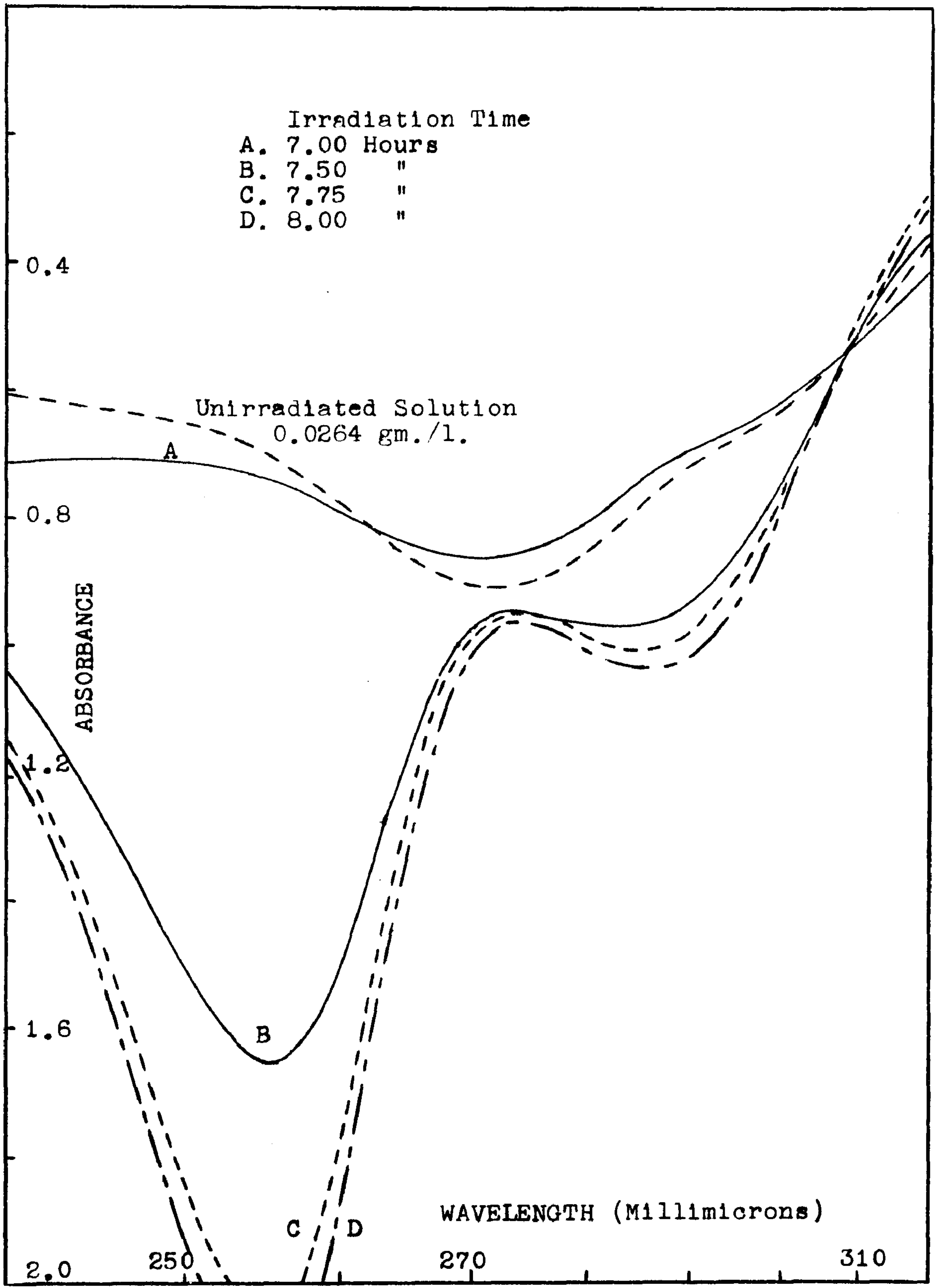


FIGURE 24: Ultraviolet Spectra of Irradiated Methanolic Solution, Aerated

seven hours which corresponds to the induction period. Longer exposures, however, result in marked changes. Succeeding spectra for 7.50, 7.75 and 8.00 hour exposures have a strong absorption at 255 mμ which is attributed to the sodium sulfanilate derivatives. There is also a weak absorption peak at 287 mμ attributed to the p-aminodiphenylamine derivatives.

An attempt was made to duplicate the ultraviolet spectrum of the solution exposed for 7.50 hours. A solution was prepared containing 0.0153 gram/liter of sodium sulfanilate, 0.0076 gram/liter of p-aminodiphenylamine and 0.0054 gram/liter of Orange IV. The ultraviolet spectrum of this solution is shown in Figure 25, and the agreement is quite good. The spectra of the sodium sulfanilate and p-aminodiphenylamine in methanol are reproduced in Figure 26.

Although the prepared solution has an almost identical ultraviolet spectrum, the concentrations used are not those expected. The dye solution contained 0.0220 gram/liter of Orange IV at the end of the seven hour induction period. After exposure for 7.50 hours the dye concentration was 0.0072 gram/liter. The loss of 0.0138 gram/liter of dye could result in the formation of 0.0071 gram/liter of sodium sulfanilate and 0.0067 gram/liter of p-aminodiphenylamine, if the azo linkage was completely reduced by hydrogen atoms, and if this was the only reaction taking place.

The post-irradiation changes reported previously in the irradiated solutions containing oxygen can also be observed by reference to the ultraviolet spectra. The solution

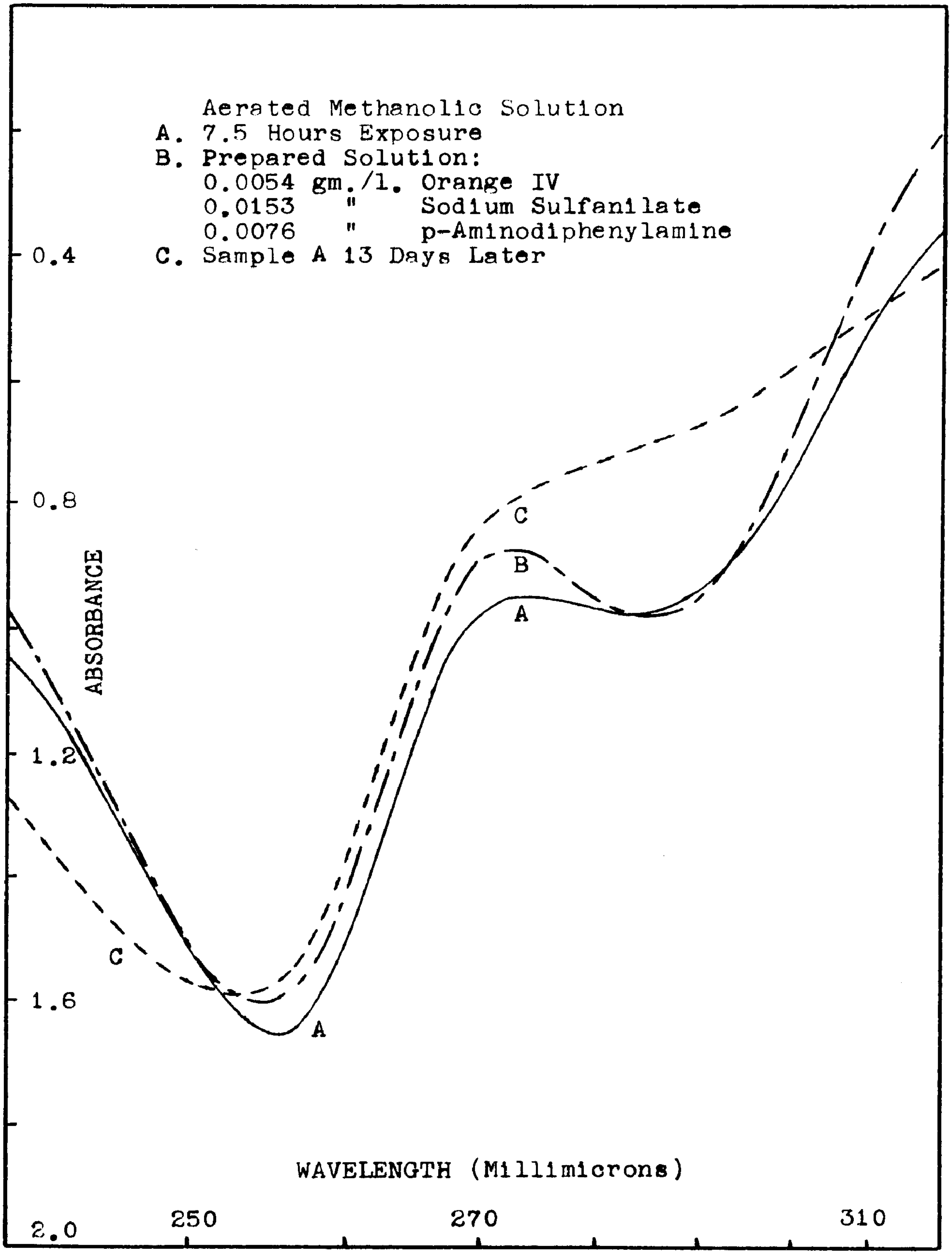


FIGURE 25: Ultraviolet Spectra of Irradiated (7.5 Hours) Methanolic Solution, Aerated

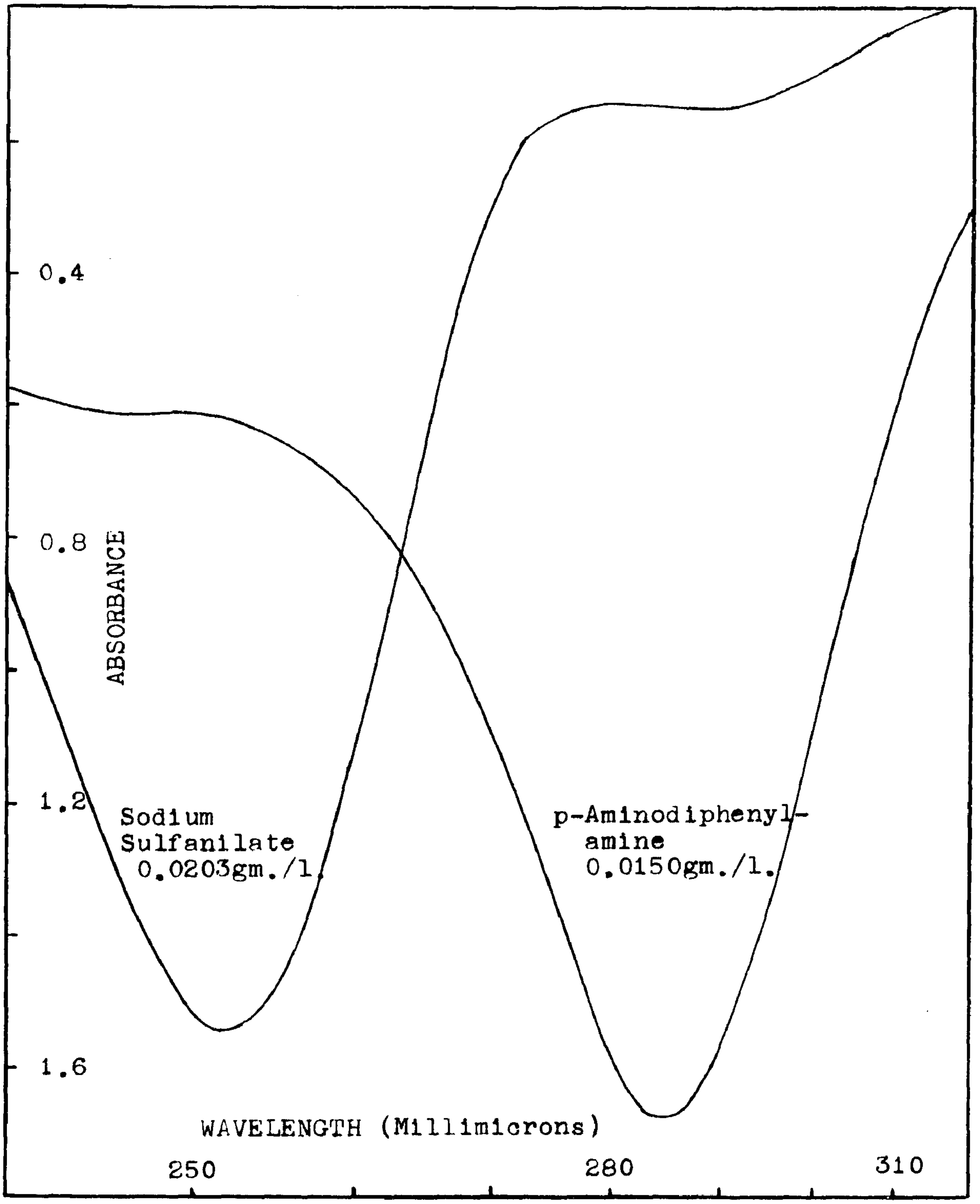


FIGURE 26: Ultraviolet Spectra of Methanolic Solutions of Dye Components

exposed for 7.50 hours was also recorded 13 days later; its ultraviolet spectrum is reproduced in Figure 25. The peak attributed to p-aminodiphenylamine derivatives has disappeared, while that attributed to sodium sulfanilate derivatives has shifted slightly to a lower wavelength.

The product mixtures observed when deaerated methanolic solutions are irradiated differ from those reported with oxygen present. With oxygen absent, the strongest absorption occurs at 287 mμ while a weaker absorption occurs at 255 mμ. The change in the ultraviolet spectrum of the deaerated dye solution with irradiation time is shown in Figure 27. The solution was decolorized in twenty minutes.

The continued irradiation after complete decolorization was also studied. A solution of almost the same initial dye concentration was irradiated for up to eight hours. The ultraviolet spectra of solutions exposed for one and eight hours are shown in Figure 28. The one hour spectrum was of the same shape but of much higher intensity than that of a solution exposed for twenty minutes. After an eight hour irradiation, however, the peak intensity at 287 mμ had decreased considerably. The absorption at 257 mμ had shifted to 253 mμ and the intensity likewise decreased.

The post-irradiation changes can also be observed in the ultraviolet spectra. The ultraviolet spectrum of the deaerated solution exposed for twenty minutes was recorded immediately after exposure and again ten days later. They are reproduced in Figure 29. The intensity of both ab-

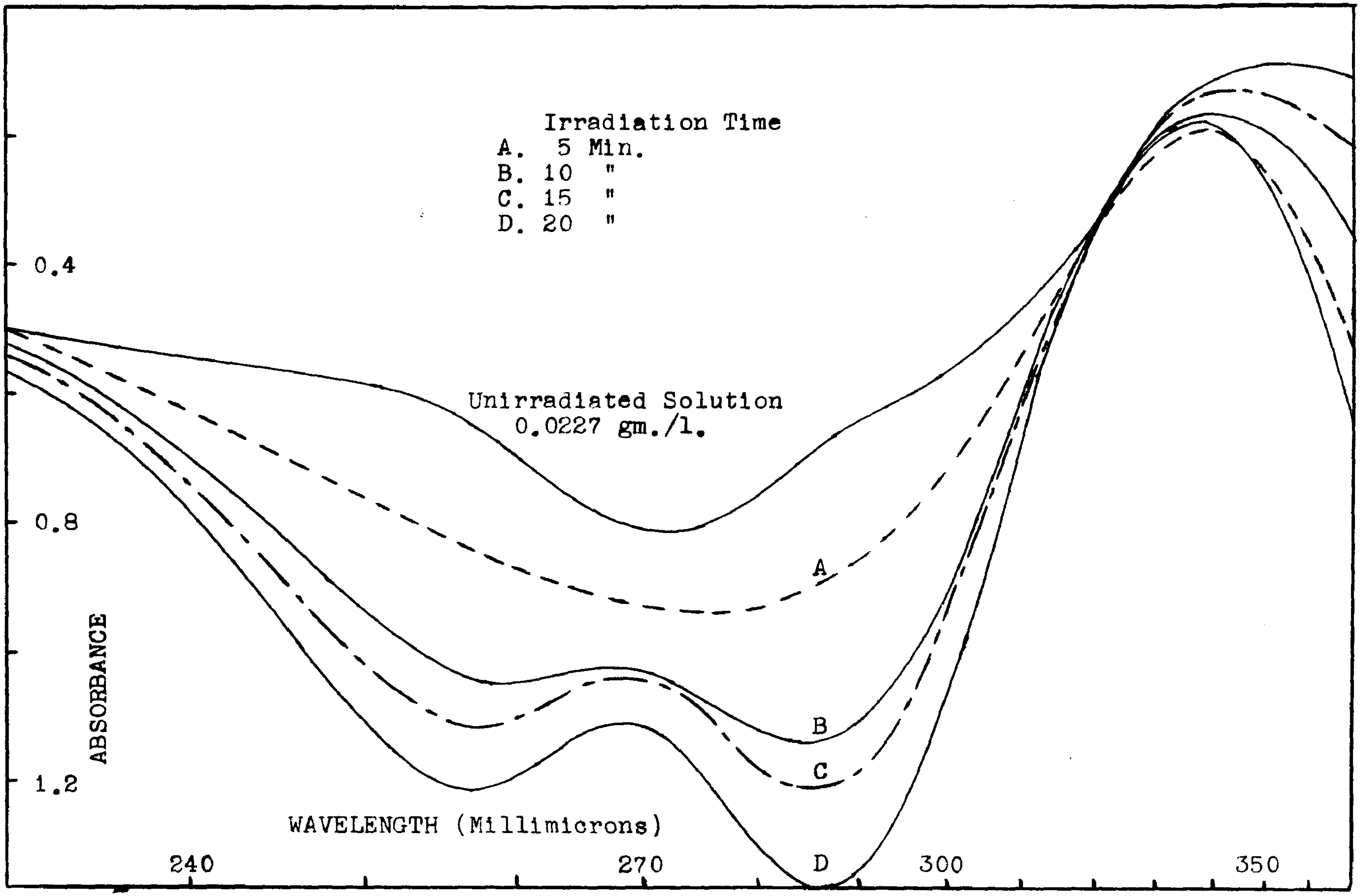


FIGURE 27: Ultraviolet Spectra of Irradiated Methanolic Solution, Deaerated

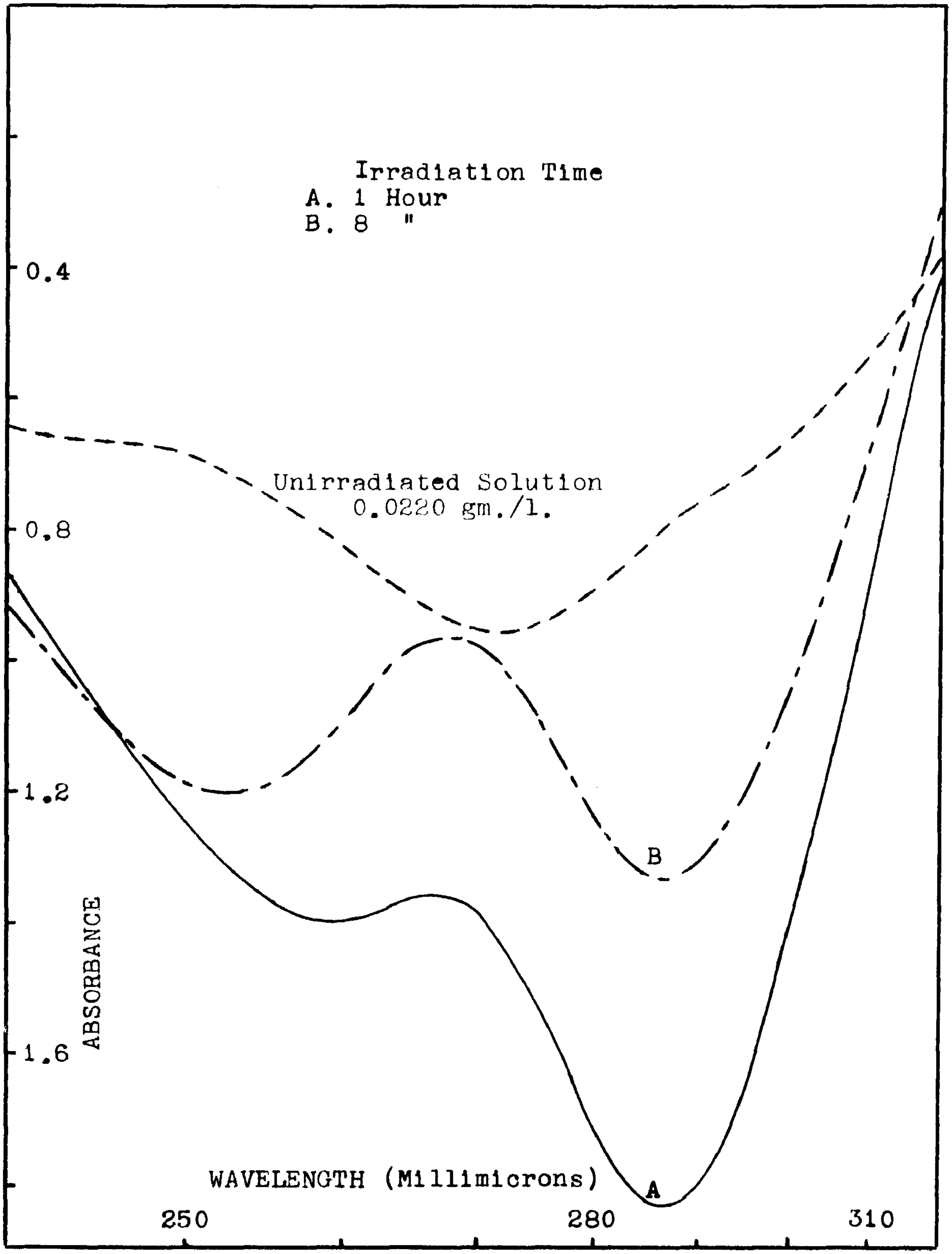


FIGURE 28: Ultraviolet Spectra of Irradiated (1 & 8 Hours) Methanolic Solution, Deaerated

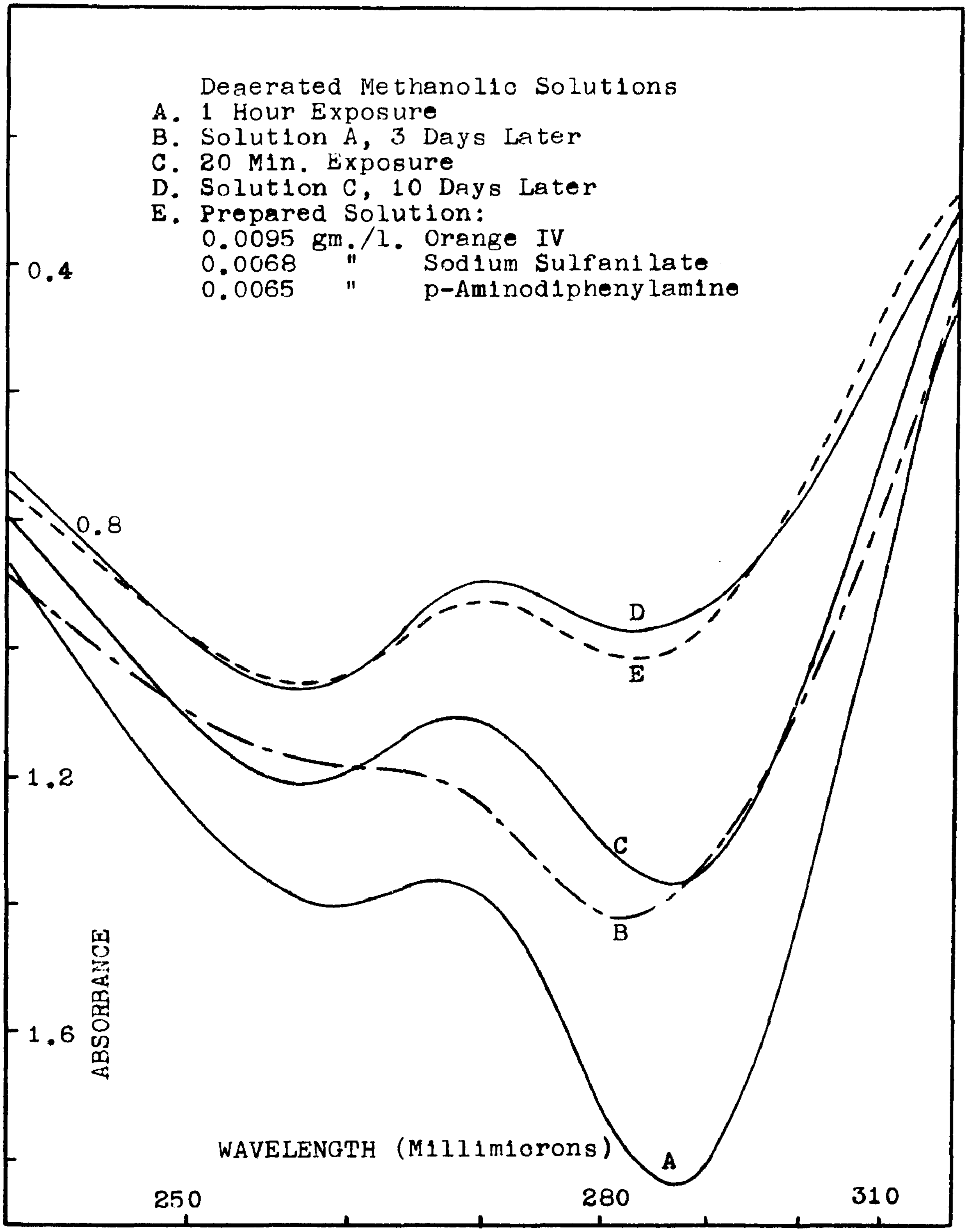


FIGURE 29: Change in Ultraviolet Spectra of Irradiated Methanolic Solutions, Deaerated

sorption peaks has decreased, and the intensity of the peak at 255 mμ then exceeded that at 287 mμ.

The spectrum of the twenty minute exposure after ten days was duplicated and is included in Figure 29. The agreement between the exposed solution and the mixture is very good. The latter solution contained 0.0095 gram/liter of Orange IV, 0.0068 gram/liter of sodium sulfanilate and 0.0065 gram/liter of p-aminodiphenylamine. This concentration of Orange IV was that observed sixty-one days after exposure. Since the initial dye concentration was 0.0227 gram/liter, 0.0132 gram/liter was permanently lost and assumed converted to the sodium sulfanilate and p-aminodiphenylamine derivatives. The concentrations of sodium sulfanilate and p-aminodiphenylamine used in the mixture were calculated from the dye permanently lost. The spectrum of the exposed solution after sixty-one days was not available. The difference should be slight.

Also shown in Figure 29 are the ultraviolet spectra of the deaerated solution irradiated for one hour and recorded immediately and then three days later. The intensity at 255 mμ has decreased and only a shoulder remains. The intensity at 287 mμ has decreased and shifted slightly to a lower wavelength.

5. **Irradiation of Solvent:** A 100 ml. sample of absolute methanol was irradiated for one hour. There was no evidence for product formation in the ultraviolet spectrum immediately after the exposure, or even after standing. A portion of the

irradiated methanol was mixed with an equal volume of a methanolic Orange IV solution and the ultraviolet spectrum was recorded. Again there was no evidence for product formation, even after standing.

6. Irradiation of Solid Orange IV: A sample (0.0108 gram) of the dye contained in a glass tube was irradiated for 17.6 days in the presence of oxygen. Part of this irradiated dye was dissolved in a sample of absolute deaerated methanol which had been irradiated for 3.50 hours. The remainder of the dye was dissolved in absolute methanol. An examination of the visible and ultraviolet spectra of both solutions failed to indicate any changes in the dye. The weight of Orange IV calculated in solution was equal to the original sample, within experimental error.

7. Light Stability of Orange IV in Methanol: Since azo compounds can occur as the <u>cis</u> or <u>trans</u> isomers, the light sensitivity of a methanolic Orange IV solution was investigated. Part of the solution was stored for four hours in a dark drawer while the remainder was exposed to direct sunlight. There was no significant difference between the visible or ultraviolet spectra of the two samples.

8. Thermal Stability of Orange IV in Methanol: There is no means of controlling the temperature in the radiation source. Therefore, the temperature of the dye solutions varies greatly so that it is necessary to know the effect of temperature on

the optical density of the solutions. This was determined by measuring the optical density of a solution as the temperature was raised from 0°C. to 55 °C. A linear relationship was found to exist between temperature and dye concentration. However, the change in concentration was slight — only 0.0007 gram/liter.

The increase in the volume of methanol as the temperature changed from 0°C. to 50°C. was calculated from data found in the literature. This expansion should be about 6.5% which is in good agreement with the concentration change, considering the method used.

9. Addition of Hydrogen Peroxide to Orange IV Solution: The ultraviolet spectrum of a methanolic dye solution was recorded. One drop of 30% hydrogen peroxide solution was added to the approximately 3 ml. sample in the optical cell and the ultraviolet spectrum was again recorded. This latter experiment was also performed with absolute methanol in place of the dye solution.

The spectrum of the dye solution is changed by the addition of hydrogen peroxide. The absorbance increases continually as the wavelength decreases from 300 mµ. This same observation was made when hydrogen peroxide was added to methanol.

10. Radiolysis of Orange I Solutions: All of the previous work has been with Orange IV. The results with another monoazo dye should be analogous. A methanolic solution of Orange I

was prepared containing 0.0218 gram/liter. The samples were deaerated in the usual manner and irradiated. The decolorization curve was similar to that obtained previously with Orange IV. The G-value calculated from the initial slope was -3.60. The dye was partially restored after standing in a dark drawer. The concentration of the sample exposed for ten minutes had increased from 0.0040 gram/liter to 0.0074 gram/liter when measured three days later. The ultraviolet absorption spectra of the irradiated Orange I solutions had absorption maxima at 255 mμ and 340 mμ. The former is attributed to the sodium sulfanilate derivatives and the latter may be due to 4-amino-1-naphthol derivatives which would also be expected from the reduction of the azo linkage.

11. The Occurrence of Naphthalene in Orange IV Solutions: A fresh stock solution of Orange IV in absolute methanol was prepared containing 0.0270 gram/liter. Nitrogen was bubbled through the stock solution for forty-five minutes and a 100 ml. sample was transferred to an exposure vessel. Nitrogen was bubbled through this sample in the vessel for an additional fifteen minutes and the sample was stoppered. The sample was irradiated for one hour, opened, and the optical density measured about five minutes later. The dye concentration had only decreased to 0.0220 gram/liter.

The ultraviolet spectrum of this irradiated solution was recorded two hours after exposure. The irradiated solution was stoppered, stored in a dark drawer, and its spectrum recorded on the following day. This procedure was repeated at intervals until the final recording was made 103 days after exposure. A few of these spectra are shown in Figure 30. A new substance was present which had a strong, characteristic absorption spectrum. Its concentration continued to increase with time.

Attempts to reproduce this strange behavior were unsuccessful. Samples of the same stock solution were exposed for one hour in the same manner. Fresh stock solutions were prepared and irradiated for one hour.

In one attempt to reproduce the strange behavior reported, a fresh bottle of absolute methanol was used to prepare the dye stock solution. The sample was deaerated and irradiated for one hour in the normal manner. Again there was no evidence of strange behavior in the irradiated solution. However, the deaerated sample of the stock solution which had not been exposed possessed the same strange characteristic absorption spectrum as observed previously in the sample exposed for one hour. This unirradiated sample was stored in a dark drawer and its ultraviolet spectrum recorded again at intervals until the final observation 45 days later. The intensity of the absorption spectrum continued to increase with time.

The concentration of this unknown substance was quite large in the unirradiated solution and the odor of the solution suggested naphthalene. The ultraviolet spectrum of naphthalene found in the literature was in good agreement with that observed. Therefore, a solution of naphthalene in metha-

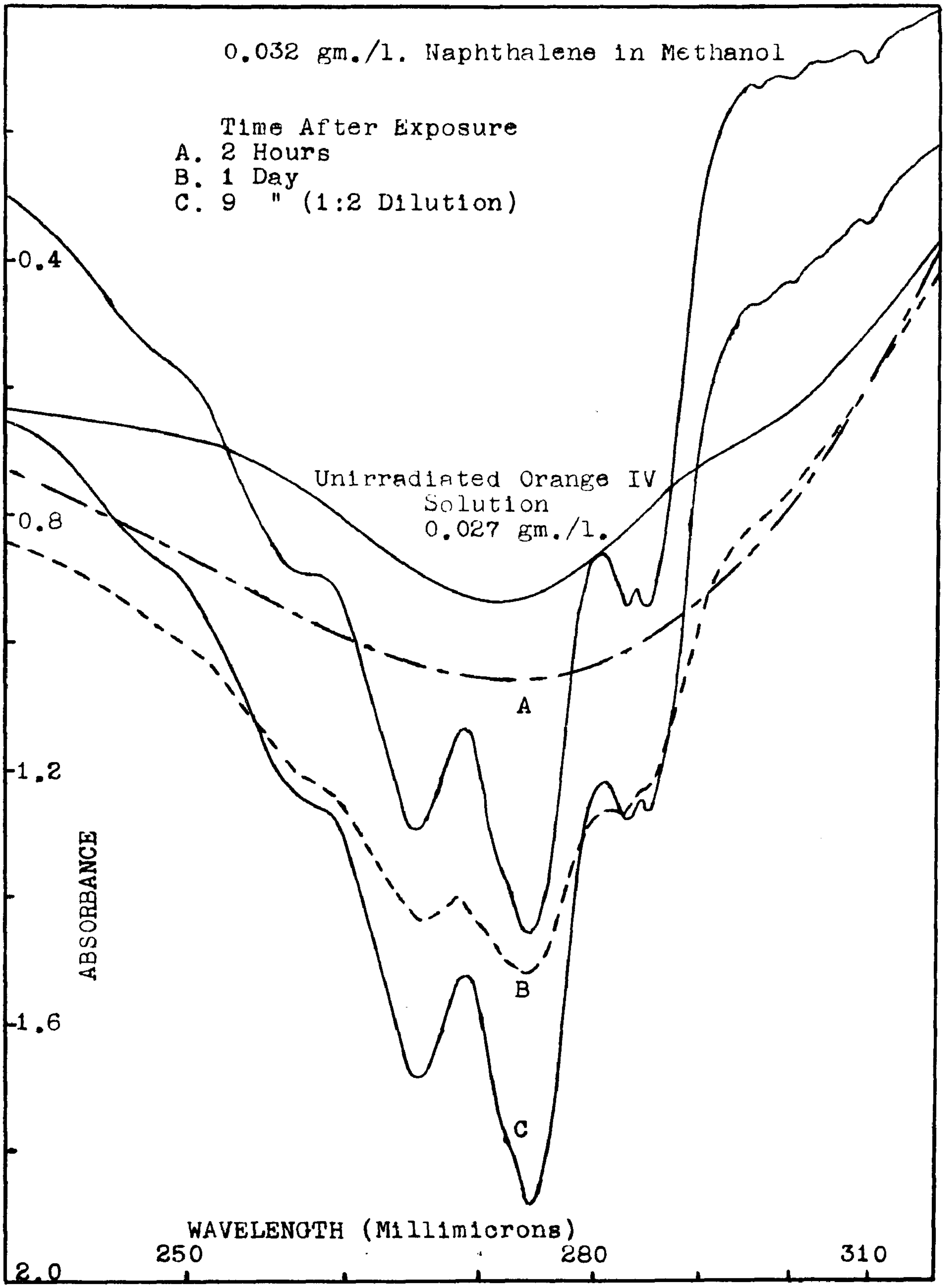


FIGURE 30: Ultraviolet Spectra of Irradiated Methanolic Dye Solution Indicating the Presence of Naphthalene

nol was prepared and its ultraviolet spectrum is included in Figure 30.

C. ETHANOL SOLUTIONS

1. Rate of Decolorization: A stock solution of Orange IV in absolute ethanol was prepared containing 0.0280 gram/liter dye. No attempt was made to exclude oxygen. Samples of 100 ml. were exposed to the source and the optical densities measured immediately after the necessary dilutions. The change in concentration with exposure time is shown in Figure 31. The decolorization proceeds slowly at first, followed by a rapid loss in dye.

A stock solution was prepared containing 0.0136 gram/liter Orange IV in absolute ethanol. Samples were carefully deaerated with dry nitrogen in the normal manner and exposed to the source. Due to the low initial concentration of dye, it was not necessary to dilute the irradiated solutions prior to measurement. They were removed from the source and the optical densities determined within three to five minutes. The change in dye concentration with exposure time is shown in Figure 32.

2. Calculation of G(-Dye): The G-value for deaerated ethanolic solution was calculated from the slope of the decolorization curve in Figure 32. This calculation is given in Table III. It was found that G = -2.76 for this solution.

FIGURE 31

Rate of Decolorization in Ethanolic Solution, Aerated.

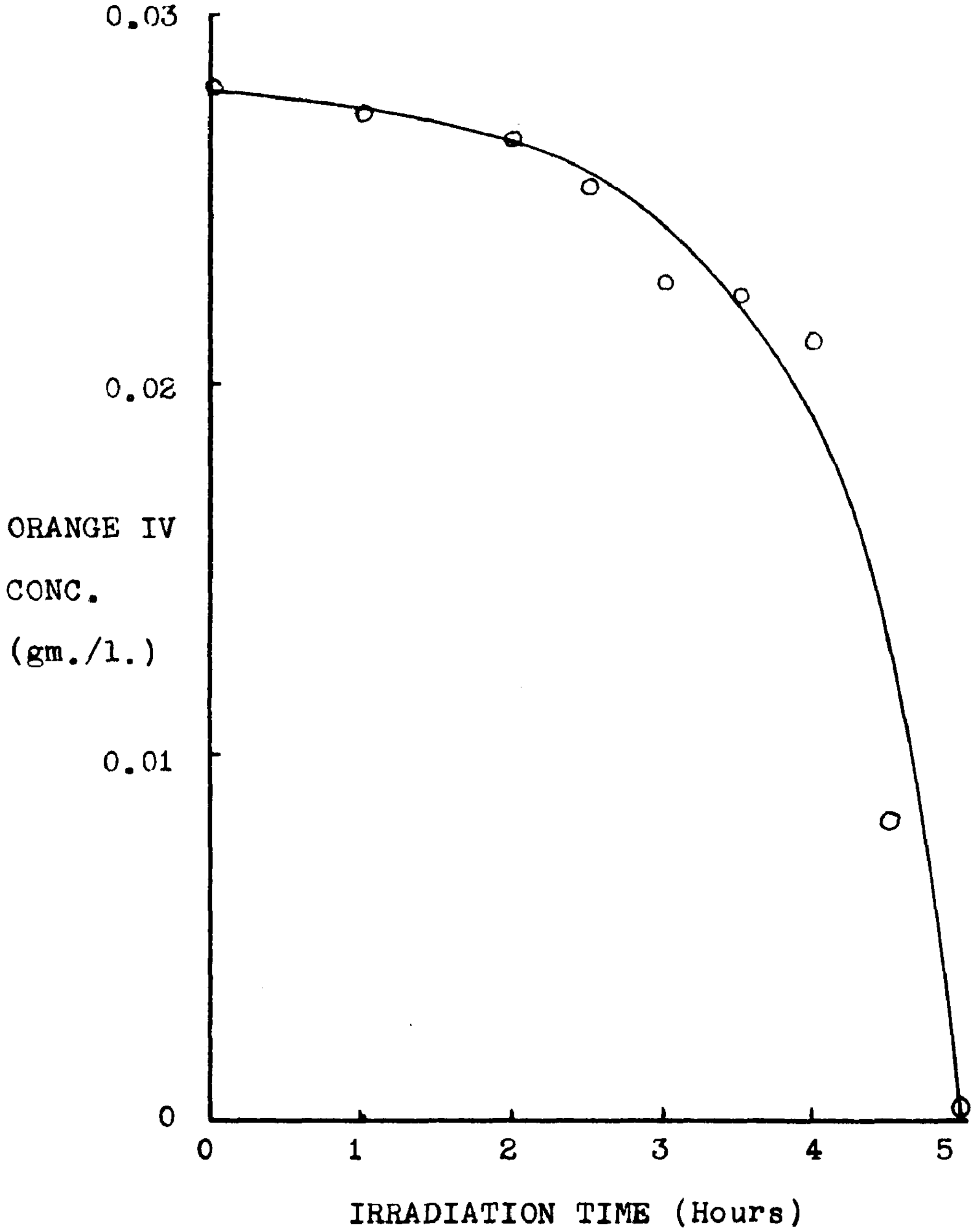


FIGURE 32

Rate of Decolorization in Ethanolic Solution, Deaerated.

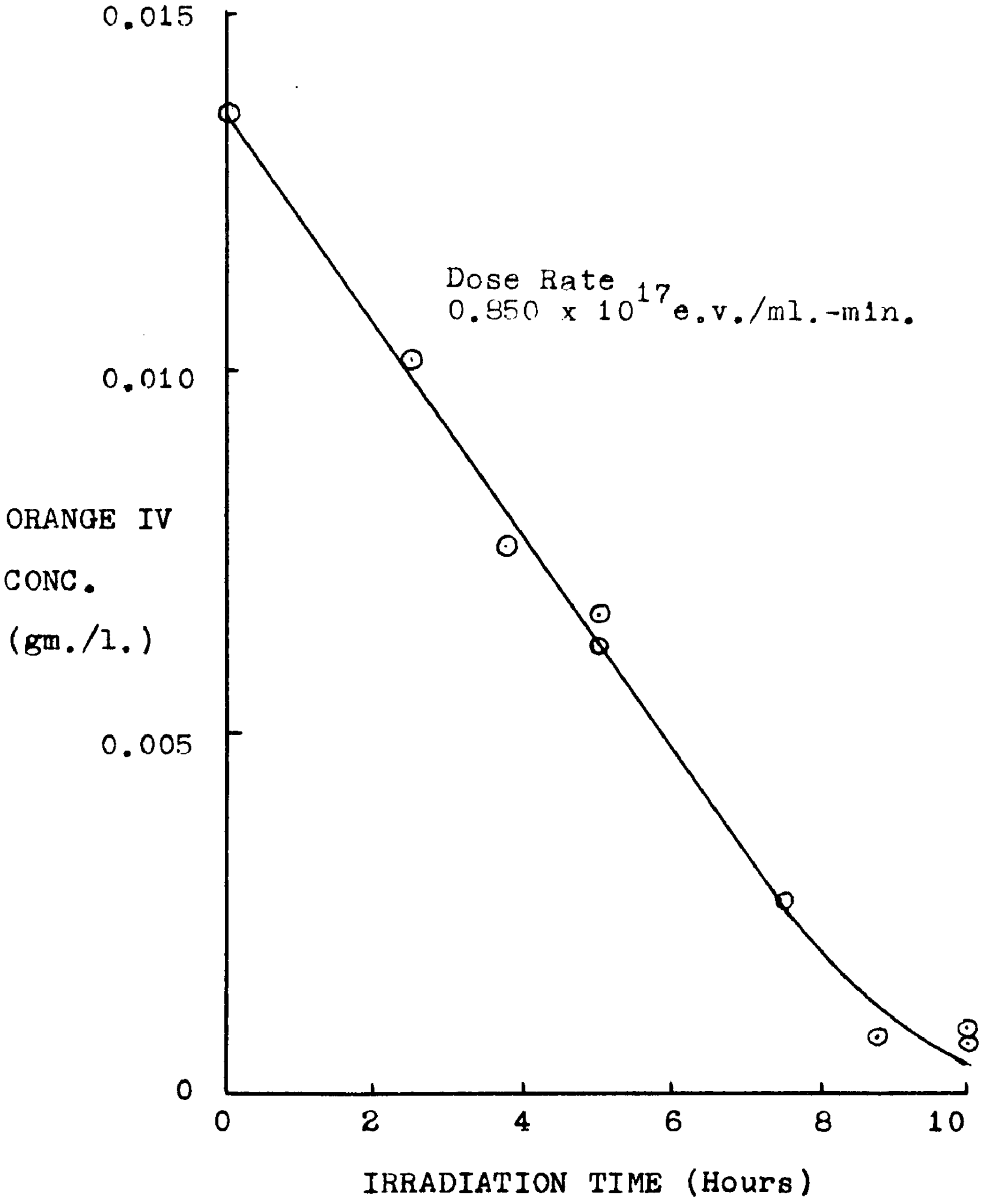


TABLE III

Calculation of G(–Dye) for Deaerated Ethanolic Orange IV Solution

Initial dye concentration: 0.0136 gram/liter

Change in dye concentration: 1.46×10^{-3} gram/liter–min.

Dose–rate: 1.06×10^{17} e.v./gram–min. for Fricke dosimeter

Dose–rate: (1.06×10^{17} e.v./gram–min.) (1.027 gram/ml.) = 1.09×10^{17} e.v./ml.–min.

Dose–rate for ethanol:[11b] (1.09×10^{17} e.v./ml.–min.)(0.780) = 0.850×10^{17} e.v./ml.–min.

$$G(-\text{Dye}) = \frac{1.46 \times 10^{-3}\ \text{gram}}{1\ \text{liter} - \text{min.}} \times \frac{1\ \text{mole}}{375\ \text{grams}} \times \frac{6.02 \times 10^{23}\ \text{mol.}}{1\ \text{mole}} \times \frac{1\ \text{liter}}{10^{3}\ \text{ml.}} \times \frac{1\ \text{ml.-min.}}{0.850 \times 10^{17}\ \text{e.v.}} \times 100$$

$G(-\text{Dye}) = 2.76$

3. Post-irradiation Effect: Irradiated ethanolic solutions which had been deaerated behaved in a manner similar to the methanolic solutions. The reaction appeared to be reversed when the solutions were removed from the source and observed, the rate being similar to that noted in Figure 19.

The original dye is almost completely restored when the irradiated solutions were allowed sufficient time. Solutions exposed for five and ten minutes were observed nine days later. Their visible spectra are reproduced in Figure 33. This indicates about 90% recovery for the solution exposed for five minutes. The spectrum for each irradiated solution is obviously that of Orange IV.

4. Product Formation: The ultraviolet spectra of the irradiated ethanolic solutions which had been deaerated are similar to those observed when the solvent was methanol. The spectra of solutions exposed for 5.0, 7.5 and 10.0 minutes are shown in Figure 34. The characteristic peaks at 287 mμ and 255 mμ are again present.

Also included in the same figure is the spectrum of the sample exposed for 10 minutes and recorded nine days later. It differs slightly from the spectrum of the dye stock solution.

5. Light Stability of Orange IV Solutions in Ethanol: It had been noted that the optical density of ethanolic Orange IV solutions seemed dependent on the light intensity. This was substantiated in the following manner. A fresh solution

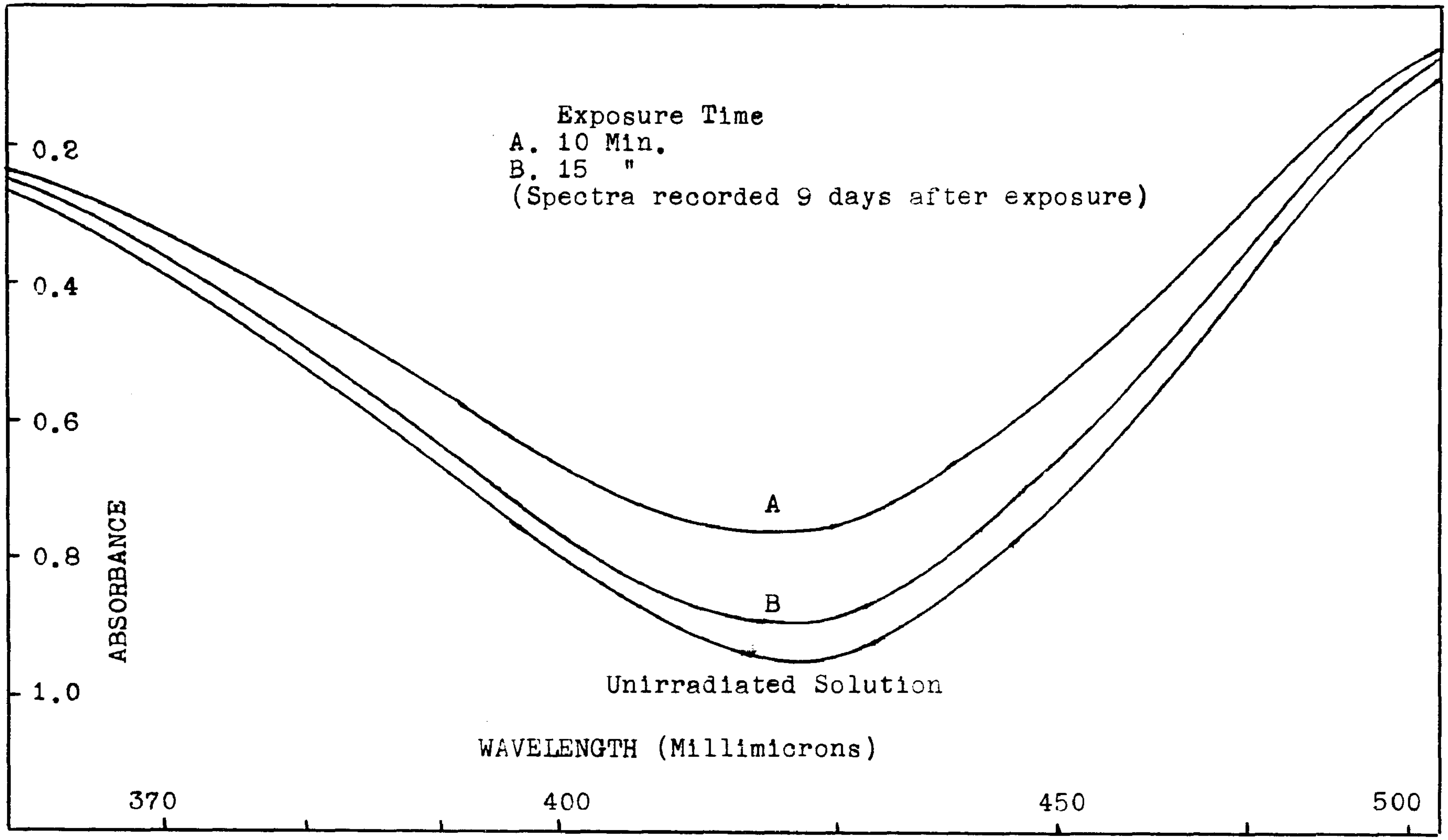


FIGURE 33: Change in Visible Spectra in Ethanolic Solution, Deaerated

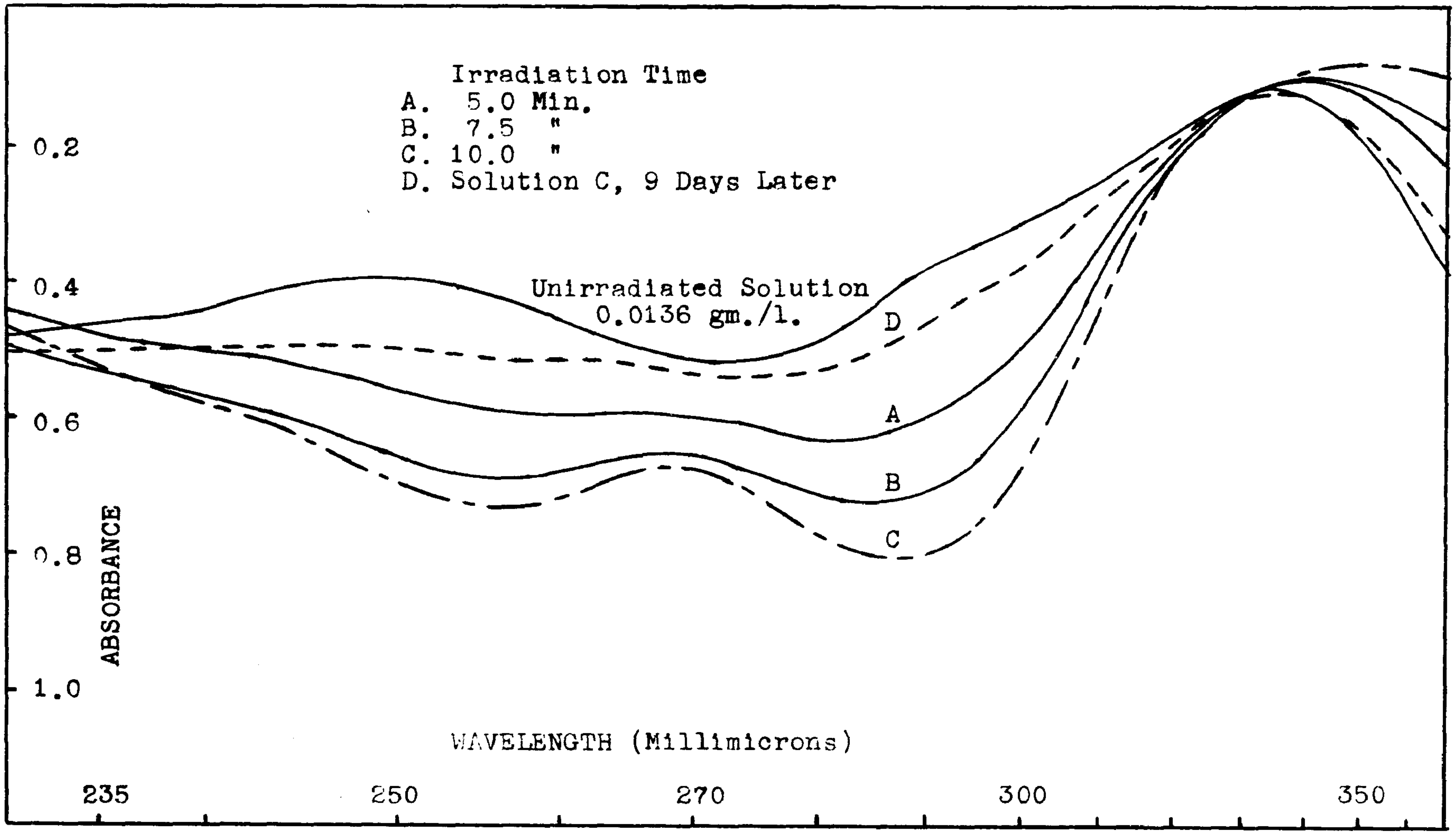


FIGURE 34: Ultraviolet Spectra of Irradiated Ethanolic Solutions, Deaerated

was prepared and divided into two portions. One sample was stored in a dark cabinet for two hours while the other was placed in the sunlight next to a window for two hours. The laboratory was darkened while the first sample was placed in the cell compartment of the "Spectracord". The visible spectrum of the solution was recorded and the optical density at 420 mμ was 1.26. The spectrum of the sample placed in the sunlight was recorded and the optical density at the same wavelength was only 0.76. This sample was allowed to remain in the dark cell compartment of the "Spectracord" for ten minutes and its spectrum was again recorded. The optical density has increased to 1.02. These spectra are reproduced in Figure 35.

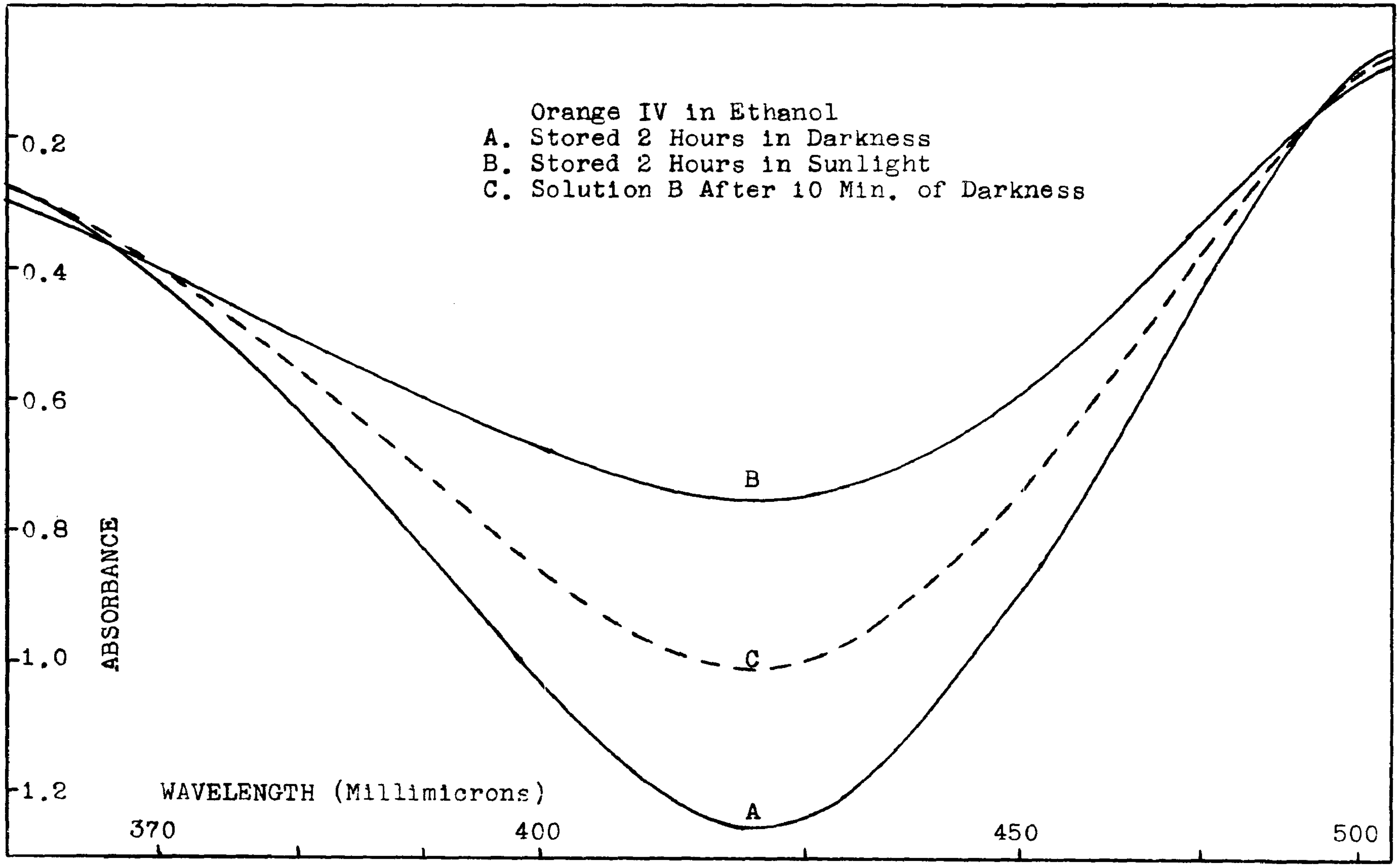


FIGURE 35: Light Sensitivity of Orange IV in Ethanol

DISCUSSION

The decolorization reaction is attributed to the highly reactive free radicals formed from the solvent by the gamma radiation. The dye molecule acts as a free radical scavenger and is susceptible to attack at the three aromatic rings, the amine or the azo linkages. The addition of free radicals to any of these positions will result in interruption of the resonance system with a resulting change in the light absorption properties of the molecule. The reaction is followed by measuring the light absorption of the irradiated dye solutions.

The destruction of Orange IV in aqueous solutions begins immediately upon exposure to the gamma radiation. The initial rate of the decolorization reaction is dependent upon the dose-rate of the source and the presence of oxygen in the solution.

In the deaerated aqueous solutions, the hydrogen atom and the hydroxyl radical are present during irradiation. They both should attack the dye molecule (D).

(1) $D + \cdot H \longrightarrow \dot{D}H$ (Reduction)

(2) $D + \cdot OH \longrightarrow \dot{D}OH$ (Oxidation)

These initial dye-radical products would be expected to be unstable in the presence of other free radicals and the following reactions are likely.

(3) $\dot{D}H + \cdot H \longrightarrow \dot{D}H_2$

(4) $\dot{D}OH + \cdot OH \longrightarrow D(OH)_2$

Due to the size and degree of unsaturation of the dye molecule, it is assumed that these products are also capable of further radical addition reactions. This is apparent from the decolorization curve which has a continuously decreasing rate of decolorization after the first thirty minutes, indicating that there is competition with the dye for the radicals.

Another reaction which has been postulated previously which helps to explain the low yields is:

(5) $\dot{D}H + \cdot OH \longrightarrow D + H_2O$

(6) $DH_2 + \cdot OH \longrightarrow \dot{D}H + H_2O$

Some general rules have been given[12] regarding the reactivity of hydrogen atoms and hydroxyl radicals in aqueous solutions. It was stated that hydrogen atoms add readily to oxygen and nitrogen atoms but less easily to carbon atoms, and that hydroxyl radicals do not add to oxygen atoms, probably not to nitrogen atoms, but very readily add to carbon atoms. Therefore, one whould expect the azo and amine linkages to be attacked by hydrogen atoms while the benzene rings should be susceptible to hydroxyl radicals.

When oxygen is present in the dye solutions during irradiation, it acts as a scavenger for hydrogen atoms. Oxygen has a strong affinity for hydrogen atoms, and the ratio of oxygen to dye molecules is 3.5:1 at the start of the exposure.

(7) $H\cdot + O_2 \longrightarrow HO_2\cdot$

Therefore, the highly reactive species in these solutions are hydroxyl and hydroperoxyl radicals, so that only oxidation reaction (2) and (8) should occur.

$$(8) \quad D + HO_2\cdot \longrightarrow \dot{D}O_2H$$

The concentration of oxygen present in the dye solution was estimated to be 2.34×10^{-4} mole/liter.[13] Assuming 100% efficiency of the oxygen scavenger for hydrogen and G(H) = 2.78, it was calculated that the oxygen concentration reached zero after 48 minutes of irradiation when the dose-rate was 1.04×10^{17} e.v./ml. -min., and after 34 minutes when the dose-rate was 1.49×10^{17} e.v./ml. -min. There is no apparent change in the decolorization curves at these two points even though the hydroperoxyl radical is believed to be replaced by hydrogen atoms as one of the attacking species.

At the lower dose-rate, the two decolorization curves are linear for approximately the first thirty minutes. There is a very slight difference in the intial rates (6.22×10^{-7} and 7.35×10^{-7} mole/l.-min.) due to the oxygen which results in the observed increase. Therefore, reactions (7) and (8) combined must proceed more rapidly than (1).

In the solutions containing oxygen, the dose-rate affects the rate of decolorization significantly, increasing the initial rate from 7.35×10^{-7} to 13.2×10^{-7} mole/l.-min. when the dose-rate increased from 1.04×10^{17} to 1.49×10^{17} e.v./ml.-min. This rate increase is about 40% greater than that expected from the different dose-rate. Such dose-rate effects are usually attributed to interference of the solute with the radical recombination reactions, so that more efficient use is made of the radicals formed initially.

The G-value increased from -0.43 to -0.53 by raising the dose-rate in the presence of oxygen, while G = -0.37 in the absence of oxygen with the lower dose-rate. These values seem rather low since G(H) = 2.78 and G(OH) = 2.28[9c] in water exposed to Cobalt-60 gamma raidation. Thus, in the absence of oxygen, about fourteen radicals would be required for each dye molecule decolorized while approximately twelve radicals would be necessary with oxygen present at the same dose-rate. This is certainly unreasonable and indicates that reactions such as (5) and (6) are occurring and thus decreasing the efficiency of the decolorization reaction.

The G-values reported for methylene blue in deaerated aqueous solutions vary from 1.3 to 2.0, and from 0.1 to 1.1 in the presence of oxygen.[14] In this case the oxygen appears to protect the dye. It was observed that oxygen increased the rate of decoloration in aqueous chlorphenol red solutions.[5] For this dye, G = -0.81 in deaerated solutions. The structure of the dye obviously determines its reactivity and the ease with which it may be decolorized. The presence of oxygen in solution can greatly influence the results, and its behavior depends upon the system under study.

The decrease in dye concentration after exposure in the solutions containing oxygen is attributed to further oxidation of the dye by the hydrogen peroxide formed during irradiation. The initial concentration of 0.0248 gram/liter of Orange IV had decreased to 0.0108 gram/liter after a forty minute exposure. An addition loss of 0.0017 gram/liter was observed upon standing. With $G(H_2O_2) = 0.67$, the concentration of hydrogen peroxide formed during the forty minute exposure at the dose-rate used is 40×10^{18} molecules/liter. This is more than adequate to account for the 2.8×10^{18} molecules/liter of dye lost. Much of the hydrogen peroxide apparently reacts further with the decolorized dye.

In the deaerated solutions, no significant changes were observed after brief exposures. This may be due to competition between oxidation of the dye and oxidation of the reduced dye by the hydrogen peroxide. Thus, the net change appears to be zero. After long exposures, however, the dye concentration is low compared to the reduced dye concentration so that the hydrogen peroxide probably oxidizes the latter and a reverse reaction is observed.

The dye oxidation products resulting from hydroxyl and hydroperoxyl radical attack when oxygen is present are undoubtedly complex and a study of the spectra of these solutions was of no value. In the deaerated solutions where both reduction and oxidation occur, a different product mixture is present. The intensity of absorption in the 270 mμ region is maintained for at least the first three hours, and the absorption at lower wavelengths is increased. This difference in products is attributed to the different behavior of hydrogen atoms and hydroperoxyl radicals. According to the rules mentioned, the former should add to the amine or azo linkages while the hydroperoxyl radicals should behave similarly to the hydroxyl radicals and add to the aromatic rings. Unfortunately the spectra are not helpful in identifying the products.

The strange behavior observed for two of the deaerated solutions is not understood. Apparently products were formed which absorb at 250 mμ, but the conditions necessary for their formation are not known. This absorption is suggestive of sodium sulfanilate which would result from the reduction of the azo linkage.

The yields of the free radicals formed when methanol is exposed to Cobalt-60 gamma radiation are reported as follows:[10b] $G(H) = 2.55$, $G(CH_2OH) = 2.75$, $G(CH_3) = 0.40$ and $G(OH) = 0.60$. The additions of these free radicals to the dye molecule have been observed with more success than the reactions in aqueous solutions.

The rapid decolorization reaction in methanolic solutions containing oxygen is preceded by an induction period. The inhibition caused by the oxygen may be due to the following type reaction.

$$(9) \quad \phi NH - HN\phi + O_2 \longrightarrow \phi N = N\phi + H_2O_2$$

This reaction of hydrazobenzene in ethanol, propanol or benzene is practically quantitative and was patented as a direct preparation of hydrogen peroxide.[15] It proceeds readily by bubbling oxygen through the hydrazobenzene solutions at room temperature.

It may be assumed that most of the radical additions to Orange IV occur at the azo linkage.

$$(10) \quad R_1N = NR_2 + R_3\cdot + R_4\cdot \longrightarrow R_1NR_3 - R_4NR_2$$

This reaction could then be followed rapidly by:

$$(11) \quad R_1NR_3 - R_4NR_2 + O_2 \longrightarrow R_1N = NR_2 + R_3OOR_4$$

The dye is, therefore, reformed and the product R_3OOR_4 may be hydrogen peroxide or a substituted peroxide, depending upon the radicals participating in reaction (10).

If the preceding theory is correct, the number of radicals formed during the seven hour induction period should be twice the number of oxygen molecules dissolved in the methanol. For a dose-rate of 0.908×10^{17} e.v./ml.-min. in methanol and assuming $G(R) = 6.3$, 2.4×10^{20} radicals would be produced in 100 ml. during a seven hour period. The Ostwald absorption coefficient for oxygen in methanol at 25°C. was calculated from data available[16] ($\lambda = 0.254$). With air at standard conditions containing 3.0×10^{-4} gram/cc of oxygen, there would be 1.4×10^{20} molecules of oxygen present in 100 ml. of methanol. This is slightly more than half the number of radicals formed and represents good agreement with this inhibition theory.

It is also possible that the inhibition effect of the oxygen could be caused by oxygen scavenging the radicals, followed by the addition of the oxygen containing radicals to the dye.

$$(12) \quad R\cdot + O_2 \longrightarrow RO_2\cdot$$

$$(13) \quad D + RO_2\cdot \longrightarrow \dot{D}O_2R$$

The slow decolorization could be due to a low rate of reaction (13) or to a low efficiency of decolorization. However, according to this reaction scheme the oxygen would be consumed in about half the induction period. If the peroxyl radical reacts with another solvent radical rather than the dye molecule, the seven hour induction period would be observed.

$$(14)\quad R\cdot \; + \; RO_2. \longrightarrow RO_2R$$

Since the ratio of oxygen to dye molecules is 33:1, it appears that the solvent radicals would react with the oxygen, rather than the dye molecules. Thus, this inhibition theory appears to be more likely. The small loss in dye during the induction period may be caused by addition of some radicals or by reaction with the peroxides.

The length of the induction period is also dependent upon the dose-rate. The ratio of induction periods (1.2:1) equals the ratio of dose-rates for the two experiments.

When the free oxygen has been consumed, the decolorization proceeds rapidly. Only about 10% of the dye had been destroyed during the seven hour induction period, apparently due to radical attacks other than at the azo linkage or to the reaction of the peroxides from (11) with the dye. The dye remaining after the induction period was destroyed within one hour. The ratio of radicals formed to dye molecules destroyed is 10:1 during this hour. The reason for the low efficiency of this reaction is perhaps the difficulty of performing a reduction in the presence of the peroxides. Also it is assumed that the decolorized dye products will compete for the radicals. The hydrazo derivatives may be reduced further to the amine derivatives.

The decolorization reaction proceeds immediately when deaerated solutions are exposed to the source. At an initial dye concentration of 0.0227 gram/liter, the ratio of radicals formed to dye molecules decolorized is 2.42:1. This suggests that all of the dye molecules decolorized have been reduced to the hydrazo form and that 20% of these have been further reduced to the amine compounds. This assumes that all of the radical attacks have been at the azo linkage and may not be valid.

At an initial concentration of 0.0136 gram/liter of dye, the ratio of radicals to dye molecules decolorized is 2.93:1. The decolorization process is less efficient at lower dye concentrations.

The decolorization rates of both solutions begin to decrease after ten minutes of exposure. This is probably due to competition of the decolorized product with the dye for the radicals.

The G-value for the solution containing oxygen initially (1.28) was about half the value (2.67) for the deaerated solution with essentially the same dye concentration prior to the rapid decolorization process. It was expected that the decolorization yields would be the same after the consumption of the oxygen. However, the peroxide concentration undoubtedly is responsible for the low yield observed.

The G-value dropped from 2.67 to 2.10 in deaerated solutions when the initial dye concentration was lowered to 60% of the original value.

It has been observed that decolorized solutions which originally contained oxygen can have some of the dye reformed if the solution is allowed to stand unopened after exposure. This may be due to an oxidation of some of the reduced hydrazo compound by the peroxides present. When these solutions are exposed to the air, a slow reaction occurs in which the product also absorbs in the visible region. The nature of this product is not known.

When deaerated solutions are opened to the air after exposure, much of the Orange IV is reformed. Since there are no peroxides present in the deaerated solutions after irradiation, the reformation of the dye is attributed to reaction (11). The rate of the oxidation of the hydrazo compound should be partly dependent upon the diffusion of oxygen into the solution. It is also possible that the peroxides formed in the reverse reaction are responsible for some of the oxidation.

If it is assumed that the final data observed in Figure 17 indicates that all of the hydrazo compound has been oxidized to Orange IV, then perhaps the dye permanently lost had been completely reduced to the amine derivatives during irradiation. This possibility was investigated in the following manner.

The ten minute exposure was chosen for study. After irradiation the dye concentration had decreased by 0.0147 gram/liter. When observed two months later, the concentration had increased by 0.0080 gram/liter when corrected for evaporation. Thus, 55% of the dye loss was temporary and is, therefore, attributed to the hydrazo compound. Since 2.36 x 10^{18} dye molecules were lost , 4.24 x 10^{18} radicals would be necessary to reduce 45% of the azo linkages completely, and 2.60 x 10^{18} radicals would be required to convert the remaining dye to the hydrazo compound. It has been calculated that 5.72 x 10^{18} radicals would be formed during the ten minute exposure, but 6.84 x 10^{18} radicals would be required if the proposed reaction scheme is correct. Therefore, it appears that less than 45% of the lost dye is reduced completely at the azo linkage.

The agreement is better when the twenty minute exposure is considered, at which time the dye is essentially completely decolorized. The temporary loss attributed to hydrazo formation was 42%, with the remainder assumed to be due to the completely reduced azo linkage. This assumption would require the addition of 11.50 x 10^{18} radicals while 11.44 x 10^{18} radicals would be formed during the twenty minute irradiation.

It has been observed that exposure to air of the deaerated dye solutions after irradiation results in the rapid reformation of the dye during the first hour after which the oxidation proceeds more slowly. The reformation of the dye was controlled by limiting the air exposure. Since this reverse reaction was believed to be due to oxygen exposure, the rate of oxidation should increase if oxygen was bubbled through the solution. This was observed in Figure 20. A similar experiment was also performed during which the dye concentration appeared constant during the addition of oxygen (Figure 21). However, this observation is regarded lightly on the basis of the other findings.

The reformation of Orange IV in these solutions upon exposure to the air is, therefore, attributed to the oxidation of the hydrazo compounds by oxygen as illustrated in (11). The rate at which the reverse reaction proceeds must be partly controlled by the rate at which oxygen diffuses into the solution. Some of the oxidation may also be due to the peroxides formed in (11).

The strange behavior observed in the sample exposed for fifteen minutes in Figure 13 remains unexplained. This sample appeared normal when observed within an hour after exposure, and finally 97 days later. However, an unknown product was present when the sample was examined 9 and 56 days after exposure. This product had an unusually high extinction coefficient in the visible region. Perhaps the product is an intermediate between the hydrazo compound and the azo dye. It has not been observed in any other solutions, however.

The ultraviolet spectra of the irradiated solutions which contained oxygen initially indicate the presence of the products expected from the reduction of the azo linkage to the amines. The spectrum of the solution exposed for 7.50

hours was duplicated with a mixture of sodium sulfanilate, p-aminodiphenylamine and Orange IV. However, the concentrations used in the mixture do not agree well with the calculated concentrations. The amount of the sulfanilate compound used in the mixture is more than twice that calculated from the dye lost. The concentration of the p-aminodiphenylamine in the mixture was only about 10% greater than that expected.

The poor agreement observed is probably due to an over-simplification of the actual reaction. The presence of the hydrazo compound and its absorption in this region has been neglected. It has been assumed that only the azo linkage is attacked by the free radicals and that the mixture of amines resulting may be duplicated spectroscopically by sodium sulfanilate and p-aminodiphenylamine. The possible reactions of the peroxides formed during the induction period have been neglected.

The spectrum of the solution exposed for 7.50 hours was observed to change upon standing. The peak attributed to the p-aminodiphenylamine derivatives disappeared. Apparently, this compound is unstable in the presence of peroxides.

The peak intensities observed for the solutions irradiated in the absence of oxygen are the reverse of those obtained when the solutions were not deaerated prior to exposure. It was also observed that the G-value found for the solution containing oxygen initially was about half the value for the deaerated solution (initial dye concentrations and dose-rate were equal). Therefore, it appears that different reactions occur in these two systems. The effect of the large concentration of peroxides formed during the induction period is not known, but is probably responsible for the difference in behavior.

The amines expected from the reduction of the azo linkage appear to be present in the spectrum of the deaerated solution exposed for ten minutes, and their concentrations increase with exposure time. It is not known at what point the absorption reaches a maximum. This may occur before, at, or after the one hour exposure whose spectrum was recorded. The spectrum of the sample irradiated for eight hours indicates that much of the p-aminodiphenylamine derivative has been destroyed by further radical additions. The same observation was made for the derivatives of the sulfanilic acid.

The destruction of the p-aminodiphenylamine derivatives may occur by radical attacks upon the amine linkage. The products expected would be derivatives of p-phenylenediamine and benzene. No evidence for the presence of these products has been observed.

The spectroscopic duplication of the solution decolorized in twenty minutes and allowed to reach equilibrium confirms the proposed theory that the free radicals formed from the methanol add almost completely to the azo linkage. The decolorization is attributed to the hydrazo compound formation. These hydrazo derivatives compete with the dye molecules for additional radicals and are reduced further to the derivatives of sodium sulfanilate and p-aminodiphenylamine. The hydrazo derivatives are converted back to the azo dye structure via reaction (11) when oxygen is admitted to the solution.

The theory that the radicals add essentially completely to the azo linkage is in agreement with the conclusions of Cropper:[2c] "If a preferred site is present, the radical may attack almost entirely at this point and the yield is high for that reaction. If a preferred site is not present, a reaction will, nevertheless, take place, but the radical is much less discriminating and less efficient in its attack, and the yield is lower."

The mixture of amines obtained is obviously complex since there are four different attacking radicals. Each of the two molecular fragments can theoretically exist as ten different compounds. However, since 84% of the radicals are either hydrogen atoms or methylol radicals, at least this proportion of each molecular fragment will exist as three compounds. If the additions of hydrogen atoms and methylol radicals are random, then almost one-third of the proportion will be a primary amine.

The use of sodium sulfanilate and p-aminodiphenylamine to spectroscopically duplicate the irradiated solutions is obviously an approximation. However, the agreement obtained is quite good. The derivatives of these two compounds which are present apparently are similar spectroscopically.

The irradiation of pure methanol and subsequent recording of the ultraviolet spectrum showed that the amounts of formaldehyde and ethylene glycol formed in one hour are insufficient to be detected. Thus, their absorption will not interfere with the spectra of the dye solutions. It has also been illustrated that these products do not interact with Orange IV.

Since the maximum dye concentration used was about 7×10^{-5} molar, the interaction of the dye molecules with the gamma radiation is negligible. Even when solid Orange IV was exposed for a long period and dissolved in methanol, there was no evidence of change in the dye.

The *cis-trans* equilibrium of Orange IV in methanol appeared stable under the conditions used. This greatly facilitated working with these solutions.

The change in optical density of a methanolic solution of Orange IV with temperature is very small over a wide temperature range. The variation appears to be due to the change in the volume of methanol with temperature.

The addition of hydrogen peroxide to methanol results in oxidation and a resulting absorption in the ultraviolet region which increases at lower wavelengths. However, the concentration of the peroxides formed in reaction (11) can be no greater than the dye concentration and is, therefore, very small.

An induction period was also observed for ethanolic solutions that initially contained oxygen. This inhibition is again attributed to the reaction of oxygen with the solvent radicals.

When the oxygen was removed, the decolorization proceeded immediately as a function of radiation time. It is assumed that the reactions are analogous to those postulated in methanol. The decolorization process is attributed to the formation of the hydrazo derivatives, followed by further reduction of these to the amine derivatives of sodium sulfanilate and p-aminodiphenylamine. The G-value of -2.76 is similar to the values in methanol.

Most of the dye was restored upon standing after exposure. Only about 10% of the hydrazo form was totally reduced to the amine derivatives in the five minute irradiation.

The ultraviolet spectra of the irradiated solutions are similar to those observed in methanol solutions. This substantiates the belief that the same type of reactions are induced in ethanol as were observed in methanol. The derivatives formed will differ slightly due to the difference in the free radicals obtained.

The *cis-trans* equilibrium of Orange IV in ethanolic solutions is greatly influenced by light. The low energy form or *trans* isomer is stable in the dark while the high energy form or *cis* isomer is formed by exposure to the light. The extinction coefficients of these isomers are quite different, that of the *trans* isomer being the maximum. This sensitivity to light increased the probability of error in measuring dye concentrations in ethanol.

The appearance of naphthalene in the irradiated solution was indeed surprising. The formation of a ten-membered conjugated ring from a structure containing only six-membered rings and with methanol as a solvent presents a challenge even for a gifted synthetic chemist. The increase in napthalene concentration even after removal from the source and storage in a dark drawer served to further unnerve the observer. It was realized that gamma radiation is certainly a powerful tool, capable of performing rare feats. However, a conceivable mechanism was not within the author's grasp.

Fortunately, the second appearance of the strange ultraviolet spectrum occurred in a solution which had not been irradiated. This led to suspicion of foul play. The discovery of a container of naphthalene nearby led to the conclusion that this had been added to both solutions by a person of questionable intentions. The increasing concentrations are attributed to solvent loss through the cork stoppers.

SUMMARY

The decolorization of deaerated aqueous solutions of Orange IV is the result of hydrogen atom and hydroxyl radical attacks. The hydrogen atoms are believed to add to the azo or amine nitrogen atoms and the hydroxyl radicals probably add to the aromatic carbon atoms. The decolorization, when oxygen is present initially, is attributed to hydroxyl and hydroperoxyl radical additions until the oxygen is consumed.

The products resulting are apparently complex and their spectra do not furnish any useful information. However, two deaerated solutions exposed for one hour had weak peaks in the region where sodium sulfanilate absorbs. Thus, some reduction of the azo linkage may occur, although these two solutions appear to be abnormal in relation to the other deaerated solutions.

The yields of these decolorization reactions in water are very low compared to the yields of hydrogen atoms and hydroxyl radicals formed. It was estimated that ten to fourteen radicals are required for each dye molecule decolorized. This fact suggests that the dye molecule may serve as a site for the recombination of a hydrogen atom and a hydroxyl radical.

Some further oxidation appears after irradiation and is attributed to the hydrogen peroxide formed with a yield of $G = 0.67$.

The decolorization of deaerated methanolic solutions of Orange IV results from its reduction to the hydrzao derivatives by the addition of hydrogen atoms, methylol, methyl and hydroxyl radicals. The hydrazo derivatives then compete with the dye molecules for the radicals and are reduced to the derivatives of sodium sulfanilate and p-aminodiphenylamine. The addition of oxygen to an irradiated solution results in the conversion of any hydrazo derivatives present to the azo form, or Orange IV. The peroxides formed in this reverse reaction may also account for some oxidation.

The azo linkage behaves as a preferred site, at which virtually 100% of the free radicals attack. This observation is in agreement with other workers. The conversion of the azo compound to the amine derivatives via the hydrazo form coincides with the photochemical study of Blaisdell with azobenzene and 4-amino-4-nitroazobenzene in isopropyl alcohol and isooctane.

The decolorization reaction in methanol containing oxygen is inhibited until the oxygen is consumed. This induction period is believed to be due to the scavenging of the radicals by oxygen to form hydrogen peroxide and its derivatives. The products formed after the induction period are apparently similar to those observed in deaerated solutions. However, much stronger absorption was observed at the sodium sulfanilate peak than can be attributed to the amount of this compound formed. The decolorization yield after the induction period was only about half that observed for deaerated solutions.

These differences in methanolic solutions containing oxygen are attributed to the peroxides formed initially. The hydrazo derivatives are also reoxidized to the dye when oxygen was admitted.

The monoazo dye Orange I behaves in a similar manner to Orange IV when deaerated methanolic solutions are irradiated. The radical additions to the azo linkage apparently yield the derivatives of sodium sulfanilate and 4-amino-1-naphthol.

The results obtained in ethanolic solutions are apparently analogous to those in methanolic solutions. The efficiency of the decolorization process is again high and indicates essentially 100% addition of the radicals to the azo linkage.

This work illustrates the use of ionizing radiation in an organic synthesis. The principal limitation to this method is the mixture of products obtained from the random addition of the free radicals formed from the solvent. However, the process is easily performed and proceeds with a very high efficiency.

It is hoped that additional work will be done on this problem. It is suggested that a product separation be attempted with deaerated methanolic solutions. Electrophoresis methods may prove of value for this work. The separate radiolysis of deaerated methanolic solutions of sodium sulfanilate and p-aminodiphenylamine could yield information concerning the results of prolonged irradiation of

Orange IV solutions. The determination of the radiation product yields of formaldehyde, ethylene glycol, hydrogen, methane and carbon monoxide in conjunction with the Orange IV products would provide more detailed information on the reaction mechanism. The study of other azo structures and solvents would also be of interest and could provide further valuable knowledge.

REFERENCES

1. Denio, A. A., M. S. Thesis, University of New Hampshire (1960).
2. a. Collinson, E., Discussions Faraday Society 12, 285 (1952).
   b. Collinson, E. and Swallow, A. J., Chem. Revs. 56, 471 (1956).
   c. Cropper, W. H., Technical Memorandum, Office of Technical Services, Dept. of Commerce, Washington 25, D. C. (1959).
   d. Hayon, E., Scholes, G. and Weiss, J. J., J. Chem. Soc., 301 (1957).
3. Wright Air Development Center, Office of Technical Services, Report No. 151,964, Dept. of Commerce, Washington 25, D. C. (1959).
4. Mongini, L. and Zimmer, E. L., J Chim. Phys. 50, 491 (1953).
5. Weber, E. N. and Schuler, R. H., J. Am. Chem. Soc. 74, 4415 (1952).
6. Seitz, W., Strahlentherapie 61, 140 (1938).
7. Patti, F., Compt. Rend. 242, 357 (1956).
8. Blaisdell, B. E., J. Soc. Dyers Col. 65, 618 (1949).
9. a. Allen, A. O., "The Radiation Chemistry of Water and Aqueous Solutions", D. Van Nostrand Co., Inc., Princeton, N. J. (1961).

b. Barr, N. F. and Allen, A. O., J. Phys. Chem. 63, 928 (1959).

c. Hart, E. J., Nucleonics 19, [10], 45 (1961).

d. Hart, E. J., Proc. Intl. Conf. Peaceful Uses of Atomic Energy, 29, 5 (1958) (United Nations).

10. a. Adams, G. E. and Baxendale, J. H., J. Am. Chem. Soc. 80, 4215 (1958).

b. Baxendale, J. H. and Mellows, F. W., J. Am. Chem. Soc. 83, 4720 (1961).

c. Baxendale, J. H. and Sedgwick, R. D., Trans. Far. Soc. 57, 2157 (1961).

d. Hayon, E. and Weiss, J. J , J. Chem. Soc., 3970 (1961).

e. Lichtin, N. N., J. Phys. Chem. 63, 1449 (1959).

f. McDonell, W. R., J. Chem. Phys. 23, 208 (1955).

g. McDonell, W. R. and Gordon, S., J. Chem. Phys. 23, 208 (1955).

h. Meshitsuka, G. and Burton, M., Radiation Research 8, 285 (1958).

i. Sullivan, P. J. and Koski, W. S., J. Am. Chem. Soc. 84, 1 (1962).

11. a. Adams, G. E., Baxendale, J. H. and Sedgwick, R. D., J. Phys. Chem. 63, 854 (1959).

b. Hayon, E. and Weiss, J. J., J. Chem. Soc., 3962 (1961).

12. Waters, W. A., Disc. Far. Soc. 12, 284 (1952).

13. Handbook of Chemistry and Physics, Cleveland: Chemical Rubber Publishing Co., 1609 (1953).

14. Swallow, A. J., "Radiation Chemistry of Organic Compounds", London: Pergamon Press, 180 (1960).

15. Walton, J. H. and Filson, G. W., J. Am. Chem. Soc. 54, 3228 (1932).

16. International Critical Tables, New York: McGraw-Hill Publishing Co., 3, 262 (1929).

APPENDIX

FIGURE 1

Calibration Curve: Orange 1V in Water at 440 mμ

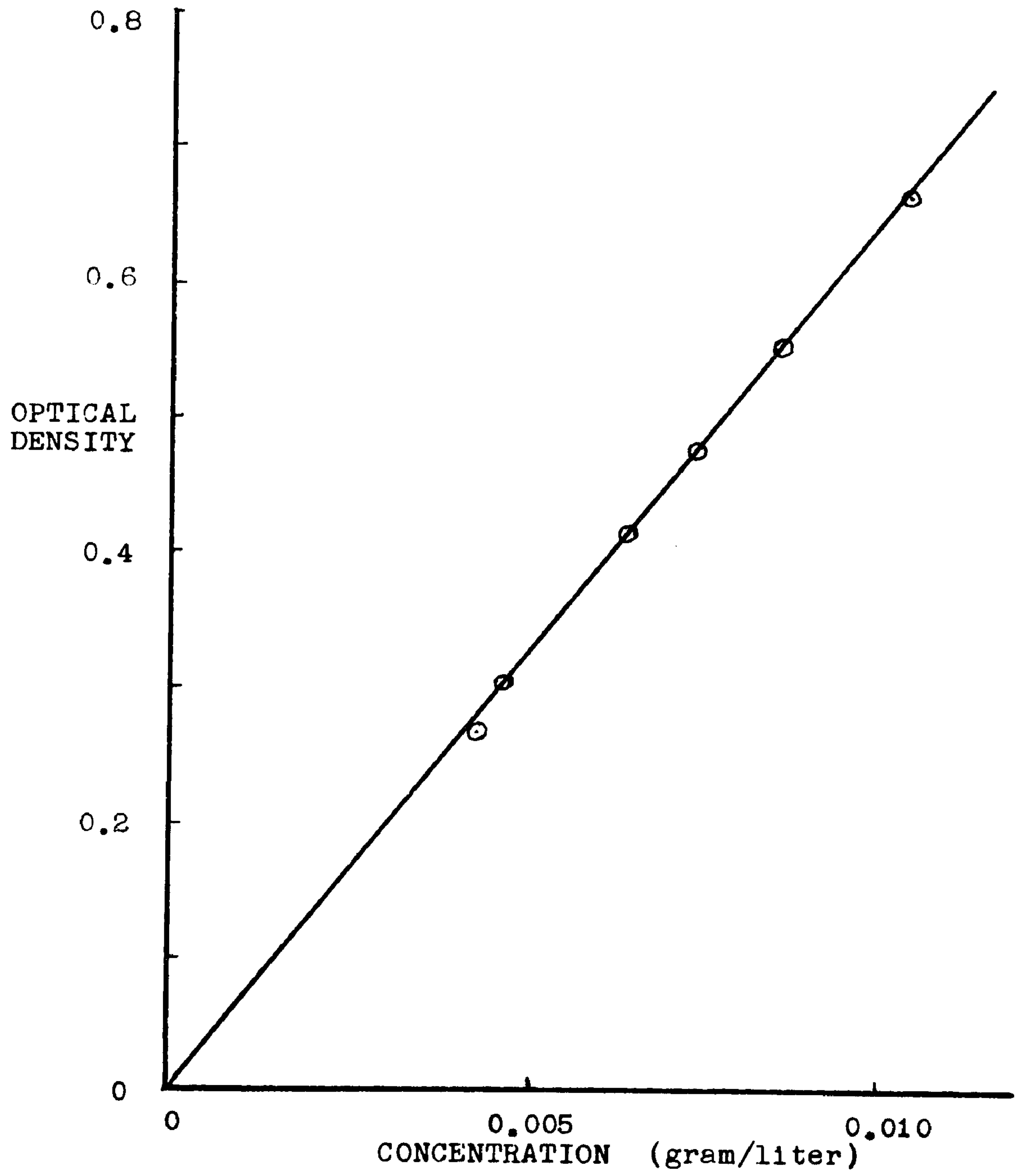


FIGURE 2

Calibration Curve: Orange lV in Methanol at 420 mμ

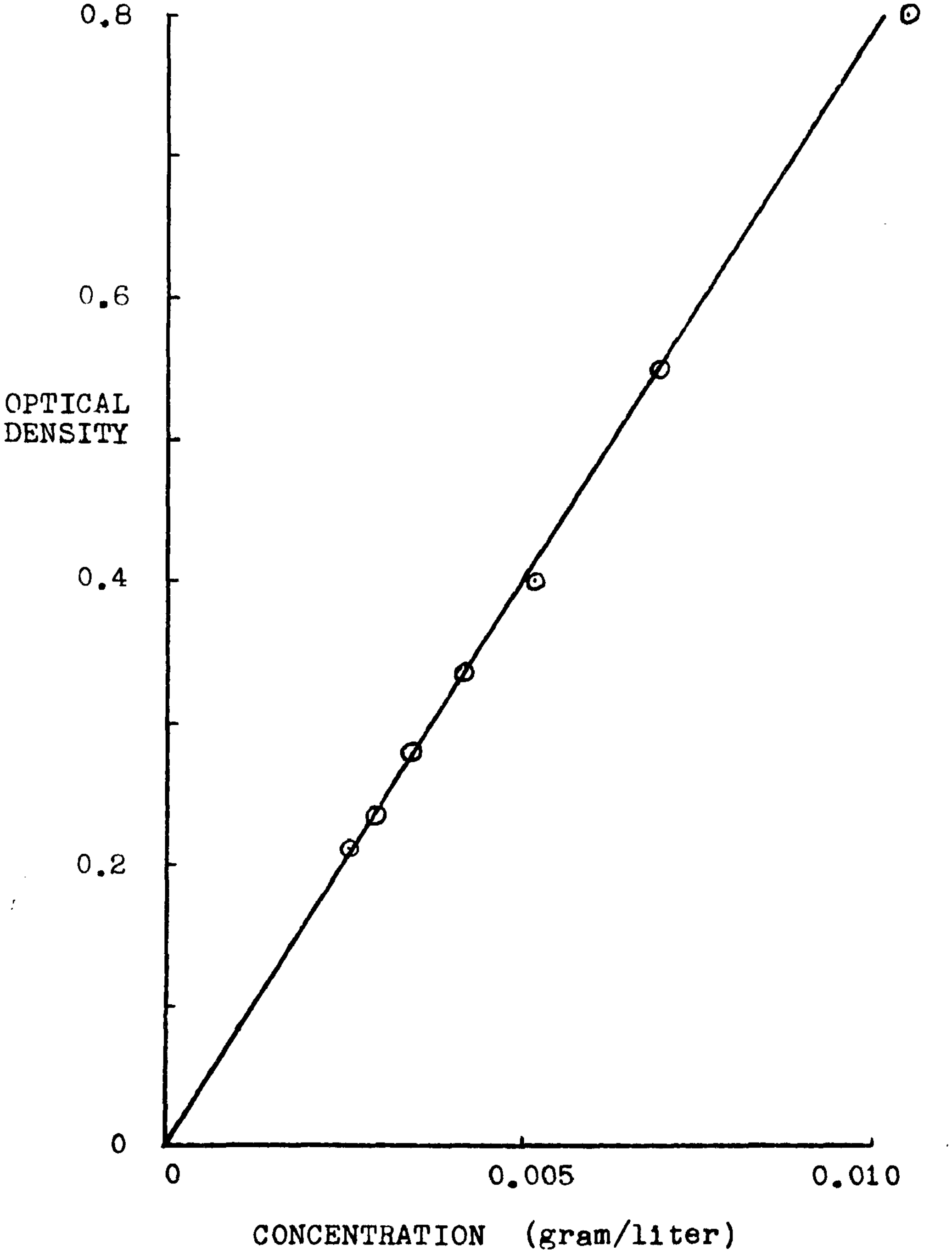


FIGURE 3

Calibration Curve: Orange lV in Ethanol at 425 mμ

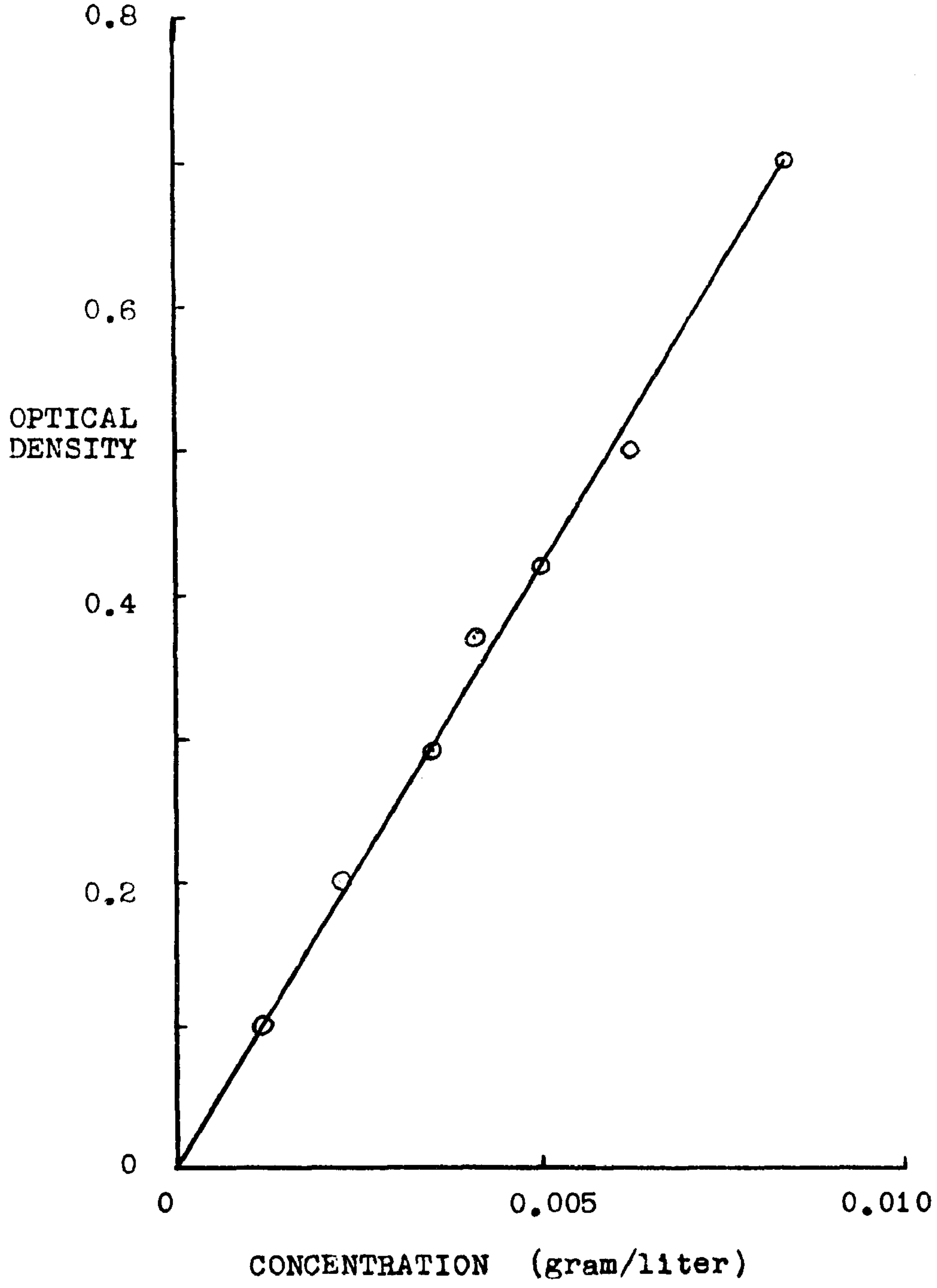


FIGURE 4

Calibration Curve: Orange lV in Methanol at 271 mμ

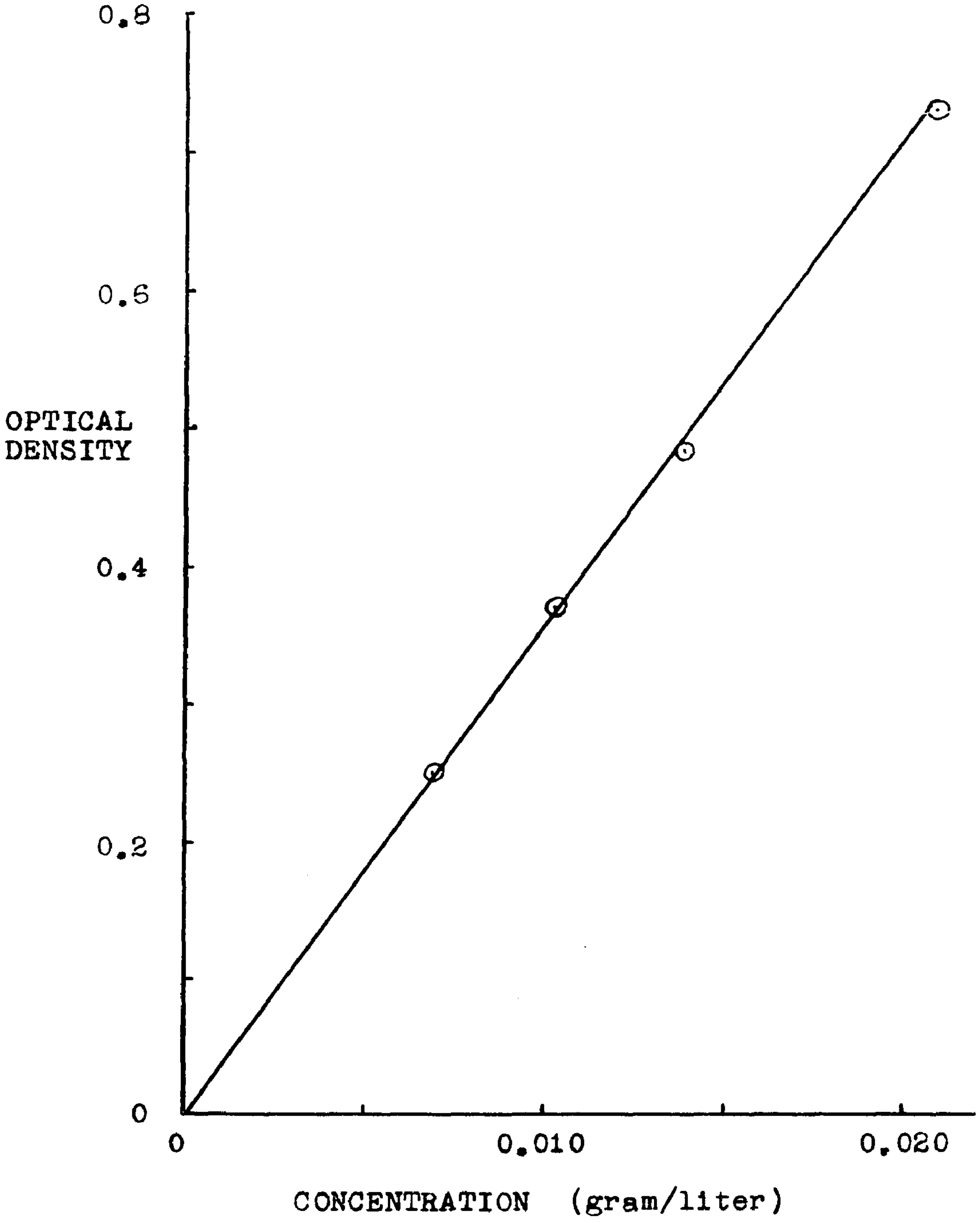


FIGURE 5

Calibration Curve: Sodium Sulfanilate in Methanol at 252 mμ

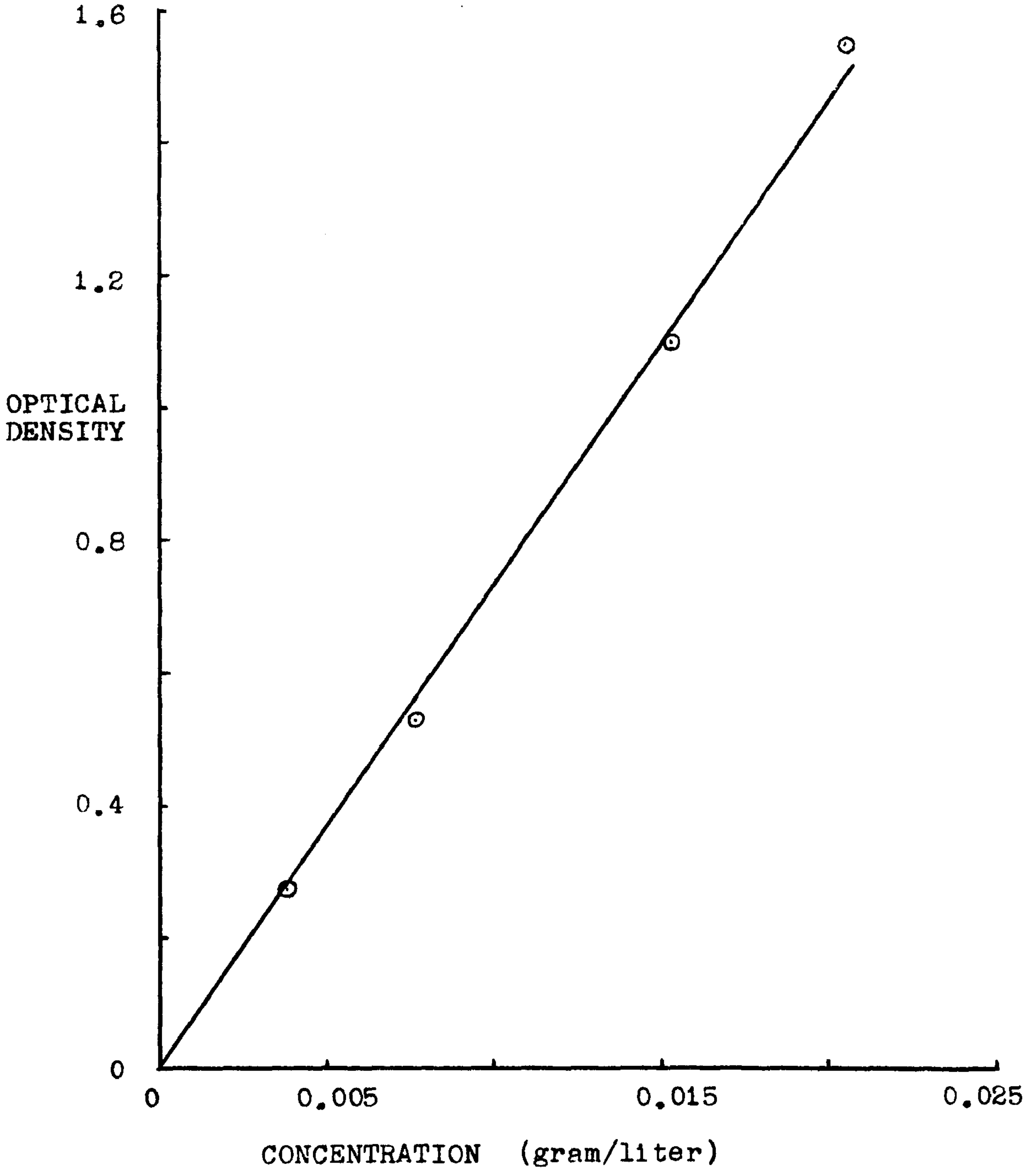
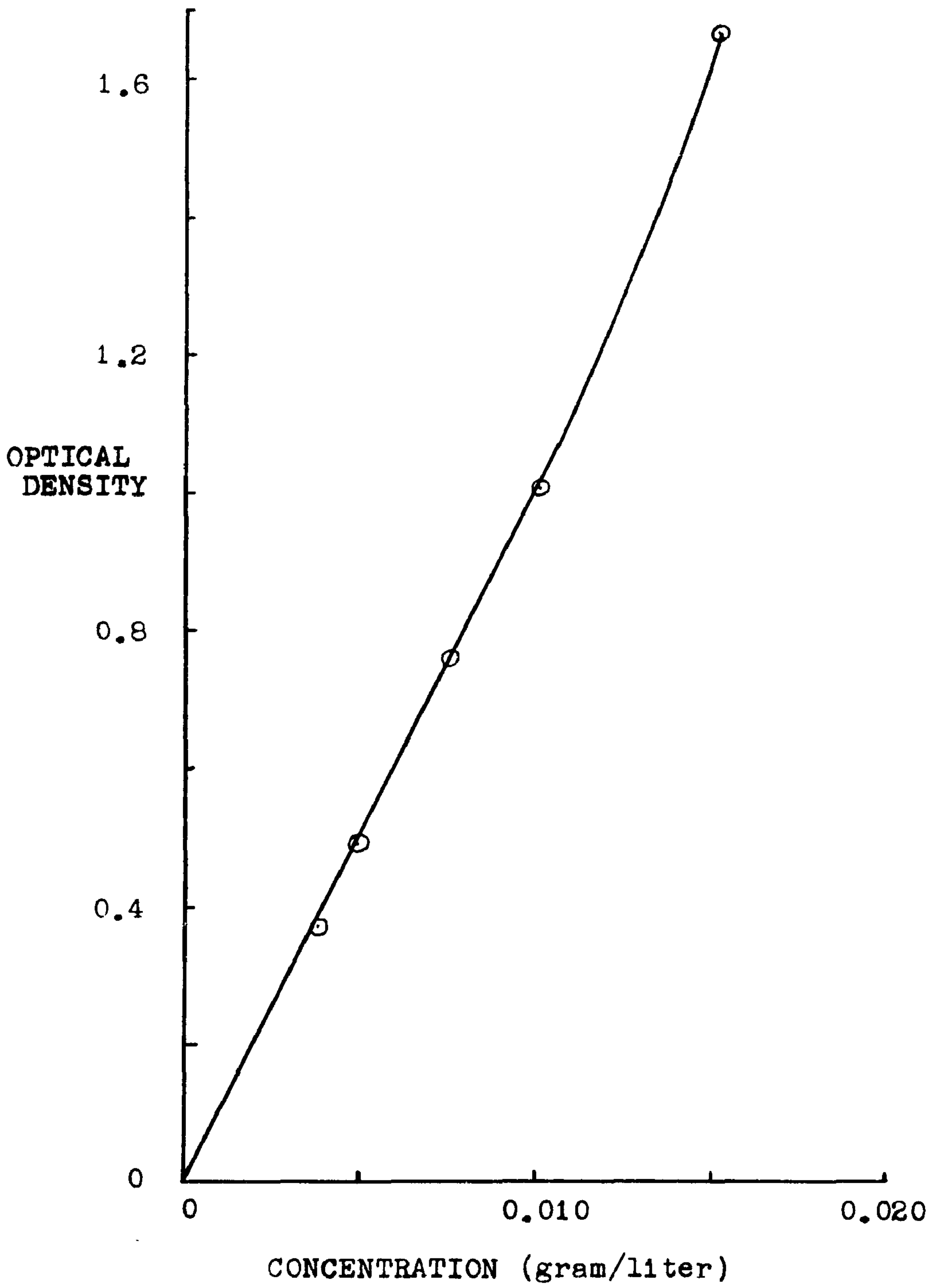


FIGURE 6

Calibration Curve: p-Aminodiphenylamine in Methanol at 285 mμ



BIOGRAPHICAL DATA

Name: **Allen Albert Denio**

Date of Birth: June 6, 1934

Place of Birth: Lowell, Massachusetts

Secondary Education: Lowell High School, Lowell, Massachusetts

Collegiate Institutions Attended:	Dates	Degree
Lowell Technological Institute	1952 – 1956	B.S. – Textile Chemistry
Lowell Technological Institute	1956 – 1957	M.S. – Textile Chemistry
University of New Hampshire	1958 – 1960	M.S. – Chemistry

Position Held: Chemist – E. I. du Pont de Nemours & Co., Inc.
Wilmington, Delaware (1957–1958)