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Major professor

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INVESTIGATIONS INTO THE USE OF O-NITROBENZALDEHYDE IN POLYMETHYL METHACRYLATE FILMS FOR THE MEASUREMENT OF LIGHT INTENSITY

By

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ABSTRACT

INVESTIGATIONS INTO THE USE OF O-NITROBENZALDEHYDE IN POLYMETHYL METHACRYLATE FILMS FOR THE MEASUREMENT OF LIGHT INTENSITY

By

Young Cheol Hong

The measurement of incidental light intensity is one of the most important and fundamental requisites in photochemical studies. Chemical actinometer systems are often used for quantitative photochemical work due to excellent reproducibility, reliability, and convenience.

This study was carried out to evaluate the use of o-nitrobenzaldehyde in polymethyl methacrylate films for measuring incidental light intensity. The o-nitrobenzaldehyde, in the form of polymeric film, undergoes a cumulative photochemical conversion in response to exposure to UV light. The extent of photochemical rearrangement by solar UV light is proportional to the length of exposure. Therefore, this actinometer can cumulatively measure the intensity of incidental UV light without loss of accuracy. Since this actinometer is a thin film, it has an advantage for measuring light intensity at surfaces and locations where currently used devices are normally unsuitable. Therefore, it can be used as a convenient and useful tool to develop better models for photochemical studies, and to better assess the rate at which xenobiotics will react photochemically by solar UV light in the environment.

ACKNOWLEDGMENTS

I would like to express sincere gratitude to my major professor, Dr. Matthew J. Zabik. I heartily thank you for your guidance and encouragement.

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INTRODUCTION

Photochemistry is the study of reactions which are caused by reaction (light) either directly or indirectly. Reactions are initiated by electronically excited molecules produced by the absorption of a quanta of suitable radiation typically in the visible and ultraviolet spectral regions.

Stark and Einstein (1908-1912) enunciated the second law of photochemistry which states that, "One light-activated molecule is produced by a primary photochemical process, when one single photo (or one quantum of light) is absorbed per molecule of reacting substance which disappears." This law forms the basis of all photochemistry (Giese, 1964).

The quantum yield (ϕ) is used to express efficiency of a photochemical reaction, and is defined as follows (Rohatgi-Mukherjee, 1978):

$$\phi = \frac{\text{number of molecules decomposed or formed per unit time}}{\text{number of quanta absorbed per unit time}}$$

$$= \frac{\text{number of molecules undergoing that process}}{\text{number of quanta absorbed}}$$

$$= \frac{\text{rate in the process}}{\text{rate of absorption}}$$

Appropriate devices for measurement of light intensity are absolutely necessary for quantitative work in photochemical studies and determination of rates in photochemical reactions. Today, photochemists primarily use three devices for measuring light intensity: thermopile-galvanometer systems, phototubes, and chemical actinometer systems (Calvert and Pitts, 1966).

Thermopile-galvanometer systems are useful for direct measurement of incidental light intensity over the entire spectral range from visible to far UV

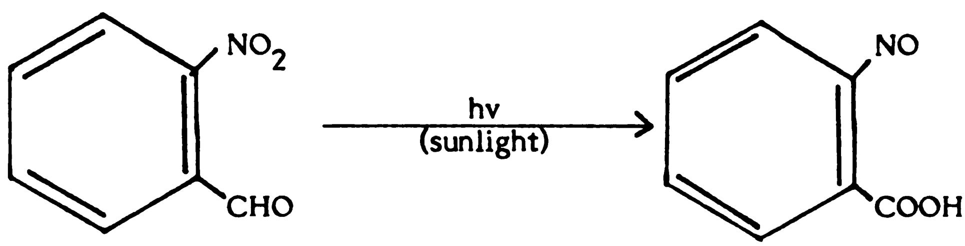
(200 nm). They have been used for light intensity measurement only at wavelengths where chemical actinometry has not been well developed. Measurements with these systems are very tedious and time consuming, frequently needing calibration against standard radiation sources supplied by the U.S. National Bureau of Standards. Besides, the thermopile is an extremely fragile piece of equipment, necessitating great care when handled (Calvert and Pitts, 1966).

Phototubes are good detectors for relative light intensity over a wide range, but are not appropriate for measurement of absolute light intensity. Their non-linear response, poor sensitivity in UV light, and fatigue during operation make them unreliable. Phototubes also must be frequently calibrated against a thermopile-galvanometer system or other standards under similar experimental conditions. They are, therefore, less desirable for quantitative work in a photochemical study (Giese, 1968).

Chemical actinometer systems, which utilize reactions of chemicals that decompose with known quantum yields under known experimental conditions, are most useful for rapid and highly accurate determinations of light intensity (Rohatgi-Mukherjee, 1978). Measurements with these actinometer systems are more reliable than those obtained with thermopile-galvanometer systems. In recent years, many chemical actinometer systems (gaseous actinometers and liquid-phase actinometers) have been developed and widely used (Calvert and Pitts, 1966).

It has been known that de Saussure made the first chemical actinometer system for measuring light intensity by applying Berthollet's discovery of chlorine water decomposition by sunlight (Giese, 1964). Leighton and Forbes (1930) used a solution of uranyl oxalate to determine quantum yields. Hatchard and Parker (1956) developed a ferrioxalate actinometer system which is very sensitive and constant over a wide range of wavelengths (McLaren, 1964 and Jagger, 1967).

The proposed actinometer system in this study is in a solid filmphase, based on Technical Support Package on UV Actinometer Films for NASA (Gupta, Coulbert and Pitts, 1980). A film of polymethyl methacrylate containing o-nitrobenzaldehyde (NBA) is made by casting from a solution of dichloromethane. Upon absorbing ultraviolet light, photochemically sensitive o-nitrobenzaldehyde undergoes a photochemical rearrangement forming o-nitrosobenzoic acid. Gupta et al. (1980) confirmed that this reaction proceeds when incorporated in a polymeric film and the quantum yield is 0.50 $\pm$ 0.03.



Since the extent of this chemical conversion is proportional to time of exposure to UV light, actinometer film can measure cumulative solar UV radiation.

This film actinometer system potentially has the following advantages which most devices currently used for measuring incidental light intensity do not have.

It can continuously integrate solar UV light intensity in the most interesting wavelength which photochemical studies generally lie (300 to 400 nm). It can be used for measuring incidental UV light accurately on any surface including areas which are normally inaccessible to other instruments. It has a large usable range, approximately up to 50% conversion of starting material, and has no deleterious effects on rate of photon absorption due to water vapor. It is not affected by visible light, and is unaffected by a temperature range of 20°C to 50°C. It is inexpensive and easy to use. It can be read conveniently by using an infrared spectrophotometer.

This study was performed to evaluate the film actinometer system in relation to its stability, reliability and capability for determination of incidental light intensity. The data obtained from this study will allow one to better assess the rate at which xenobiotics will photoreact in the environment, and to develop models for environmental photochemistry by using the film actinometer system.

EXPERIMENTAL

MATERIALS AND METHODS

Reagents

1. o-Nitrobenzaldehyde (NBA): 98%, M.W. 151.12, Aldrich Chemical Company.
2. Polymethyl methacrylate (PMMA): secondary standard, Aldrich Chemical Company.
3. Dichloromethane: Omnisolv for spectroscopy and chromatography, glass distilled, MCB reagent.
4. Nitric acid: diluted with distilled water (1:1).
5. Mercury: acid washed.

Equipment

1. Infrared spectrophotometer: Perkin-Elmer 337, and 137 Infracord.
2. UV-Vis spectrophotometer: Gilford 252.
3. Ultraviolet lamp: Blak-Ray UVL-56, 365 nm.
4. Incubator: Blue M.
5. Petri dish: glass, 13 cm in inside diameter.
6. Slide film holder: cardboard, 5 x 5 cm.
7. Tray: polyethylene, 8" x 6" x 3".

Mercury Decontamination

Dirty and soiled mercury was placed in a polyethylene tray to expose a large surface area. Diluted nitric acid was added and the two-phase mixture was stirred slowly with a glass rod. After approximately ten minutes, the acid solution was discarded, replaced with fresh acid, and again stirred for ten minutes. After discarding the second acid solution, the mercury was washed three times with distilled water. The mercury was then passed twice, by gravity, through a small pin hole in a filter paper in a glass funnel (Koch and Hanke, 1948).

Preparation of Actinometer Films

The casting solution was prepared by dissolving 0.05 to 0.1 g of NBA with 1 g of PMMA in 100 ml of dichloromethane. The casting solution was poured on clean mercury in a Petri dish, which was then covered carefully with a lid so that the casting solution was not disturbed. The dish was allowed to stand until a thin polymer film containing NBA was formed by complete and slow solvent (dichloromethane) evaporation. Using a thin, wide plastic ruler (or metal spatula), the transparent film was carefully lifted off the mercury and cut with scissors into proper size. The film was then inserted into a slide film holder, and both sides were covered with dull black paper to prevent light exposure. One side of the dull black paper was taped on to the holder permitting the system to be opened in a book-like fashion. The film, when mounted in the holder, fitted directly into the sample slot of an IR spectrophotometer.

Measurement of Photons Absorbed by a Film

One side of the dull black paper cover was opened, and the film exposed to the sun or experimental light source for a given period. The exposed film was then examined on the IR spectrophotometer and the spectrum was recorded (see Figures 1 and 2). The amount of unreacted NBA in the film was determined by measuring the height of a band at 1530 cm^{-1} of the IR spectrum (Meloan, 1963). The amount of reacted NBA was obtained by subtracting the amount of unreacted NBA from the amount of NBA presented prior to exposure. The number of photons absorbed by the film was determined using the following equation (Gupta, Coulbert and Pitts, 1980):

Figure 1. IR Spectrum of a PMMA Film without o-NBA

IR SPECTRUM OF A PMMA FILM WITHOUT O-NBA

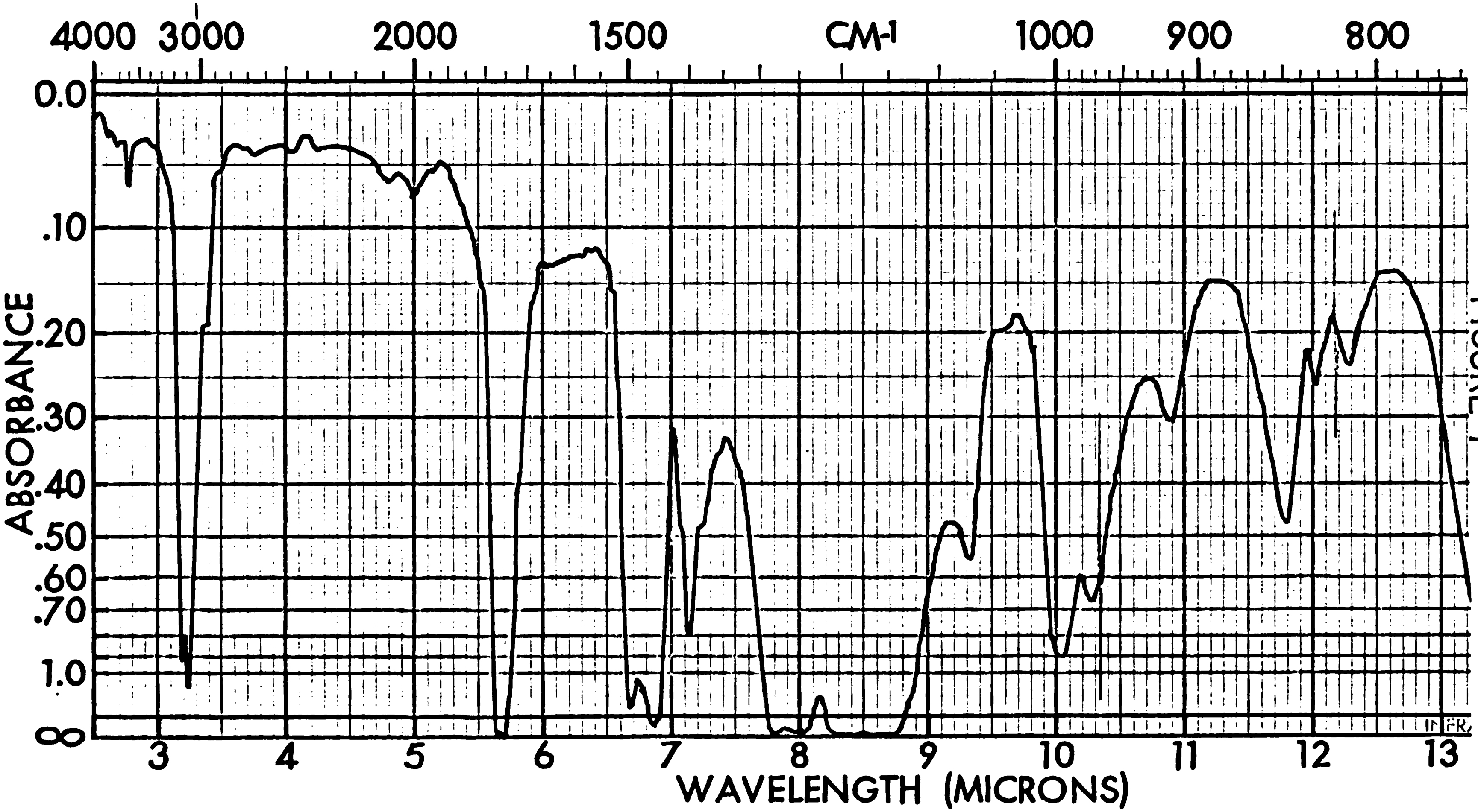
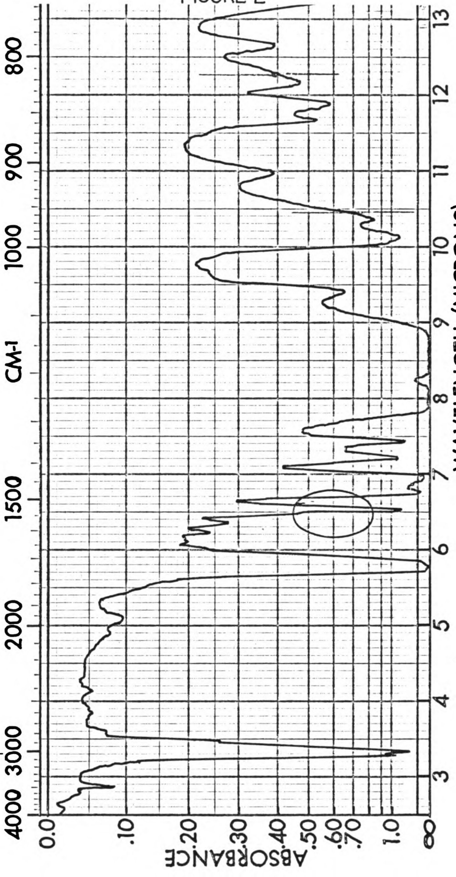


FIGURE 1

Figure 2. IR Spectrum of a PMMA Film containing o-NBA

FIGURE 2

IR SPECTRUM OF A PMMA FILM CONTAINING O-NBA



Equation 1

$$\text{photons (n)} = \frac{C \times 10^{-3}}{M} \times 2 \times N$$

where C = amount of NBA reacted (mg/cm^2 film)

M = molecular weight of NBA (151.12)

N = Avogadro's number (6.02×10^{23})

Preparation of Calibration Curve for Actinometer Films

Films with five different concentrations of NBA (0.10, 0.15, 0.20, 0.25 and 0.30 mg NBA/cm^2 film) were prepared by casting from solutions which contained five different amounts of NBA to a given amount of PMMA (200 mg per 10 ml of casting solution) when dissolved in solvent (dichloromethane). Ten ml of each solution was used for casting in a Petri dish, 13 cm in diameter (area = 132.73 cm^2). The concentration of NBA in a film was obtained from the following equation:

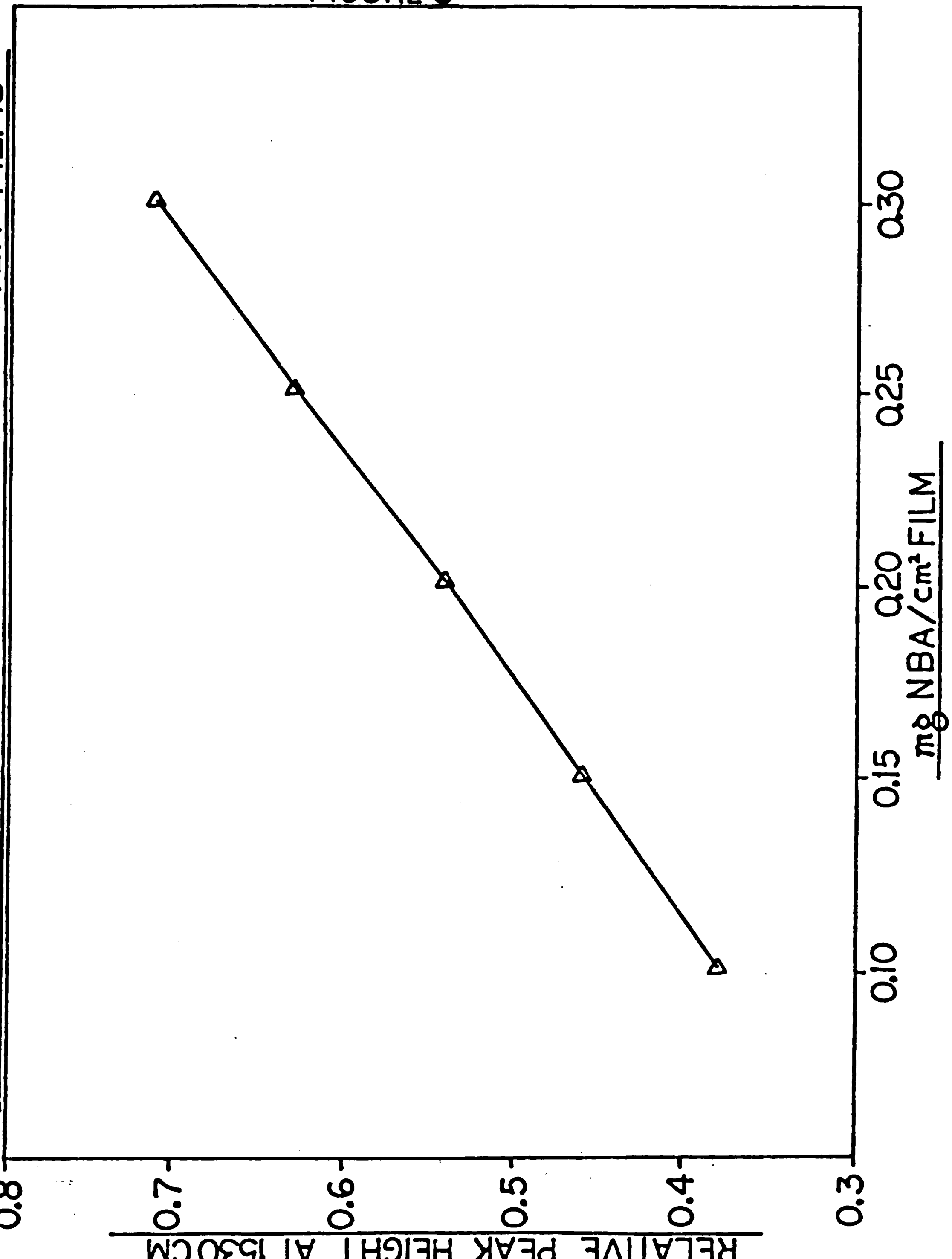
Equation 2

$$\frac{\text{amount of NBA cast (mg)}}{\text{area of Petri dish used } (cm^2)} = \text{mg NBA}/cm^2 \text{ film}$$

After mounting the film into film holders, they were examined by IR spectroscopy and the height of the band at 1530 cm^{-1} was measured. This experiment was performed twice with two replicates. The calibration curve was drawn by plotting the mg of NBA per cm^2 of film versus the relative height of the band at 1530 cm^{-1} (Figure 3). Results are given in Tables 1 and A-1.

Figure 3. Calibration Curve for Actinometer Films

FIGURE 3



CALIBRATION CURVE FOR ACTINOMETER FILMS

Effect of Varying Volume of Casting Solution

A Petri dish with an inside diameter of 13 cm was used for casting films. 4000 mg of NBA and 2.0 g of PMMA were dissolved in 100 ml of dichloromethane to make the casting solution. Five respective volumes (5, 8, 10, 15, and 20 ml) of the solution were cast on the surface of clean mercury to prepare the films for this experiment. After mounting the films into side film holders, they were examined by IR spectroscopy to observe the height of the band at 1530 cm^{-1} by which the amount of NBA present was determined. This experiment was performed twice with two replicates. Results are given in Tables 2 and A-2, and a plot of the relative band height at 1530 cm^{-1} versus volume of casting solution is shown in Figure 4.

Table 1. Relative Height of the Band at 1530 cm^{-1} against the mg NBA per cm^2 of Film

mg NBA casted	mg PMMA casted	mg NBA per cm^2 of film	relative height at 1530 cm^{-1}
13.3	200	0.10	0.380
20.0	200	0.15	0.462
26.5	200	0.20	0.542
33.0	200	0.25	0.630
40.0	200	0.30	0.715

Effect of Angle of Incidental Light

Using a long wavelength (365 nm) UV lamp, ultraviolet light was used to irradiate films which were set at four different angles (0, 30, 60, and 90 degrees) to the direction of light (Figure 5). After exposure for a given period, the films

Figure 4. Effect of Varying the Volume of Solvent on Casting the Film

FIGURE 4

EFFECT OF VARYING THE VOLUME OF SOLVENT ON CASTING THE FILM

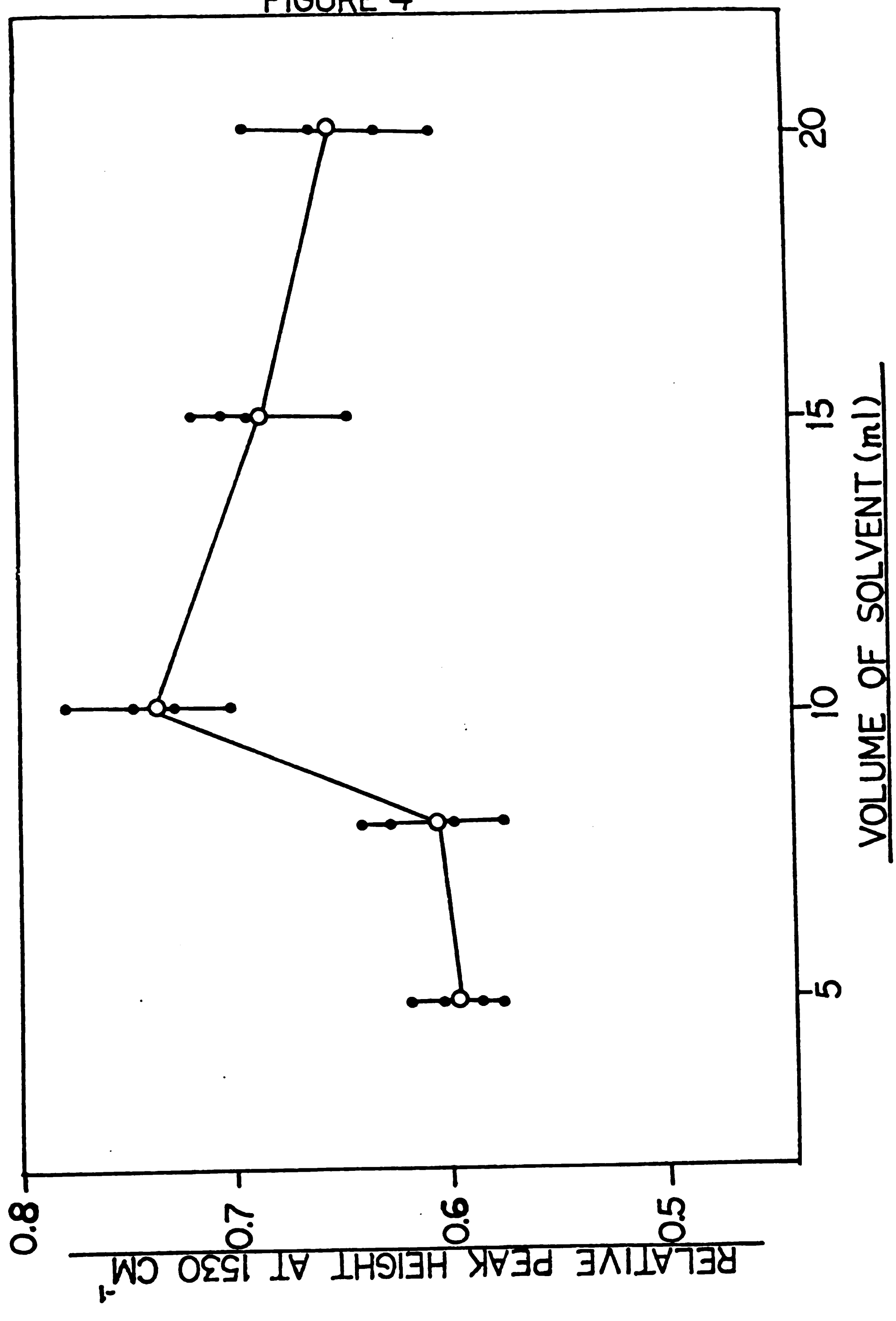
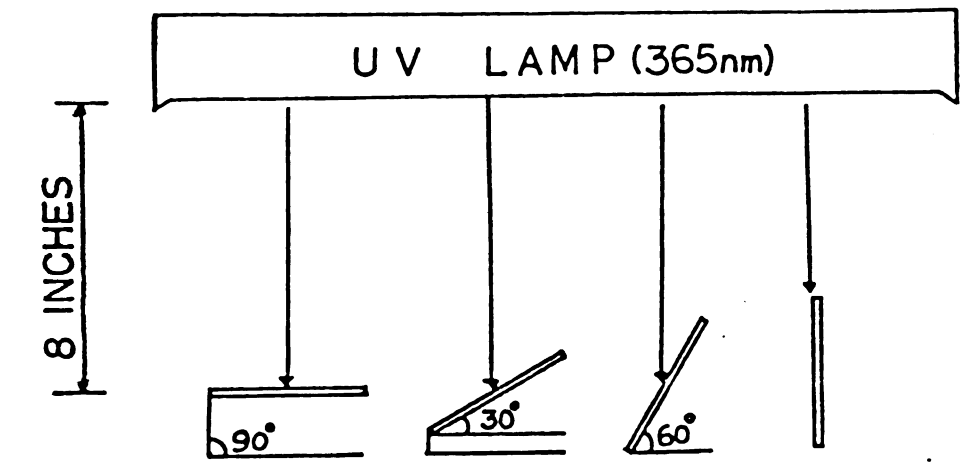


Figure 5. Irradiation of UV Light to Films

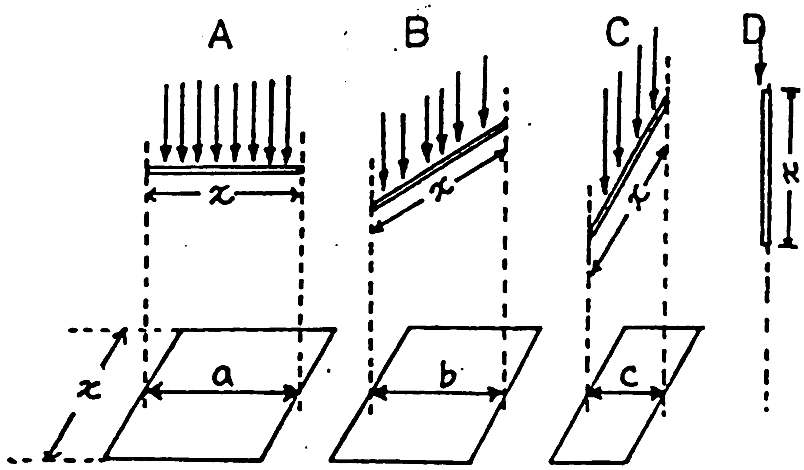
Figure 6. Plane Figures on the Area of Films Irradiated at Various Angles of Incidence

FIGURE 5
IRRADIATION OF UV LIGHT TO FILMS



FILM	A	B	C	D
ANGLE OF INCIDENCE	90°	60°	30°	0°(180°)

FIGURE 6
PLANE FIGURES ON THE AREA OF FILMS IRRADIATED AT VARIOUS ANGLE OF INCIDENCE



$a = x$

$b = x \cdot \text{Cosine } 30°$

$c = x \cdot \text{Cosine } 60°$

were examined by IR spectroscopy to observe changes in height of the absorbance band at 1530 cm^{-1}. The number of photons absorbed by each film was calculated by using equation 1, and results are given in Tables 3, A-3, 4, A-4, 5, A-5, 6, and A-6. A plot of number of photons against time of exposure is shown in Figure 7. This experiment was performed twice.

Effect of Temperature

A long wavelength (365 nm) UV lamp was used to irradiate films for a given period at selected temperatures: 4°C, 37°C, and 50°C. At respective temperatures, three or four films were irradiated at a 90° angle. The same experiment without UV light was also carried out simultaneously to evaluate film stability at these temperatures. After the films were examined on the IR spectrophotometer, the amount of reacted NBA was measured and the number of photons absorbed by each film was calculated by using equation 1. Number of photons absorbed versus time was plotted (Figures 8, 9, and 10). Results are given in Tables 7, A-7, 8, A-8, 9, A-9, 10, A-10, 11, A-11, 12, and A-12.

Table 2. Relative Height of the Band at 1530 cm^{-1} against the Thickness of Film

volume used for casting, ml	amount of PMMA, mg	mg NBA per cm^2 of film	relative height at 1530 cm^{-1}
5	100	0.15	0.60
8	160	0.24	0.61
10	200	0.30	0.74
15	300	0.45	0.69
20	400	0.60	0.65

Figure 7. Effect of Angle of Incidence on Photon Interception by Actinometer Films

EFFECT OF ANGLE OF INCIDENCE ON PHOTON INTERCEPTION BY ACTINOMETER FILMS

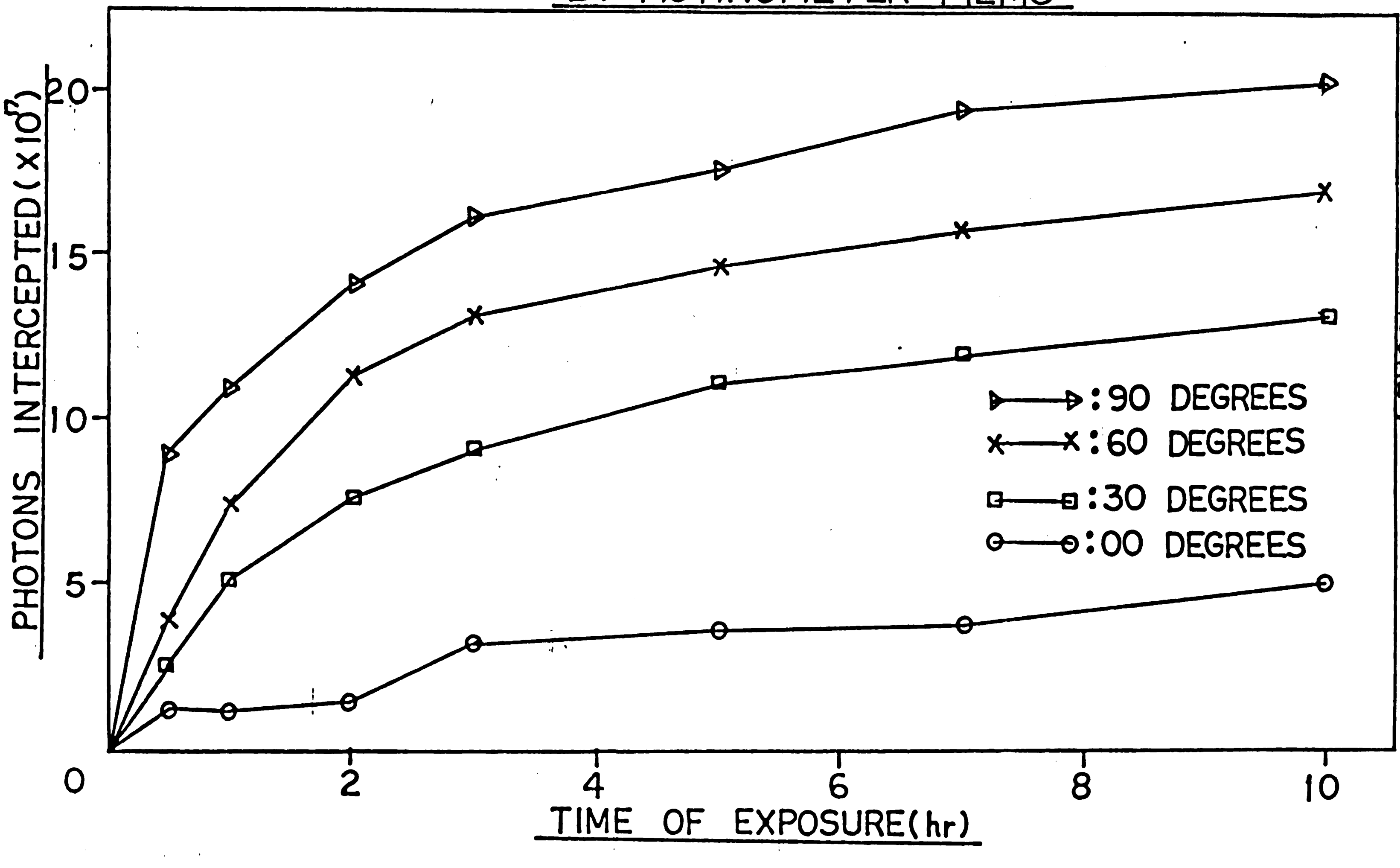


FIGURE 7

Figure 8. Effect of Temperature (4^oC) on Photon Interception by Actinometer Films

EFFECT OF TEMPERATURE(4°C) ON PHOTON INTERCEPTION BY ACTINOMETER FILMS

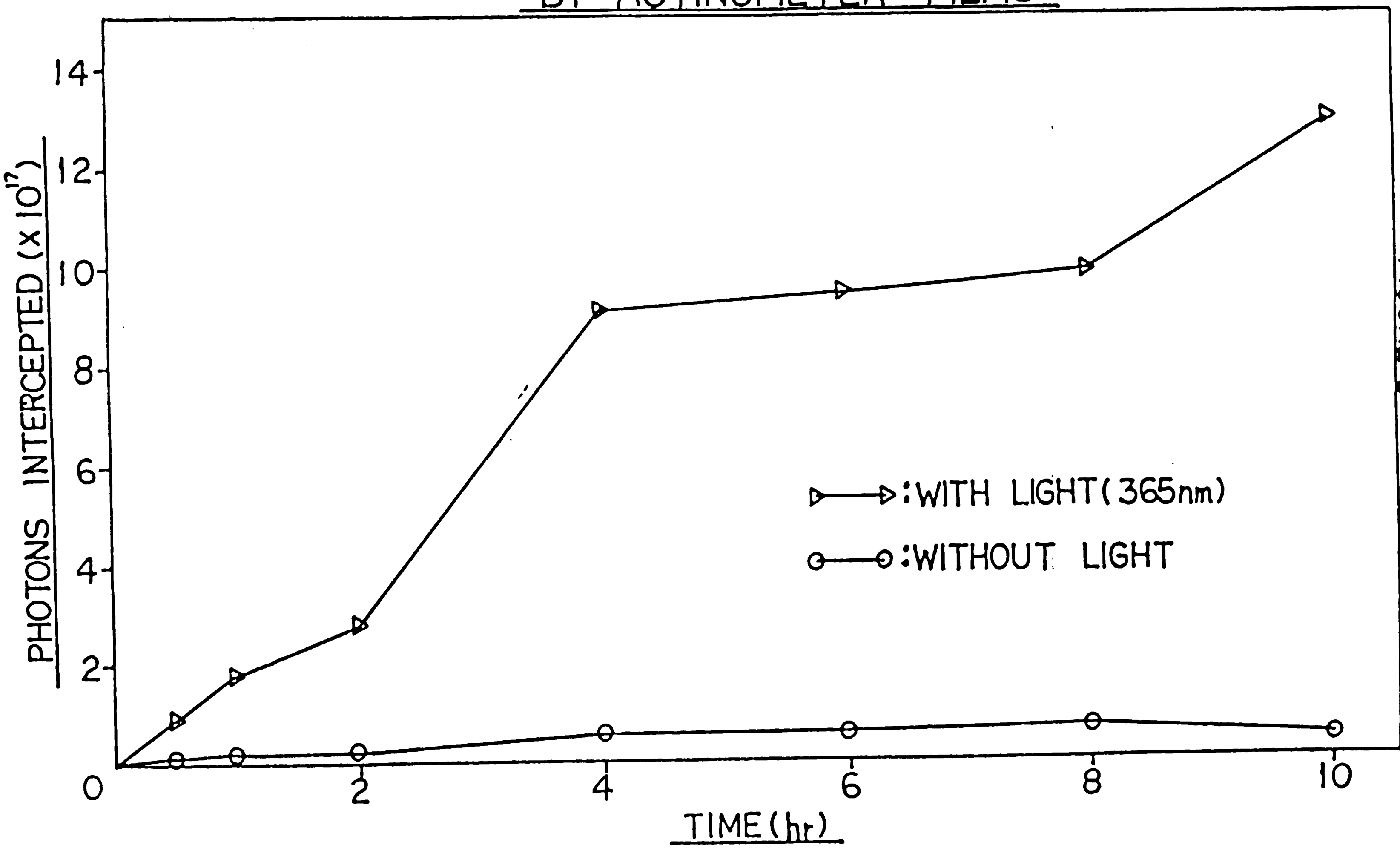


FIGURE 8

Figure 9. Effect of Temperature (37°C) on Photon Interception by Actinometer Films

EFFECT OF TEMPERATURE(37°C) ON PHOTON INTERCEPTION BY ACTINOMETER FILMS

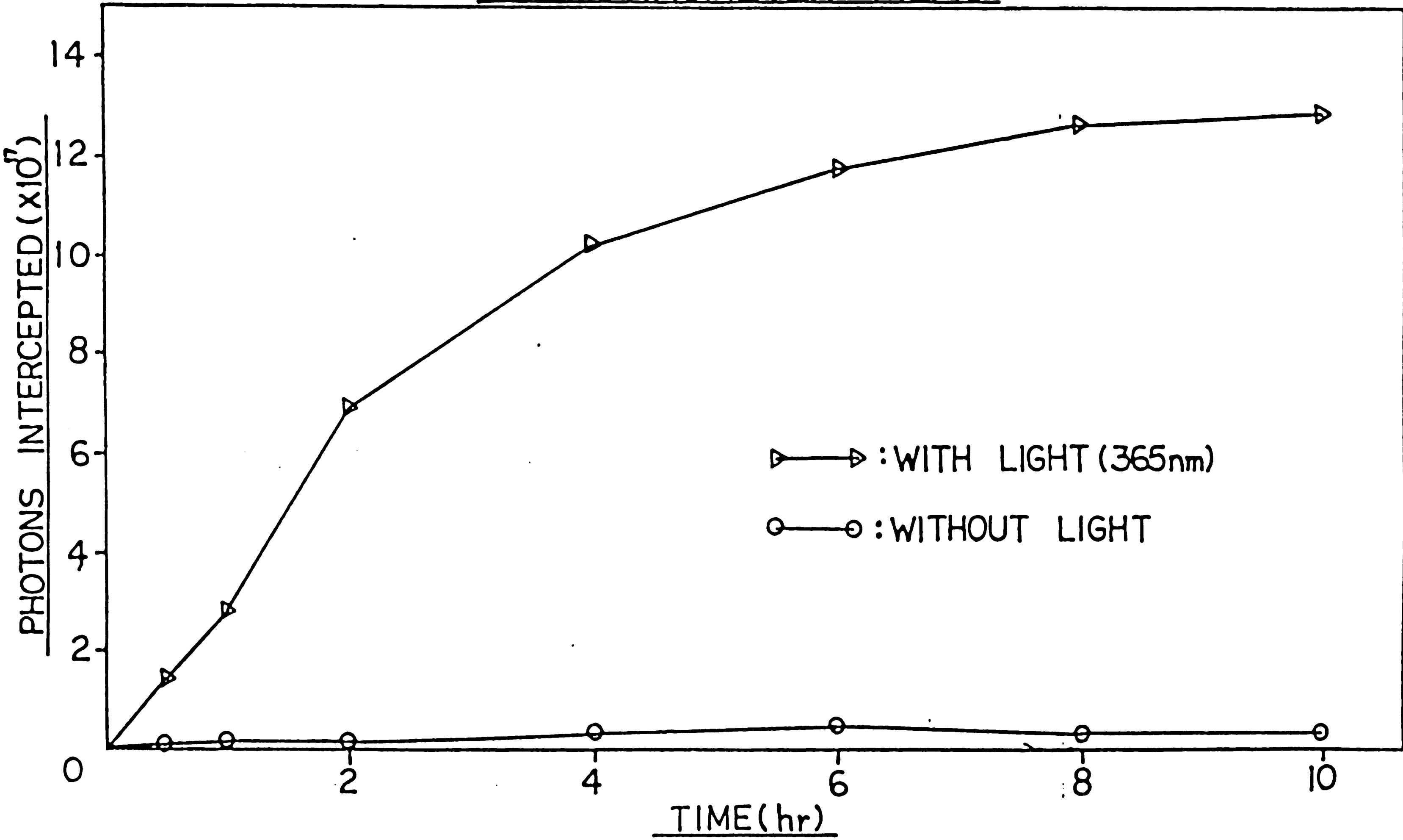


FIGURE 9

Figure 10. Effect of Temperature (50°C) on Photon Interception by Actinometer Films

EFFECT OF TEMPERATURE(50°C) ON PHOTON INTERCEPTION BY ACTINOMETER FILMS

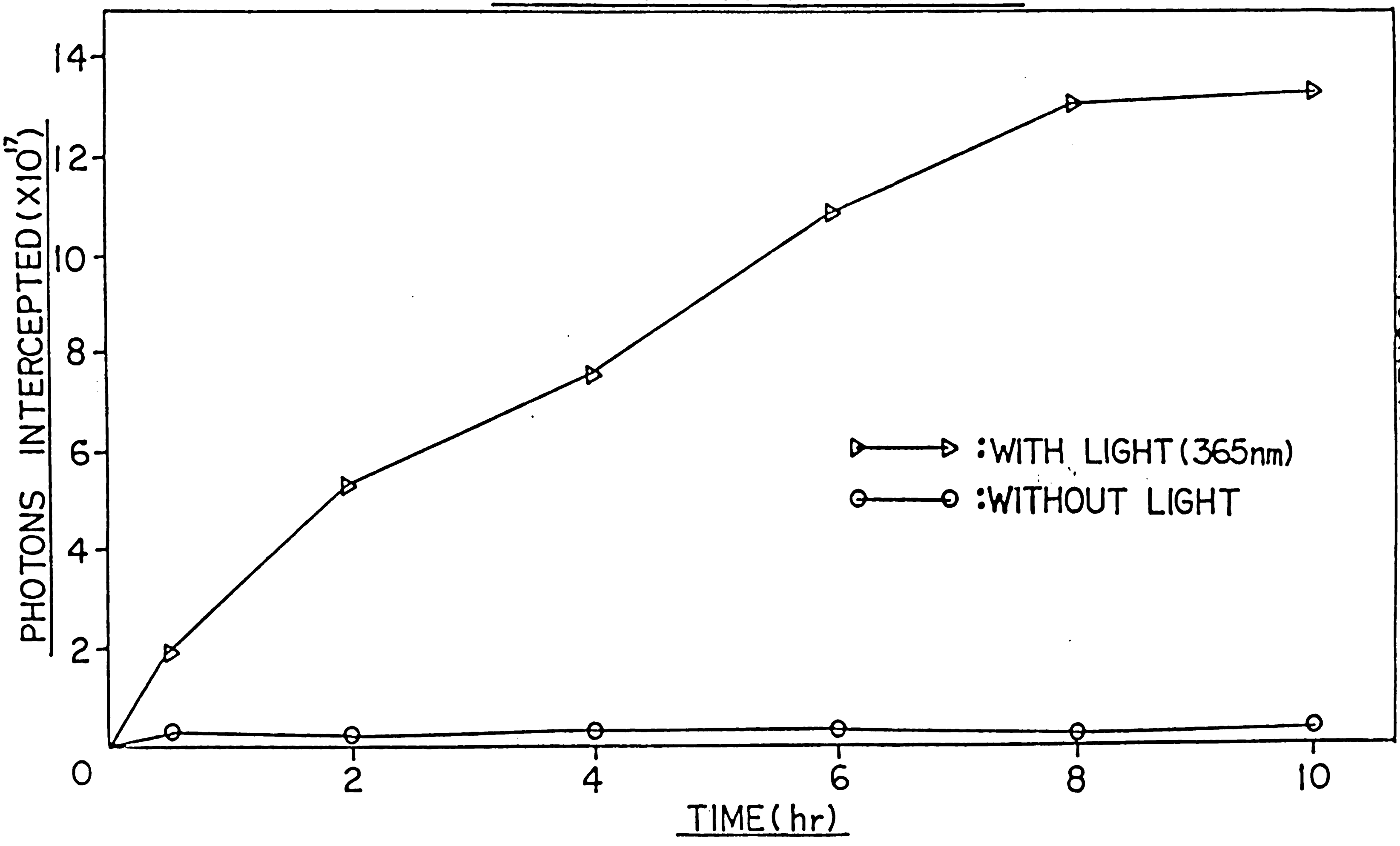


FIGURE 10

Effect of Wavelength

Films were inserted into the sample slot of a UV-Vis spectrophotometer, and irradiated at various wavelengths for four hours. Wavelengths at 10 nm intervals from 300 nm to 400 nm were used for this experiment. This experiment was carried out twice at each wavelength. Films stored at room temperature without irradiation were used as control for the irradiated films. After four hours of irradiation, films were examined by IR spectroscopy, and amount of reacted NBA was determined. Using equation 1, the number of photons absorbed was calculated and wavelength versus number of photons was plotted (Figure 11). Results are given in Tables 13, A-13, and A-14.

Table 3. The Number of Photons Absorbed by Actinometer Films with Time at 90^{o} Angle of Incidence

time, hr	amount of NBA reacted, mg/cm^2 film	photons ($x10^{17}$)
1/2	0.1117	8.91
1	0.1376	10.97
2	0.1757	14.01
3	0.2014	16.06
5	0.2210	17.62
7	0.2437	19.43
10	0.2547	20.31

Figure 11. Effect of Wavelength on Photon Interception by Actinometer Films

EFFECT OF WAVELENGTH ON PHOTON INTERCEPTION BY ACTINOMETER FILMS

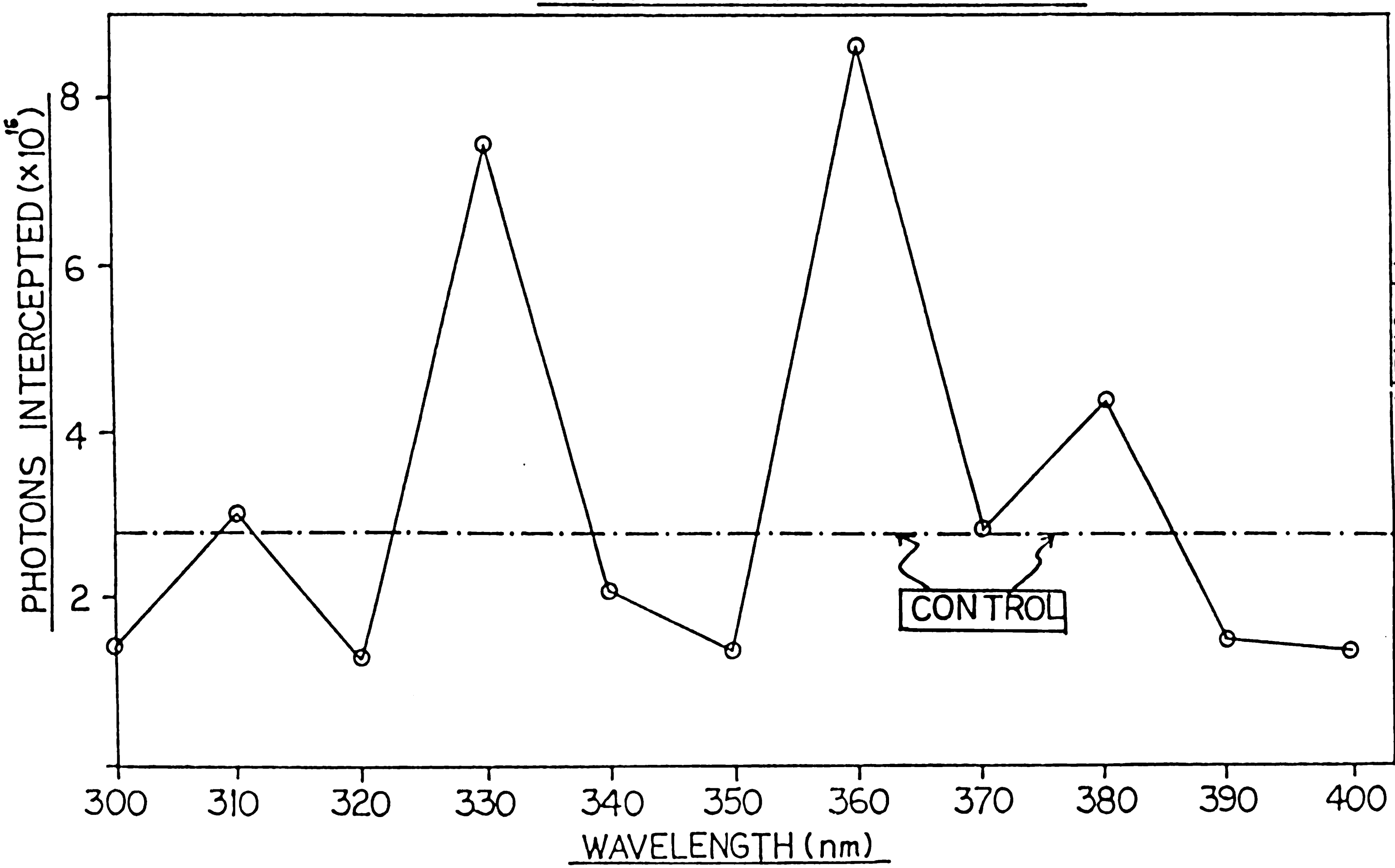


FIGURE 11

Table 4. The Number of Photons Absorbed by Actinometer Films with Time at 60^{o} Angle of Incidence

time, hr	amount of NBA reacted, mg/cm^2 film	photons ($\times 10^{17}$)
1/2	0.0473	3.77
1	0.0927	7.39
2	0.1420	11.32
3	0.1654	13.19
5	0.1839	14.66
7	0.1978	15.77
10	0.2127	16.96

Table 5. The Number of Photons Absorbed by Actinometer Films with Time at 30^{o} Angle of Incidence

time, hr	amount of NBA reacted, mg/cm^2 film	photons ($\times 10^{17}$)
1/2	0.0316	2.52
1	0.0630	5.02
2	0.0949	7.57
3	0.1134	9.04
5	0.1382	11.02
7	0.1505	12.00
10	0.1658	13.22

Table 6. The Number of Photons Absorbed by Actinometer Films with Time at 0^{o} C (or 180^{o}) Angle of Incidence

time, hr	amount of NBA reacted, mg/cm^2 film	photons ($x10^{17}$)
1/2	0.0143	1.14
1	0.0138	1.10
2	0.0243	1.94
3	0.0413	3.29
5	0.0458	3.65
7	0.0536	4.27
10	0.0647	5.16

Effect of Water

About one ml of distilled water was applied on films, and afterward irradiated with UV light by using a long wavelength (365 nm) UV lamp for a given period of time. Exposed films were then examined by IR spectroscopy and the number of photons absorbed by the films was calculated. Films without irradiation were used as control for irradiated films and also examined by IR spectroscopy. Three films were used for irradiation of each run in this experiment. A plot of number of photons absorbed versus time is shown in Figure 12, and results are given in Tables 14, A-15, 15, and A-16.

Figure 12. Effect of Water on Photon Interception by Actinometer Films

FIGURE 12

EFFECT OF WATER ON PHOTON INTERCEPTION BY ACTINOMETER FILMS

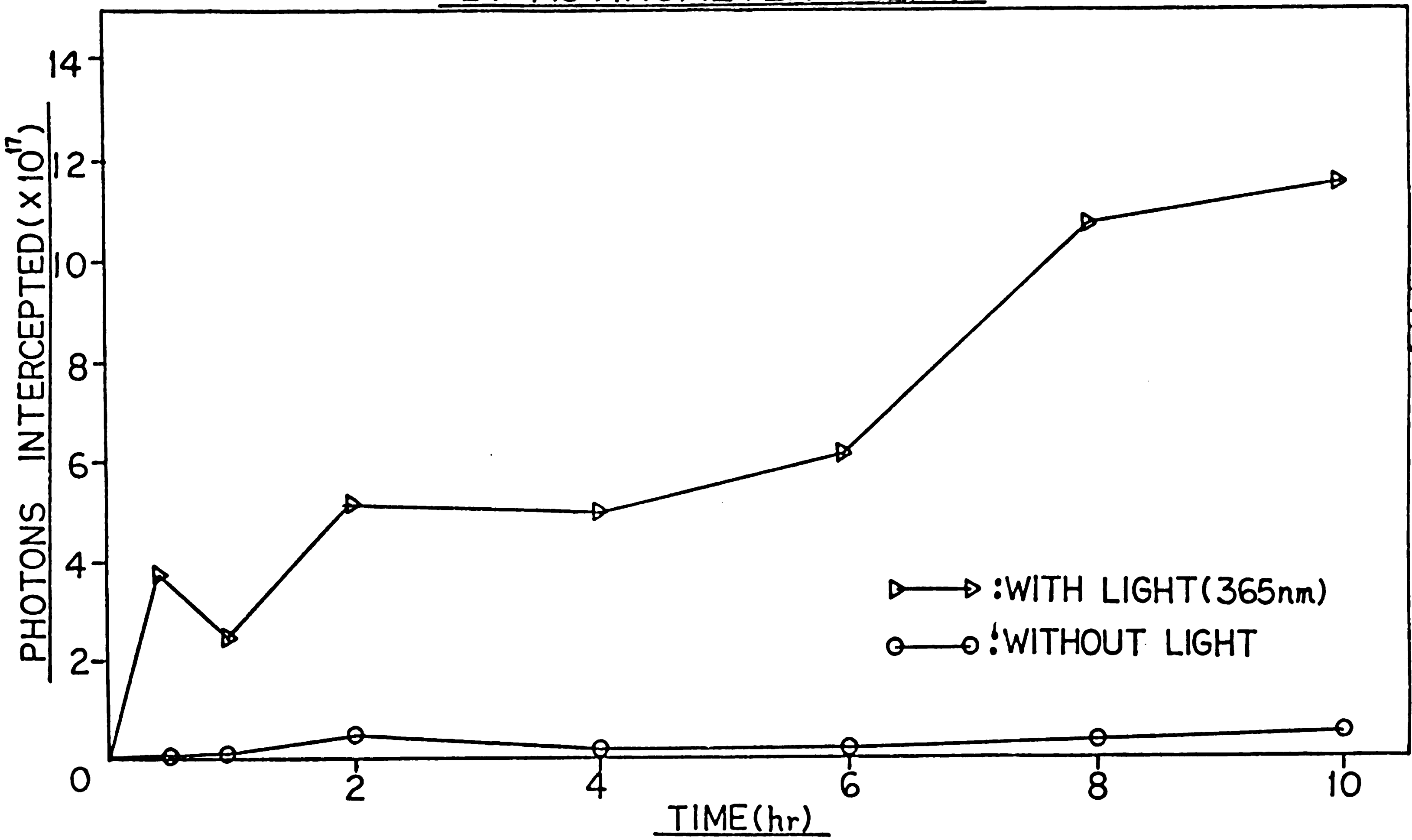


Table 7. The Number of Photons Absorbed by Actinometer Films with Time at 4^{o} C (With Exposure to 365 nm)

time, hr	amount of NBA reacted, mg/cm^2 film	photons ($x10^{17}$)
1/2	0.0110	0.88
1	0.0221	1.77
2	0.0339	2.70
4	0.1135	9.05
6	0.1175	9.37
8	0.1239	9.88
10	0.1610	12.83

Table 8. The Number of Photons Absorbed by Actinometer Films with Time at 4^{o} C (Without Irradiation)

time, hr	amount of NBA reacted, mg/cm^2 film	photons ($x10^{17}$)
1/2	0.0013	0.10
1	0.0028	0.23
2	0.0029	0.23
4	0.0067	0.53
6	0.0065	0.52
8	0.0082	0.65
10	0.0055	0.44

Table 9. The Number of Photons Absorbed by Actinometer Films with Time at 37° C (With Exposure to 365 nm)

time, hr	amount of NBA reacted, mg/cm^2 film	photons (x10^{17})
1/2	0.0192	1.53
1	0.0352	2.81
2	0.0865	6.90
4	0.1280	10.21
6	0.1473	11.75
8	0.1568	12.50
10	0.1612	12.85

Table 10. The Number of Photons Absorbed by Actinometer Films with Time at 37° C (Without Irradiation)

time, hr	amount of NBA reacted, mg/cm^2 film	photons (x10^{17})
1/2	0.0020	0.16
1	0.0024	0.19
2	0.0022	0.18
4	0.0040	0.32
6	0.0052	0.41
8	0.0035	0.28
10	0.0048	0.38

Table 11. The Number of Photons Absorbed by Actinometer Films with Time at 50° C (With Exposure to 365 nm)

time, hr	amount of NBA reacted, mg/cm^2 film	photons (x10^{17})
1/2	0.0246	1.96
2	0.0667	5.32
4	0.0948	7.56
6	0.1367	10.90
8	0.1636	13.04
10	0.1653	13.18

Table 12. The Number of Photons Absorbed by Actinometer Films with Time at 50° C (Without Irradiation)

time, hr	amount of NBA reacted, mg/cm^2 film	photons (x10^{17})
1/2	0.0022	0.17
2	0.0018	0.15
4	0.0030	0.24
6	0.0028	0.22
8	0.0029	0.23
10	0.0035	0.28

Table 13. The Number of Photons Absorbed by Actinometer Films for Wavelength (300 to 400 nm)

wavelength, nm	amount of NBA reacted, mg/cm^2 film	photons ($x10^{16}$)
300	0.0018	1.42
310	0.0037	2.94
320	0.0016	1.30
330	0.0093	7.38
340	0.0026	2.08
350	0.0017	1.39
360	0.0107	8.54
370	0.0036	2.89
380	0.0055	4.38
390	0.0018	1.46
400	0.0017	1.39
control film	0.0035	2.80

Measurement of Cumulative Solar Light Intensity

An actinometer film was exposed to sunlight for a given period of time on July 6, 1982 (location: Lansing, Michigan). After examining the film on the IR spectrophotometer, the film was again exposed to sunlight under the same conditions. Two films with different concentration of NBA/cm^2 film were used to perform this experiment at two different times (2 P.M. and 5 P.M.) on the same day. The number of photons absorbed by the film each time was determined by using equation 1, and a plot of the number of photons absorbed versus time of exposure is shown in Figure 13. The correlation coefficient of the determinations by linear regression was obtained using a curve fitting program on a Hewlett-Packard 97 calculator. Results are given in Tables 16 and 17.

Measurement of Solar Light Intensity Using NBA Actinometer Films

A 2.7 m tall and 1.8 m wide round-shaped honeysuckle (Lonicera tatarica) which stood solitarily in the middle of a field at the Michigan Department of Public Health, Lansing, Michigan was selected for this purpose. Actinometer films (approximately 0.3 mg NBA/cm^2 film) were vertically hung on leaves of the bush at four different directions (east, west, south, and north), and at two different heights (2.1 m and 0.6 m). They were exposed to sunlight for ten minute periods at four different times of the day (10 A.M., 12 Noon, 2 P.M., and 4 P.M. on August 12, 1982). After examining the films by IR spectroscopy, the number of photons absorbed by the films was calculated by using equation 1. Results are given in Tables 18, 19, 20, 21, 22, 23, 24, and 25. The plots of photons absorbed by each film versus time of exposure are shown in Figures 14 and 15.

Table 14. The Number of Photons Absorbed by Actinometer Films with Water (With Exposure to 365 nm)

time, hr	amount of NBA reacted, mg/cm^2 film	photons (x10^{17})
1/2	0.0477	3.80
1	0.0324	2.58
2	0.0634	5.06
4	0.0620	4.94
6	0.0764	6.09
8	0.1336	10.65
10	0.1433	11.42

Figure 13. Measurement of Cumulative Solar Light Intensity by Actinometer Films

FIGURE 13

MEASUREMENT OF CUMULATIVE SOLAR LIGHT INTENSITY BY ACTINOMETER FILM

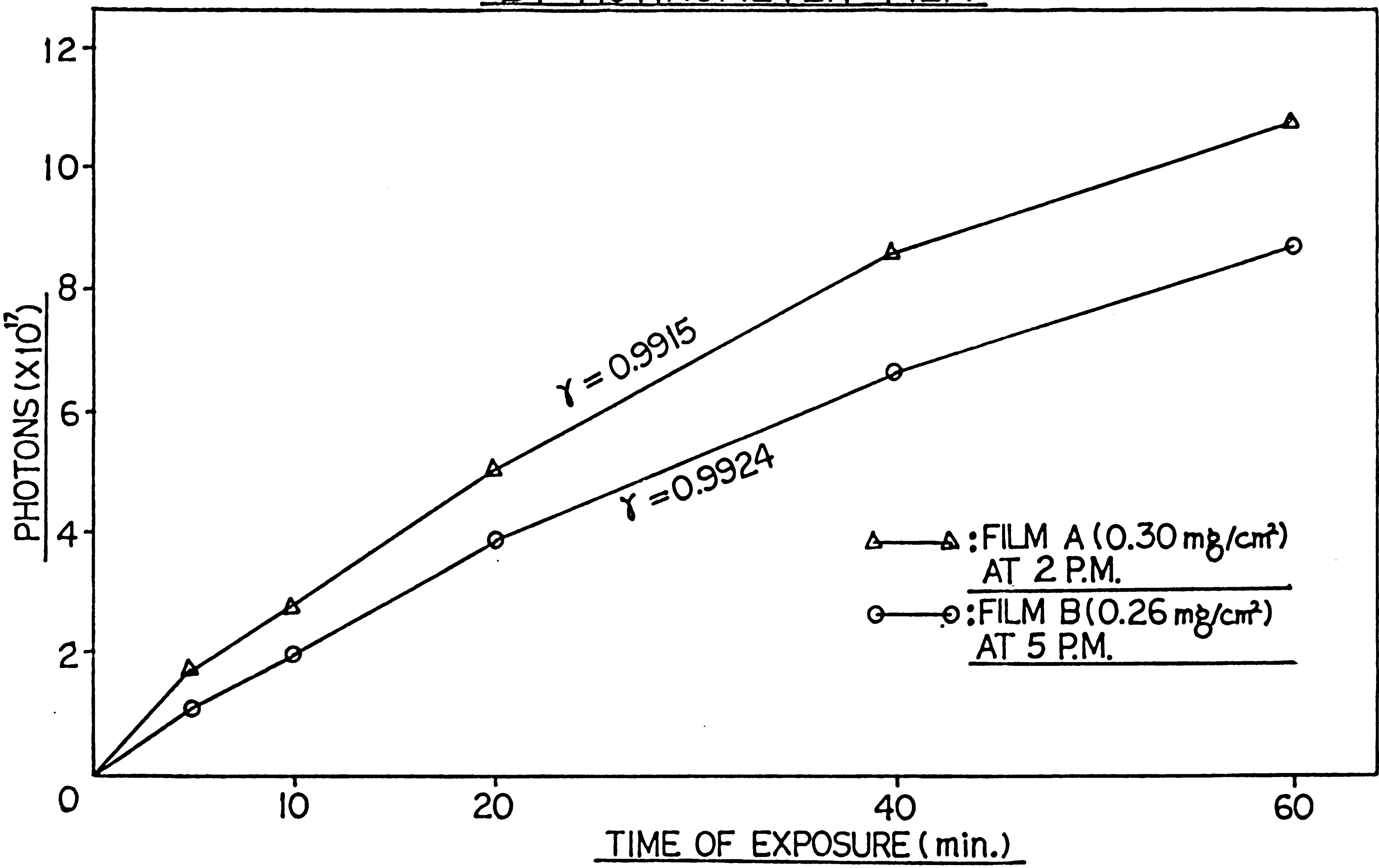


Table 15. The Number of Photons Absorbed by Actinometer Films with Water (Without Irradiation)

time, hr	amount of NBA reacted, mg/cm^2 film	photons ($x10^{17}$)
1/2	------	----
1	------	----
2	0.0058	0.45
4	------	----
6	------	----
8	0.0027	0.21
10	0.0058	0.45

Table 16. Measurement of Cumulative Solar Light Intensity at 2 P.M. on July 6, 1982

time, minutes	height of band at 1530 cm^{-1}	amount of NBA remained, mg/cm^2	amount of NBA reacted, mg/cm^2	photons ($x10^{17}$)
0	0.720	0.3039	-----	-----
5	0.665	0.2807	0.0232	1.85
10	0.640	0.2701	0.0338	2.69
20	0.570	0.2406	0.0633	5.04
40	0.465	0.1963	0.1076	8.58
60	0.400	0.1688	0.1351	10.76

Table 17. Measurement of Cumulative Solar Light Intensity at 5 P.M. on July 6, 1982

time, minutes	height of band at 1530 cm^{-1}	amount of NBA remained, mg/cm^2	amount of NBA reacted, mg/cm^2	photons ($x10^{17}$)
0	0.650	0.2622	-----	-----
5	0.615	0.2481	0.0141	1.12
10	0.590	0.2380	0.0242	1.93
20	0.530	0.2138	0.0484	3.86
40	0.445	0.1795	0.0827	6.59
60	0.385	0.1553	0.1069	8.52

Table 18. Measurement of Solar Light Intensity Irradiated on a Tree (at 2.1 m high and East)

time	amount of NBA reacted, mg/cm^2 film	photons ($x10^{17}$)
10 A.M.	0.0675	5.38
12 Noon	0.0676	5.39
2 P.M.	0.0123	0.98
4 P.M.	0.0061	0.49

Table 19. Measurement of Solar Light Intensity Irradiated on a Tree (at 2.1 m high and West)

time	amount of NBA reacted, mg/cm^2 film	photons ($x10^{17}$)
10 A.M.	0.0020	0.16
12 Noon	0.0031	0.25
2 P.M.	0.0061	0.49
4 P.M.	0.0140	1.12

Table 20. Measurement of Solar Light Intensity Irradiated on a Tree (at 2.1 m high and South)

time	amount of NBA reacted, mg/cm^2 film	photons ($x10^{17}$)
10 A.M.	0.0324	2.58
12 Noon	0.0551	4.39
2 P.M.	0.0810	6.46
4 P.M.	0.0762	6.08

Table 21. Measurement of Solar Light Intensity Irradiated on a Tree (at 2.1 m high and North)

time	amount of NBA reacted, mg/cm^2 film	photons ($x10^{17}$)
10 A.M.	0.0250	1.99
12 Noon	0.0375	2.99
2 P.M.	0.0188	1.50
4 P.M.	0.0094	0.75

Table 22. Measurement of Solar Light Intensity Irradiated on a Tree (at 0.6 m high and East)

time	amount of NBA reacted, mg/cm^2 film	photons ($x10^{17}$)
10 A.M.	0.0438	3.49
12 Noon	0.0375	2.99
2 P.M.	0.0031	0.25
4 P.M.	0.0031	0.25

Table 23. Measurement of Solar Light Intensity Irradiated on a Tree (at 0.6 m high and West)

time	amount of NBA reacted, mg/cm^2 film	photons ($x10^{17}$)
10 A.M.	0.0031	0.25
12 Noon	0.0033	0.27
2 P.M.	0.0100	0.80
4 P.M.	-----	----

Table 24. Measurement of Solar Light Intensity Irradiated on a Tree (at 0.6 m high and South)

time	amount of NBA reacted, mg/cm^2 film	photons ($x10^{17}$)
10 A.M.	0.0032	0.26
12 Noon	0.129	1.03
2 P.M.	0.0385	3.07
4 P.M.	0.0726	5.79

Table 25. Measurement of Solar Light Intensity Irradiated on a Tree (at 0.6 m high and North)

time	amount of NBA reacted, mg/cm^2 film	photons ($x10^{17}$)
10 A.M.	0.0032	0.26
12 Noon	0.0032	0.26
2 P.M.	-----	-----
4 P.M.	0.0061	0.49

Figure 14. Measurement of Solar Light Intensity Irradiated on a Tree (at 2.1 m high) by the Actinometer Films

MEASUREMENT OF SOLAR LIGHT INTENSITY IRRADIATED ON A TREE (AT 2.1 m HIGH) BY THE ACTINOMETER FILMS

FIGURE 14

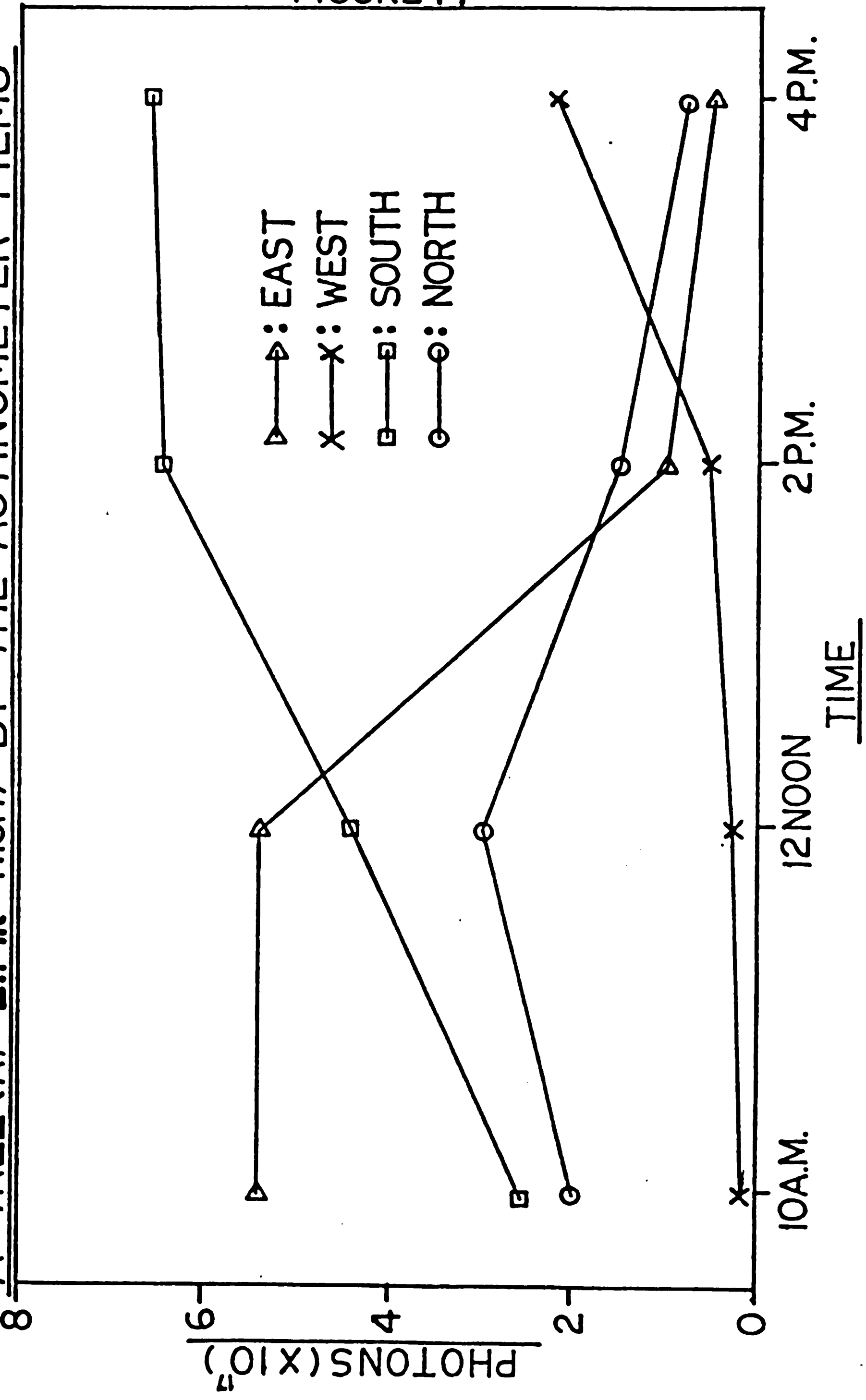


Figure 15. Measurement of Solar Light Intensity Irradiated on a Tree (at 0.6 m high) by the Actinometer Films

MEASUREMENT OF SOLAR LIGHT INTENSITY IRRADIATED ON A TREE (AT **0.6 m** HIGH) BY THE ACTINOMETER FILMS

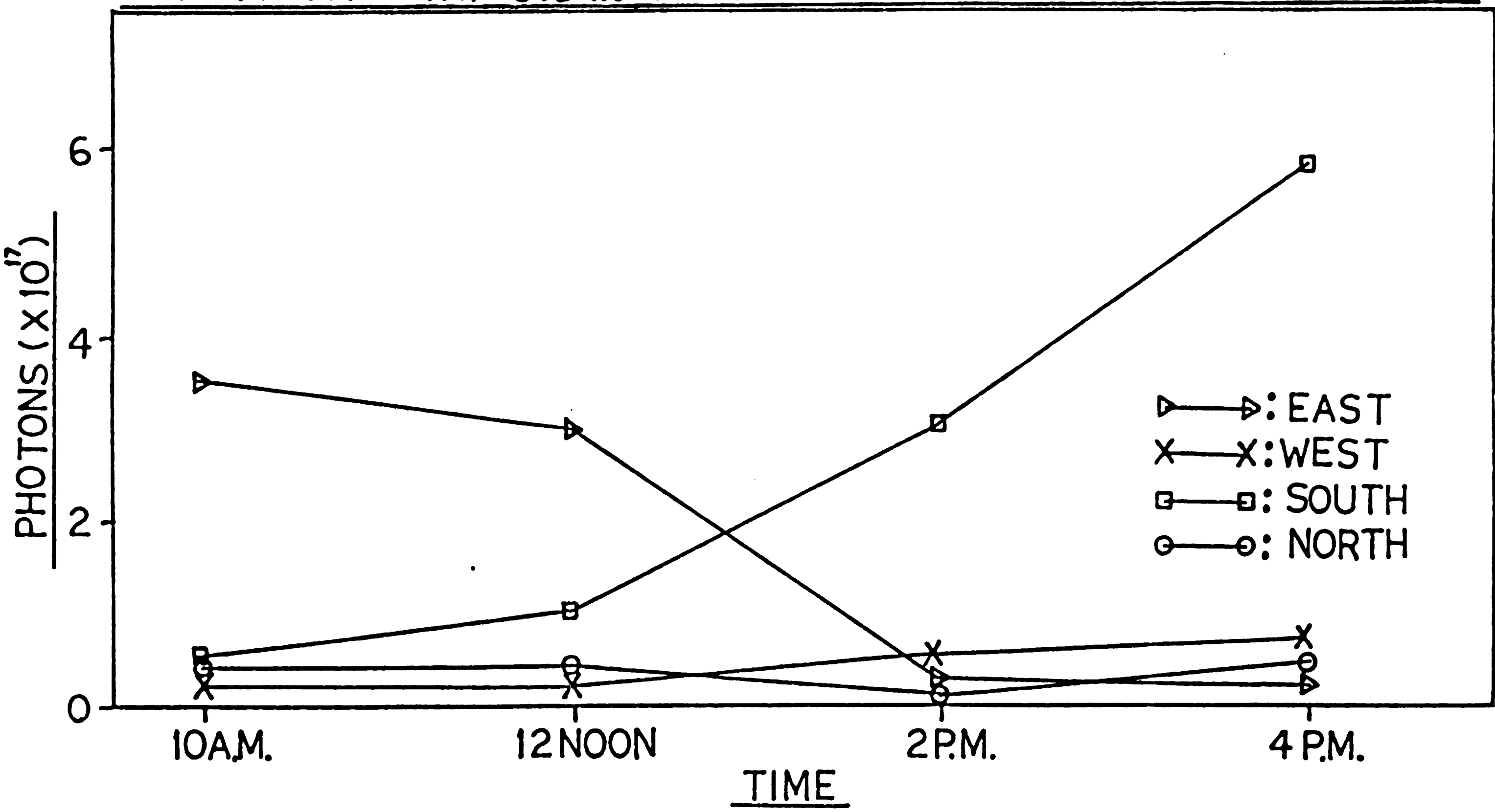


FIGURE 15

RESULTS AND DISCUSSION

Preparation of Calibration Curve for Actinometer Films

Gupta et al. (1980) have shown that calibration curves for orthonitrobenzaldehyde actinometer films have excellent linearity.

From the linear regression calculations, the calibration curve for actinometer films has very good linearity with r = 0.9997. These results show that the absorbance at 1530 cm^{-1} is proportional to the concentration of NBA in the film (mg/cm^2 film). Thus, the concentration of NBA in a film can be obtained easily from this linear calibration curve, after measuring the height of the IR band at 1530 cm^{-1}.

Effect of Varying Volume of Casting Solution

Of the five respective volumes evaluated, the 10 ml casting solution, containing 200 mg of PMMA, showed the highest absorbance band at 1530 cm^{-1}. The absorbance band at 1530 cm^{-1} from the larger volume of casting solution tends to be interfered with more than that from the smaller volume, due to an increase in intensity and overlap of adjacent bands from the polymer. The best results were obtained from films containing 0.3 mg NBA per cm^2 of film and 200 mg of PMMA.

Effect of Angle of Incidental Light

Assuming that the length (x) of a film exposed to light as shown in Figure 6 is 1 cm, the area of the incidental light which had fallen on the film at 90^o angle is the same as the area of the film (1×1 cm^2) because the incidental light falls directly on the whole length (1 cm) of the film. However, at 60^o angle of incidence, the area of the incidental light which falls on the film becomes smaller than that at 90^o angle of incidence, due to the oblique angle of the film to the light. The length (b in Figure 6) of the incidental light which had fallen on the film at 60^o angle is actually equal to the cosine 30^o (= 0.866 cm). In the same manner, a 30^o angle of incidence is equal to cosine 60^o (= 0.5 cm). Therefore, the area of the incidental light for a 90^o angle of incidence is 1 x 1 cm^2, 1 x 0.866 cm^2 for a 60^o, and 1 x 0.5 cm^2 for a 30^o angle of incidence. The ratio of the area of the incidental light which had fallen on the film at various angles of incidence of 90^o: 60^o: 30^o equals 1: 0.87 : 0.5, respectively.

From the results as shown in Tables 3, 4, and 5, the number of photons absorbed by a film in 3 hours was 16.06 x 10^{17} at 90^o angle, 13.19 x 10^{17} at 60^o angle, and 9.04 x 10^{17} at 30^o angle by which the ratio of the number of photons absorbed by each film was 1 : 0.82 : 0.56. Again, the number of photons absorbed in 10 hours at 90^o, 60^o, and 30^o angle of incidence was 20.31 x 10^{17}, 16.96 x 10^{17}, and 13.22 x 10^{17}, respectively, and gives the ratio of 1 : 0.84 : 0.65.

These experiments show that the number of photons absorbed by films depends on the area (quantity) of incidental light which has fallen on the film, and angle of incidence has an effect on the absorption of the number of photons by film, due to changes in area of incidental light.

<u>Effect of Temperature</u>

Without irradiation, the actinometer films were little affected by the various temperatures (4^oC, 37^oC, and 50^oC) for the three experiments. Chemical conversion by photochemical reaction which occurred at all temperatures had equal rates and photon absorption.

These experiments demonstrate that actinometer films are not sensitive to variations of temperature from 4^oC to 50^oC, and that temperature has little influence on the stability and capability of films to measure photons produced by various wavelengths of light. It is well known that temperature has little or no effect on primary photochemical reactions, but has a marked effect on secondary reactions, since the secondary processes are thermal reactions (Ellis, 1941). Therefore, they may be used as a stable and reliable device for measuring photons caused by a primary photoreaction at these temperatures.

Effect of Wavelength

As shown in Figure 11, films generally reflected an insensitivity of response to a variation in wavelength except wavelengths at 330 nm and 360 nm which had conspicuous effect on the actinometer films. Of ten respective wavelengths evaluated, the wavelength at 360 nm had the greatest effect on photochemical conversion of o-nitrobenzaldehyde in a film. Thus, it is likely that an effective wavelength for the NBA film actinometer lies in the range of 320 nm and 380 nm.

Effect of Water

Without irradiation, water had little effect on the stability of actinometer films. With irradiation of UV light, water had an effect on the absorption of UV incidental light by actinometer films as shown in Figure 12. The films irradiated for less than five hours gave a fluctuation in the absorption of photons versus time. However, comparing with the results from effect of angle of incidence, films irradiated from six to ten hours gave an effect similar to films which were irradiated in the absence of water. The long irradiation caused the vaporization of the distilled water which had been applied to the films. This was due to the heat produced by the UV lamp. This experiment shows that water interferes with the absorption of incidental light by preventing some light from reaching the films.

Measurement of Cumulative Solar Light Intensity

As shown in Figure 13, the correlation coefficient of plots of photons absorbed versus time of exposure was 0.9915 for film A (0.3 mg NBA/cm^2 film), and 0.9924 for film B (0.26 mg NBA/cm^2 film), respectively. Thus, these results show that the plots of the determinations (photons absorbed versus time of exposure) have good linearity, and that the concentration of NBA in films has little effect on the rate of photochemical conversion of o-nitrobenzaldehyde by solar UV light. Therefore, o-nitrobenzaldehyde in a film is cumulatively altered by exposure to sunlight, and the extent of photochemical conversion of NBA depends on length of exposure.

This experiment demonstrates that the actinometer films can measure continuously the intensity of solar UV light. It has been reported by Gupta et al. (1980) that the o-nitrobenzaldehyde films have a linear range of up to about 50% conversion by photoreaction. Thus, they may be used for measuring cumulatively the intensity of solar UV light until 50% conversion of initial amount of NBA in films occurs.

Measurement of Solar Light Intensity Using Actinometer Films

In the morning (10 A.M. and 12 Noon), the strongest light intensity was measured from the films at the east side, and the intensity of light then faded as time progressed.

In the afternoon (2 P.M. and 4 P.M.), the strongest intensity of sunlight was absorbed by the films on the southern part, and the lowest intensity of light was detected from those films at the west side even though the sun had moved westward.

At 2.1 m high, the greatest absorption of incidental light by the actinometer films was observed, and the smallest absorption occurred at 0.6 m of height.

Again, this experiment shows that actinometer films are capable of measuring solar UV light intensity in obedience to the intensity of incidental light which has fallen on the films.

SUMMARY AND CONCLUSIONS

The following results were derived from this study on the o-nitrobenzaldehyde film actinometer system:

1. Film actinometer can be easily prepared by casting from dichloromethane containing polymethyl methacrylate.
2. It is stable at a temperature range of 4°C to 50°C.
3. Angle of incidence has an effect on the absorption of the number of photons by film actinometer.
4. The most effective range in wavelengths for film actinometer lies between 320 nm and 380 nm.
5. Water interferes with the absorption of incidental light by film actinometer.
6. Film actinometer can continuously measure solar UV light without loss of accuracy up to 50% depletion of initial amount of o-nitrobenzaldehyde.
7. Film actinometer can be used for determination of incidental light intensity at any surface and locations to which currently used devices are normally inaccessible.
8. Determination of photons absorbed by films can be obtained conveniently by using an IR spectrophotometer.

Therefore, the film actinometer system may be used as a convenient, useful tool for measuring incidental light intensity to develop better models for photochemical studies, and to better assess the rate at which xenobiotics will react by solar UV light in the environment.

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APPENDIX

Table A-1. Relative Height of the Band at 1530 cm^{-1} versus the mg NBA per cm^2 of Film

mg NBA per cm^2 film	relative band height at 1530 cm^{-1}			
	1	2	2	4
0.10	0.390	0.345	0.385	0.400
0.15	0.470	0.475	0.478	0.425
0.20	0.505	0.575	0.550	0.538
0.25	0.625	0.600	0.645	0.650
0.30	0.700	0.690	0.715	0.755

Table A-2. Relative Height of the Band at 1530 cm^{-1} versus Volume of Casting Solution

volume of casting solution, ml	relative band height at 1530 cm^{-1}			
	1	2	3	4
5	0.585	0.600	0.620	0.585
8	0.570	0.635	0.625	0.600
10	0.700	0.730	0.775	0.745
15	0.690	0.705	0.715	0.645
20	0.635	0.660	0.700	0.610

Table A-3. The Number of Photons Absorbed by Actinometer Films with Time at 90° Angle of Incidence

time, hr	amount of NBA unreacted mg/cm^2 film	amount of NBA reacted mg/cm^2 film	photons ($x10^{17}$)
1/2	0.2480	0.1020	8.13
	0.2284	0.1216	9.69
1	0.2065	0.1435	11.44
	0.2184	0.1316	10.49
2	0.1724	0.1776	14.16
	0.1763	0.1737	13.85
3	0.1518	0.1982	15.80
	0.1454	0.2046	16.31
5	0.1295	0.2205	17.58
	0.1286	0.2214	17.66
7	0.0956	0.2544	20.29
	0.1171	0.2329	18.57
10	0.0940	0.2560	20.40
	0.0963	0.2537	20.21

Table A-4. The Number of Photons Absorbed by Actinometer Films with Time at 60° Angle of Incidence

time, hr	amount of NBA unreacted mg/cm^2 film	amount of NBA reacted mg/cm^2 film	photons (x10^{17})
1/2	0.2426 0.2630	0.0574 0.0370	4.58 2.95
1	0.2117 0.2029	0.0883 0.0971	7.04 7.74
2	0.1735 0.1427	0.1265 0.1573	10.09 12.55
3	0.1402 0.1289	0.1598 0.1711	12.74 13.64
5	0.1201 0.1123	0.1799 0.1877	14.34 14.97
7	0.1066 0.0979	0.1934 0.2021	15.42 16.12
10	0.0938 0.0808	0.2062 0.2192	16.44 17.47

Table A-5. The Number of Photons Absorbed by Actinometer Films with Time at 30° Angle of Incidence

time, hr	amount of NBA unreacted mg/cm^2 film	amount of NBA reacted mg/cm^2 film	photons ($x10^{17}$)
1/2	0.2723	0.0277	2.21
	0.2144	0.0356	2.84
1	0.2267	0.0733	5.85
	0.1975	0.0525	4.19
2	0.1851	0.1149	9.16
	0.1749	0.0751	5.99
3	0.1690	0.1310	10.44
	0.1542	0.0958	7.64
5	0.1424	0.1576	12.57
	0.1312	0.1188	9.47
7	0.1316	0.1684	13.42
	0.1172	0.1328	10.59
10	0.1186	0.1814	14.47
	0.1000	0.1500	11.96

Table A-6. The Number of Photons Absorbed by Actinometer Films with Time at 0^o (or 180^o) Angle of Incidence

time, hr	amount of NBA unreacted mg/cm^2 film	amount of NBA reacted mg/cm^2 film	photons ($x10^{17}$)
1/2	0.2876	0.0124	0.99
	0.2838	0.0162	1.29
1	0.2880	0.0120	0.96
	0.2844	0.0156	1.24
2	0.2714	0.0286	2.28
	0.2800	0.0200	1.59
3	0.2538	0.0462	3.69
	0.2638	0.0362	2.88
5	0.2492	0.0508	4.05
	0.2592	0.0408	3.25
7	0.2409	0.0591	4.71
	0.2519	0.0481	3.83
10	0.2277	0.0723	5.76
	0.2428	0.0572	4.56

Table A-7. The Number of Photons Absorbed by Actinometer Films with Time at 4°C (With Exposure to 365 nm)

time, hr	amount of NBA reacted mg/cm² film	photons (x10¹⁷)
1/2	0.0140	1.12
	0.0080	0.64
	0.0095	0.76
	0.0125	1.00
1	0.0238	1.90
	0.0204	1.63
	0.0184	1.47
	0.0258	2.06
2	0.0282	2.25
	0.0395	3.15
	0.0342	2.72
	0.0335	2.67
4	0.1026	8.19
	0.0966	7.70
	0.1244	9.91
	0.1304	10.39
6	0.1037	8.26
	0.1128	8.99
	0.1222	9.74
	0.1316	10.48
8	0.1032	8.22
	0.1222	9.74
	0.1446	11.52
	0.1256	10.01
10	0.1552	12.37
	0.1667	13.28
	0.1737	13.85
	0.1483	11.82

Table A-8. The Number of Photons Absorbed by Actinometer Films with Time at 4°C (Without Irradiation)

time, hr	amount of NBA reacted mg/cm^2 film	photons ($x10^{17}$)
1/2	0.0010	0.08
	0.0016	0.13
1	0.0028	0.22
	0.0029	0.23
2	0.0028	0.22
	0.0030	0.24
4	0.0055	0.44
	0.0079	0.63
6	0.0062	0.49
	0.0068	0.54
8	0.0072	0.57
	0.0092	0.73
10	0.0072	0.57
	0.0038	0.30

Table A-9. The Number of Photons Absorbed by Actinometer Films with Time at 37°C (With Exposure to 365 nm)

time, hr	amount of NBA reacted mg/cm^2 film	photons (x10^{17})
	0.0164	1.31
1/2	0.0203	1.62
	0.0209	1.67
	0.0288	2.29
1	0.0402	3.20
	0.0366	2.92
	0.0776	6.18
2	0.0825	6.57
	0.0994	7.92
	0.1238	9.86
3	0.1307	10.41
	0.1295	10.32
	0.1368	10.90
5	0.1495	11.91
	0.1556	12.40
	0.1594	12.70
8	0.1500	11.95
	0.1610	12.83
	0.1611	12.84
10	0.1588	12.65
	0.1637	13.04

Table A-10. The Number of Photons Absorbed by Actinometer Films with Time at 37°C (Without Irradiation)

time, hr	amount of NBA reacted mg/cm^2 film	photons (x10^{17})
1/2	0.0016	0.13
	0.0024	0.19
1	0.0020	0.16
	0.0028	0.22
2	0.0020	0.16
	0.0024	0.19
3	0.0032	0.25
	0.0048	0.38
5	0.0046	0.37
	0.0058	0.46
8	0.0043	0.34
	0.0027	0.22
10	0.0058	0.46
	0.0038	0.30

Table A-11. The Number of Photons Absorbed by Actinometer Films with Time at 50°C (With Exposure to 365 nm)

time, hr	amount of NBA reacted mg/cm^2 film	photons ($\times 10^{17}$)
	0.0198	1.58
1/2	0.0306	2.44
	0.0234	1.86
	0.0538	4.29
2	0.0788	6.28
	0.0675	5.38
	0.0886	7.06
4	0.0992	7.90
	0.0966	7.70
	0.1028	8.19
6	0.1527	12.17
	0.1546	12.32
	0.1432	11.41
8	0.1805	14.38
	0.1671	13.31
	0.1449	11.54
10	0.1815	14.46
	0.1695	13.50

Table A-12. The Number of Photons Absorbed by Actinometer Films with Time at 50°C (Without Irradiation)

time, hr	amount of NBA reacted mg/cm^2 film	photons ($\times 10^{17}$)
1/2	0.0018	0.14
	0.0025	0.20
2	0.0014	0.11
	0.0022	0.18
4	0.0033	0.26
	0.0027	0.22
6	0.0026	0.21
	0.0029	0.23
8	0.0028	0.22
	0.0029	0.23
10	0.0028	0.22
	0.0042	0.33

Table A-13. The Number of Photons Absorbed by Actinometer Films for Wavelength (300 to 400 nm)

wavelength, nm	amount of NBA reacted mg/cm^2 film	photons ($x10^{16}$)
300	0.00168	1.338
	0.00188	1.498
310	0.00416	3.314
	0.00322	2.565
320	0.00172	1.370
	0.00154	1.227
330	0.00851	6.780
	0.01001	7.975
340	0.00292	2.326
	0.00230	1.832
350	0.00154	1.227
	0.00194	1.546
360	0.01011	8.055
	0.01133	9.027
370	0.00365	2.910
	0.00361	2.876
380	0.00624	4.972
	0.00476	3.792
390	0.00157	1.251
	0.00209	1.665
400	0.00166	1.322
	0.00182	1.450

Table A-14. The Number of Photons Absorbed by Actinometer Films (Control for Wavelength Effect)

film #	amount of NBA reacted mg/cm^2 film	photons ($x10^{16}$)
1	0.00203	1.617
2	0.00432	3.442
3	0.00345	2.749
4	0.00438	3.490
5	0.00451	3.593
6	0.00287	2.287
7	0.00198	1.578
8	0.00273	2.175
9	0.00386	3.075
10	0.00497	3.960

Table A-15. The Number of Photons Absorbed by Actinometer Films with Water (With Exposure to 365 nm)

time, hr	amount of NBA reacted mg/cm^2 film	photons ($x10^{17}$)
	0.0443	3.53
1/2	0.0507	4.04
	0.0481	3.83
	0.0312	2.49
1	0.0346	2.76
	0.0314	2.50
	0.0493	3.93
2	0.0756	6.02
	0.0653	5.20
	0.0673	5.36
4	0.0584	4.65
	0.0603	4.80
	0.0865	6.89
6	0.0621	4.95
	0.0806	6.42
	0.1440	11.47
8	0.1248	9.94
	0.1320	10.52
	0.1488	11.86
10	0.1523	12.13
	0.1288	10.26

Table A-16. The Number of Photons Absorbed by Actinometer Films with Water (Without Irradiation)

time, hr	amount of NBA reacted mg/cm^2 film	photons ($x10^{17}$)
1/2	------	----
1	------	----
2	0.0050	0.40
	0.0064	0.51
4	------	----
6	------	----
8	0.0023	0.18
	0.0030	0.24
10	0.0049	0.39
	0.0067	0.53