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ASSESSMENT OF A WATER TREATMENT SYSTEM UTILIZING OXIDIZING SPECIES PRODUCED AT THE TAL OXIDE-WATER INTERFACE UNDER ILLUMINATION

JOHN H. CAREY

UNPUBLISHED REPORT
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1. INTRODUCTION

Water treatment processes that can replace chlorination for disinfection or which can be used in conjunction with biological treatment to remove dissolved organics are needed. It is possible that oxidizing species produced on semiconductor surfaces by irradiation can be utilized. Such a process would have several advantages over conventional photochemical techniques.

(a) it is a "sensitized" process and hence does not require that the substance to be oxidized absorb the light;

(b) the photochemical transition usually involved interatomic electron transfer and therefore, oxidizing and reducing agents are produced as primary species;

(c) the semiconductors can be solids that do not dissolve under irradiation and therefore, are easily removed by physical means, i.e., no costly chemical removal of sensitizers.

In order to understand the route by which illumination of a semiconductor surface produces reactive species in solution, it is necessary to visualize the electronic levels at the solid/liquid interface. When a semiconductor is illuminated with light of energy greater than its optical band gap, an electron is transferred to the conduction band, leaving an electron vacancy or 'hole' in the valence band. At the interface, electron transfer can occur either from the conduction band to an electron acceptor in solution or from a donor in solution to the valance band hole. These processes are depicted in Fig. 1.

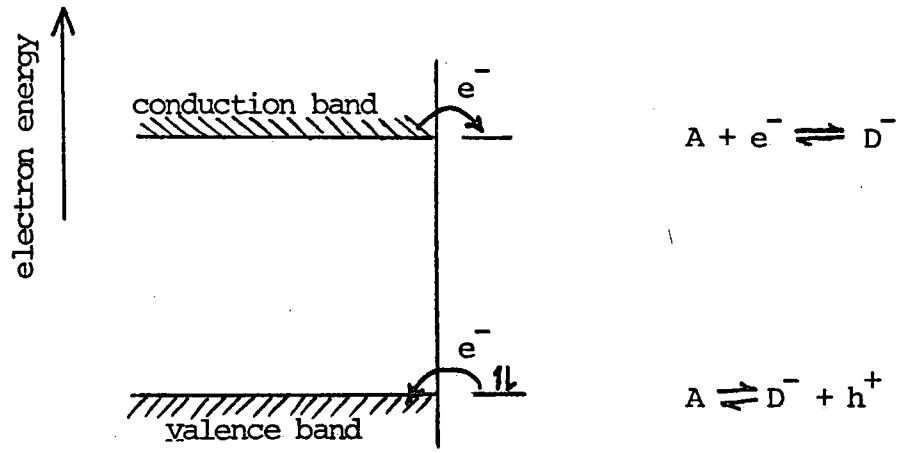


Fig. 1. Energy correlations for electron-transfer processes at the semiconductor-electrolyte interface.

The principle of conservation of energy demands that electron exchanges occur between electron states of the same energy ($\pm$ kT). Thus, potential acceptors with energy levels more than kT below the conduction band edge and donors of energy more than kT above the valance band edge do not participate in radiationless electron-transfer processes. It is possible to picture which processes are thermodynamically possible by comparing the relative position between the energy levels of the redox components and the band edge of the semiconductor using some common reference energy, usually the vacuum level.

The electronic energy levels in a semiconductor can be calculated from thermodynamic work functions using the band model for metals. For example, for the wide band gap semiconductor TiO_2 (rutile), the conduction band is 4eV below the vacuum level, the Fermi level 4.3 eV and the valence band 7eV below vacuum. The

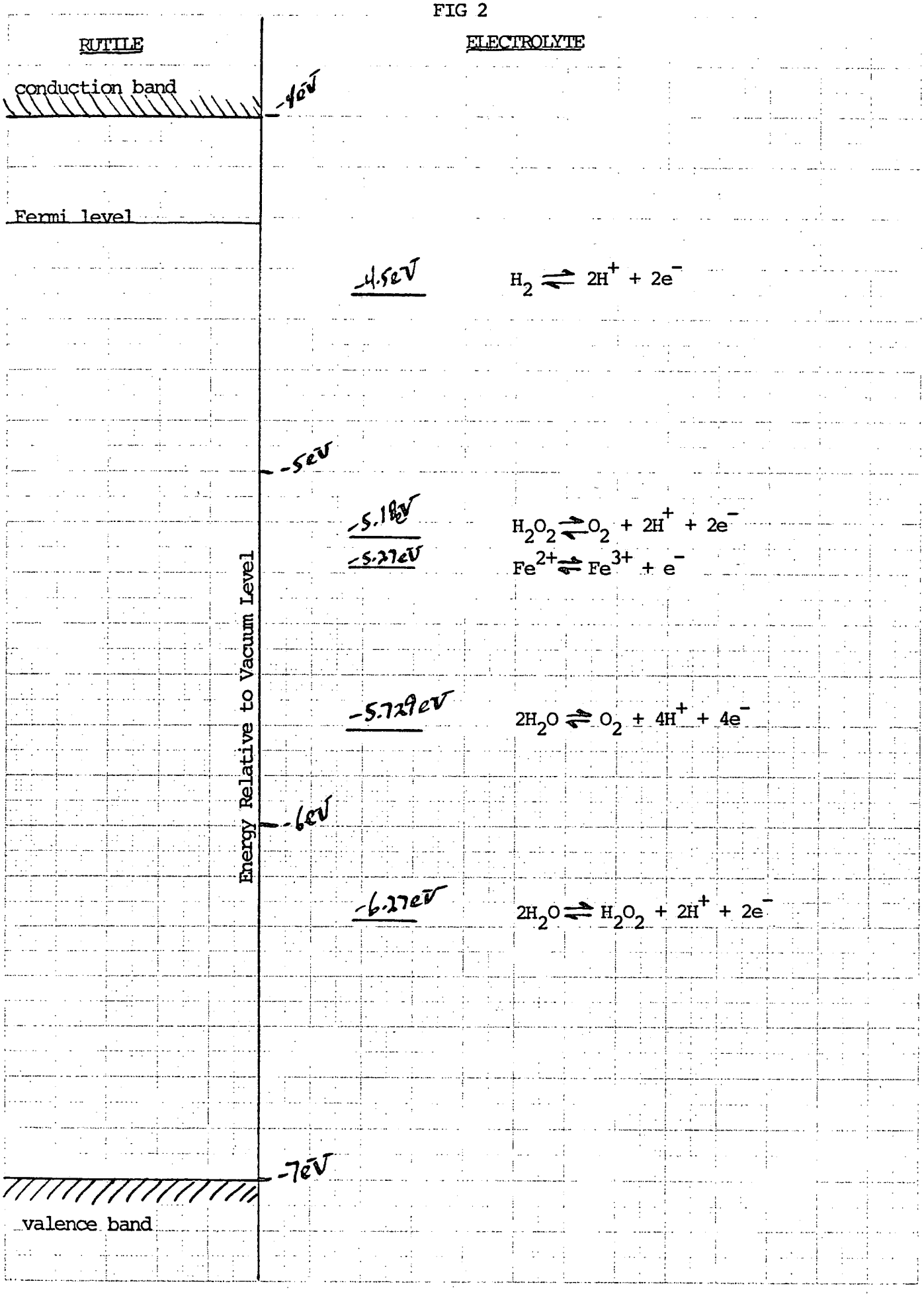
optical band gap is 3 eV and thus illumination with light of wavelength less than 410 nm will cause the formation of an electron/hole pair.

The calculation of the equivalent levels for dissolved species is more complex due to various solvation states of one species and the changes in solvation energy that can accompany changes in oxidation states. Gerischer[1] has dealt with this matter in detail. The Fermi level of the Normal Hydrogen Electrode (NHE) at pH = 0 has been reported to be 4.5 eV below vacuum. Thus only the position of a given redox pair relative to the NHE is needed to determine possible interactions between the pair and semiconductor levels. The relationship between the rutile levels and redox levels involving water and oxygen are shown in Fig. 2.

While the preceding discussion can be used to determine what processes are thermodynamically possible, it gives no indication of the kinetics. The rate of electron transfer is proportional to the density of occupied state in one phase and unoccupied states in the other phase that are on the same energy level. Because of the energy level distribution, an integration has to be performed over all corresponding energy levels. Thus, the rate of electron transfer is directly proportional to the concentration of donors and acceptors.

For wide band gap semi-conductors, surface states can function as additional donor or acceptor levels. The importance of this type of process can be demonstrated by reference to Fig. 2. Due to the considerable separation between the rutile valence band edge and the

FIG 2


RUTILE
ELECTROLYTE
conduction band
-4eV
Fermi level
-4.5eV
$H_2 \rightleftharpoons 2H^+ + 2e^-$
-5eV
-5.18eV
$H_2O_2 \rightleftharpoons O_2 + 2H^+ + 2e^-$
-5.27eV
$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$
-5.729eV
$2H_2O \rightleftharpoons O_2 + 4H^+ + 4e^-$
-6eV
-6.27eV
$2H_2O \rightleftharpoons H_2O_2 + 2H^+ + 2e^-$
-7eV
valence band
Energy Relative to Vacuum Level

redox potential for the water/oxygen couple, it might be expected that rutile holes would not efficiently oxidize water to oxygen. In fact, the process occurs with high efficiency. The processes involved in electron transfer via surface states are depicted in Fig. 3. The arrows show the direction of electron transfer. The sequence starts with the production of an electron/hole pair by light absorption (process 1).

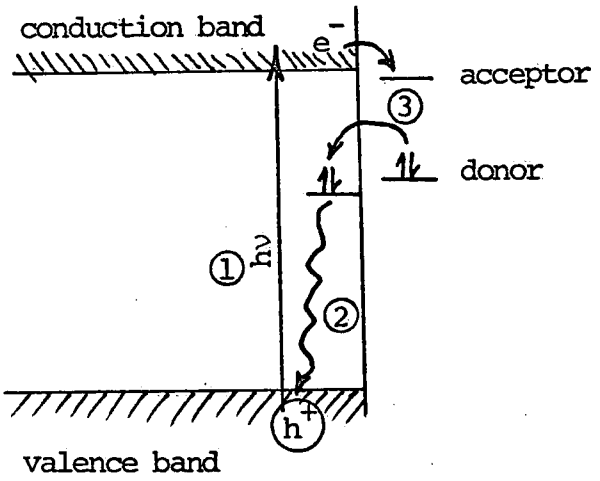


Fig. 3. Energy correlations for electron transfer involving surface states.

An electron from the surface state then populates the valence band hole (process 2), leaving an electron vacancy in the surface state. This vacancy is then filled by an electron from the donor in solution (process 3).

As in most photochemical reactions involving electron transfer, recombination of the primary products will be an extremely rapid process. It is necessary, therefore, to prevent recombination to achieve significant yields of photoproducts. This can be done by

making the semiconductor an electrode and applying a polarizing potential. In this case, the electrons and holes are separated by the potential and react at different electrodes, thus preventing recombination.

It is also possible to prevent recombination at the surface by having all reactive sites in solution occupied by the appropriate electron donor or acceptor. The fraction of either electrons or holes reacting with a scavenger would be related to

$$\frac{k_1[s]}{k_1[s] + \text{rate comb.}}$$

Thus at high scavenger concentrations, the fraction approaches 1. It is necessary to have scavengers present for both electrons and holes since the rate of recombination is proportional to $k[e^-][h^+]$ and if the concentration of either species were allowed to increase, the rate of recombination would increase, thus cancelling the effect of scavenging for other species.

It is clearly desirable, from an economic standpoint, if both the electron donors and acceptors are present in the water to be treated. Reference to Fig. 2 reveals that major electron acceptors already present in the area of the conduction band are H^+ and O_2 while H_2O is the only electron donor present in large concentrations. Thus, for electron transfer reactions to be efficient enough to compete with recombination, the following reactions should readily occur.

$$e^- + H^+ \rightarrow H\cdot \quad (1)$$

$$H\cdot + O_2 \rightarrow HOO\cdot \quad (2)$$

$$e^- + O_2 \rightarrow O_2^- \quad (3)$$

$$O_2^- + H^+ \rightarrow HOO\cdot \quad (4)$$

$$h^+ + H_2O \rightarrow \cdot OH + H^+ \quad (5)$$

Either hydroperoxyl (HOO·) or hydroxyl (·OH) radicals could attack the organics present, resulting in organic oxidation. In this way, the system efficiency does not depend on organic concentration.

2. RESULTS AND DISCUSSION

2.1 Preliminary Evaluation

Since stability under irradiation is an important prerequisite of any metal oxide which is to be used as a photocatalyst for water treatment, this factor was evaluated first. Of the ten semiconductors evaluated, two proved unstable under illumination in neutral aqueous solution. These were V_2O_5 and ZnO. Some vanadium dissolved from V_2O_5 in the dark since supernatants from an unirradiated slurry were yellow, indicating the presence of small amounts of dissolved vanadium (V) species. However, after irradiation, the supernatants were blue, indicative of the presence of vanadium (IV) species such as $VO(H_2O)_5^{2+}$. Zinc Oxide did not dissolve in the dark but after irradiation several drops of the supernatant were tested with 0.2M $K_4Fe(CN)_6$. A bluish-grey precipitate formed which proves the presence of zinc. The other eight oxides listed in TABLE 1 all contained titanium. No titanium

was found when supernatants from irradiated solutions were tested with H_2O_2.

The remaining eight semiconductors were then evaluated to determine their relative photoreactivities for organic oxidations. Methanol and isopropanol were chosen as substrates for oxidation since they react with a wide variety of oxygen containing radicals, including those expected to result from the photooxidation of water on the metal oxide surface. In order to suppress chain reactions, ferric perchlorate was included at a concentration large enough to react with all alcohol radicals formed. Alcohol concentrations were chosen from studies of iron photochemistry and were large enough to scavenge all hydroxyl and hydroperoxyl radicals in solution. The presence of iron allowed the solutions to be degassed which removed the possible complication of peroxyl radical formation by reaction of the alcohol radicals with dissolved oxygen. Thus the degree of alcohol oxidation can be expected to be a true measure of primary photoefficiency for each catalyst. The results of these irradiations are listed in TABLE 1.

The results clearly show anatase to be superior to all semiconductors tested by an order of magnitude. Attempts were made to alter the photoactivity of these catalysts by pretreatment. Heating anatase and rutile at 150°C for 72 hours did not measurably alter the photoefficiencies. The photoactivity of anatase at the gas-liquid interface decreases with increasing temperature due to loss of strongly bound water but this effect can be reversed by cooling in the presence

TABLE 1

PRIMARY PHOTOEFFICIENCY FOR VARIOUS SEMICONDUCTORS

SEMICONDUCTOR	Φ Fe(II)	Φ CH_2O
TiO_2 (anatase)	.334	.076
TiO_2 (rutile)	.020	.005
$ZnTiO_3$	.010	.0001
$MgTiO_3$	.034	.0006
$CaTiO_3$	.030	.0006
$BaTiO_3$	.012	.0001
$SrTiO_3$	.020	.0005

$[HClO_4] = 0.5M$, $[CH_3OH] = 0.494M$, $[(CH_3)_2CHOH] = 0.260M$, $[Fe^{3+}] = 0.01M$

of water vapour. Since the changes on the anatase surface are reversed in the presence of water, and the proposed use is as a catalyst for water treatment, it is unlikely that heat treatment can be used to advantage. Indeed, at very high temperatures, anatase is irreversibly converted to rutile and thus would exhibit drastically lower yields.

When rutile or anatase are heated at moderate temperatures in a vacuum, oxygen defects are produced in the surface which increase the conductivity and give the oxides a blue colour. These defects can

also be produced by irradiation of the oxides with far UV light in a deoxygenated system. Samples of anatase and rutile which had been pretreated in this manner were added to the iron perchlorate/alcohol system. In the dark prior to the irradiation, the blue colour disappeared and iron(II) was produced. The blue colour also disappeared in the presence of oxygen. The samples of TiO_2 which had been pretreated and reoxidized in this manner exhibited similar photooxidation quantum yields to the parent material. Because of its reasonably high yield of photooxidants and its low price (50¢ per lb in commercial quantities), anatase was chosen for further evaluation as a water treatment catalyst and all attempts at pretreatment were abandoned.

2.2 Attempted Disinfection of Secondary Effluent with Anatase/UV

In order to determine whether the reactive species produced in the anatase-UV system could be used as a viable alternative to chlorine for disinfection, studies were conducted on secondary effluent from the Burlington Skyway sewage treatment facility. Since disinfection of this effluent by direct irradiation with light in the far UV region (254 nm) had already been studied and compared to chlorination, it was decided to compare the far UV efficiency with that of anatase-near UV (365 nm). Using the value 6×10^{-8} einsteins/ml as the dose required to kill 99% of the pathogenic bacteria, it was estimated that 0.25 min in the Rayonet should have been sufficient to achieve a comparable kill if the anatase system worked as well as direct irradiation at 254 nm.[2] For comparison purposes, a sample was

given a dose of far UV of comparable intensity. The results are listed in TABLE 2.

TABLE 2

ATTEMPTED DISINFECTION OF SECONDARY EFFLUENTS

WAVELENGTH & CATALYST	IRRADIATION TIME	COUNTS/ml	EFFICIENCY
none	0 min	9.7×10^5	-
254 nm, direct	1 min	1	100%
365 nm, direct	10 min	6.6×10^5	32%
365 nm, .5% anatase	0 min	9.5×10^5	-
365 nm, .5% anatase	2 min	8.7×10^5	-
365 nm, .5% anatase	4 min	9.1×10^5	-
365 nm, .5% anatase	6 min	8.5×10^5	-
365 nm, .5% anatase	10 min	8.8×10^5	9% *
365 nm, 1% anatase	3 min	9.3×10^5	-
365 nm, 4% anatase	3 min	8.8×10^5	-

* This value may not be significantly different from the control.

It is apparent from these values that anatase cannot be suggested as a photocatalyst for disinfection. Indeed, the efficiency with anatase was lower than an equivalent dose of the same wavelength light without anatase which indicates that the anatase was protecting the

bacteria from exposure to the light. Further attempts at disinfection with anatase were abandoned. Although the species produced on irradiation of anatase can oxidise organics, they don't appear capable of disinfection, probably because they react so efficiently with the dissolved organics they don't survive long enough to encounter the bacteria.

2.3 Photolysis of Anatase in the Presence of Chlorinated Organics

Our preliminary studies had indicated that PCBs could be dechlorinated upon irradiation with anatase but the identity and toxicity of the photoproducts were not determined.[3] Identities of the photoproducts are difficult to determine since electron capture detectors cannot detect dechlorinated products at the ppb level and other detectors are also not sensitive enough. An additional problem is that some of the products are likely phenolic and difficult to extract from water at the ppb level. At the saturation (30 ppb) concentration however, Aroclor 1254 strongly suppresses growth of the algae Scenedesmus quadricauda. In order to study the effect of the photoproducts on this algae, a 500 ml sample of saturated Aroclor 1254 solution containing .25% anatase was irradiated for one hour at 365 nm. Another sample in an opaque red flask was placed in the irradiation chamber to be used as an unirradiated control. After irradiation and filtration, three 100 ml aliquots of each solution were taken. The nutrients required for CHU-#10 algal growing medium were added to each sample and also to three 100 ml samples of distilled water[4]. The

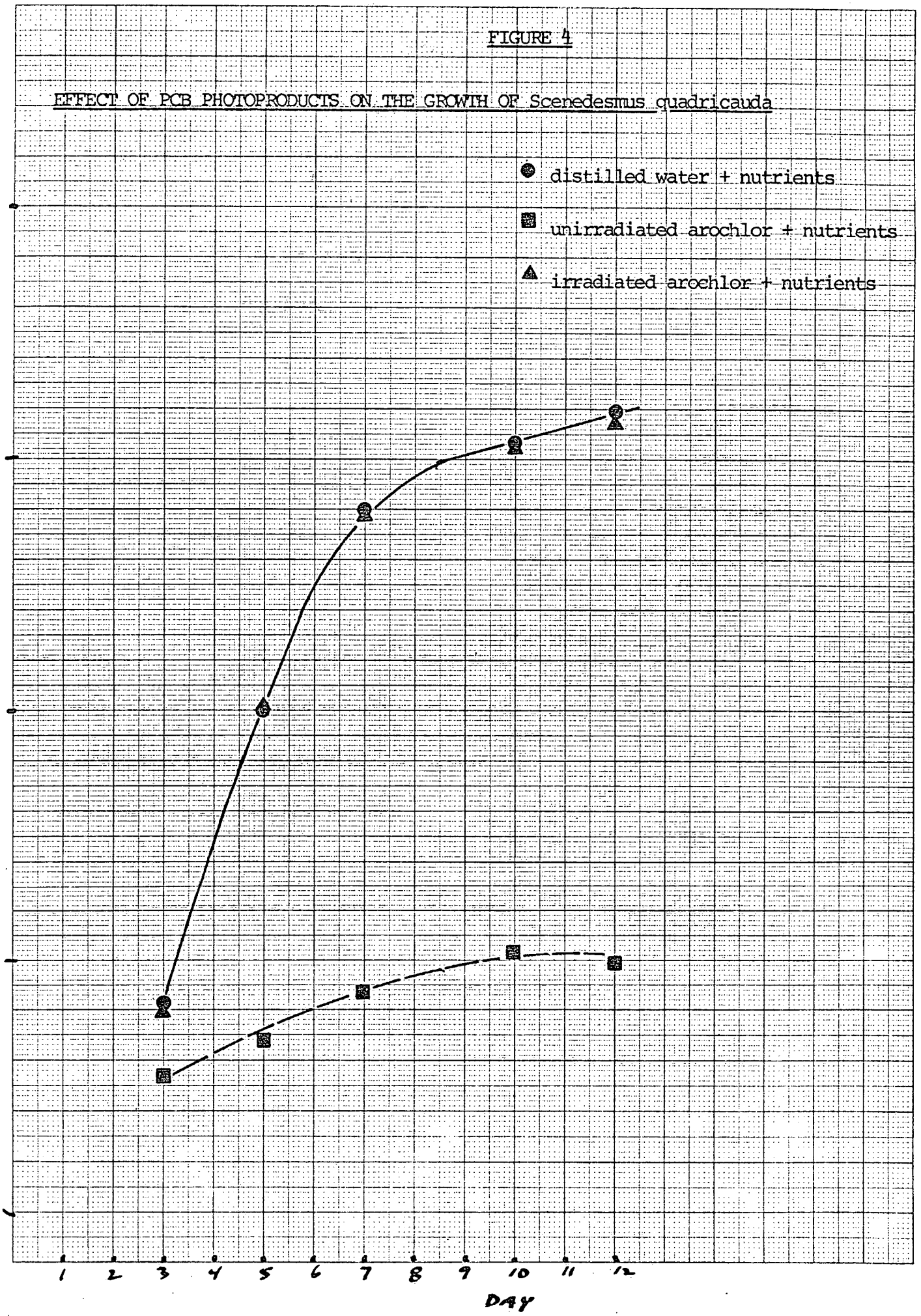
pH was adjusted to 7.0 - 7.5 and all flasks were inoculated with Scenedesmus and incubated. Growth was measured by monitoring the optical density of 540 nm and data was treated following techniques in Stein. The resulting growth curves are shown in Fig. 4 (numerical values for these curves are given in Appendix 1). No difference could be noted between the distilled water controls and the irradiated samples while the unirradiated Aroclor strongly suppressed growth as expected. Unfortunately, concentrations of chloride released from 30 ppb solutions are too low to accurately measure for quantum yield determination.

In order to get some idea of the quantum efficiencies of dechlorination, chlorobenzoic acids were used as model chlorinated aromatics. Photolytes consisted of the appropriate benzoic acid (0.003M), ferric perchlorate (0.01M), perchloric acid (0.1M) and anatase (0.5%) and were not deaerated prior to irradiation. Ferric ion was added to scavenge conduction band electrons and organic radicals. Plots of chloride concentration as a function of irradiation time were linear for conversions of less than 30%. Quantum yields for chloride release calculated from these plots are listed in TABLE 3 along with several other yields of interest.

The yields for chloride release from all three isomeric chlorobenzoic acids are higher than the yield for salicylic acid production from benzoic acid in spite of the fact that there are two possible sites of hydroxylation of benzoic acid to produce salicylic acid but only one site of dechlorination. The system appears to exhibit a

FIGURE 4

EFFECT OF PCB PHOTOPRODUCTS ON THE GROWTH OF Scenedesmus quadricauda



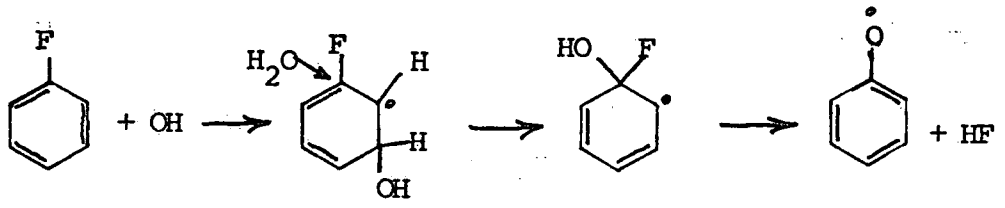
$\log_2$ OD $\times 10$

TABLE 3

QUANTUM YIELDS FOR PHOTOOXIDATION OF BENZOIC ACIDS

Acid	Φ Fe(II)	Φ Cl^-	Φ Salicylic Acid
benzoic	0.121 ± .007		0.017 ± .003
o-chlorobenzoic	0.139 ± .006	0.041 ± .005	< .010
m-chlorobenzoic		0.026 ± .004	
p-chlorobenzoic		0.037 ± .005	

preference for dechlorination. It is of interest to note that the mechanism of fluoride release from fluorobenzene as a result of hydroxyl radical attack appears to involve an acid catalyzed rearrangement of the initially formed hydroxycyclohexadienyl radical to give a phenoxy radical at the point of substitution, regardless of the point of hydroxyl attack.[5] It may be that such a mechanism is



operative in the present case although a phenoxy radical would be expected to react with iron (II) to form a phenol and the yields in TABLE 3 indicate that salicylic acid is not being produced in the dechlorination of o-chlorobenzoic acid.

Assuming that two ferrous ions are produced for each benzoic acid oxidized in the hydroxylation pathway, we find that the yield of iron(II) arising from the production of salicylic acid should be .034 (i.e., 2 x .017). Instead, the quantum yield of iron (II) production is .121, indicating that 70% of the iron reduced did not come from the production of salicylic acid. The most obvious explanation for this discrepancy is that the other two isomeric hydroxybenzoic acids were also produced. To examine this possibility, an acidic photolyte was extracted several times with ether, dried with sodium sulfate and methylated with diazomethane. After evaporation of the excess ether, the concentrate was subjected to gas chromatography using a Carbowax 20M/Gas Chrom Q column and flame ionization detector. Along with peaks for methyl benzoate and methyl salicylic, there were small peaks just above noise level where the methylated derivatives of meta- and para-hydroxybenzoic acid were expected. From the peak sizes, it appeared that salicylic acid was in at least 20-fold excess over the other two isomers. Thus the unaccounted for iron(II) did not come from the hydroxylation of benzoic acid at the meta- and para- positions.

In the absorption spectrum of the benzoic acid photolyte, a peak is observed for the ferric salicylate complex at 530 nm. This peak was broader than that of a synthetic sample of ferric salicylate due to the presence of a broad, featureless band between 350 and 600 nm. In the γ-radiolysis of aqueous solutions of benzene, a similar band is observed and has been attributed to the production

of a dialdehyde via a ring cleavage mechanism involving oxygen.[6] The products to prove that such a mechanism occurred in the present case could not be isolated from the photolyte.

Although photodechlorination was the major reaction pathway observed when aqueous solutions of pure chlorinated aromatics were irradiated in the presence of anatase, it was not proven that the same reactions would occur in a chlorinated industrial effluent. A variety of chlorinated aromatics arise as a result of the chlorination and have been observed in pulp mill bleach plant effluents. A sample of chlorinated bleach plant effluent was obtained from Eddy Forest Products Ltd., Espanola. The effluent had a pH of 1.8, was amber in colour and was low in residual chlorine. Anatase suspensions (0.5% w/v) of this effluent were irradiated at 350 nm for times up to 18 hrs. Reaction was followed both spectrophotometricly and by measuring chloride and formaldehyde levels in the photolytes. The results are listed in TABLE 4.

Absorbance at all wavelengths decreased while formaldehyde and chloride concentrations increased as a result of irradiation. Both chloride and formaldehyde apparently reached limiting concentrations after which no further increase occurred even though the absorbance continued to decrease. To confirm the effect of irradiation, 100 ml aliquots of a sample that had been irradiated 1080 min and an unirradiated sample were extracted with ether and the extracts dried with sodium sulfate. After evaporation of the ether, a brown liquid was left from the unirradiated sample while the photolyte extract was

TABLE 4

IRRADIATION OF CHLORINATED BLEACH PLANT EFFLUENT

IRRADIATION TIME	ABSORBANCE * 250 nm	300 nm	350 nm	Cl^-	CH_2O
-	1.062	.499	.187	.0317M	1.22×10^{-4}M
60 min	1.012	.453	.154	.0328	1.53×10^{-4}
180 min	.900	.381	.144	.0327	1.95×10^{-4}
360 min	.892	.360	.126	.0349	2.44×10^{-4}
540 min	.773	.291	.106	.0338	2.38×10^{-4}
720 min	.686	.253	.086	.0336	2.59×10^{-4}
1080 min	.520	.182	.068	.0338	2.39×10^{-4}

* Absorbance was determined for a 1:10 dilution.

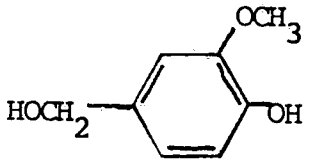
concentrated to a pale yellow liquid. Organic chlorine content of each residue was determined by oxidizing weighed quantities in an oxygen atmosphere and analysis of the chloride produced. The unirradiated sample was found to contain $0.64 \pm .1\%$ chlorine while the irradiated one contained $0.19 \pm .04\%$. Although both samples seemed low in organic chlorine, the results indicated that irradiation with anatase had accomplished a 70% reduction in chlorine content of the ether extractable organic fraction. This reduction, however, does

not necessarily mean that the effluent has been rendered less toxic.

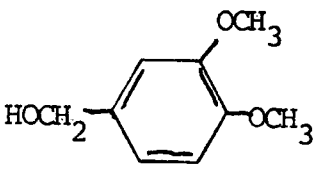
To determine toxicities, bioassays with rainbow trout were conducted. A 12 litre effluent/anatase suspension (.5% w/v) was irradiated at 365 nm for 48 hrs until the absorbance at 250 nm had decreased to half its initial value. From TABLE 4 it can be seen that by the time this decrease in absorbance had occurred, the limiting concentrations of chloride had been reached. Total mortality was observed for both control and irradiated samples between 8 and 12 hours after the start of the bioassay. Therefore, there was no observable change in toxicity as a result of irradiation.

2.4 Irradiation of Lignin Model Compounds

The production of formaldehyde in the irradiation of bleach plant effluent was taken as an indication that some oxidation of lignin compounds was occurring. To verify this observation, two lignin model compounds were chosen for further study. These were vanillyl and veratryl alcohols. Initial checks of the biodegradability of these compounds with bacteria capable of degrading aromatics such as PCBs were conducted in shake flasks, using the alcohols as sole carbon source. While vanillyl alcohol was rapidly metabolized with a half life at the 100 ppm level of less than 2 days, veratryl alcohol was more persistent, having a half life greater than 7 days.



vanillyl alcohol



veratryl alcohol

Upon irradiation of either compounds with 0.5% anatase, formaldehyde was produced with a quantum yield of $\simeq .05$. Prior to irradiation, there was little difference in the absorption spectra of veratryl alcohol in acidic and basic solution with both exhibiting a peak at 278 nm. After irradiation, however, a new shoulder was noted at 310 nm in the acidic solution. More changes were apparent in the spectrum in basic solution. A new shoulder appeared at 244 nm, the 278 peak of veratryl alcohol was shifted to 288 nm and new peaks appeared at 292 and 348 nm. These spectral changes are depicted in Fig. 5. These spectral features are similar to those observed for unirradiated vanillyl alcohol in acid (peaks at 226 and 278 nm) and in base (peaks at 248 and 292 nm). Taken with the observation of formaldehyde as a product, the results are consistent with the photocatalysed conversion of veratryl to vanillyl alcohol. The peak at 348 nm remains unassigned but may be some type of quinone or hydroquinone. The irradiation solutions were brown in colour due to this absorption but the species giving rise to this colour could not be extracted into organic solvents such as ether.

Bacterial degradation studies, using seed cultures from the preliminary examinations, were conducted on unirradiated and irradiated samples of veratryl alcohol. Spectra taken of samples before and after one week of bacterial degradation in the shake flasks are depicted in Fig. 6(a) and (b). The unirradiated veratryl was less than 50% degraded in agreement with preliminary results. The irradiated sample was substantially degraded after one week.

Fig. 5

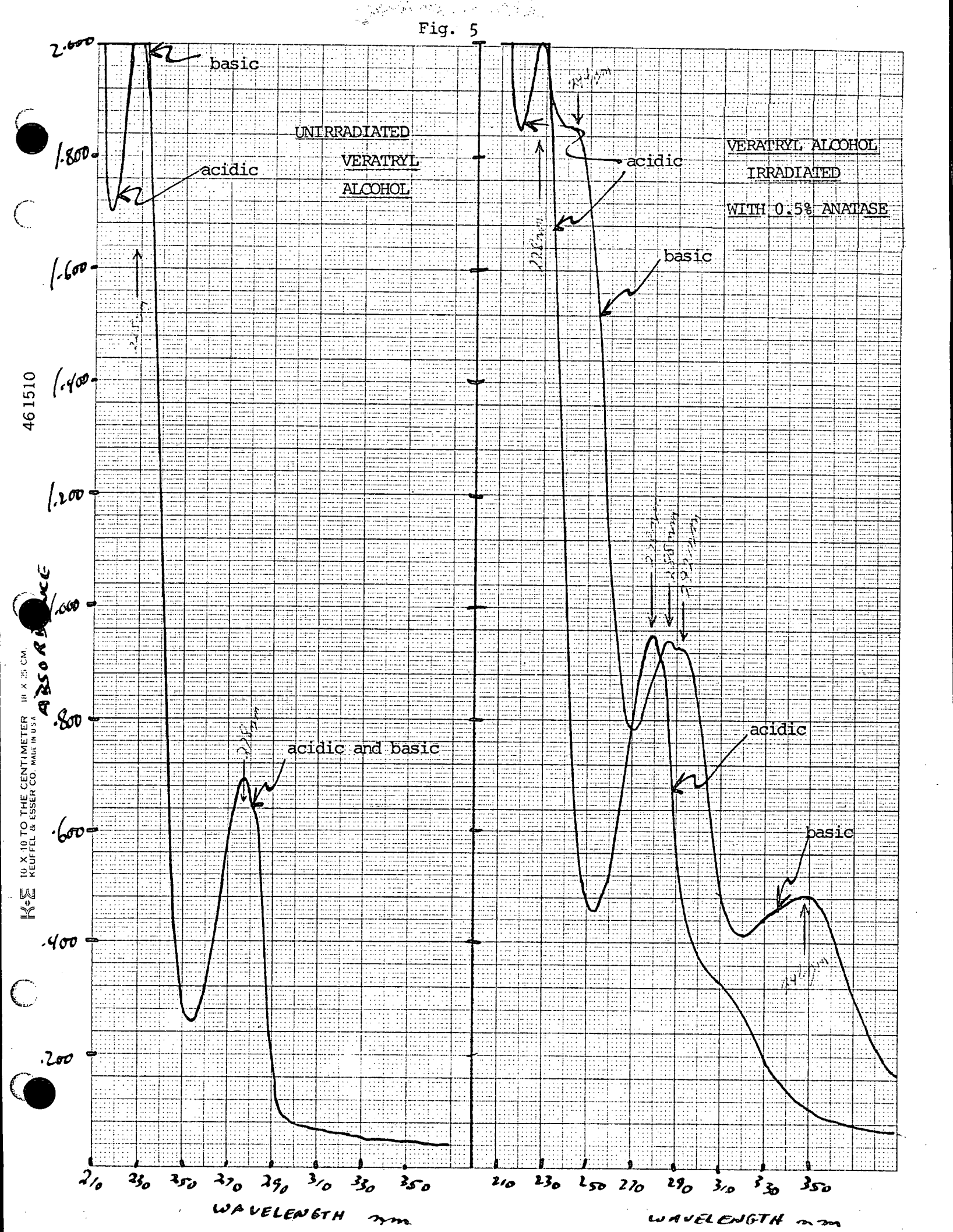

UNIRRADIATED VERATRYL ALCOHOL
VERATRYL ALCOHOL IRRADIATED WITH 0.5% ANATASE
basic
acidic
acidic
basic
acidic and basic
acidic
basic
2.000
1.800
1.600
1.400
1.200
1.000
.800
.600
.400
.200
ABSORBANCE
210 230 250 270 290 310 330 350
WAVELENGTH nm
210 230 250 270 290 310 330 350
WAVELENGTH nm
10 X 10 TO THE CENTIMETER 11" X 25 CM.
KEUFFEL & ESSER CO. MADE IN U.S.A.
46 1510

Fig. 6(a)

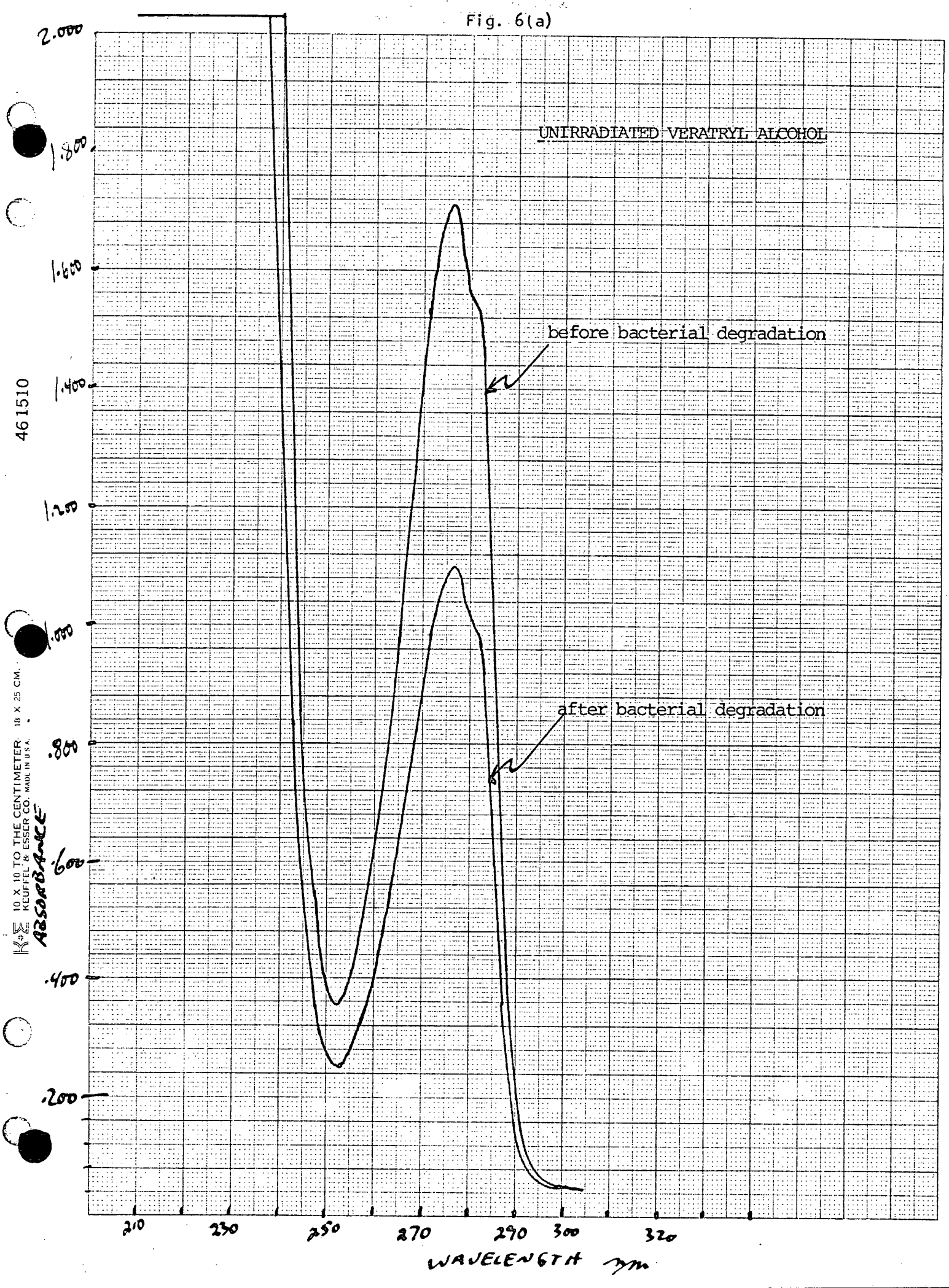
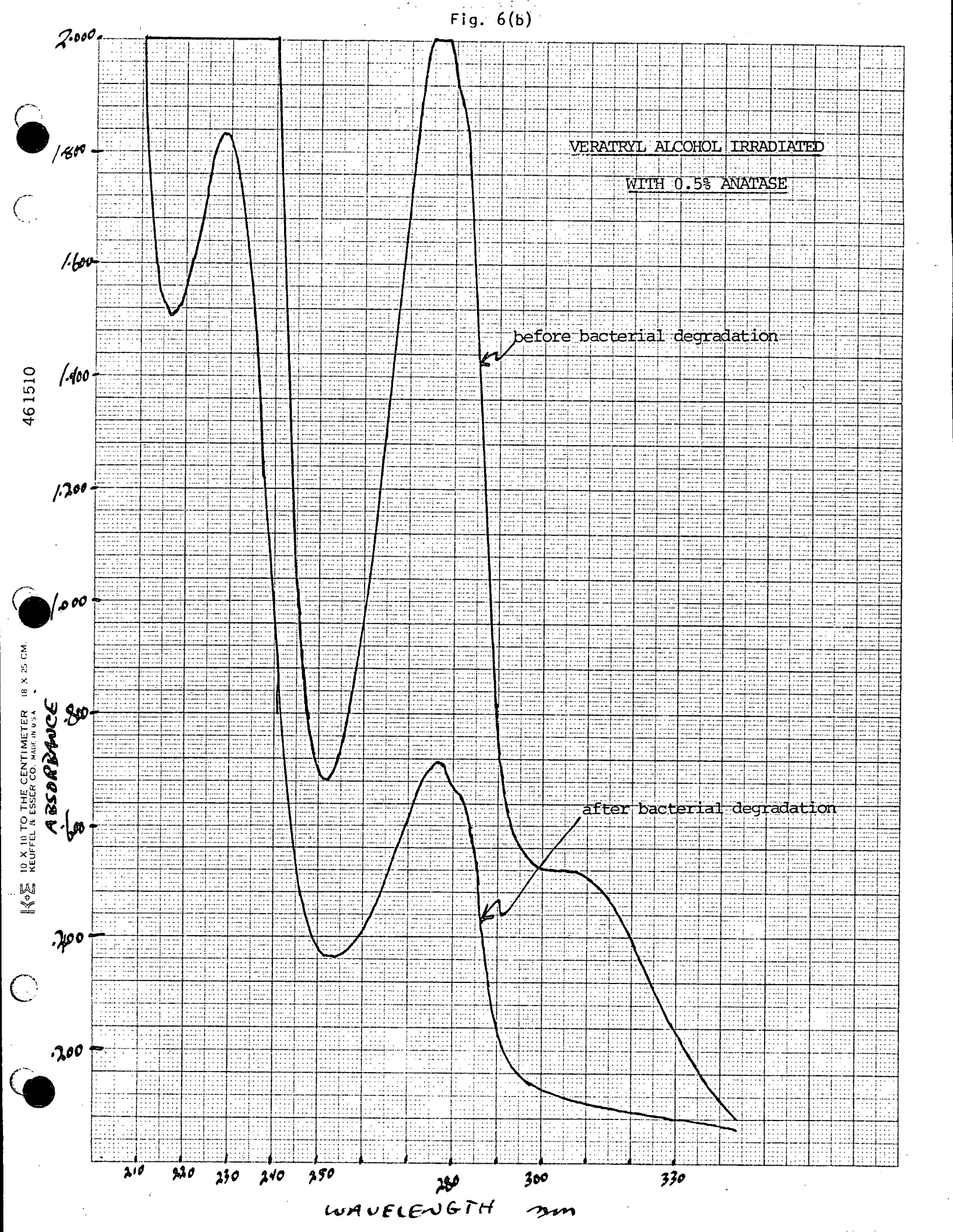

UNIRRADIATED VERATRYL ALCOHOL
before bacterial degradation
after bacterial degradation
2.000
1.800
1.600
1.400
1.200
1.000
.800
.600
.400
.200
ABSORBANCE
210
230
250
270
290
300
320
WAVELENGTH mμ
461510
10 X 10 TO THE CENTIMETER 18 X 25 CM.
KEUFFEL & ESSER CO. MADE IN U.S.A.

Fig. 6(b)



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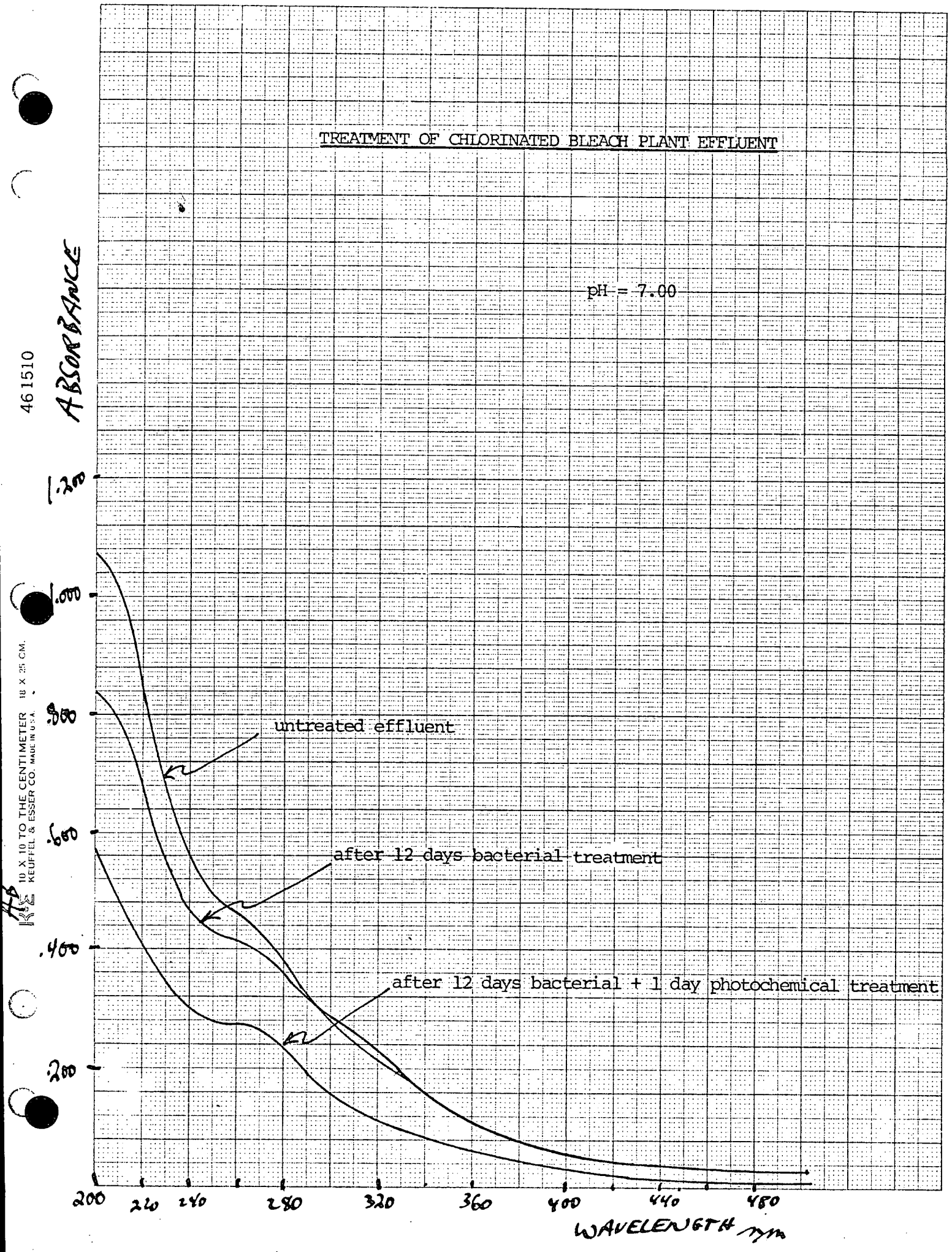
10 X 10 TO THE CENTIMETER 18 X 25 CM.
KEUFFEL & ESSER CO. MADE IN U.S.A.

Fig. 6



In addition, the peak at 310 nm had disappeared and the remaining material behaved similar to veratryl alcohol in acidic and basic solutions, leading to the conclusion that the photolysis products had been metabolized and what was left in the flasks was veratryl alcohol that had not been converted in the irradiation.

This observation gave rise to the interesting possibility that anatase treatment of non-degradable compounds could be used to convert them to a more biodegradable form and thus reduce their persistence. To examine this possibility, a sample of the chlorinated bleach plant effluent, seeded with activated sludge bacteria, was circulated for 12 days in a cyclone fermenter. Substantial bacterial growth but little colour removal occurred. After removal of the bacteria, part of the treated effluent was irradiated 24 hours at 350 nm in the presence of 0.5% anatase. Colour was substantially reduced. The irradiated samples were returned to a cyclone fermenter along with an unirradiated sample in a second fermenter. Unfortunately, no growth occurred in either fermenter when seeded with bacteria from the previous experiment. Spectra for these samples are depicted in Fig. 7.

3. CONCLUSIONS AND RECOMMENDATIONS

The disinfection studies clearly indicate that photolysis of semiconductors such as anatase cannot be used for disinfection. The species that are produced are too reactive towards each other, or towards trace organics, to survive long enough to encounter a bacterium. No further investigation in this area is recommended. Instead, some attention should be devoted to the photochemical generation of singlet oxygen using heterogeneous dye sensitizers. The dyes could be absorbed on semiconductors such as anatase or on polymer supports such as ion exchange resins. The photoreactions which generate singlet oxygen are well studied and suitable dyes are methylene blue and rose bengal. Singlet oxygen can oxidize lipid membranes and peptides and is antagonistic towards life in general. Since it reacts selectively and in fact undergoes no reaction with many common organics, its solution phase life time is much longer than the radicals in the current study and, therefore, should be a more efficient disinfectant. The lifetime is short enough that the singlet oxygen itself should not pose a threat to receiving waters. However, the same may not be true for the reaction products, many of which are peroxides, and this area would require study. Advantages of such a system over direct photolysis would be the use of sunlight instead of high energy UV for disinfection since both the dyes mentioned have high quantum efficiencies in the visible region.

The studies of organic oxidation offer more encouragement. The photoproducts from heterogeneous photooxidation of PCBs are less toxic than the starting material and the photoproducts of chlorinated aromatics in general appear to be substantially dechlorinated. Lignin model compounds are more biodegradable after irradiation. The studies with pulp mill bleach plant effluent deserve some comment. This effluent is extremely complex and failure of the anatase system to eliminate toxicity or increase apparent biodegradability does not necessarily indicate a total failure of anatase treatment. The bioassays merely indicate that toxic components are still present; indeed, in view of the production of formaldehyde as a photoproduct, they can hardly be avoided. If time had permitted, a complete study of LC_{50} of both treated and untreated effluent would have indicated to what extent anatase had altered the toxicity. It is likely that with a less complex effluent containing persistent aromatics such as refinery waste streams, anatase treatment would be of use. In view of the report published near the end of this project that anatase photolysis is effective in oxidizing cyanide to cyanate[6], plating industry wastes should also be examined. In view of the dismal performance of other semiconductors examined, future work should be centered on anatase.

APPENDIX

Abosrbance values for Scedesmus quadricauda growth experiments in Fig. 4.

Sample	A_{540}	$\log_2$ OD + 10	
	Day 3, August 16, 1976		
#1 control	.055	5.92	
#2 control	.059	5.92	5.84
#3 control	.053	5.77	
#4 unirradiated PCB	.045	5.53	
#5 unirradiated PCB	.048	5.62	5.58
#6 unirradiated PCB	.047	5.59	
#7 irradiated PCB	.051	5.71	
#8 irradiated PCB	.053	5.77	5.80
#9 irradiated PCB	.059	5.92	
	Day 5, August 18, 1976		
#1	.124	6.99	
#2	.142	7.19	7.00
#3	.110	6.82	
#4	.048	5.62	
#5	.051	5.71	5.68
#6	.051	5.71	
#7	.112	6.84	
#8	.122	6.97	7.02
#9	.150	7.26	
	Day 7, August 20, 1976		
#1	.222	7.83	
#2	.234	7.91	7.80
#3	.197	7.66	
#4	.059	5.92	
#5	.058	5.92	5.87
#6	.053	5.76	
#7	.201	7.67	
#8	.218	7.80	7.78
#9	.227	7.86	

Sample	A_{540}	$\log_2$ OD + 10	
	Day 10, August 23, 1976		
#1	.265	8.09	
#2	.276	8.14	8.07
#3	.248	7.99	
#4	.060	5.94	
#5	.065	6.06	6.03
#6	.066	6.08	
#7	.252	8.01	
#8	.254	8.02	8.04
#9	.268	8.10	
	Day 12, August 25, 1976		
#1	.296	8.24	
#2	.290	8.22	8.19
#3	.270	8.11	
#4	.069	6.14	
#5	.060	5.94	5.98
#6	.057	5.87	
#7	.267	8.10	
#8	.278	8.15	8.15
#9	.285	8.19	

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