

AQUEOUS PHASE OXIDATION WITH ACTIVATED OXYGEN  
SPECIES FOR WASTEWATER TREATMENT

by

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## CHAPTER I

### INTRODUCTION

Recently some 900 chemical species were listed by the Environmental Protection Agency (EPA) as being known or suspected carcinogens. Moreover, many of these compounds have been found in the water sources for municipal supplies and in the aqueous effluents from industrial operations. Their genesis is sometimes well known and in other instances only suspected. In any event their removal is necessary if potential damage to human health and the environment is to be avoided.

One technique for removing these chemical species is to oxidize them to carbon dioxide, water, etc. Ozone has been suggested as an oxidizer in this approach. Ozone has the advantage of forming two oxygen fragments: singlet oxygen and atomic oxygen. These and other activated species such as peroxides which may form in water, make it one of the most powerful oxidizing agents known to man. Only fluorine and chlorine trifluoride rank higher than ozone in oxidizing power (1). Ozone has been successfully used to completely oxidize organic and inorganic materials and to remove color, taste and odor-causing compounds through partial oxidation. Usually, the partially oxidized degradation products which are generated are also innocuous. As previously suggested, singlet oxygen by itself is known to be an energetic oxygen species which may participate in aqueous phase oxidation processes. It is considered to be essential in metabolic oxidations. Singlet oxygen is generated by radiation at high altitudes or, in our case, by the polymer-based sensitizers which mimic biological processes. In aqueous solution,



these polymer-based sensitizers have been known to be <sup>^</sup>ery stable and capable of generating singlet oxygen continuously when irradiated with ultraviolet light. In this process a large number of repetitive generation steps are possible before sensitivity is lost (2). Even though they are powerful oxidants, chemical oxidation processes using only ozone or chlorine dioxide fail to completely remove all the chemical species on the EPA list. This is due to the fact that sometimes the oxidation sequence can result in highly stable, complex compounds in an intermediate step. Therefore, a combination of processes is needed if one desires to treat wastewater to meet the projected 1983 "zero" discharge standards.

The combination of new processes which we will consider in this research, combine ozone, a polymer-based sensitizer and ultraviolet radiation. The purpose of the ultraviolet radiation is to activate ozone and its subspecies. In addition, it simultaneously excites the organic reactants in the reaction system. For the polymer-based sensitizer the UV acts as a trigger for the singlet oxygen transfer medium. Hence, it prolongs singlet oxygen's residence time in the aqueous phase. The combination of these oxidizing mechanisms can promote complete oxidation.

The objectives of this study involved the examination of the following oxidants in aqueous solutions: 1) ozone, 2) ozone with UV, 3) photosensitizer with UV, 4) ozone with photosensitizer, and 5) a combination of ozone, photosensitizer and UV. The effectiveness of these oxidizers was determined by their ability to destroy potassium cyanide and hydrazine in aqueous solutions. All the experiments were performed

at constant temperature (20°C) and atmospheric pressure. The effect of pH was also investigated because of its reported contribution to ozone stability in water. UV intensity was kept at the constant level of approximately 100 watts per square meter. No attempt was made to investigate UV attenuation in water or examine wavelengths other than the 254 nm produced by the G.E. germicidal lamp.

## CHAPTER II

### LITERATURE REVIEW

#### Ozonation

Ozone is a highly reactive allotrope of oxygen containing three oxygen atoms per molecule. It is one of the three most powerful oxidizing agents known to man. One of the best known applications of ozone is in purification of drinking water. The first large scale ozone-water purification plant was built in Nice, France in 1906 (3). Since 1906, the use of ozone in water treatment facilities has grown to include various chemical oxidation processes, in addition to bacterial disinfection and viral deactivation. Many recently constructed municipal water treatment facilities use ozone as a biocide to replace chlorine (4). This has become necessary because of problems associated with the formation of chlorinated byproducts which are toxic or potentially carcinogenic.

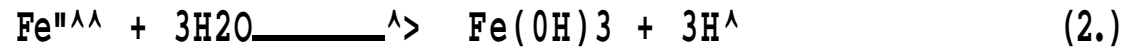
Even so, ozone now has more varied industrial uses than municipal applications. These processes are not as well documented since many of them are proprietary, and industrial companies often wish to keep them that way.

Wastewater treatments which do utilize ozone and are described in the literature can be classified in the following way.

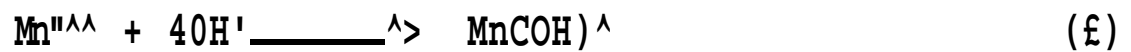
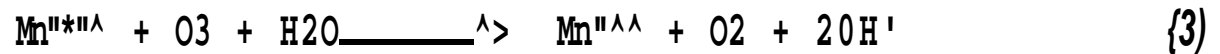
#### 1). Oxidation of inorganic materials.

An example would be soluble ferrous ions which are oxidized rapidly by ozone to ferric ions. The less soluble ferric ions then hydrolyze, coagulate, and precipitate according to the

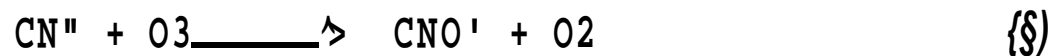
following reactions:



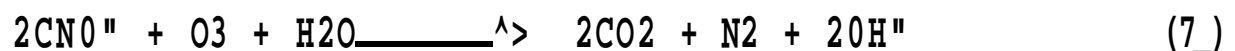
Similarly, manganous ions can be oxidized to manganic ions, which then form insoluble manganese dioxide:



Highly toxic cyanide ions are also readily oxidized by ozone to form the much less toxic cyanate ions:

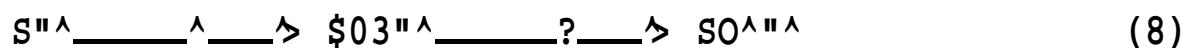


At high pH, cyanate ions hydrolyze to produce carbon dioxide and nitrogen:



Over the last four decades, these cyanide oxidation reactions have been studied by at least eight different investigators: Neuwirth (5a), Tyler (5b), Walker, Zabban (5c), Khandelwal (5d), Dodge, Sondak (5e), and most recently Bollyky (5f). In every instance, the reaction of cyanide with ozone was reported to be very rapid, and to proceed by first producing cyanates.

Sulfide ions are easily oxidized to sulfite and finally, to sulfate:



2). Oxidation of organic materials.

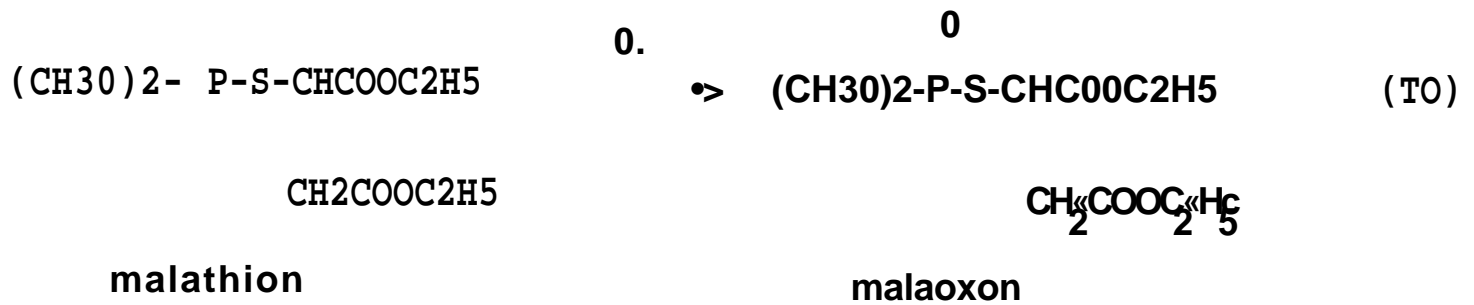
Phenols, especially the non-chlorinated phenols, generally can be oxidized with ozone:



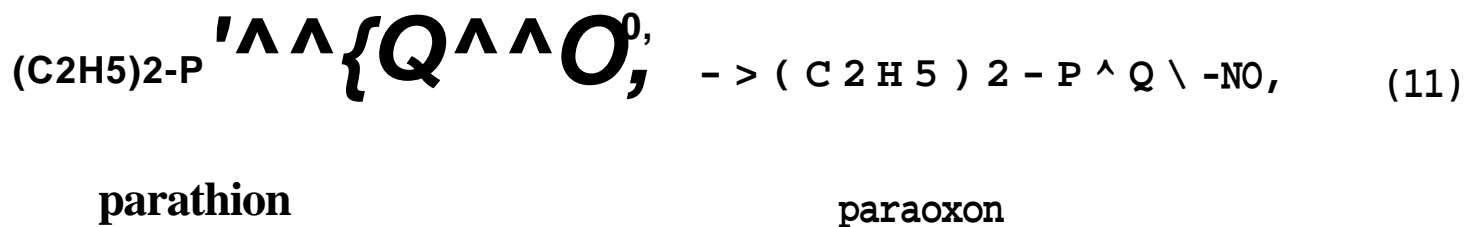
Detergents can be classified as either linear alkyl sulfonates, linear alkylbenzene sulfonates or aliphatic quaternary amine compounds (3, 6). Given sufficient time, the biodegradable detergents will decompose in sewage treatment plants or in rivers and streams. However, many raw water supplies are contaminated from time to time by detergents or their partial decomposition products. These compounds can be oxidized by ozone much faster than by biodegradation.

Pesticides and insecticides differ widely in their reactivity with ozone. For example, phosalone and aldrin are readily oxidized with small amounts of ozone. Dieldrin, chlordane, lindane, dichloro-diphenyl-trichloro ethane (DDT), polychlorinated biphenyl (PCB) and endosulfan, however, are only slightly reactive with ozone under normal conditions (3). Some pesticides, such as malathion and parathion should not even be treated by ozone. These compounds proceed through intermediates (oxons) which are more toxic than the starting thions (7, 8), as shown in the

following equations:



0.  
(decomposed)



0.  
v  
(decomposed)

### 3). Color removal (3).

Artificial color is usually caused by the presence of unsaturated organic moieties conjugated in the compounds. By the contacting the conjugated compounds with ozone under suitable conditions, the conjugation is disrupted and the color will disappear.

### 4). Taste and odor removal (3).

In general, taste and odor are caused by organic compounds, although many inorganic sulfides also are encountered which are highly odorous. Many of these organic compounds which cause unacceptable tastes and odors are formed from natural vegetation during anaerobic decomposition in the ground or on the surface of water in which the dissolved oxygen content may be too low to

support aerobic colonies. They are readily oxidized by ozone.

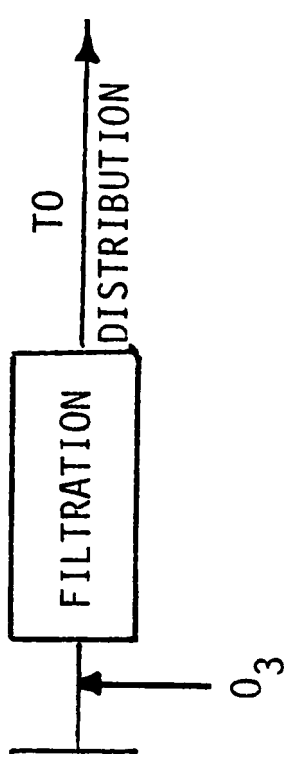
Because of the many potential constituents of wastewater streams it is possible that ozonation might be installed for a single purpose or multiple applications for wastewater treatment. Some candidate treatment sequences are shown in Figure 1.

### Photooxidation Processes

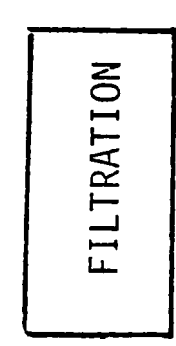
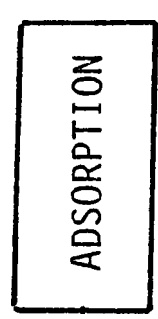
Singlet oxygen is another energetic oxygen species which may participate in aqueous phase oxidation processes. This form of free molecular oxygen is described in Table I. Here the electronic transitions can be observed both in absorption and in emission (9, 10).

The measurements of the integrated absorption coefficients for these transitions yield radiative lifetimes of 45 minutes (10, 11, 12) for the first excited state molecule ( $A$ ) and between 7 to 12 seconds (9, 13, 14) for the second excited state molecule ( $Z$ ). The observed lifetimes are usually shorter because of the collisions with other molecules, and in the liquid oxygen phase they are very short indeed ( $T^Z = 10^{-10}$  Sec,  $T^A = 10^{-6}$  Sec; estimates)(9).

While singlet oxygen can be created by direct radiation in rarefied gases, dye-sensitized photooxidation has been demonstrated as being feasible in aqueous mediums. The possibility that electronically excited, metastable singlet oxygen molecules might be involved as reactive intermediates in dye-sensitized photooxidation reactions was first suggested by Kautsky over 40 years ago (15). Since then the dye-sensitized photooxidation of organic compounds has been studied



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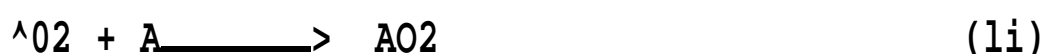
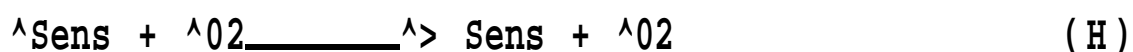


TABLE I

POSSIBLE ARRANGEMENT OF ELECTRONS IN  $\pi^*$  2P ORBITALS AND  
 POTENTIAL DIFFERENCE IN THE LOWEST ELECTRON  
 CONFIGURATION OF OXYGEN (9, 10)

State of the oxygen molecule	Occupancy of highest orbitals	Energy above ground state
2 nd excited state ( S )		37 Kcal
1 St excited state ( A )		22 Kcal
ground state ( $^3Z^-$ )		

extensively by many investigators and represents a *wery* convenient method for introducing oxygen in a highly specific fashion into organic compounds (16-21). Two mechanisms have been suggested for the photo-oxidation process (10, 23, 24). Both begin with excitation of the sensitizer to promote to the singlet state, followed by intersystem crossing to the triplet state (3 p) where the energy is 50 Kcal above the ground state (25). The first mechanism was originally proposed by Kautsky in 1931 (10, 26). In this mechanism, energy is transferred from triplet sensitizer to oxygen to give the excited singlet molecular oxygen. The singlet molecular oxygen then reacts with acceptor (A) to give the peroxide (A02) as shown in the following reactions:



This mechanism was largely ignored after 1940. The other mechanism, which was originally suggested by Schonberg (10, 27) and has been advocated by Schenck and others (10, 23), is now generally accepted. In this mechanism (Eqn. 12\_, H, 16., ]7), the triplet sensitizer reacts with triplet oxygen to give a sensitizer-oxygen complex. This complex then reacts with the acceptor (A) to give the product peroxide (A02) and regenerated sensitizer.

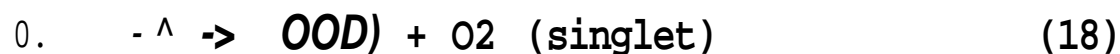


Although several sources of singlet oxygen are now available, the photosensitized formation of singlet oxygen using various dyestuffs remains the method of choice for most applications. However, several limitations have been observed for the photooxidation method. First, the sensitizer (dye) must be soluble in the reaction solvent, limiting the dye-solvent combinations which can be used. Second, the dye is often bleached over long reaction time, thereby rendering it ineffective. Finally, the dye itself may interact with products, or the separation of the dye from the products can be difficult (28).

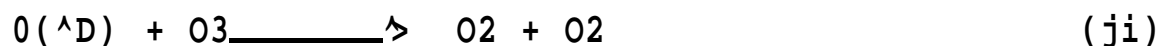
Polymer-based sensitizers have several advantages over the use of free soluble sensitizers in solution. They can be used in solvents in which the unbound dye is insoluble, and therefore unable to sensitize singlet oxygen formation efficiently. Also they are significantly more stable toward bleaching than are the free sensitizers. The polymer-based sensitizers can also be subsequently reused with little or no loss in efficiency (28).

### Combination Processes with Ultraviolet

The reactivity of both ozone and singlet oxygen can be enhanced in the introduction of ultraviolet radiation. The primary step in the ultraviolet photolysis of ozone almost certainly gives rise to an electronically activated nascent oxygen atom,  $\text{O}(^1\text{D})$ . Moreover, if there is conservation of spin, then product oxygen molecule should be a singlet.

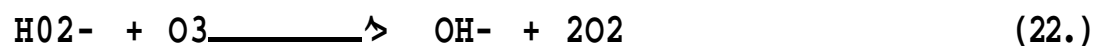


The reactions of  $O(^1D)$  might also give rise to excited molecules in the ozone photolysis. The reaction would proceed in the following way:



This is exothermic to the extent of 138 Kcal mole<sup>-1</sup>, and  $K = 4.2 \times 10^9$  liter mole<sup>-1</sup> Sec<sup>-1</sup> (29).

Ozone-ultraviolet photooxidation is known to not only generate singlets of molecular oxygen, activated atomic nascent oxygen ( $O(^1D)$ ), but also other excited species (29). For example, the activated oxygen atom,  $O(^1D)$ , reacts with water to form hydroxy ( $OH^-$ ) and hydroperoxy ( $HO_2^-$ ) radicals (30, 31).



Each of these reactive species greatly enhance the overall oxidation rate and eventually permit complete oxidation of any unoxidized compounds in the aqueous solution.

### pH Effect

The pH effect of ozone concentration decomposition is important. It was found that dissolved ozone concentration drops from 3.5 mg/l to

0.2 mg/l when the pH changes from 8.0 to 9.5 (32). Figure 2 shows this drop of ozone concentration over a period of 30 minutes.

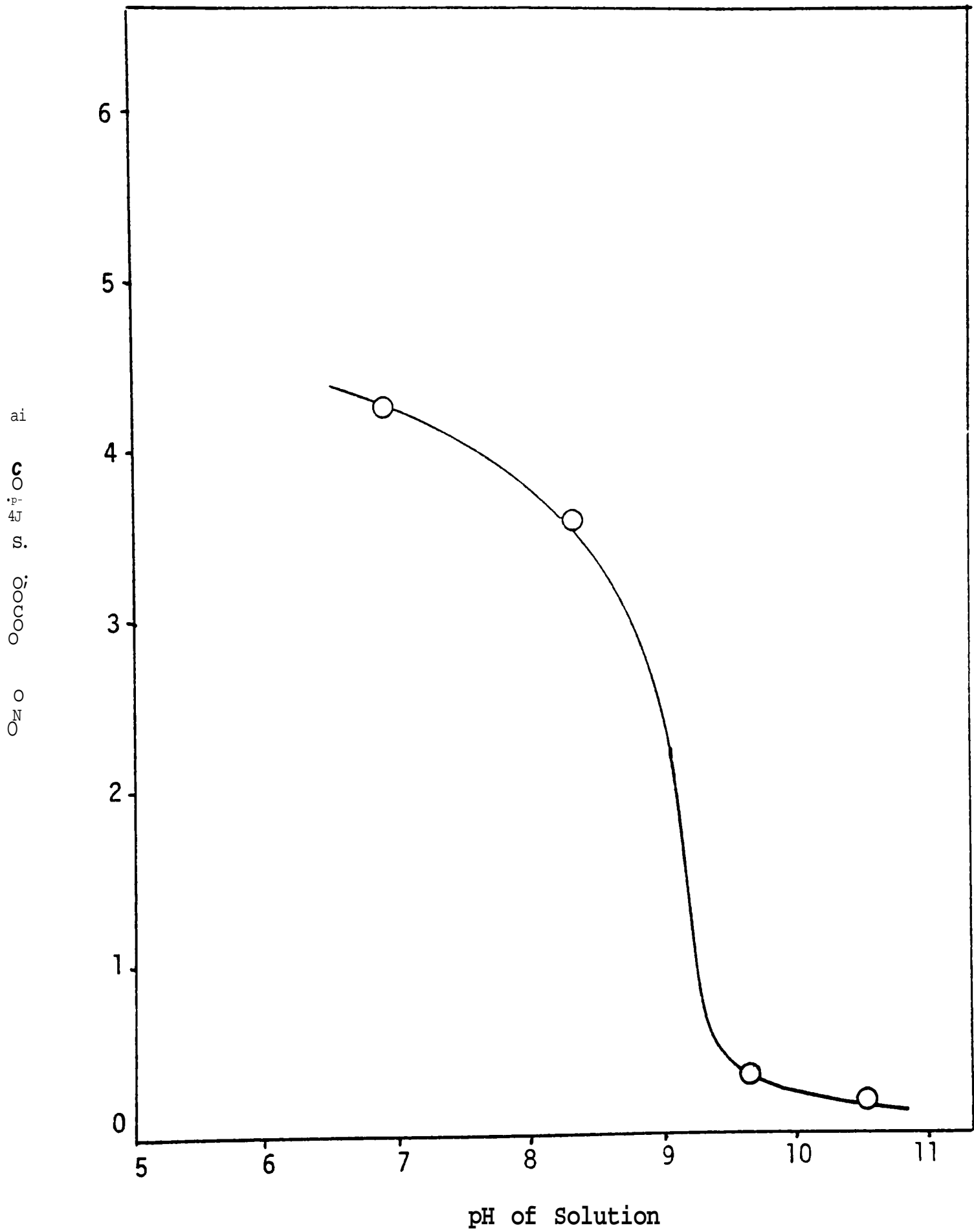


Figure 2, Effects of pH on Ozone Decomposition (32)

## CHAPTER III

### EXPERIMENTAL

#### Experimental Equipment and Materials

A Welsbach T-816 Laboratory Ozonator was used to generate the ozone. For the high ozone concentration used, an oxygen flow rate of 3 standard liter per minute (SLPM) and a setting of 70 volts were used on the generator.

For safety purposes, a Mast 724-2 Ozone Meter with KI solution was used to detect any leakage from the ozonation system. This instrument has a sensitivity range of 0.01 parts per million (PPM) to 1.00 PPM.

To continuously saturate the aqueous solution with ozone or oxygen, a Pyrex<sup>^</sup>-<sup>^</sup>gas washing bottle (250 ml) with a fritted disc was used as a contactor. This arrangement permitted synthetically generated aqueous solutions to be treated in a batchwise manner.

A George W. Model MR-4 Light and GE Germicidal Lamp (wavelength 254 nm) were used as the source of ultraviolet, because the strongest absorption by ozone in the UV Spectra is the wavelength 254 nm (Figure 3). The radiant flux emitted from the light was determined by a Yellow Spring Instrument (YSI) Model 65-A Radiometer. The operational range is 0-2500 watts per square meter.

A YSI Model 54 Dissolved Oxygen Meter (operational range is 0-20 PPM) was used to determine the solubilities of oxygen in the aqueous solution.

Analysis of reactants was performed with a Bausch & Lomb Spectronic 21 Spectrophotometer which operated in the wavelength range 200-1000 nm

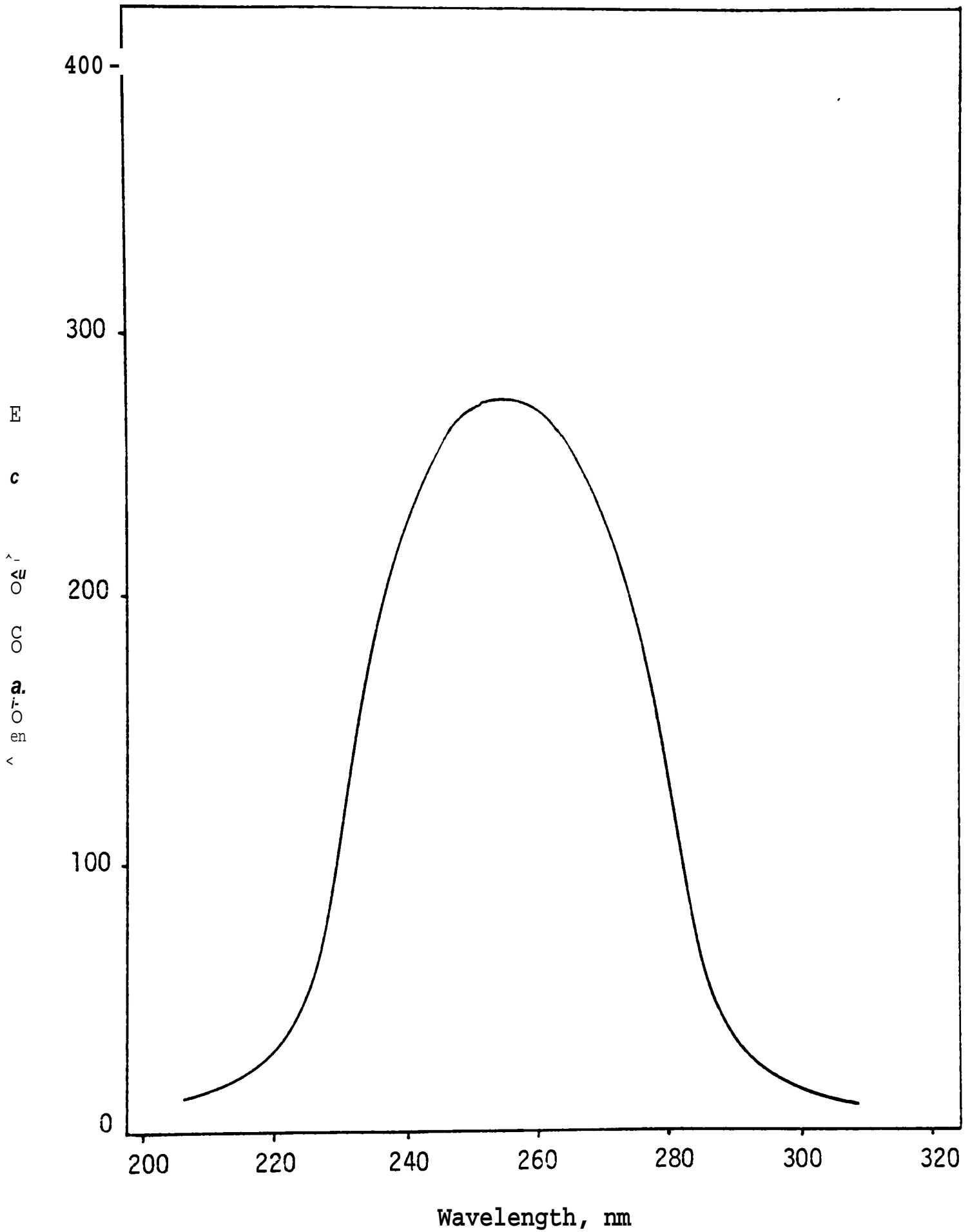


Figure 3. Absorption Spectrum of Ozone in the Ultraviolet (33)



An Orion 701 A pH Meter with Orion Model 91-01 Electrode and Probe were used to determine the value of pH of the solutions.

It was imperative that all glassware used in this research be kept scrupulously clean. Consequently, after each run all glassware was submerged in chromic acid and thoroughly rinsed with distilled water.

All chemical compounds not prepared by the author were obtained from commercial sources and were used as received unless otherwise indicated.

The polymer-based sensitizer was prepared from porous styrene-divinylbenzene copolymer beads (Bio bead S-X ix 200 mesh) with the sensitizer, Rose Bengal, in dimethylformamide (DMF) solution. The procedure used was as follows (27):

To 2.0 g porous styrene-divinylbenzene copolymer beads in 60 ml of DMF, 1.55 m mole of Rose Bengal (approximately 1.56 g) was added. The mixture was stirred with a Teflon<sup>®</sup>-coated magnetic stirrer and heated to 60°C for 20 hours. The reaction mixture was then cooled to ambient temperature and filtered through a sintered-glass funnel. The residue was washed thoroughly with 200-ml portions of solvent in the following order: ethyl acetate, ethanol, ethanol-water (1:1), water, methanol-water (1:1), and methanol. The polymer beads were then extracted with methylene chloride and methanol in a Soxhlet extractor for at least 2<sup>^</sup> hr. or until no visible color appeared in the solvent. The polymer-sensitizer was then dried in an oven at 60°C for 12 hrs.

The chemical impurities in the synthetic wastewater studied in this research program were: potassium cyanide and p-nitrophenylhydrazine. Cyanide is extremely toxic and occurs primarily in industrial effluents. Metal cleaning and electroplating baths, gas scrubbers, gas works and coke ovens, and other various chemical treatments are the main sources of the cyanide found in industrial waste. A 0.01-mg/l cyanide limit is recommended by the U.S. Public Health Service as the maximum allowable cyanide concentration in public drinking water supplies. Hydrazine on the other hand is used as an oxygen scavenger for high pressure boilers in power plants and industry to reduce corrosion of metal pipes and fittings. Its concentration is also limited in the industrial effluents.

### Experimental Procedure

Before the experimental data were taken, some preliminary work was required. A YSI 54 Dissolved Oxygen Meter was calibrated with fresh water saturated with oxygen at a known temperature and partial pressure of oxygen. An Orion 701 A pH Meter was also calibrated with standard buffer solution at a known temperature.

The object of this experiment was to study the oxidation reaction processes using different oxidizers and contacting schemes. These were: 1) ozone; 2) polymer-based sensitizer for singlet oxygen; and 3) the combination of both with ultraviolet radiation. The reaction time and pH value of solution at ambient temperature were the measured dependent experimental variables.

The schematic diagram of the contacting apparatus for ozone, photosensitizer and UV, or combination operations is shown in Figure 1. The



following procedure was used for each experimental run with ozone:

- 1) Set the inlet oxygen pressure of the ozone generator to 5 psig.
- 2) Initiate the flow of cooling water and turn on the power switch.
- 3) Set the voltmeter of the ozone generator at 70 volts (- 72 watts) and the ozone flow rate of 3 SLPM.
- 4) Wait 5-10 minutes to allow the system to approach steady state.
- 5) Open the valve to the contactor and turn on the timer.
- 6) After a predetermined time interval, close the ozone inlet valve and record the elapsed time.
- 7) Aliquots of the solution are checked for pH and analyzed for any remaining contaminant.

For the combination of ozone with ultraviolet radiation, the above procedure was repeated for steps 1) to 4). The following additional steps were then taken:

- 1) Turn on the UV light and radiometer.
- 2) Open the ozone valve to the contactor and allow ozone to contact with the solution and start the timer,
- 3) After a predetermined time interval, close the valve, turn off the UV light and radiometer and then record the elapsed time.
- 4) Take aliquot samples and check the pH value and perform the product analysis.

For the photooxidation of polymer-based sensitizer process, 1000 PPM concentration of sensitizer was used. The following procedure was used for each experimental run:

- 1) Place a dissolved oxygen meter probe and an oxygen saturated probe in a 1 liter beaker of water and set it on a magnetic stirring plate. Place the radiometer sensor probe directly under the UV light.
- 2) Turn the dissolved oxygen meter on and saturate the solution with oxygen from a laboratory gas cylinder.
- 3) Mix the polymer-based sensitizer until it is completely dispersed throughout the solution.
- 4) Turn on the UV light and radiometer.
- 5) Record the energy input and the oxygen concentration changes vs. time.
- 6) Take aliquot samples of the solution, check the pH value, and perform an analysis of the reactants.

The conditions for combinations of ozone and polymer-based sensitizer with ultraviolet were the same as previous processes. The following procedure was used for each experimental run:

- 1) Mix the polymer-based sensitizer until complete suspension is obtained in the solution.
- 2) Set the inlet oxygen pressure on the ozone generator to 5 psij.
- 3) Turn on the cooling water flow and the power switch.

- 4) Set the voltmeter of the ozone generator at 70 volts (~ 72 watts) and the rotameter for the ozone to a flow rate of 3 SLPM.
- 5) Wait 5-10 minutes to allow the system to approach steady state.
- 6) Open the valve to the contactor and simultaneously turn on the UV light and timer.
- 7) Following the test time interval, close the valve and turn off the light source.
- 8) Take aliquot samples, and check for pH value followed by an analysis of the product solution.

#### Analytical Methods for Ozone

There are several different ways to determine ozone in the wastewater. In this research, the iodometric method and the orthotolidine-manganese sulfate method were used.

In the iodometric method, ozone was absorbed in KI solution. After absorption of the ozone, the iodide solution was acidified which liberated the iodine, this solution was then titrated with standard sodium thiosulfate solution. The procedures used were as follows:

- 1) Preparation of reagents.

Potassium iodide solution: Dissolve 40 g KI, free from iodine, in 1.0 liter distilled water. Store in a brown bottle.

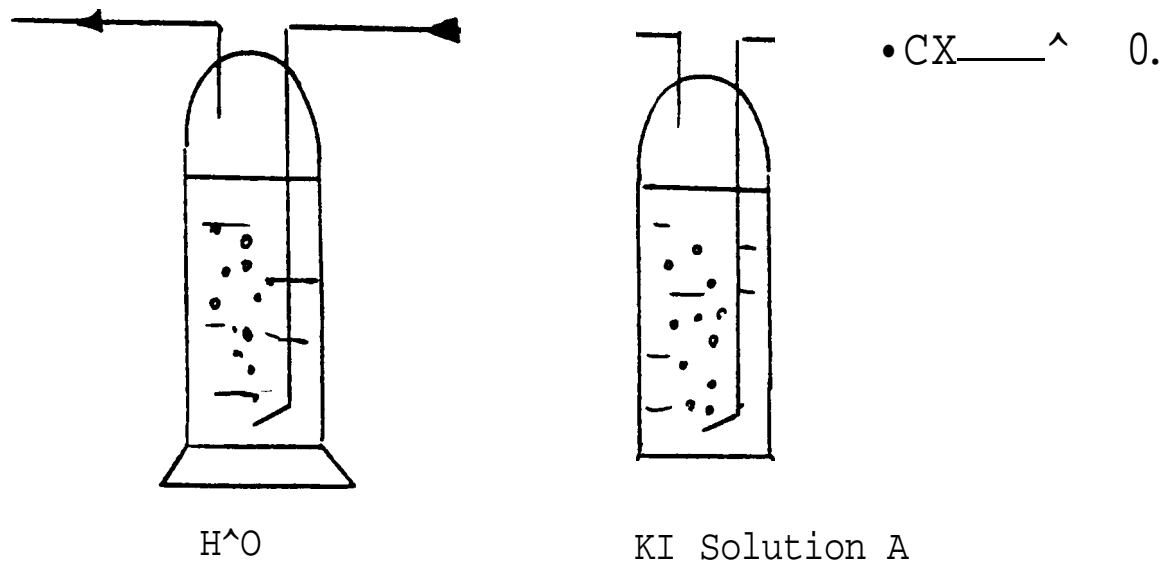
Standard Sodium thiosulfate titrant, 0.005 N: Dissolve 0.25 g  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in 1.0 liter distilled water.

Starch indicator solution: To 5.0 g soluble starch in a mortar, add a little cold distilled water and grind to a thin paste. Pour into 1.0 liter distilled water, stir and allow to settle overnight. Use the clear supernatant.

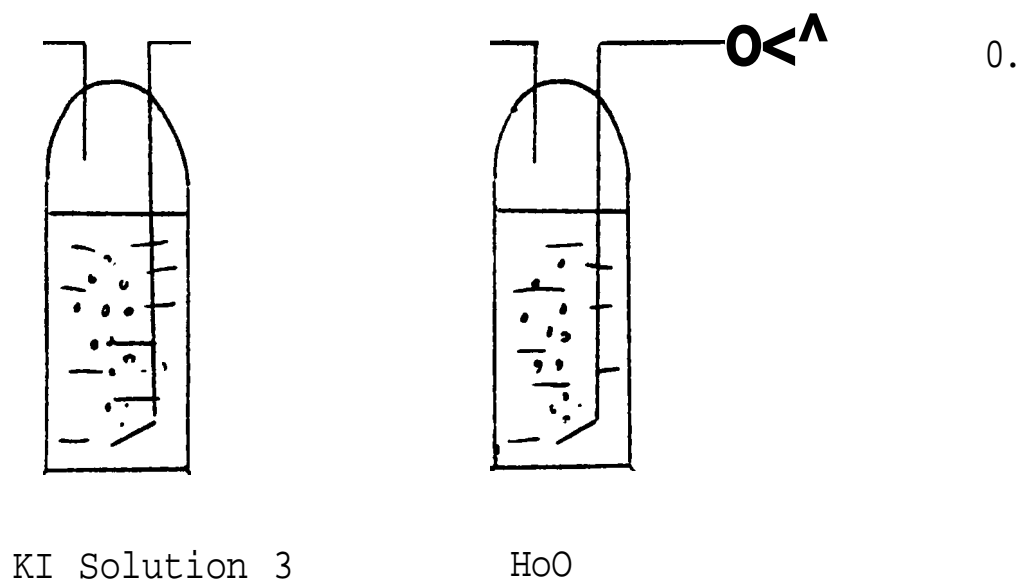
Standard iodine solution, 0.1 N: Dissolve 40.0 g KI in 25 ml distilled water. Add 13.0 g resublimed iodine and stir until dissolved. Dilute to 1.0 liter.

Standard iodine solution, 0.005 N: Dissolve 16.0 g KI in a little distilled water in a volumetric flask (1000 ml), add 50 ml of 0.1 N iodine solution, and dilute to the mark. For accurate work, standardize daily. Store the solution in a brown bottle or in the dark. Protect from direct sunlight at all times and prevent all contact with rubber.

- 2) Connect two gas washing bottles together. Fill with potassium iodide solution and distilled water separately (shown on Figure 5).
- 3) Turn the ozone generator and timer on for 50 seconds. The solution will turn to a yellow color. At this time, the titration is begun.
- 4) Titration: Transfer 30 ml KI solution A (Figure 5a) to 125 ml Erlenmeyer flask and add a small amount of  $H^+SO_4^-$  to this solution. When the  $pH$  has dropped below 2.0, titrate with 0.005 N sodium thiosulfate titrant until the yellow of the liberated iodine is almost discharged. Add 5  $\mu$ l starch ind-: ^ .cor solution to



(a)



(b)

Figure 5. Schematic Diagram for Testing Ozone Concentration



impart a blue color and continue the titration carefully but rapidly to the end point at which the blue color just disappears.

- 5) Blank test. Take 30 ml of KI solution, a small amount of H<sub>2</sub>SO<sub>4</sub> and 5 drops starch indicator solution. Perform whichever one of the blank titrations below applies: First, if a blue color occurred, titrate with 0.005 N sodium thiosulfate solution until the disappearance of the blue color and record the amount. Or, if no blue color occurred, titrate with 0.005 N iodine solution until a blue color appears. Back-titrate with 0.005 N sodium thiosulfate solution and record the difference.
- 6) Before calculating the ozone concentration, subtract the amount of the blank titration in the first part of next step 7) from the amount of sample titration, A, or add the amount to them.
- 7) Calculate the ozone concentration by the following equation:

$$\text{mg/l O}_3 = \frac{(A + B) \times N \times 24000}{\text{ml sample}} \quad (23)$$

where A = ml titration of sample, B = ml titration of blank (positive or negative), and N = normality of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.

- 8) Repeat the steps 3) to 7) for KI solution (Figure 5b).

- 9) The difference between KI solutions A and B should equal the concentration of ozone in the water solution (Figure 5).
- 10) Take the water sample from above (Figure 5) and then follow the orthotolidine-manganese sulfate method procedures for the spectrophotometer. Using these data draw a calibration curve for the Spectronic 21.

In the orthotolidine-manganese sulfate method, the residual ozone oxidizes manganous ion to manganic state. This in turn reacts with acidic orthotolidine reagent. The final yellow color was measured visually with a Spectronic 21 at the wavelength of 435 nm. The following procedures were used for each experimental run:

- 1) Take 25 ml sample in a 125 ml Erlenmeyer flask.
- 2) Dissolve 1 pillow manganese sulfate reagent (33) in the solution. Then add 1.0 ml orthotolidine reagent (34). Stopper and shake to mix. A yellow color should form immediately. Allow at least 20 min. for proper color development but no more than 30 min. before taking the reading.
- 3) Record the reading of percent of transmittance on Spectronic 21 at 435 nm. Transfer the percent of transmittance to mg/l by the calibration curve (Figure 6).

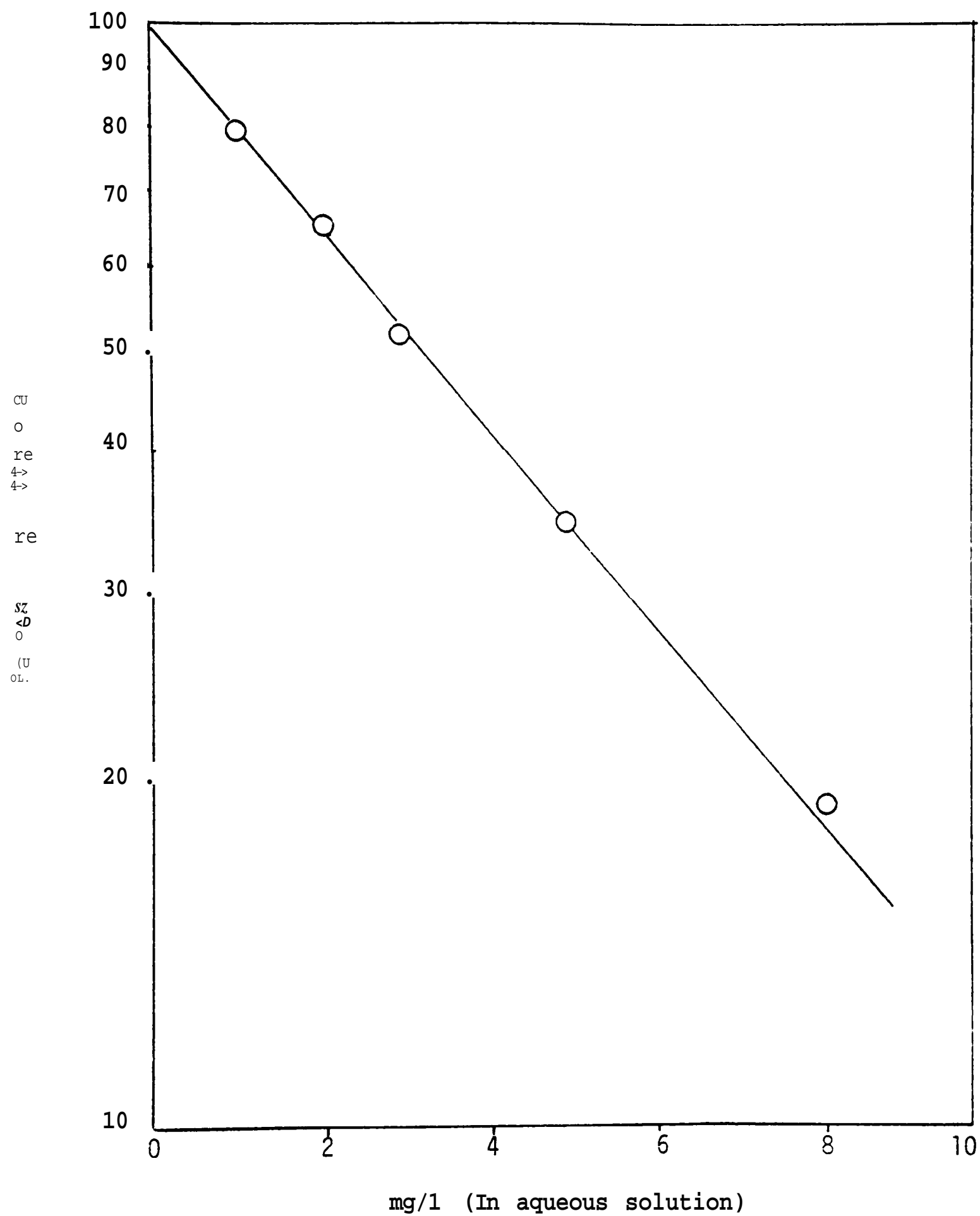
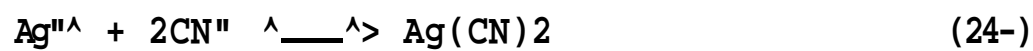


Figure 6. Calibration Curve of Ozone for Bausch & Lomb Spectronic 21

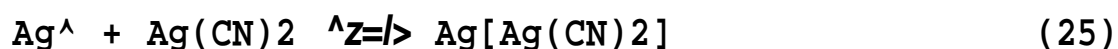
### Analytical Methods for Cyanide

The cyanide v/as determined either by volumetric titration (The Liebig Titration) or by colorimetric measurement.

In the Liebig Titration method, a solution containing cyanide ions was titrated with standard silver nitrate solution. Two cyanide ions reacted with one silver ion to form a soluble, colorless complex:



The overall formation constant,  $K$ , of this reaction was  $1.25 \times 10^8$ . Upon the addition of the first slight excess of silver nitrate solution, the following reaction occurred:



The solubility product expression of the form,  $K_{sp} = [\text{Ag}^+][\text{Ag}(\text{CN})_2^-]$ , may be written, for which the solubility product is  $K_{sp} = 5.0 \times 10^{-12}$ . The turbidity is caused by the precipitation of white  $\text{AgCN}$  or  $\text{Ag}[\text{Ag}(\text{CN})_2]$ . This signaled the end point of titration.

In the colorimetric measurement, the cyanide was converted to cyanogen chloride,  $\text{CNCl}$ , by reaction with chloramine-T at a pH less than 8.0 and without hydrolyzing to cyanate. After the reaction was completed, the color was formed by the addition of pyridine-pyrazolone reagents. The procedures used were as follows:

1) Preparation of pyridine-pyrazolone solution (35):

Add 0.25 g of 3-methyl-1-phenyl-2-pyrazolin-5-one to 50 ml of distilled water, heat to 60°C with

- stirring. Cool to room temperature. The 3-methyl-1-phenyl-2-pyrazolin-5-one saturated solution form. Dissolve 0.01 g of bispyrazolone in 10 ml of pyridine to form pyridine solution. Then pour the 3-methyl-1-phenyl-2-pyrazolin-5-one saturated solution which is prepared previously, through nonacid-washed filter paper. Collect the filtrate. Through the same filter paper pour solution of pyridine (above). Collect the filtrate. Mix the two filtrates well. This mixed reagent develops a pink color, but does not appear to affect the color production with cyanide if it is used within 24 hours of preparation.
- 2) Collect 25 ml sample in a 125 ml Erlenmeyer flask and add 5 drops 1 N sodium hydroxide standard solution to prevent cyanide from hydrolyzing to cyanate.
  - 3) Add 3 drops of m-nitrophenol indicator solution to the sample and swirl to mix.
  - 4) Add 0.1 N HCl standard solution dropwise to the sample until the color changes from yellow to colorless. Proceed immediately with step 5).
  - 5) Add chloramine-T to sample followed by adding pyridine-pyrazolone reagent. Shake well and a blue color should form. Wait 30 minutes to completely develop the color before taking reading.

- 6) Read the transmittance on the Spectronic 21 at 612 nm.  
Record the percentage of transmittance and transfer to mg/l by a calibration curve (Figure 7).

#### Analytical Method for Hydrazine

Since aldehydes reacted with hydrazine will give hydrazones, the p-dimethylaminobenzaldehyde method was used to test the hydrazines for portion of the experiment.

The reagent p-dim.ethylaminobenzaldehyde was purchased from a commercial source (34). The procedures used were as follows:

- 1) Collect 25 ml sample in a 125-ml Erlenmeyer flask.
- 2) Add 1.0 ml reagent in the sample solution and mix well. A yellow color should form. Allow 12 minutes for the color to fully develop.
- 3) Read the spectrophotometer indicator for the wavelength of 455 nm.
- 4) Record the transmittance and then convert to mg/l by a calibration curve (Figure 8).

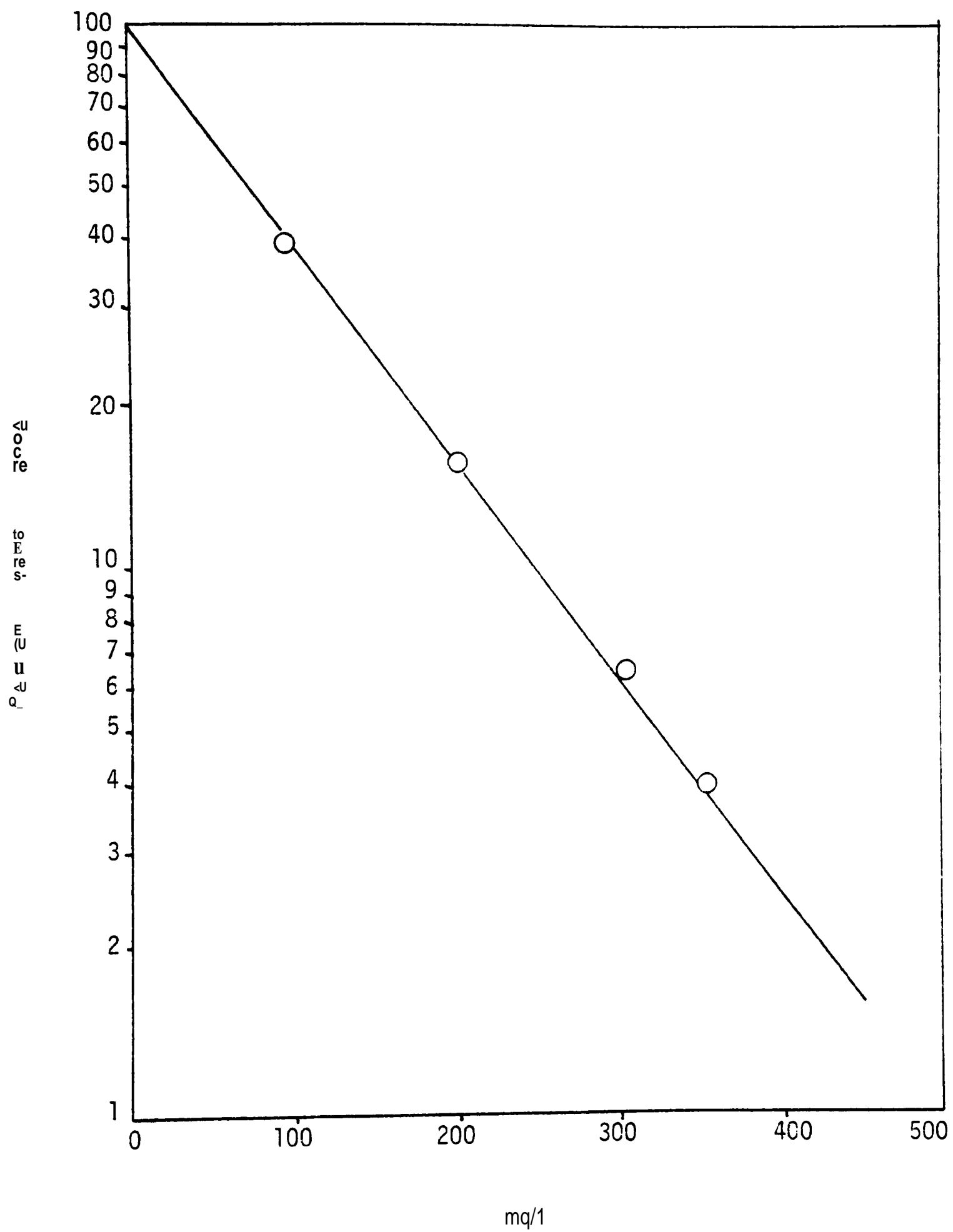


Figure 7 Calibration Curve of Cyanide Compound for Bausch & Lomb Spectronic 21

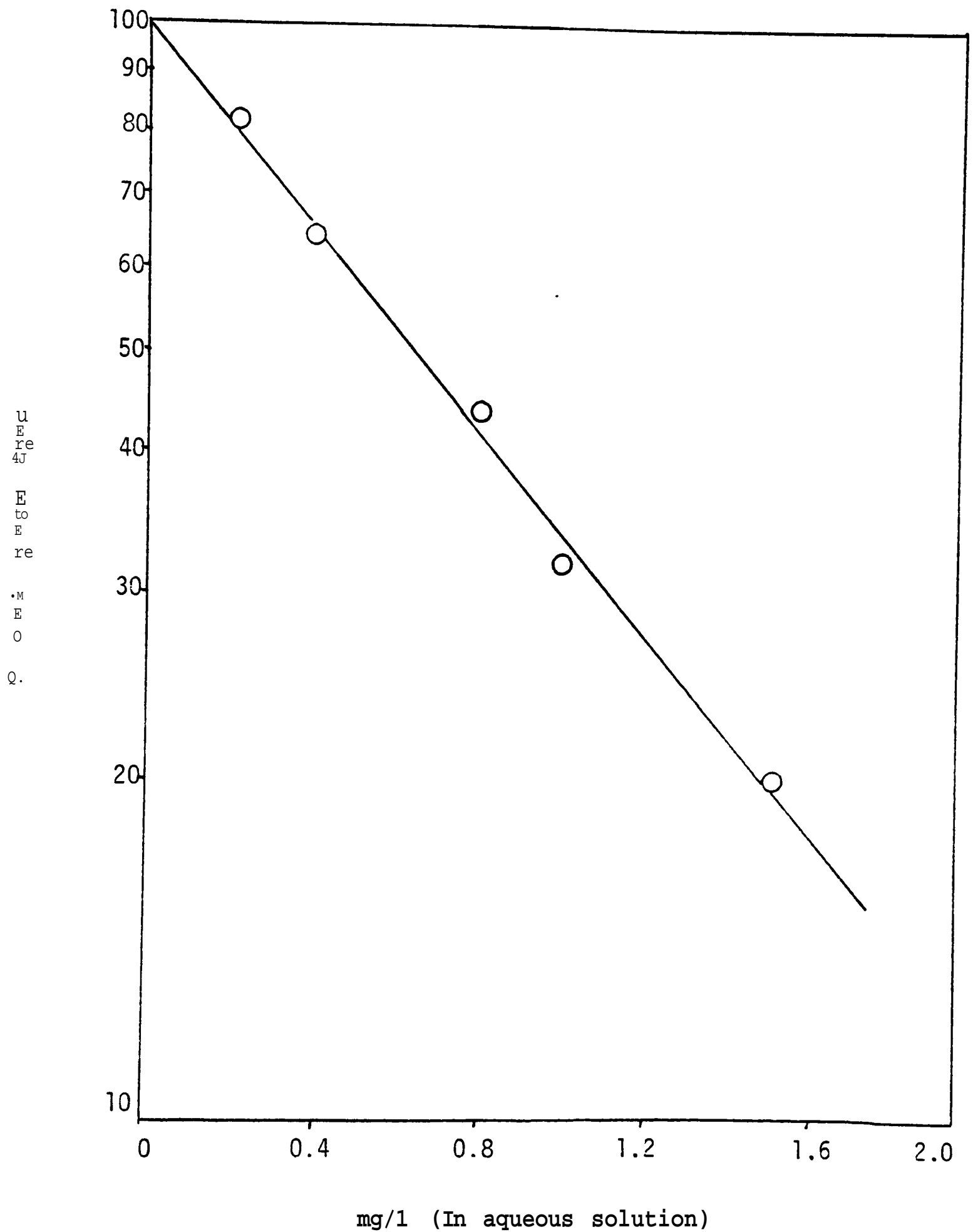


Figure 8. Calibration Curve of p-Nitrophenylhydrazine for Bausoh&Lomb Soectronic 21



## CHAPTER IV

### DISCUSSION OF RESULTS

#### Oxidant Concentration

The initial studies involved the determination of ozone degradation rates in pure water at constant temperature but at different pH levels. For these decay studies, distilled water having a pH adjusted to 3.0 by HCl and pure distilled water (pH 7.0) was saturated with ozone at 20°C. In neither case was the pH buffered. The ozone supply was then turned off. Figure 9 shows the drop in dissolved ozone concentration over a period of 40 minutes. A reduction from 40 mg/l to 2.7 mg/l was observed with a pH of 7.0 and from 50 mg/l to 32 mg/l with a pH of 3.0 solution. This indicated that ozone decay is favored in a high pH solution. There is no firm theoretical explanation for such behavior, however. This result was similar to Adams' result (32). The only difference being that our data were collected for solution pH values of 3.0 and 7.0. Adams' study covered the pH range from 7.0 to 10.5 (Figure 2).

For the dissolved oxygen with photosensitizer studies (Figure 10), the solution containing 1000 mg/l photosensitizer was saturated with oxygen from the air. Pure oxygen could not be used without exceeding the concentration range of the dissolved oxygen meter. The dissolved oxygen concentration was observed to increase slightly when the UV light was turned on. After reaching a maximum, the air probe was removed and a loss or decay in the dissolved oxygen concentration was observed. When steady state was reached, air was re-introduced. As

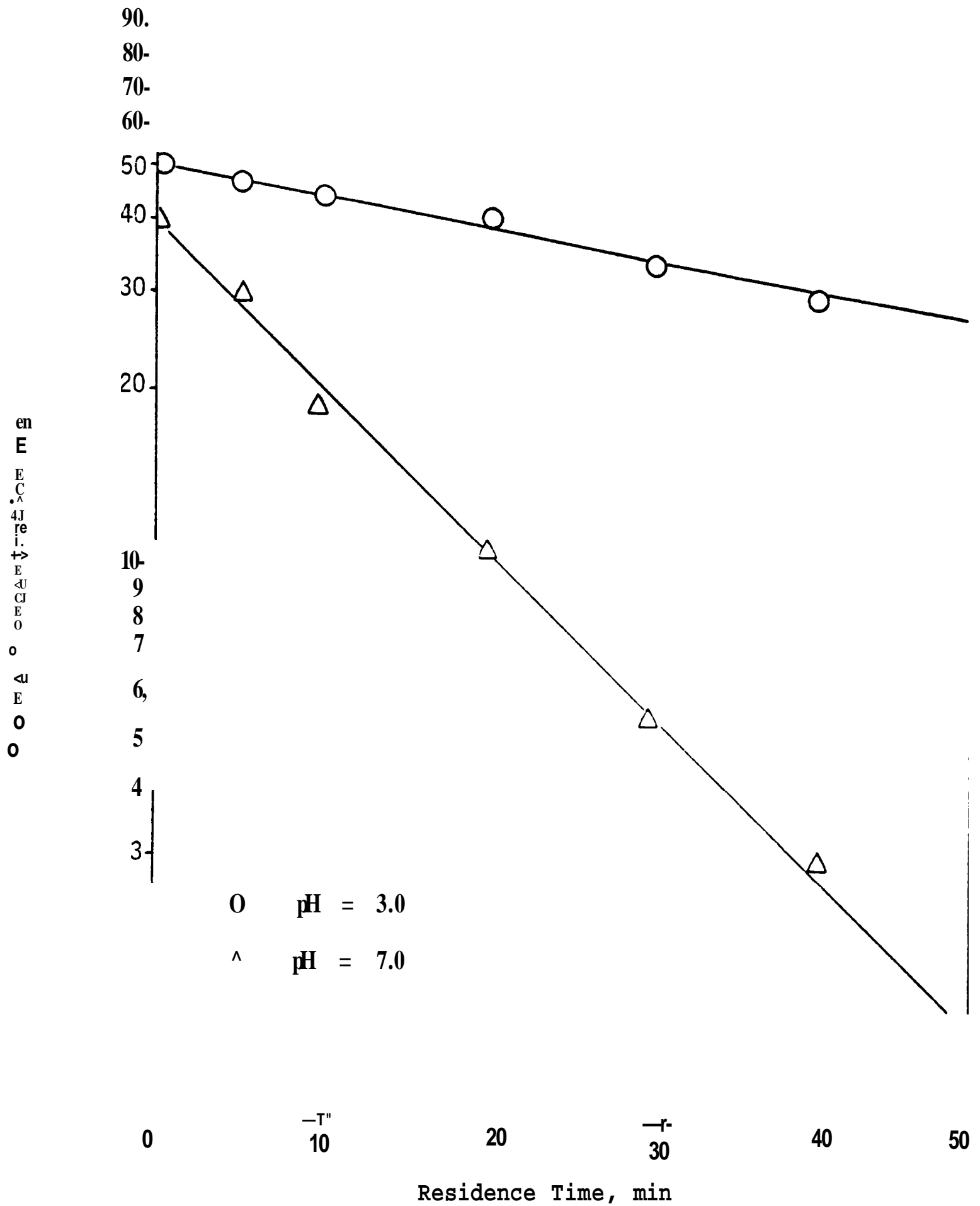


Figure 9. Ozone Decay in Pure Water with pH = 3.0 and 7.0 at Atmospheric Pressure, 20°C

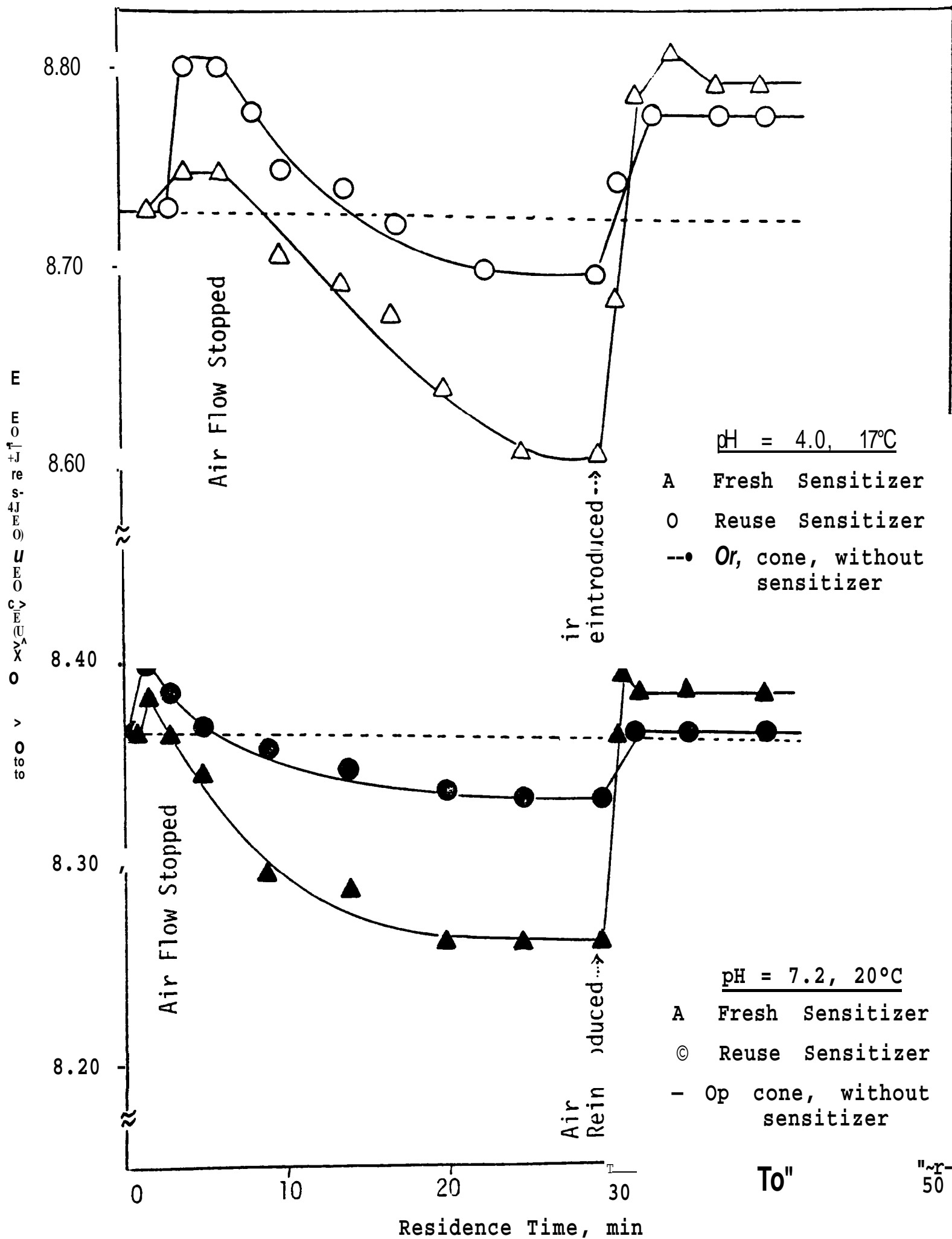


Figure 10 Dissolved Oxygen Concentration in Pure water as a Function of pH at Atmospheric P-essure

shown, the dissolved oxygen concentration again increased until it reached a maximum. The general configuration of decay and generation of dissolved oxygen were nearly the same for different pH levels (Figure 10). The maximum and minimum concentration levels varied. There was a higher dissolved oxygen level for the low pH value. This is similar to the ozone decay behavior with regard to the effect of pH.

For the photosensitizer studies in which the sensitized polymer was reused the results are also shown in Figure 10. The only observed difference between fresh and reused photosensitizer material was the slight disparity in the levels of dissolved oxygen concentration. This might be caused by the gradual losses in sensitivity during operation, but additional data are needed for confirmation of this hypothesis.

#### Hydrazine Studies

The rate of oxidation of p-nitrophenylhydrazine with photosensitizer is shown in Figure 11. The p-nitrophenylhydrazine concentration dropped from 20 mg/l to 2.5 mg/l in 12 hours. This was relatively slow when compared to the results of the ozone studies and various combinations. These data are all grouped as shown in Figure 12. It is to be noted that the time scale in Figure 12 is seconds rather than hours as was the case in Figure 11. It is obvious that p-nitrophenylhydrazine concentration with ozone dropped from 20 mg/l to 16 mg/l in 60 seconds. Moreover, a combination of photosensitizer, under the same conditions, but with ozone and UV light gave the most efficient oxidation rate as shown in Figure 12.

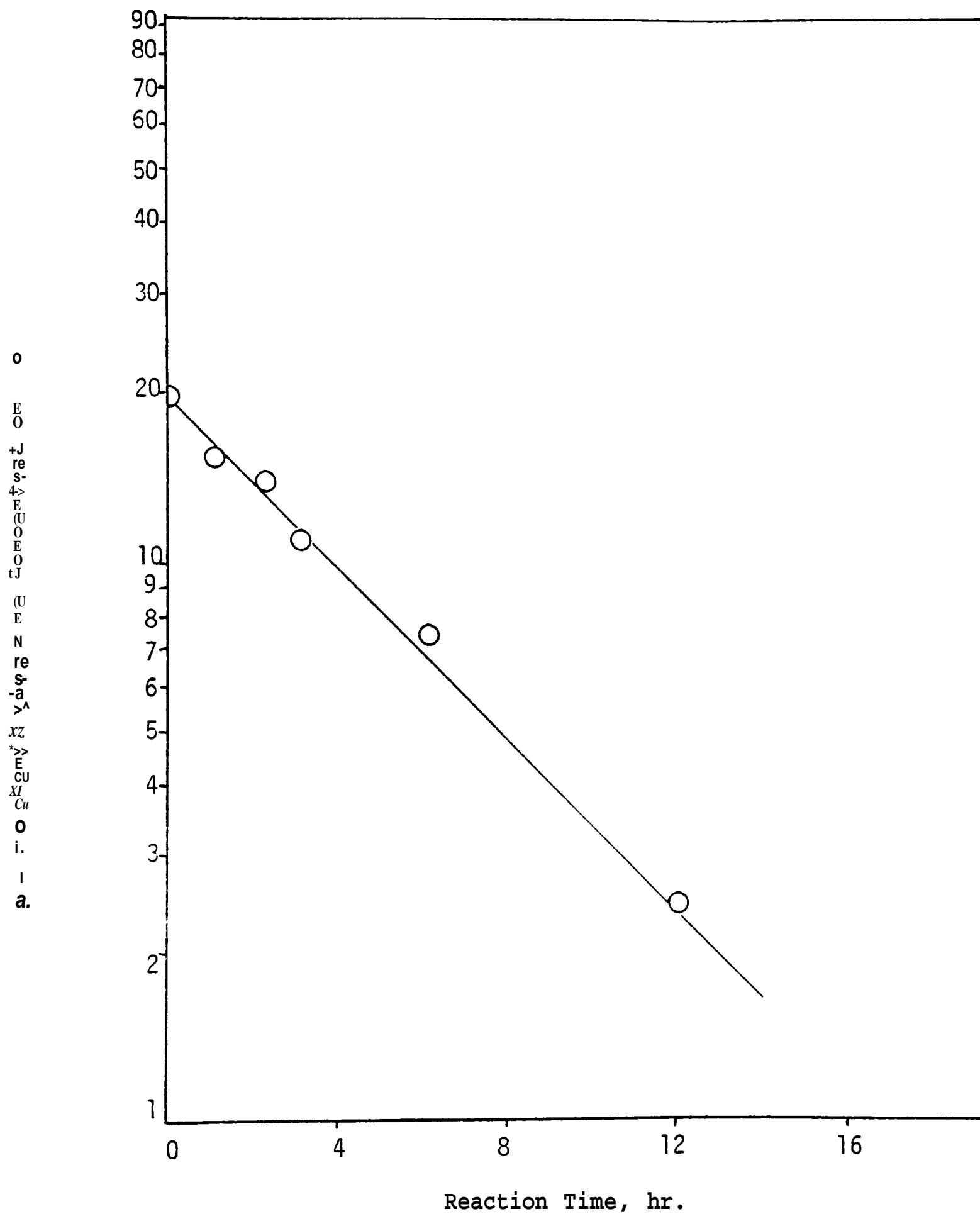


Figure 11. Degradation of p-Nitrophenylhydrazine with Photosensitizer in pH = 7.0 at Atmospheric Pressure, 20°C

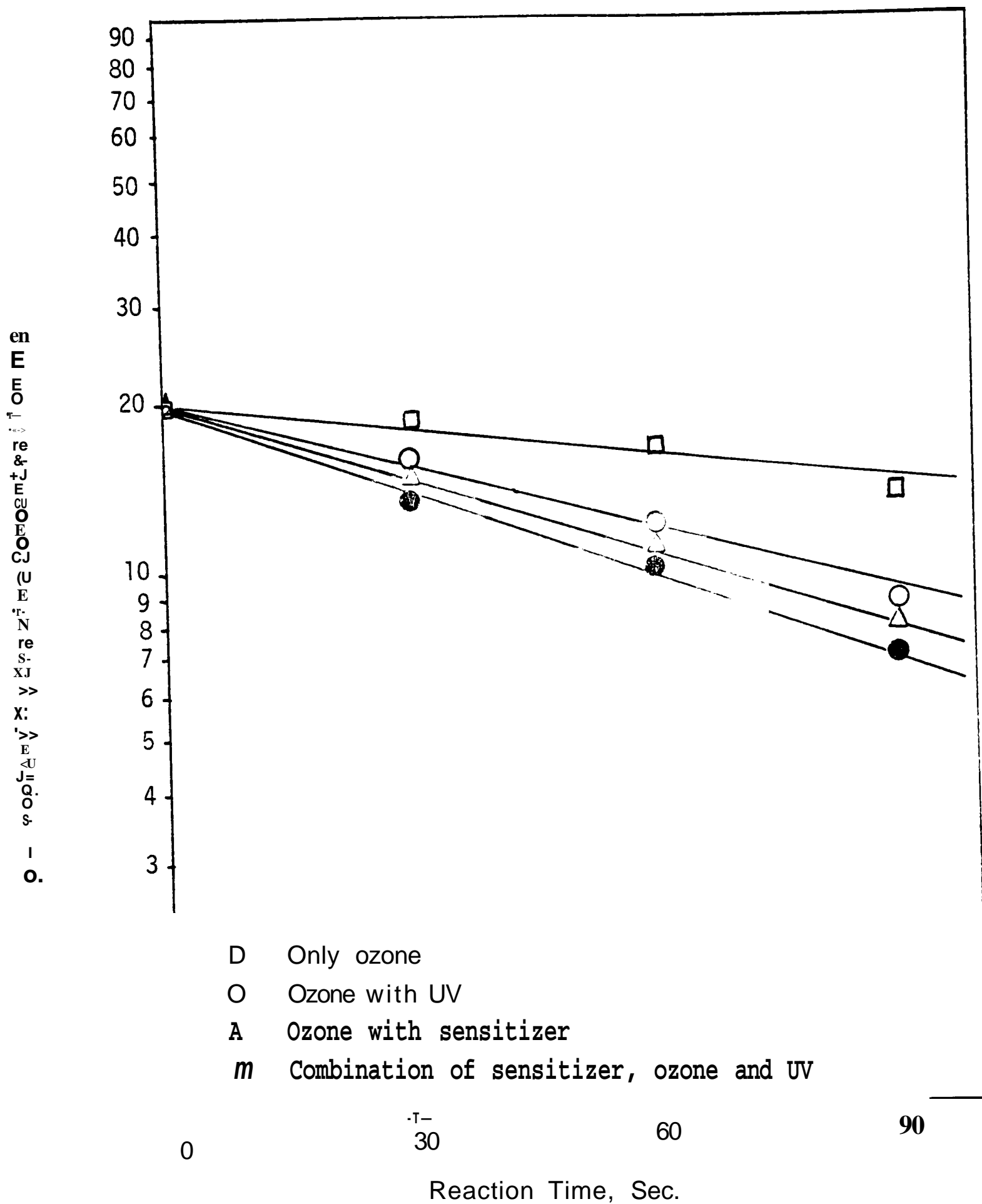


Figure 12 Oxidation of p-Nitrophenylhydrazine in pH = 7.0 at Atmospheric Pressure and 20°C by Various Combination Oxidizers

## Cyanide Studies

Figure 13 shows the results of 20 mg/l potassium cyanide treated with photosensitizer for 3 hours. About 14 mg/l KCN was oxidized after this time period. With only ozone the same amount KCN was oxidized in 60 seconds. Using ozone/UV in combination, 16.3 mg/l KCN had disappeared in 60 seconds. Using ozone with sensitizer, 16.7 mg/l KCN was oxidized. The most efficient process was still the combination of the ozone; photosensitizer and UV, where about 17.5 mg/l KCN had been destroyed in 60 seconds. These results (Figure 14) were similar to those for the hydrazine studies with regard to the effectiveness of the oxidizers.

## First Order Reaction Model

The experimental data indicate that the oxidation rates are first order with respect to the impurity reactant (hydrazine or cyanide). Thus the following simplified equation (27<sup>^</sup>) can be written to describe the rate of disappearance of the contaminant:

$$-\frac{d[A]}{dt} = k[A] \quad (21)$$

[A] is the concentration of impurities (mg/l), t is time (hr), and k is the "apparent" reaction rate constant (hr<sup>-1</sup>)- Equation (21) is actually a simplification of a more involved bimolecular reaction between an impurity molecule and an oxidizing molecule. By assuming that the concentration of the oxidizing species is constant throughout the experiment, it can be incorporated into the assigned "apparent" reaction rate constant. Hence, the units on k values are not simply inverse

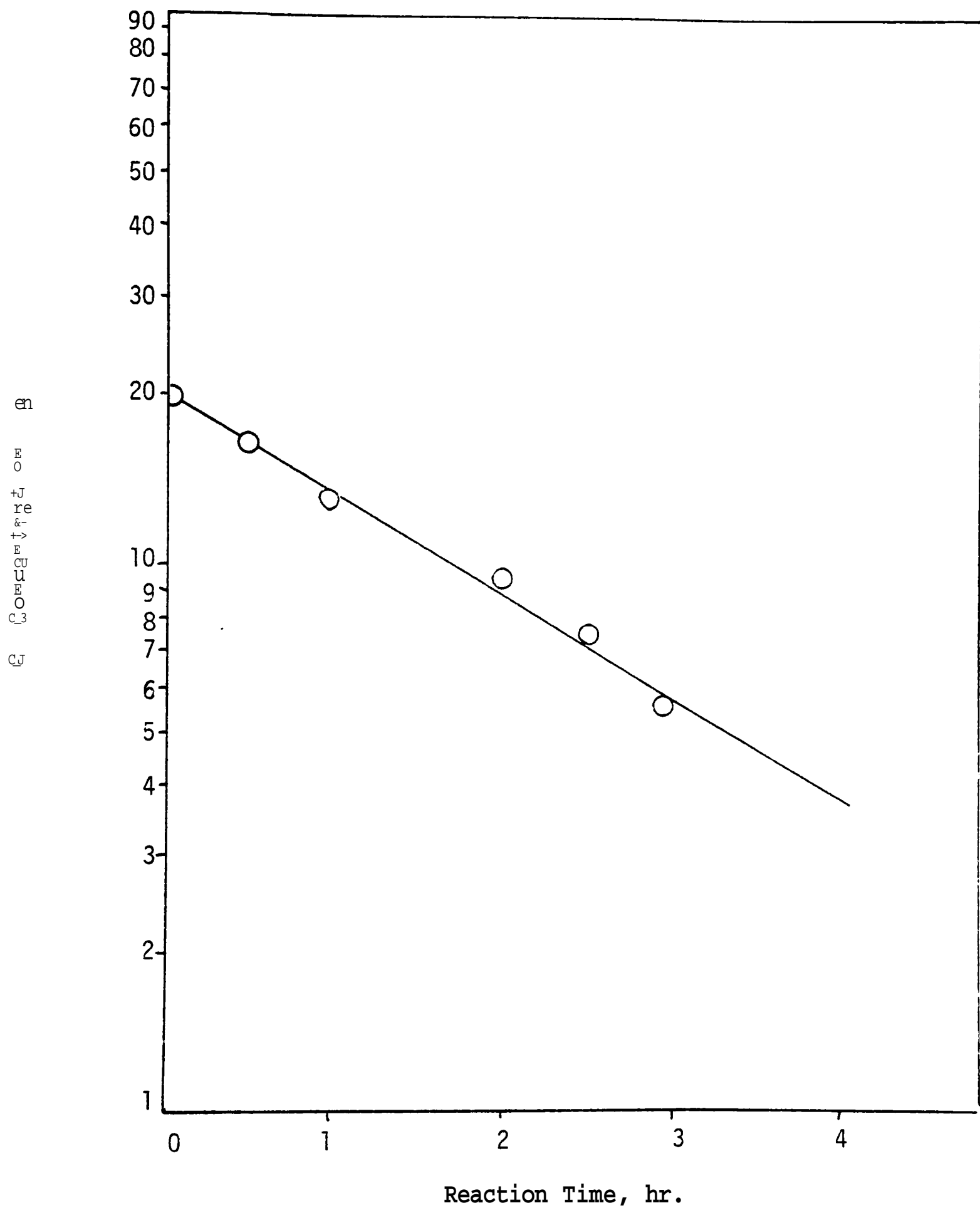


Figure 13. Degradation of Potassium Cyanide with Photosensitizer in pH = 8.0 at Atmospheric Pressure, 20°C



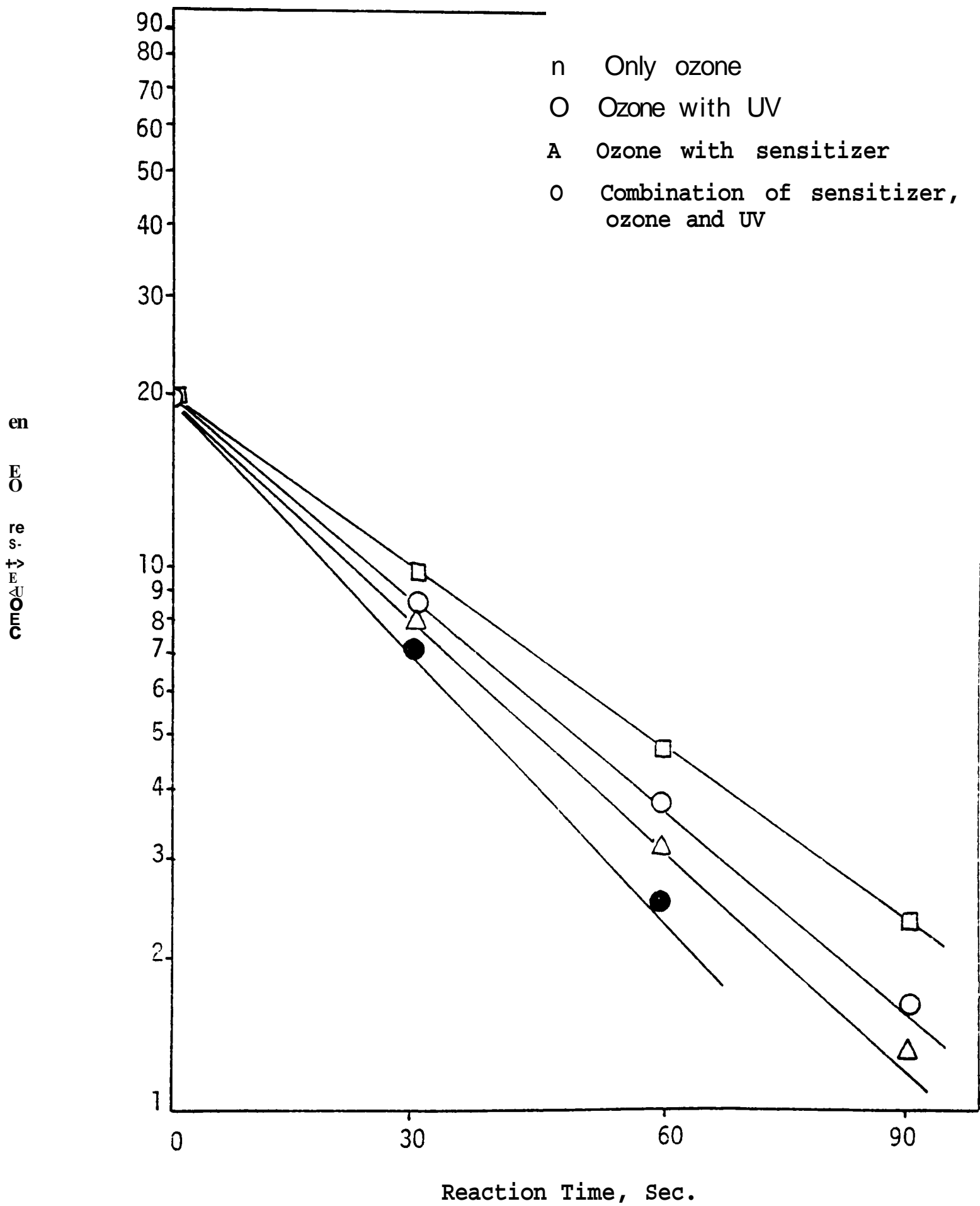


Figure 14, Degradation of Potassium Cyanide in pH = 8.0 at Atmospheric Pressure and 20°C by Various Combination Oxidizers

time, but rather the inverse of oxidant concentration times time. This distinction is most apparent when the  $k$  values from our experiments are compared with those of other investigators. Agreement can be expected only after the  $k$ 's are normalized to the same oxidant concentration.

The results of graphical analysis based on a least squares regression of the equation (21) are shown in Table II. These regression data (Table II) show the apparent reaction rate constants,  $k$ 's, for the different processes. The different rates can only be attributed to qualitative reasons at this time. For example, the ozone is known to be a very reactive oxidizer and hence should give a faster rate than the photosensitizer which triggers only a singlet molecular oxygen degradation process. Moreover, the ultraviolet radiation is known for its ability to excite both the oxidizing molecule and impurity atoms. Hence, its use should also increase the overall reaction rates. The combination of ozone with photosensitizer in the absence of UV was something of a surprise, however, in that the observed rate was faster than ozone. Obviously the ozone is interacting in some way with the photosensitizer to destroy the impurity molecules. In any event, the combination processes can be conceived as providing multiple parallel reaction paths for the destruction of the cyanide and hydrazine molecules.

Bollyky studied the ozone oxidation of cyanide with different catalysts (5f) and his results are shown in Figure 15. His data were fit to the first order model by a least squares regression analysis. He reported that the fastest reaction was obtained using copper sulfate as a catalyst. The apparent reaction rate constant,  $k$ , for this

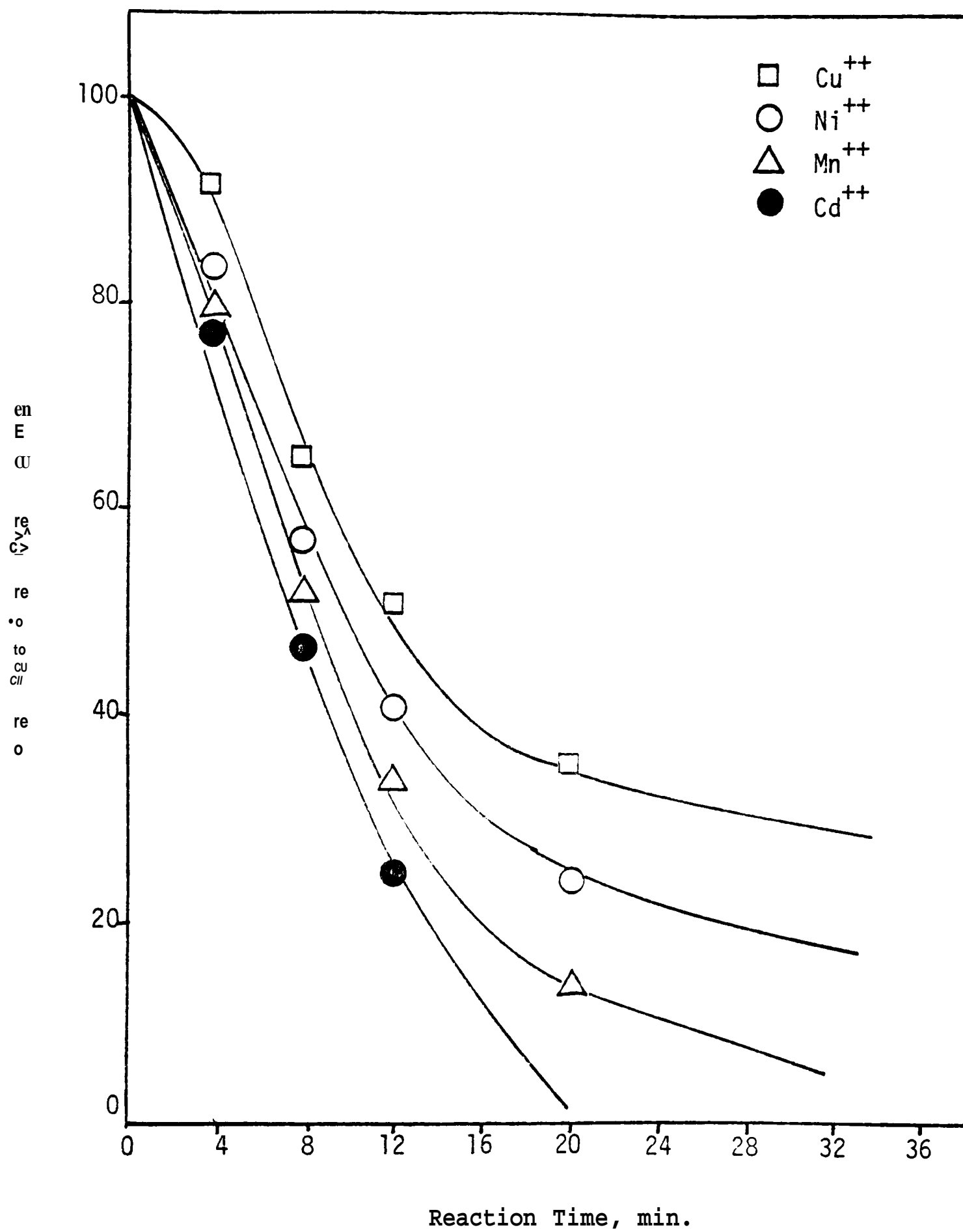


Figure 15. Ozonation of KCN Catalyzed by Various Metal Sulfates (5f)

TABLE II

REGRESSION ANALYSIS OF RATE DATA BASED  
ON FIRST ORDER REACTION MODEL

Process	Rate constant, k(hr <sup>-1</sup> )
O <sub>3</sub> decay at pH = 3.0	0.,7
O <sub>3</sub> decay at pH = 7.0	4..3
3. Hydrazine with photosensitizer	1..7
4. Hydrazine with only O <sub>3</sub>	16,.9
Hydrazine with O <sub>3</sub> /UV	35,.7
6. Hydrazine with O <sub>3</sub> /sensitizer	38 .4
7. Hydrazine with O <sup>^</sup> , sensitizer, and UV	42.8
8, Cyanide with photosensitizer	0,4
9. Cyanide with only O <sub>3</sub>	88.2
10, Cyanide with O <sub>3</sub> /UV	101.1
11, Cyanide with O <sub>3</sub> /sensitizer	109.4
12 Cyanide with O <sub>n</sub> , sensitizer, and UV	124.8

catalyst was 11.5 hr" . This result compares favorably with our research findings when only O<sub>3</sub> was used, and the difference in ozone concentration is corrected to a value consistent with that which Bollyky would obtain using air as his oxygen source.

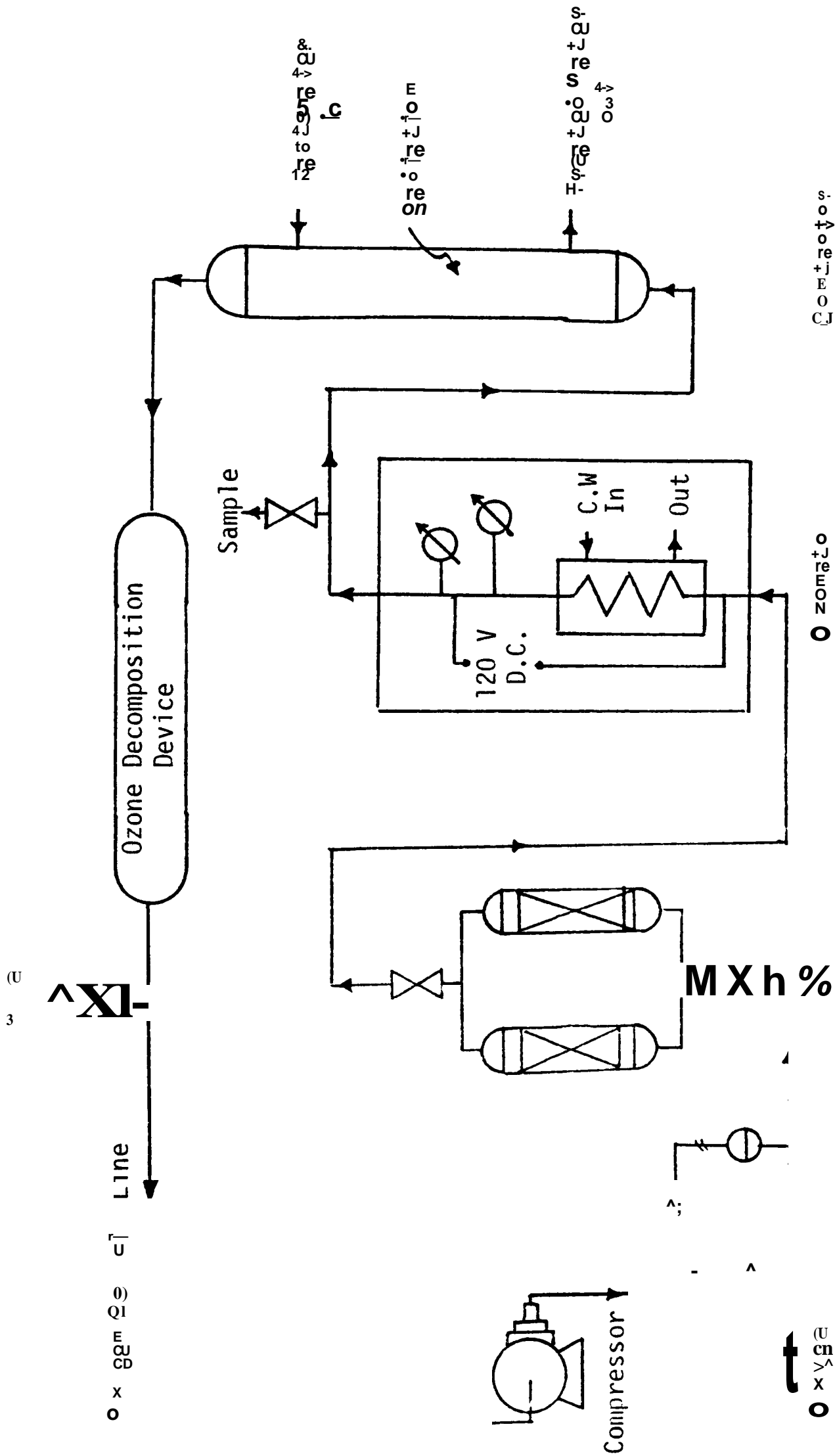
#### Limitations on Scale-up

In order to scale-up from a laboratory to a prototype system, it is necessary that the kinetic data be obtained for multi-component systems. Also more information is needed on the effect of varying UV intensity and the depth of penetration of UV radiation into aqueous solutions.

Of secondary importance is the effect temperature since most wastewaters have a rather narrow range of temperature. Even so, the rate of chemical reaction would be expected to increase with increasing wastewater temperature. However, the relative stability and solubility of ozone or dissolved oxygen should decrease with increasing wastewater temperature so that the overall effect of increasing temperature might be to lower the rate of oxidation rather than increase it.

The effects of pH are also quite important, as shown in Figures 2 and 9. If hydrocarbon compounds are completely oxidized, it is possible that CO<sub>3</sub>" ions could conceivably produce higher pH levels in the solution. This would destroy the ozone's effectiveness unless buffers were added.

A diagram of a hypothetical combination process using ozone, photosensitizer and UV for wastewater treatment is shown in Figure 16.



Ozone detector  
 Ozone decomposition device  
 Sample  
 120 V D.C.  
 C.W. In  
 C.W. Out  
 MXh %  
 Compressor  
 LINE  
 Ozone detector  
 Ozone decomposition device  
 Sample  
 120 V D.C.  
 C.W. In  
 C.W. Out  
 MXh %  
 Compressor  
 LINE

## CHAPTER V

### CONCLUSION AND RECOMMENDATIONS

#### Conclusion

The following conclusion was made based upon the experimental data obtained. This is the combination process of ozone, sensitizer and UV was found to be the most effective process for the destruction of potassium cyanide and p-nitrophenylhydrazine at 20°C and atmospheric pressure.

#### Recommendations

1. Future work should seek to better define the actual mechanisms for the varied reaction processes.
2. More information is needed on the effects of changing UV intensity and on the degree of attenuation of UV radiation by aqueous solutions.
3. Actual wastewater samples should be studied using these procedures.
4. Additional experimentation should be designed to examine the possibilities of using a continuous process for treating wastewater with various combinations of ozone, ultraviolet radiation and photosensitized materials.

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