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TOXIC EFFECTS OF COLOR PHOTOGRAPHIC
PROCESSING WASTES ON BIOLOGICAL SYSTEMS

Edward E. LeFebvre, et al

Environmental Health Laboratory
Kelly Air Force Base, Texas

August 1970

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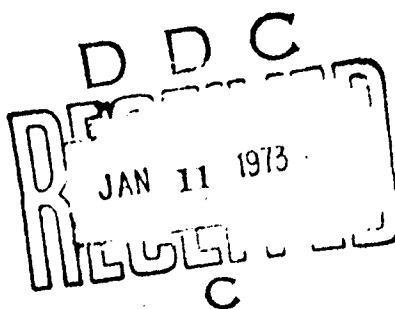
TECHNICAL

Report

TOXIC EFFECTS OF COLOR PHOTOGRAPHIC PROCESSING WASTES
ON BIOLOGICAL SYSTEMS

August 1970

EHL(K) 70-9



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Bioassay

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USAF ENVIRONMENTAL HEALTH LABORATORY (AFLC)

UNITED STATES AIR FORCE


KELLY AFB, TEXAS 78241

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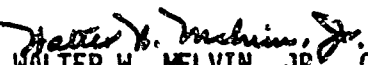

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I. INTRODUCTION

Federal installations are required by Executive Order 11507, Feb 1970, to conform to state and federal laws concerning water pollution. This order directs the head of each federal branch to maintain surveillance of installations under his purview. Executive Order 11514, March 1970, directs federal agencies to provide national leadership in protecting and enhancing the environment and requires that each agency monitors the pollution activities on its installations. State laws all forbid the disposal of waste effluents that poison aquatic habitats designated for use as potable water, contact recreation or fish culture. These designations apply to the vast majority of rivers in the United States.

The Clean Water Act of 1965 assigned the responsibility of defining anti-pollution criteria to the Federal Water Pollution Control Administration (FWPCA) which recently changed its name to the Federal Water Quality Administration (FWQA). This organization has stated as its policy concerning the disposal of wastes "...all effluents containing foreign materials should be considered harmful and not permissible until bioassay tests have shown otherwise. It should be the obligation of the agency producing the effluent to demonstrate that it is harmless in the concentrations to be found in the receiving waters."⁽¹⁾

Color photographic processing is one of the major industrial waste sources on Air Force bases engaged in aerial photographic reconnaissance. Since these bases do not usually have industrial waste treatment plants, disposal of the photographic processing waste through the domestic sewage treatment plant would be desirable. Little information was available on

this disposal method so toxicity studies were initiated at the USAF Environmental Health Laboratory, Kelly AFB TX, in February 1969, to determine the effects of these wastes on a biological systems.

Three color film processes, ECO-2, ME-4, and EA-4, use similar chemicals. The EA-4 process is associated with portable processing laboratories. Disposal of waste from these units into a nearby sanitary manhole would be desirable as the EA-4 processing unit is moved from place to place.

There are eight separate baths that the film is passed through during development in the EA-4 process as well as water washes at various intervals. Waste containing high oxygen demand salts, heavy metals, and organic material are generated. This report covers biodegradability studies and bioassays on EA-4 wastes received from Shaw AFB SC and Forbes AFB KS.

II. SUMMARY OF RESULTS

A. Photographic chemical wastes generated by the Kodak Ektachrome RT Processor using Kodak EA-4 processing chemicals were tested for degradability by, and toxicity to sewage treatment plant microorganisms. Desilvered waste is successfully degraded by and is non toxic to such organisms at concentrations as high as 0.05% chemical waste.

B. The effluents from treatment plants receiving photowaste must be diluted at least 10 fold by their receiving streams to satisfactorily dilute undegraded effluent cyanides.

C. Desilvered EA-4 waste cannot be disposed of without degradative treatment unless such action is justified as defined in Executive Orders 11507 and 11514. When so justified, EA-4 waste may be introduced untreated into streams with a volume of at least 3.4 cubic feet per second (CFS) and with flow characteristics as described in Appendix 5.

D. Desilvering EA-4 fixer bath prior to disposal is mandatory regardless of the disposal technique. Non desilvered waste is extremely toxic to all biological systems tested.

E. These studies indicate that more investigations concerning the toxicology of photowaste are necessary before truly non pollutional disposal techniques can be proposed with a high degree of confidence. Appropriate investigations are recommended.

III. DISCUSSION

A. Description and Waste Sources from the Kodak Ektachrome RT Processor:

1. A full description of the EA-4 color photographic (Ektachrome RT Processor is contained in the operational training manual⁽⁶⁾ prepared for the Air Training Command. Appendix 1 is an extract of Section II of the manual which describes the Kodak Ektachrome RT Processor, Model 1411-M using the EA-4 chemical process. The RT Processor is designed for continuous processing and drying of reconnaissance-type Ektachrome aerial roll film. Being mobile, the unit can be readily deployed from base to base depending upon the operation mission. The mission of portable photographic processing laboratories at times places them in remote locations without access to any sewage treatment plant. Therefore, investigations included the toxicity of untreated EA-4 waste to aquatic organisms and recommendations for the disposal of untreated waste when such disposals are authorized under Executive Order 11507.

2. There are eight separate baths or chemical process stages passed through during development of the film. Additionally, there are two intermediate and one final washing stages using water at 90°F prior to drying. Each separate bath produces a waste with individual chemical characteristics. The wasting rate of each chemical bath is dependent upon the quantity of film processed per unit time. Washing water is usually discharged at a constant rate of about six gallons per minute when the unit is operating regardless of the rate or quantity of film processed. The states of processing in order are:

- a. Prehardener

- b. Neutralizer
- c. First Developer
- d. First Stop
- e. Wash
- f. Color Developer
- g. Second Stop
- h. Wash
- i. Bleach
- j. Fix
- k. Wash
- l. Dryer

3. All baths and washing waters are discharged to a common trough and effluent line from the unit. The chemical properties of the raw chemicals used in each bath are altered somewhat by reaction with the film as it is processed and/or by reaction with each other when combined for discharged.

B. Scope of Biodegradability and Bioassay Studies:

1. Initial biodegradability studies consisted of a Warburg Oxygen (O_2) Uptake Study and batch activated sludge treatment study of the total waste including wash waters from an Ektachrome RT processing unit using the EA-4 process located at Shaw AFB SC. After completion of these initial studies, a detailed study of the EA-4 process and chemical analysis of subsequent waste samples submitted from Shaw AFB it was recognized that the total waste including washing water varied greatly in chemical composition. This variation is due to the constant wash water discharge rate regardless of the quantity of film processed, while wasting of process baths (chemicals) is dependent upon the

quantity of photographic film processed.

2. Recognizing the difficulty of establishing sufficient controls using a variable total waste as a parameter, samples were obtained from each discharge line of the eight individual chemical processing baths during actual film processing. This unit was located at Forbes AFB KS. By sampling in this manner all wash waters were excluded. Fractions of the samples from each individual chemical processing bath were then combined (composited) in the same ratios by volume they would be wasted during processing. In this manner a concentrated waste of consistent chemical composition and whose volumetric rate of discharge could be related to the quantity of film processed was obtained.

3. Warburg studies were conducted separately on the wastes from each of the EA-4 chemical process baths to determine which ones might be amenable to biological treatment systems. Warburg studies were also conducted on the combined composited waste. Biological treatment studies using a bench top continuous flow activated sludge plant measured the biodegradation actually achieved in a biological system. Most of the silver was then removed from the combined waste and a further treatment study using the continuous flow activated sludge bench top plant was accomplished.

4. Bioassays for 96 hours were conducted on the composited waste from Forbes AFB KS prior to, and after treatment in the bench top continuous flow activated sludge plant. These studies measured the toxicity of the composited waste before and after treatment and changes in this toxicity over a limited period of time. Similar bioassays were conducted on the combined

waste after silver removal. Data from these studies:

(a) Were used in devising a protocol for disposing of untreated wastes.

(b) Indicated biological treatment of EA-4 wastes produced an effluent meeting state and federal requirements concerning toxicity when disposed of as recommended in this report.

C. Biodegradability Studies:

1. EA-4 Processing Waste Including Wash Waters from Shaw AFB SC.

The waste received from Shaw AFB was primarily inorganic with only a trace of organic material. Laboratory analysis of the waste as received is presented in Table 1. The waste included a large quantity of water used in the wash steps of the process. The calculated effluent composition of the EA-4 process as provided by the manufacturer is presented in Table 2.

Table 1
ANALYSIS OF WASTE DISCHARGED FROM EA-4
PHOTOGRAPHIC PROCESS, SHAW AFB

<u>Constituent</u>	<u>Concentration (mg/l)</u>
COD	2,234
Dissolved Solids	5,942
Suspended Solids	70
Volatile and Fixed Suspended Solids	70
Oils and Greases (as Heptane)	22
Surfactants (as LAS)	13
Phenols	0
Nitrates	48
Phosphates	380
Sulfates	1,100
Cyanides	260
Silver	6.70
Iron	1.96
Zinc	0.20
Copper	0.08
Manganese	0.05
Chromium	0.05
Lead	<0.05
Cadmium	<0.01

Table 2

CALCULATED EFFLUENT COMPOSITION FROM EA-4 PROCESS*
(9 1/2-inch film at 3.2 ft/min)

<u>Chemical</u>	<u>Concentration (mg/l)</u>
Acetate Ion	1,340
Benzyl Alcohol	100
Bicarbonate	50
Bromide Ion	405
Citrazinic Acid, sodium salt of	33
Ethylenediamine	63
Ethylene glycol	76
Ferrocyanide Ion	414
Formaldehyde	128
Hydroquinone	136
Hydroxylamine	90
Kodak Color Developing Agent (free base) CD-3, 4-amino-N-ethyl-N-(B-methanesulfonamidoethyl)-n-toluidine	
Phenidone	7
Phosphate Ion	350
Quadrafos**	143
Succinaldehyde	20
Sulfate Ion	540
Sulfite Ion	1,170
Tertiary butylamine borane	2
Thiocyanate Ion, CNS	450
Thiosulfate Ion	1,130
p-toluenesulfinic Acid, sodium salt	3
Total Dissolved Solids***	6,653

*Sodium potassium ions not reported.

**Marketed by Rumford Chemical Co.

***Calculated from above data.

Several comparisons between Tables 1 and 2 can be made showing the similarity of the calculated and measured composition. The measured dissolved solids of 5942 mg/l is lower than the 6653 mg/l probably due to experimental error in the gravimetric analysis and the loss of some components by evaporation during the drying process. However, the results are in close proximity when taking this into account. The phosphates seem to be in close agreement. The difference in sulfate quantities is undoubtedly caused by oxidation of some of the sulfite to sulfate. At first, the cyanides appear to be very divergent. However, the analysis method does not record the ferrocyanide due to the difficulty of converting this to free cyanide. When the thiocyanate is calculated in terms of CN, the result is 210 mg/l which agrees quite closely with the measured 260 mg/l CN.

a. Warburg O₂ Uptake Study of Dilute EA-4 Processing Waste from Shaw AFB:

Warburg studies were run on the waste from Shaw AFB according to the method employed by this laboratory.⁽²⁾ These studies were conducted to estimate the approximate percentage of the waste that might be toxic to conventional activated sludge processes. These studies indicated the dilute waste from Shaw AFB was not toxic up to a concentration of 20 percent of the total volume. Figure 1 contains the Warburg O₂ uptake curves for the waste.

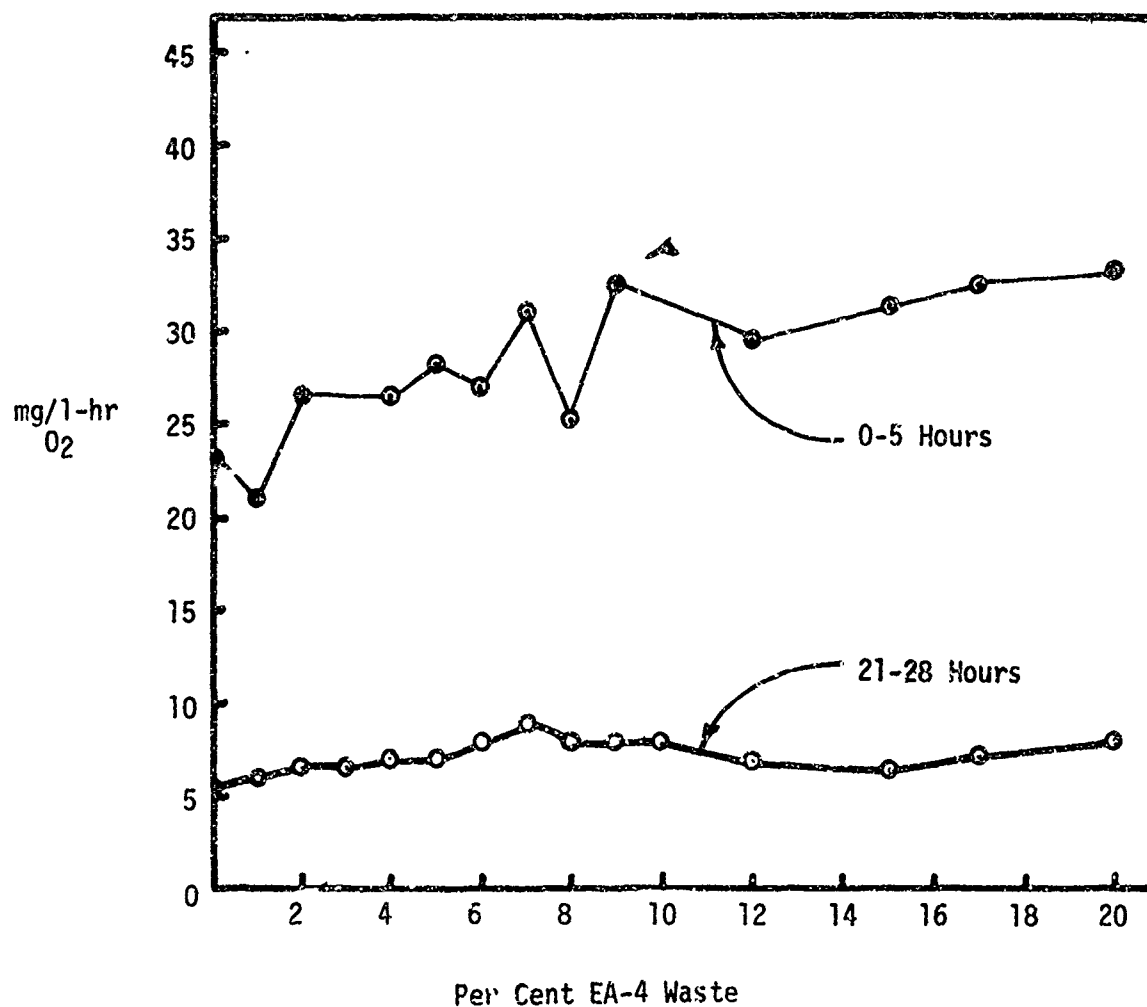


Figure 1. Warburg O₂ Uptake, Diluted EA-4 Waste from Shaw AFB SC

b. Batch Activated Sludge Treatment of Dilute EA-4 Processing Waste from Shaw AFB SC.

(1) Two batch activated sludge treatability studies were conducted on the waste from Shaw AFB according to the methods employed by this laboratory⁽²⁾. The contents of each of the five compartments of each of the two batch treatment units were made up according to Table 3.

The composition of the synthetic sewage used is shown in Table 4.

Table 3
COMPOSITION OF BATCH ACTIVATED SLUDGE UNITS

		Compartment			
	Control	A	B	C	D
Settled Sludge (ml)	900	900	900	900	900
Synthetic Sewage (ml)	2,600	2,582.5	2,565	2,495	2,425
Photowaste (ml)	0	17.5	35	105	175
Per Cent Photowaste	0	0.5	1	3	5

Table 4
COMPOSITION OF SYNTHETIC SEWAGE

<u>Substrate</u>	<u>mg/l</u>
Glucose	150
Glutamic Acid	150
Surfactant (LAS)	5
Sodium Phosphate, Monobasic ($\text{NaH}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$)	95

(2) Samples from each compartment of the two batch units were analyzed prior to aeration and after six and 24 hours of aeration. Complete results are contained in Appendix 3. BOD removal was over 90 per cent in six hours for all compartments. Nitrification was shown for the control, 0.5 per cent and 1.0 per cent compartments in the first six hours of aeration and in all compartments after 24 hours. Phosphates reflected

little or no change in six hours. Cyanides were partially removed at the 0.5 per cent and 1.0 per cent photowaste concentrations but appeared higher at the 3.0 per cent and 5.0 per cent levels. This was probably due to conversion in the treatment plants of CN-complexes to a free CN measurable by the analytical procedure used, Method B, Standard Methods⁽³⁾.

c. Both the Warburg O₂ uptake study and the batch activated sludge studies of the dilute EA-4 processing waste from Shaw AFB SC indicated that the waste was not acutely (short term) toxic to biological treatment systems in the range of concentrations of the waste used in the studies. Concentrations of the photographic waste above 1.0 per cent in the batch studies, however, appeared to retard nitrification. These studies did not predict what might occur during long term discharges to a biological treatment system where accumulation of heavy metals and cyanides may occur in the biological mass. With the constant wash water rate and varying amounts of chemicals being discharged, it was impossible to predict toxicity of the waste based on these studies alone. The need for further information on the waste without wash water became readily apparent.

2. Warburg Oxygen Uptake of EA-4 Individual Unit Process (Bain) Wastes from Forbes AFB KS:

a. Samples for Warburg O₂ uptake studies of each of the eight individual EA-4 process baths were obtained from a unit at Forbes AFB KS as described in paragraph B.3. These samples contained no dilution with wash waters. Manufacturers information⁽⁵⁾ indicates a BOD for each of these baths. Table 5 contains BOD values calculated from this information and COD values determined at this laboratory for each sample obtained from

Forbes AFB.

Table 5
BOD'S AND COD'S OF PROCESS WASTE SOLUTIONS

	<u>BOD (mg/l)</u>	<u>COD (mg/l)</u>
Prehardener	66,500	100,000
Neutralizer	8,200	20,000
First Developer	9,600	260,000
First Stop Bath	22,800	24,000
Color Developer	11,900	35,000
Second Stop Bath	13,200	29,000
Bleach	900	41,000
Fixing Bath	35,000	136,000

(1) Prehardener: The prehardener reduces emulsion swelling which results from the gelatin' coating of the film becoming soft on contact with water. Its total chemical content is approximately 20 percent. In addition to inorganic and organic salts, the prehardner contains formaldehyde and dimethoxytetrahydrofuran. The formaldehyde concentration is approximately 10 grams per liter. Previous studies at this Laboratory show that the average microorganism activity is decreased by about 10 percent in a 10 mg/l formaldehyde concentration. The activity of the microorganisms is further reduced until it reaches zero at concentrations between 100 and 500 mg/l

formaldehyde (4). Warburg O₂ uptake studies with prehardner indicate a toxic effect at a concentration of 0.05 percent by volume (approximately 500 mg/l). These results are shown in Figure 2. The microorganisms showed no indication of acclimation in 28 hours.

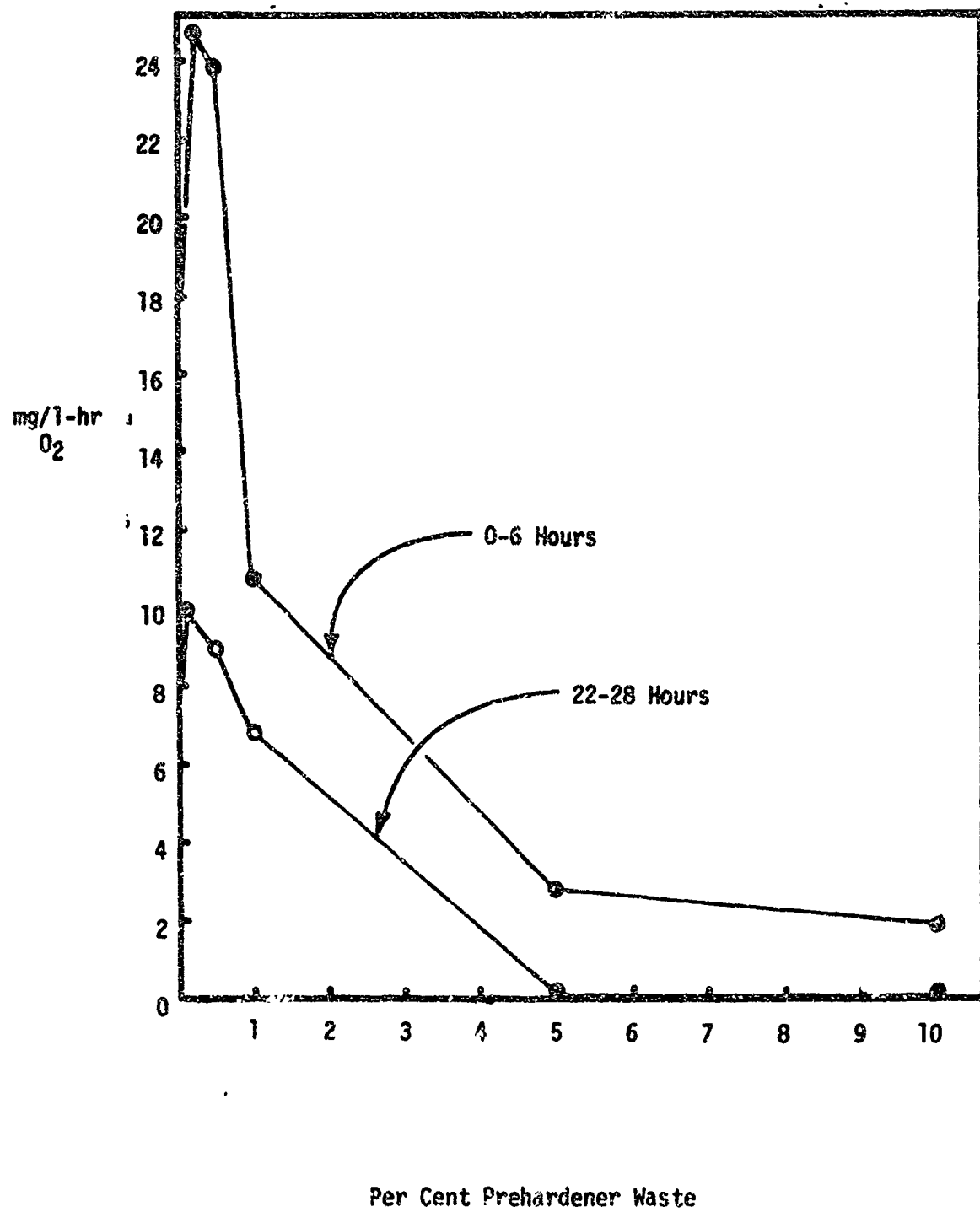


Figure 2. Warburg Study, Prehardener O₂ Uptake

(2) Neutralizer: The neutralizer solution inactivates the chemicals from the previous step. The neutralizer is composed of organic and inorganic salts including bromides, sulfates, acetates, and proprietary chemicals. Warburg studies (see Figure 3) show toxicity to microorganisms at concentrations as low as 0.01 per cent by volume. Below this concentration there seems to be little reaction to the waste.

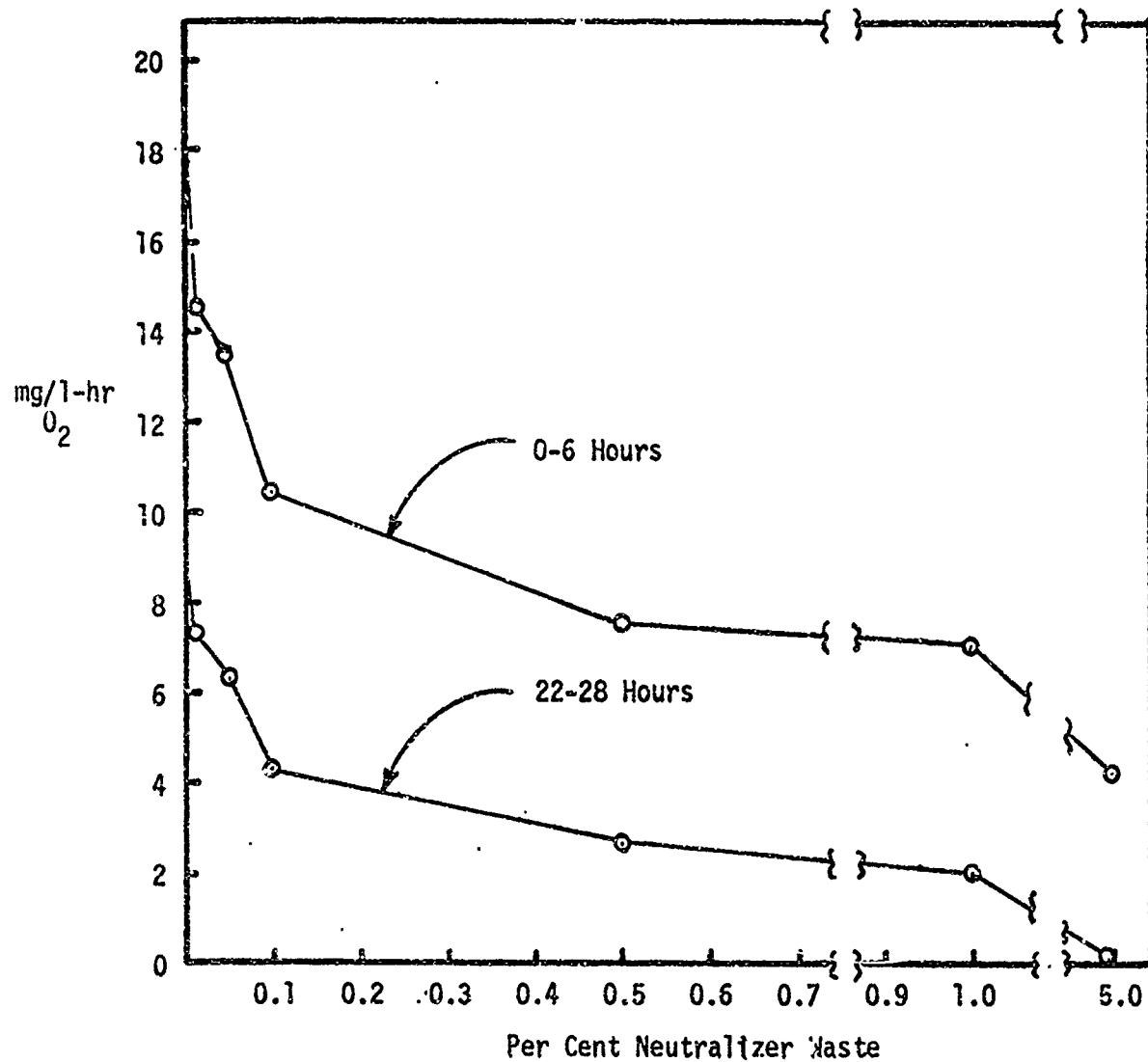


Figure 3. Warburg Study, Neutralizer O₂ Uptake

(3) First Developer: The first developer is considered the most critical step in the process. The first developer's function is to form a black and white image in all three layers of the color emulsion. Consequently, it contains a wide variety of chemicals including sulfites, sulfates, bisulfites, carbonates, bromides, thiocyanates, phosphates, and hydroquinone. Warburg studies (see Figure 4) were conducted both with and without microorganisms in the solution. The oxygen uptake of the microorganisms was impossible to determine due to the presence of the large quantity of sulfites but was probably negligible. Because of the sulfites, the BOD as reported in Table 5 probably had a positive interference.

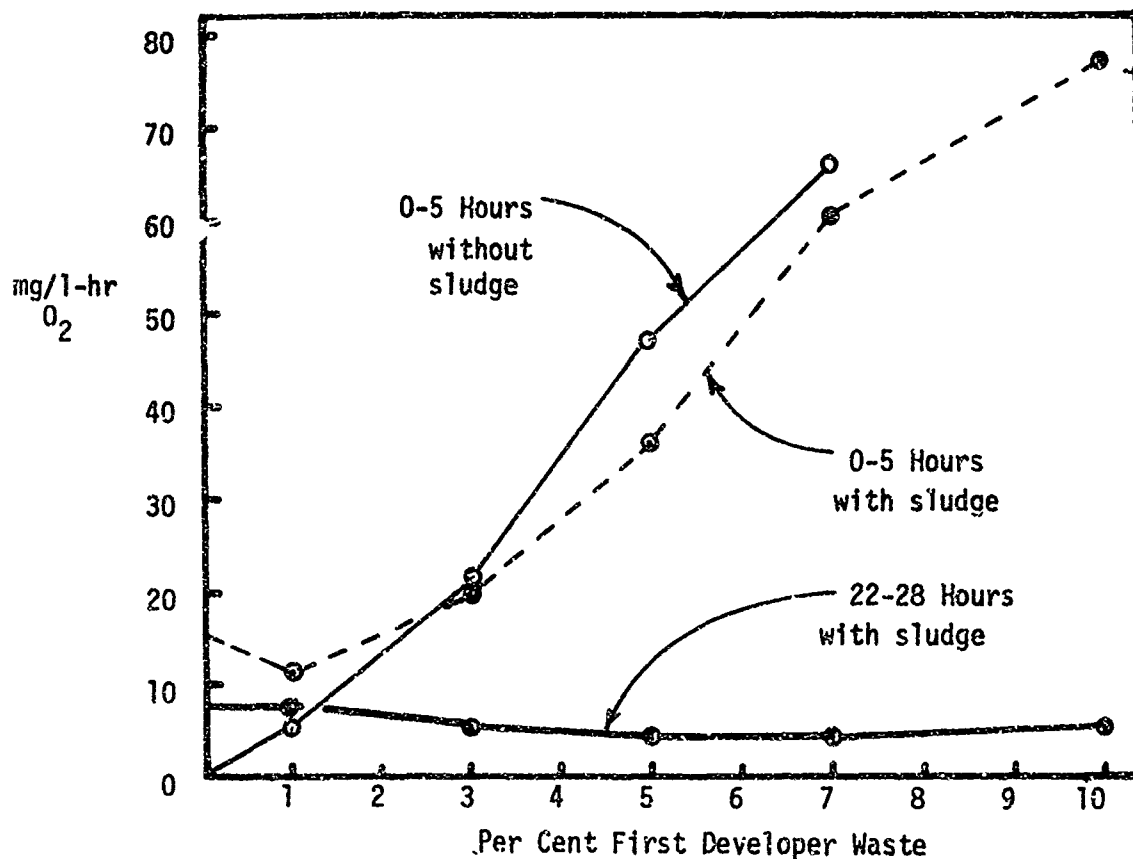


Figure 4. Warburg Study, First Developer O₂ Uptake

(4) First Stop Bath: As the name implies, this solution is to stop the action of the previous bath. It also provides additional hardening to protect the emulsion in subsequent process steps. It is a dilute solution of acetic acid and inorganic salts. Warburg studies (Figure 5) show this waste to be acutely toxic to the sludge microorganisms above 0.5% by volume in the first five hours. However, there is indication that some acclimation occurs between five and 21 hours so that up to 1% waste by volume may be tolerated. There is complete aerobic inhibition at 5% by volume.

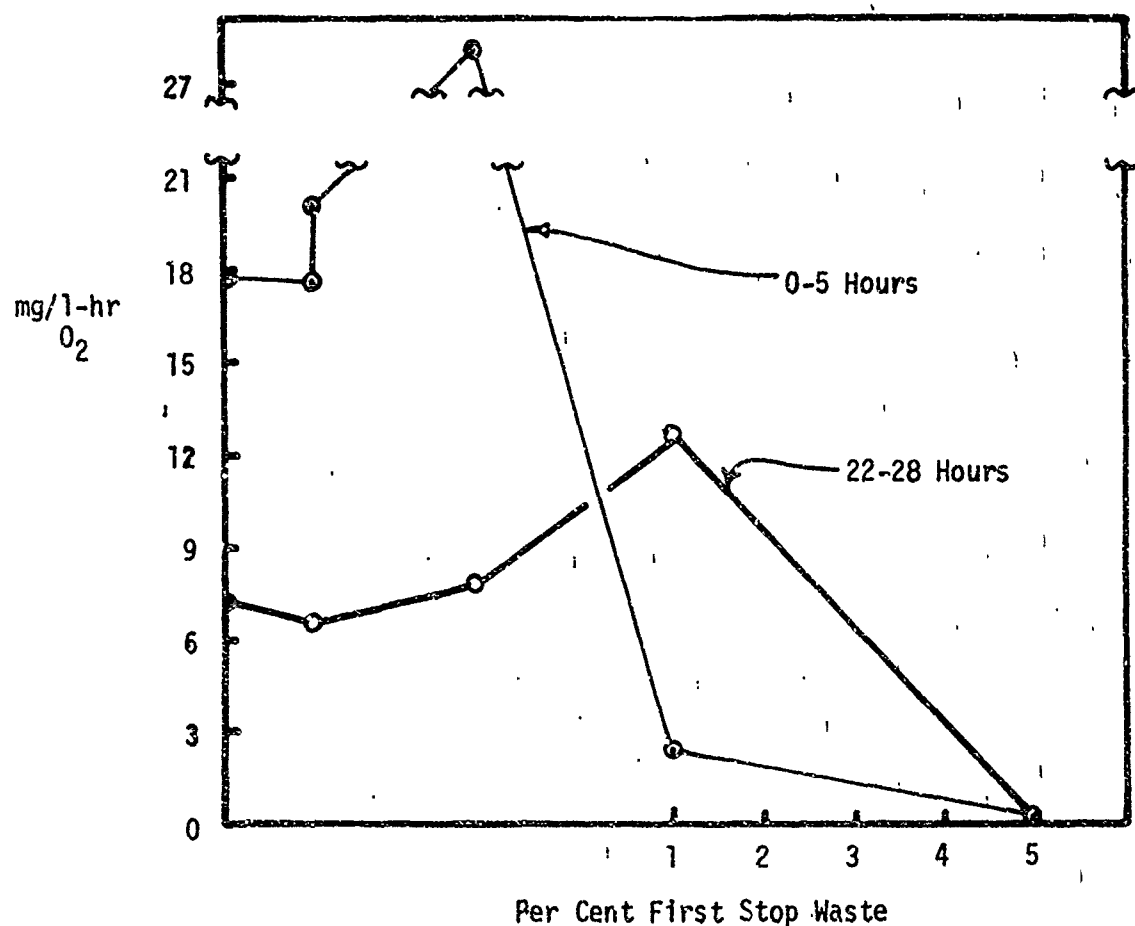


Figure 5. Warburg Study, First Stop O₂ Uptake

(5) Color Developer: After a water wash to remove the first stop bath chemicals, the next step is the production of colored dyes in areas where fogged silver has previously been developed in the three color-sensitive layers of the film. When prepared for use, the solution contains a total chemical content of 10% which includes sodium hydroxide, tert-butylamine borane, phosphates, sulfites, bromides and organic salts. Warburg studies (Figure 6) show toxicity to microorganisms at approximately 1% by volume (12,000 ppm).

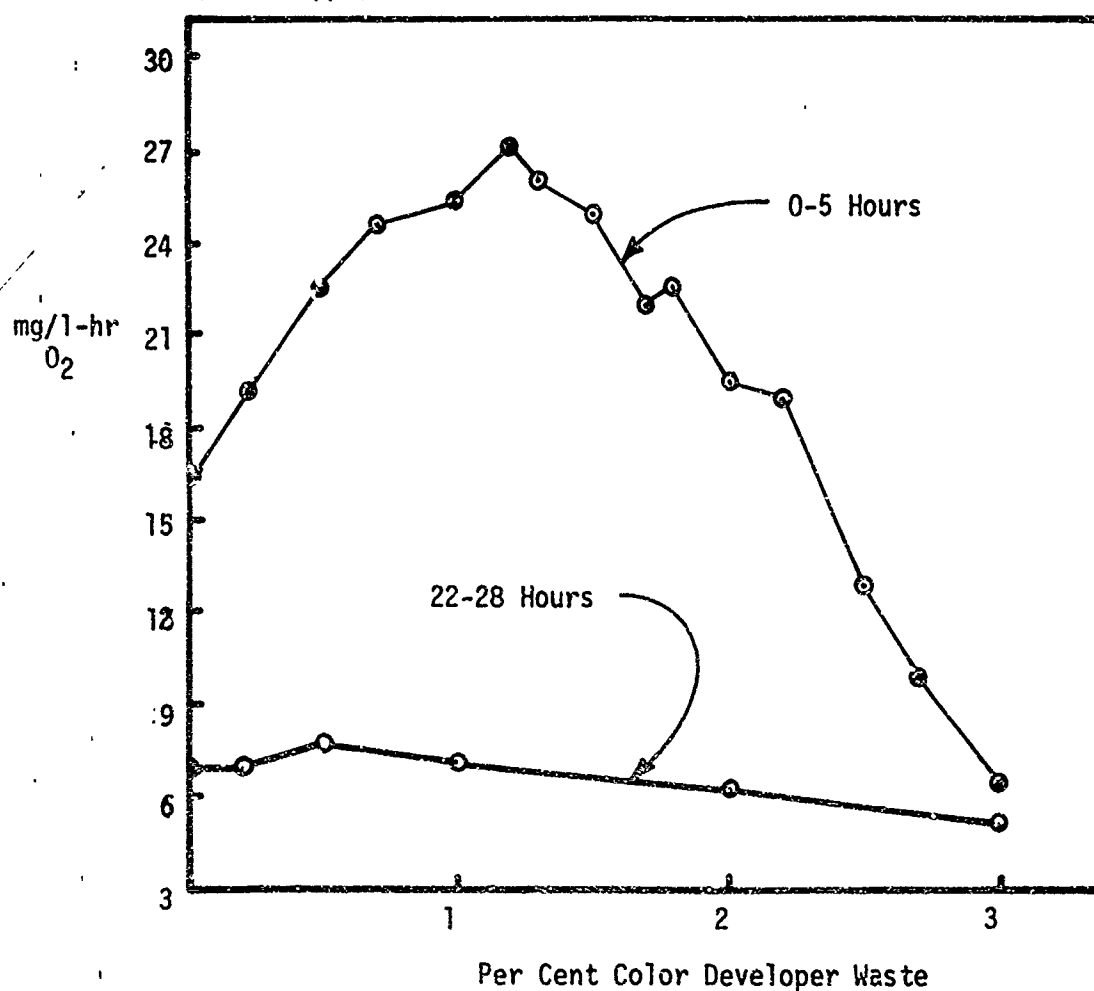


Figure 6. Warburg Study, Color Developer O₂ Uptake

(6) Second Stop Bath: The second stop bath deactivates and leaches out the color developer from the previous step. This is essentially the same waste as the first stop bath. Warburg studies (Figure 7) gave the same results as for the first stop bath.

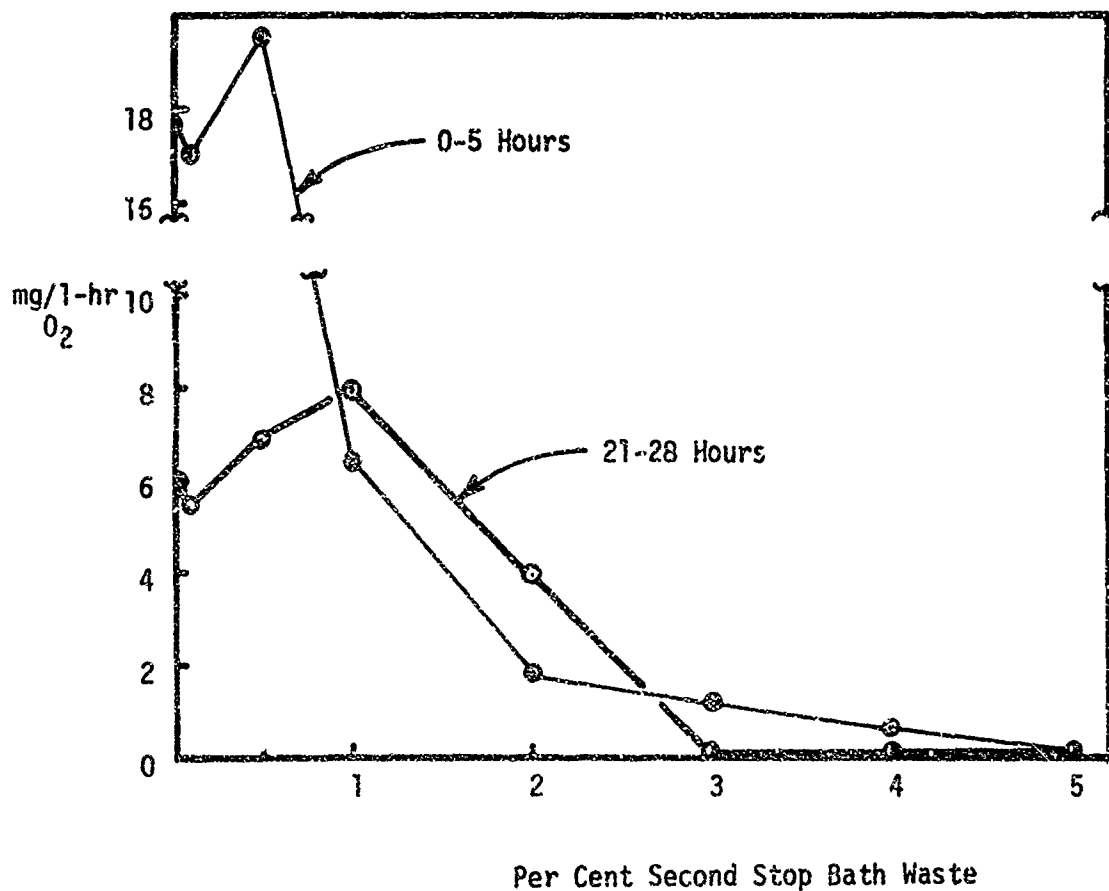


Figure 7. Warburg Study, Second Stop O₂ Uptake

(7) After a second water wash, the film is passed through the bleach bath. This is a solution of inorganic salts and includes ferrocyanides. Its purpose is to convert metallic silver to silver salts that are soluble in the next bath. According to Warburg studies (Figure 8) it can only be tolerated by the microorganisms below 100 mg/l.

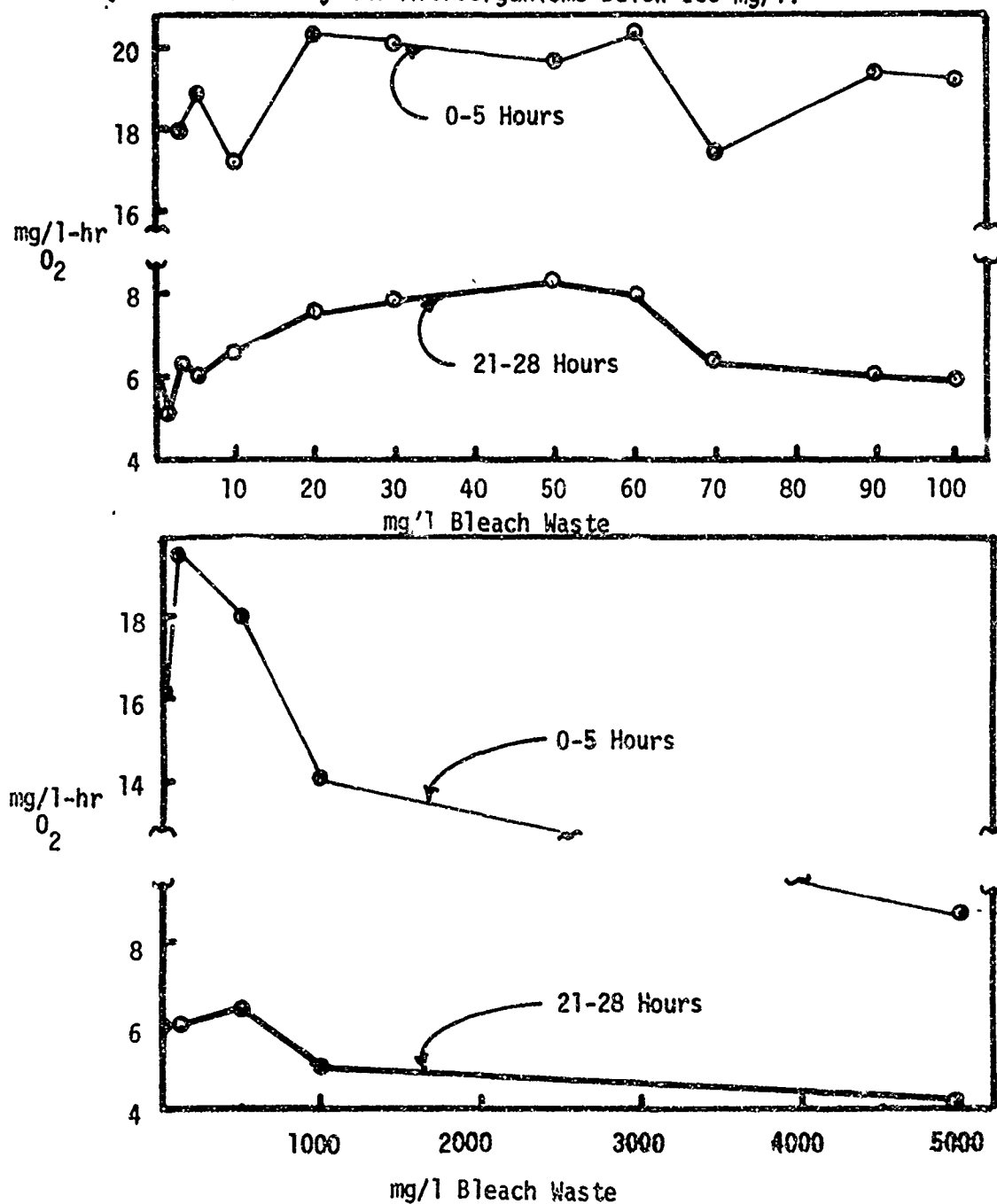


Figure 8. Warburg Study, Bleach O_2 Uptake

(8) Fixing Bath: This is the final chemical step prior to the last wash and drying of the film. This bath dissolves the silver salts and stabilizes the dye somewhat. Some additional hardening of the gelatin takes place. The fixer is primarily made up of sulfites, thiosulfate and formaldehyde. Warburg studies (Figure 9) show it to be quite toxic above 0.1% by volume

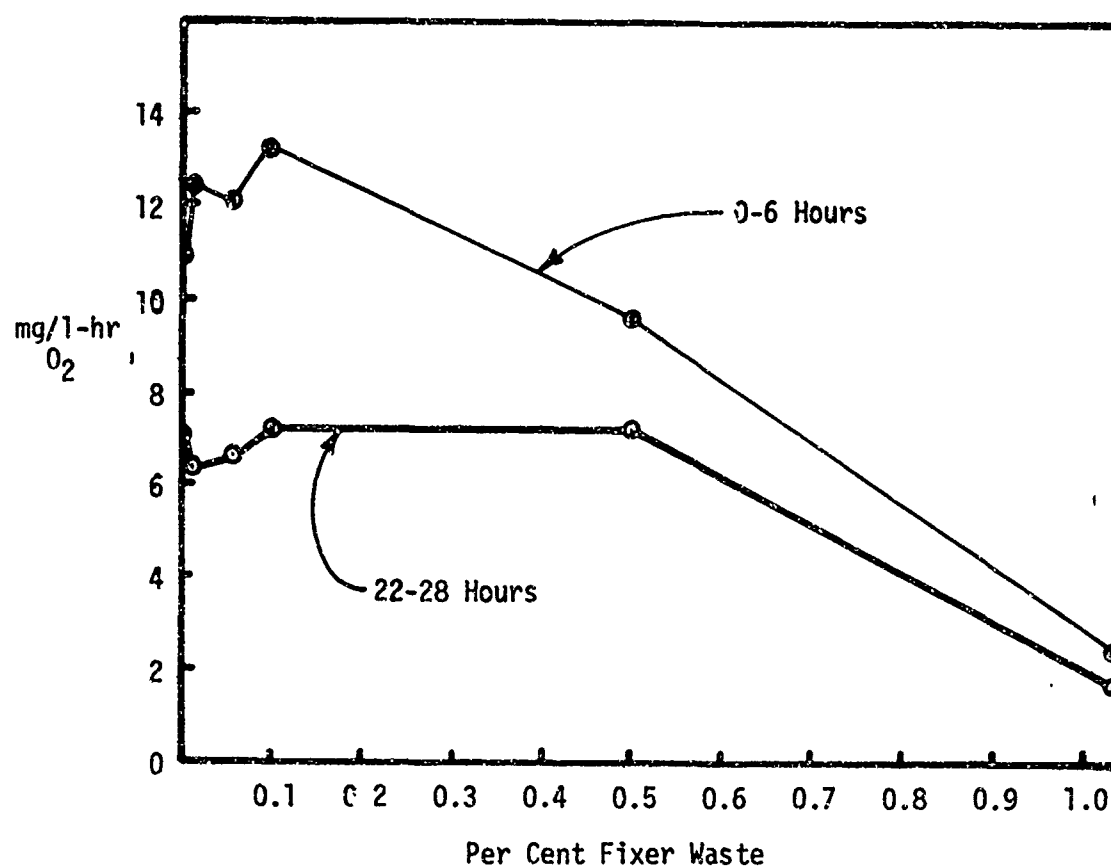


Figure 9. Warburg Study, Fixing Bath O₂ Uptake

b. The individual chemical process bath wastes are extremely toxic to biological treatment systems. The inhibitory effects on micro-organisms appear in concentrations from 0.01 percent by volume (about 100 ppm) in the neutralizer and bleach to 1% by volume in the color developer. The offending substances in the bleach may be cyanides. The offending substances in the neutralizer remain to be determined.

3. Composite EA-4 Processing Wastes Excluding Wash Wastes from Forbes AFB KS:

Composite EA-4 waste samples were formulated from the individual processing bath wastes obtained from Forbes AFB SC based on flow rates shown in Table 6. These rates represent the maximum processing conditions stated in the operational training manual⁽⁶⁾. Wash water, which was not included in the composite, would account for about 90 per cent of the total waste emerging from the Ektachrome RT processor under these conditions. At lower film processing rates or with intermittent film processing while the processing equipment is still operating, the per cent wash water would increase.

Table 6
CHEMICAL FLOW RATES FROM FILM PROCESSING
(9.5 inch film at 3.2 ft/min)

<u>Bath</u>	<u>ml/sq ft</u>	<u>ml/min</u>
Prehardener	60	150
Neutralizer	50	125
First Developer	175	427.5
First Stop	225	562.5
Color Developer	225	562.5
Second Stop	200	500
Bleach	60	150
Fix	60	150
		<u>2,637.5</u>
Wash (3 x 2 gal/min = 6 gal/min)		22,711.5
		<u>25,349.0</u>

The metal analysis of the formulated composite waste (wash water excluded) is shown in Table 7.

Table 7
METALS IN COMPOSITE EA-4 WASTE

	<u>mg/l</u>		<u>mg/l</u>
Lead	0.57	Cadmium	0.09
Copper	0.15	Silver	214
Manganese	<0.05	Chromium	2.66
Zinc	0.30	Iron	15.00

a. Warburg O_2 studies were conducted on the formulated composite EA-4 waste (Figure 10). The studies indicated the waste was not acutely toxic up to a 2 per cent concentration by volume although there were significant amounts of metals, notably silver and chromium, present in the waste. For some unexplainable reason there was, however, a drop in the O_2 uptake at the 0.05 per cent waste concentration. The most likely explanation of this deviation is experimental error. As there are chemicals in some of the baths, such as sulfites, that spontaneously bind with dissolved oxygen, a Warburg study was also conducted on the composite waste without biological sludge. Little oxygen scavenging by the chemicals occurred. Since the first developer bath was previously shown to have a substantial spontaneous oxygen demand (para 2a(3)) evidently compositing the waste baths satisfies this demand.

b. Treatment of Formulated Composite EA-4 Waste in Bench Top Continuous Flow Activated Sludge Plant:

(1) The composite EA-4 processing waste was fed to a continuous flow activated sludge treatment plant and various parameters monitored. Based on the Warburg O_2 uptake studies of this waste the initial feed concentration was selected at 2 per cent photowaste by volume. However, the plant showed signs of deterioration so the waste concentration

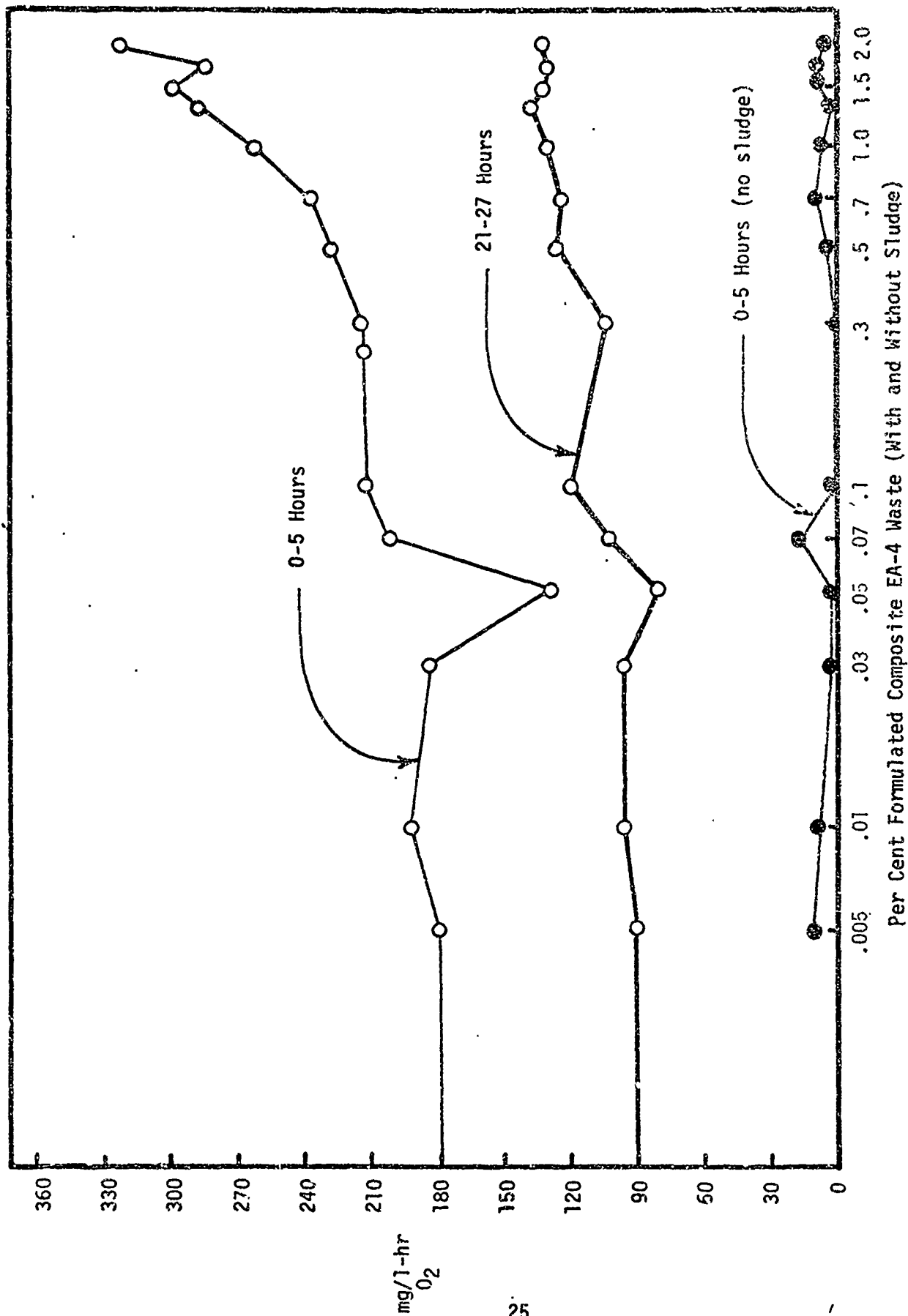


Figure 10. Warburg Studies, Formulated EA-4 Waste O₂ Uptake

was dropped in steps to 0.5 percent and finally terminated when the plant would not recover. The total volumetric feed rate (waste and synthetic sewage) allowed a 12 hour aeration time. The average Total Oxygen Demand (TOD) and COD removal was 63 percent and 64 percent respectively.

Appendix 3, Table 13 contains the Laboratory data collected from this first attempt to treat the waste in a dynamic flow through system.

(2) Subsequently, a second continuous flow treatment study was begun with new activated sludge obtained from the San Antonio TX activated sludge treatment plant. The feed rate to the pilot plant allowed a 12 hour aeration time. The initial composite EA-4 waste concentration was 0.1 percent. The plant appeared to be operating satisfactorily so the feed rate was increased to allow a 9 hour aeration time. At this feed rate the plant began to deteriorate producing a cloudy effluent. The photowaste concentration was reduced to 0.05 percent while maintaining the 9 hour detention time for five days. The plant continued to deteriorate with loss of mixed liquor suspended solids due to poor settling and demise of the plant. Appendix 3, Table 14 contains the Laboratory data collected from this second attempt to treat the waste in the bench top continuous flow activated sludge plant.

(3) In a third attempt to treat the EA-4 composite waste, the concentration of waste fed to the plant indicated above was dropped to 0.005 percent with a 6 hour aeration time. However, the sludge remained very light, mixed liquor suspended solids decreased and the plant never recovered after five days of operation. A new plant was started at this point with new sludge. A feed concentration of 0.001 percent EA-4 waste

and a 6 hour aeration time were maintained. The plant ran successfully for 22 days with good O_2 uptake rate and an overall COD removal of 82.5 per cent. As this was the first successful treatment using the bench top activated sludge treatment plant, a 96 hour bioassay was conducted on the plants effluent during this period. To determine if there had been some acclimation of the treatment plants biological sludge to accept higher EA-4 waste loadings, the plants feed concentration of composite waste was increased to 0.5 per cent for a period of 5 days. There was a marked increase in O_2 uptake, however, the sludge became light and would not settle resulting in a reduction of mixed liquor solids. The study was then terminated. Appendix 3, Table 15 contains the laboratory data collected during this phase of the pilot treatment studies.

c. Treatment of Desilvered Composite EA-4 Waste in Bench Top Continuous Flow Activated Sludge Plant:

Because of the high concentration of silver in the composite waste from the EA-4 process, it was felt that silver was one of the prime toxic substances in the previous pilot treatment studies. The effects of cyanides was discounted somewhat as previous studies have shown that the activated sludge process acclimates to cyanides⁽¹⁷⁾. Silver is also well known for its bactericidal power and dosages of 0.000001 to 0.5 mg/l of silver have been reported as sufficient to sterilize water⁽⁹⁾. By using the iron replacement technique⁽¹⁵⁾ the silver concentration of the formulated composite EA-4 waste was reduced from 214 mg/l to 52.3 mg/l or reduced to approximately one-fourth its original concentration. The desilvered waste was then used as feed in two treatment studies using the bench top continuous

flow activated sludge plants at rates of 0.2 per cent and 0.4 per cent EA-4 desilvered composite waste.

(1) The pilot activated sludge plant fed 0.4 per cent EA-4 desilvered composite waste immediately lost mixed liquor solids by carryover in the effluent. After nine days, damage to the plant was too severe for recovery although the feed concentration of desilvered composite waste was reduced to 0.1 per cent. No laboratory data was collected on the operation of this plant due to its early signs of failure.

(2) The pilot activated sludge treatment plant fed 0.2 per cent EA-4 desilvered composite waste functioned well with an average of 82 per cent COD removal. Operational performance was similar to the previous successful treatment study using 0.001 per cent EA-4 waste without the silver removed. The actual silver concentration fed at the 0.2 per cent desilvered waste, however, was comparable to a concentration of 0.05 per cent waste without silver removed. The previous treatability study at 0.05 per cent waste without silver removal was in a pilot plant that had been initially fed a concentration of 0.1 per cent waste without silver removed nor was wasting of sludge practiced. In the operation of the plant fed 0.2 per cent desilvered waste, sludge was wasted daily. Laboratory analysis of the sludge showed accumulation of silver in the sludge. Daily wasting of sludge reduced the accumulation of silver in the mixed liquor suspended solids. Appendix 3, (Tables 16, 17 & 18) contains the data collected from this phase of the pilot treatment studies.

d. The Warburg O₂ uptake studies of the formulated composite EA-4 waste indicated the waste was not acutely toxic to an activated sludge at concentrations up to 2 per cent waste by volume. Treatment of the

formulated composite EA-4 waste was not successful at concentrations above 0.001 per cent waste by volume in a pilot activated sludge unit when the activated sludge was not wasted. Treatment of the formulated EA-4 waste was successful at a concentration of 0.2 per cent waste after reduction of the initial silver content from 214 mg/l to 52.3 mg/l and daily wasting of sludge was practiced. Indications are that one main factor that limits treating waste in a biological system is the silver content both initially and by concentration in the biological sludge.

D. Bioassay Tests of Toxicity

1. Bioassay Technique - The Measurement of Acute Toxicity

a. Over the past year this laboratory has developed a bioassay system capable of accurately testing the toxicity of water solutions under standard conditions to various species of aquatic animals. The theory, physical structure, and sensitivity of this system will be reported in detail at a later date.

b. Briefly, the toxicity of chemical solutions are tested as follows: A control of artesian well water and five known dilutions of the test solution are continuously pumped through glass troughs at a known and equal rate. Each trough contains six nylon mesh baskets each containing five individuals of the test species. At times, five individuals of two compatible species are placed in each basket providing a direct comparison of sensitivity between species. All assay solutions were aerated vigorously therefore dissolved oxygen levels were near saturation. Mortality in these tests is therefore independent of BOD (Biological Oxygen Demand) depletion of dissolved oxygen. The maximum BOD untreated photowaste could exert in a stream was measured in a

separate procedure.

c. The resulting mortality response curves were analyzed by probit analysis⁽⁷⁾ a statistical technique that calculates the LC(50) (lethal concentration to 50% of the test species) with fiducial limits. The 95% confidence intervals were calculated for these data. The probability is 95 out of 100 that the true LC(50) of each test lies between the bounds of this interval. The size of this interval is therefore a measure of the consistency of the dose-mortality relationship from which it was derived. Differences between LC(50) data with overlapping intervals were considered to be statistically and practically insignificant.

(1) Additionally, analysis of variance⁽⁸⁾ was performed on all tests in which treated solutions killed more animals than control solutions but the mortality apparently was not dose related. A water solution was considered to exhibit no acute toxicity when F was not significant at the 40% level. At this level of significance, small differences in mortality will appear significant from the control unless such differences approximate a random distribution within treatments; in other words, they are not treatment related. Mortality that was not dose related was considered to be aberrant and such tests were discarded. At the 40% level of significance data that is really not significant will often appear to be; however, the probability of truly significant mortality appearing insignificant is minimized. This is therefore an ecologically conservative technique.

d. Bioassay tests were run for at least 96 hours under the following conditions: Temperature 20-22°C, pH 7.2-8.0, hardness 200-210 mg/l as CaCO₃ in the dilution and control H₂O. The LC(50) was calculated at 24, 48, 72, 96 and occasionally at 117 hours in each test. These

calculated LC(50)'s were plotted against time. When the LC(50) became stable as a function of time, the lower limit of acute toxicity was considered to be reached. This value was then used in making judgments concerning acute toxicity of the waste. As mentioned in the Introduction the FWQA considers it the responsibility of the disposing agency to determine the toxicity of waste effluents to all beneficial aquatic life⁽¹⁾. Testing the acute toxicity of disposed materials to hundreds of bacterial, plant, and animal species is presently beyond the capability of the USAF. The acute toxicity of treated and untreated photowaste was therefore tested on three diverse forms of aquatic life commonly used in assessing toxicity, and judgments were made from these data as to toxicity in nature.

(1) The acute toxicity of the composite EA-4 waste, silver present, was determined for D. magna (the Giant Water Flea, a crustacean) before and after treatment in activated sludge treatment plants. The acute toxicity of treated and untreated desilvered waste was also determined for daphnia and the fry of Pimephales promelas (the Fathead minnow, a pisces). Additionally, the toxicity of EA-4 waste, silver present and desilvered, to the activated sludge community of microorganisms was monitored as described previously⁽²⁾.

(2) The effluents of bench top activated sludge plants were tested, as described above (para 1,b,c and d), using the treated plant effluent as the toxicant solution and the effluent from a control plant as the diluent and control H₂O. Using sewage plant effluent as the diluent and control solution minimized experimental errors due to water quality not related to the EA-4 chemical fed to the treatment plant and also provided a valid control.

(3) The EA-4 waste used in all tests was collected as it emerged from the individual baths of a Kodak 1411 Automatic Processing Unit which was processing 364.8 square inches of film per minute. The origin, handling and mixing of the composite waste prior to testing has been described in Section III, C (3) above. The wash water was excluded from the samples to increase stability. All results are therefore in terms of milliliters of actual chemical solution per liter of dilution water.

2. The Acute Toxicity of Untreated EA-4 Photowaste:

a. Table 8 presents the LC(50) data of untreated and desilvered EA-4 waste for Daphnia magna and Pimephales promelas at 24 hour intervals. P. promelas was tested only in composite waste of which the fixer component had been desilvered. The slope of the response of the fish data (Figure 11) was so steep that most dilutions gave 0 to 100% mortality. The 1 to 2 intermediate points provided inadequate data for meaningful statistical treatment. The LC(50) data for fish fry are therefore estimates of the true LC(50)'s and were computed by eye fitting the regression line to the mortality data. This technical weakness has been corrected by replacing the inflexible proportional diluter system used to provide chemical dilutions with a more flexible pumping system.

b. Figure 12 presents the changes in LC(50) of the composite EA-4 waste as a function of time. The data show that desilvering the waste does not affect its acute toxicity to daphnia. Desilvered waste appears slightly more toxic to D. magna at 72 hours than to fish fry. This difference is minor and of little practical significance. The data indicate the probability is greater than 95 chances out of 100 that the 96 hour

Table 8
LC50 of UNTREATED AND DESILVERED EA-4 PHOTOWASTE TO
DAPHNIA MAGNA AND PIMEPHALES PROMELAS*

	DAPHNIA MAGNA				PIMEPHALES PROMELAS*
	Untreated EA-4		Desilvered EA-4		Desilvered EA-4
Time	LC50	.05 interval	LC50	.05 interval	
24	38.0**		34.28**	-	38.02*
48	15.33	12.64-18.59	17.3**	-	17.78*
72	9.39	7.44-11.83	10.45	8.81-12.42	14.29*
96	7.63	5.08-10.05	7.23	6.25-7.98	10.0*
117	-				7.96*
96	No mortality 4 ml/l	-			

*ml/l EA-4 waste, wash water excluded

**Estimated from data with insufficient dose-responses for valid statistical analysis.

PROBIT REGRESSION LINE OF DESILIVERED EA-4 PHOTOWASTE TO P. PROMELAS FRY

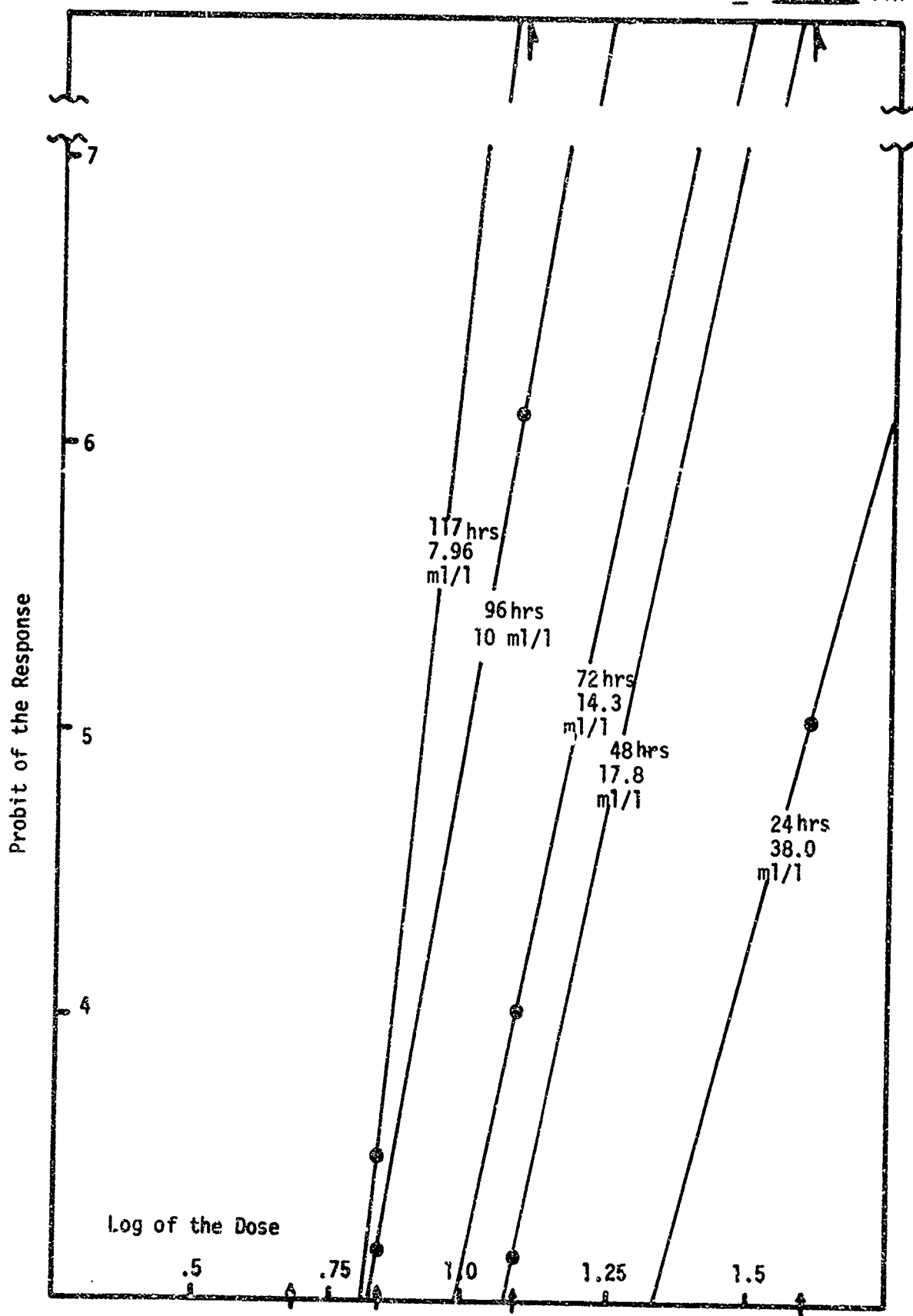


Figure 11
34

LC50 OF EA-4 WASTE TO D. MAGNA AND P. PROMELAS AS A FUNCTION OF TIME

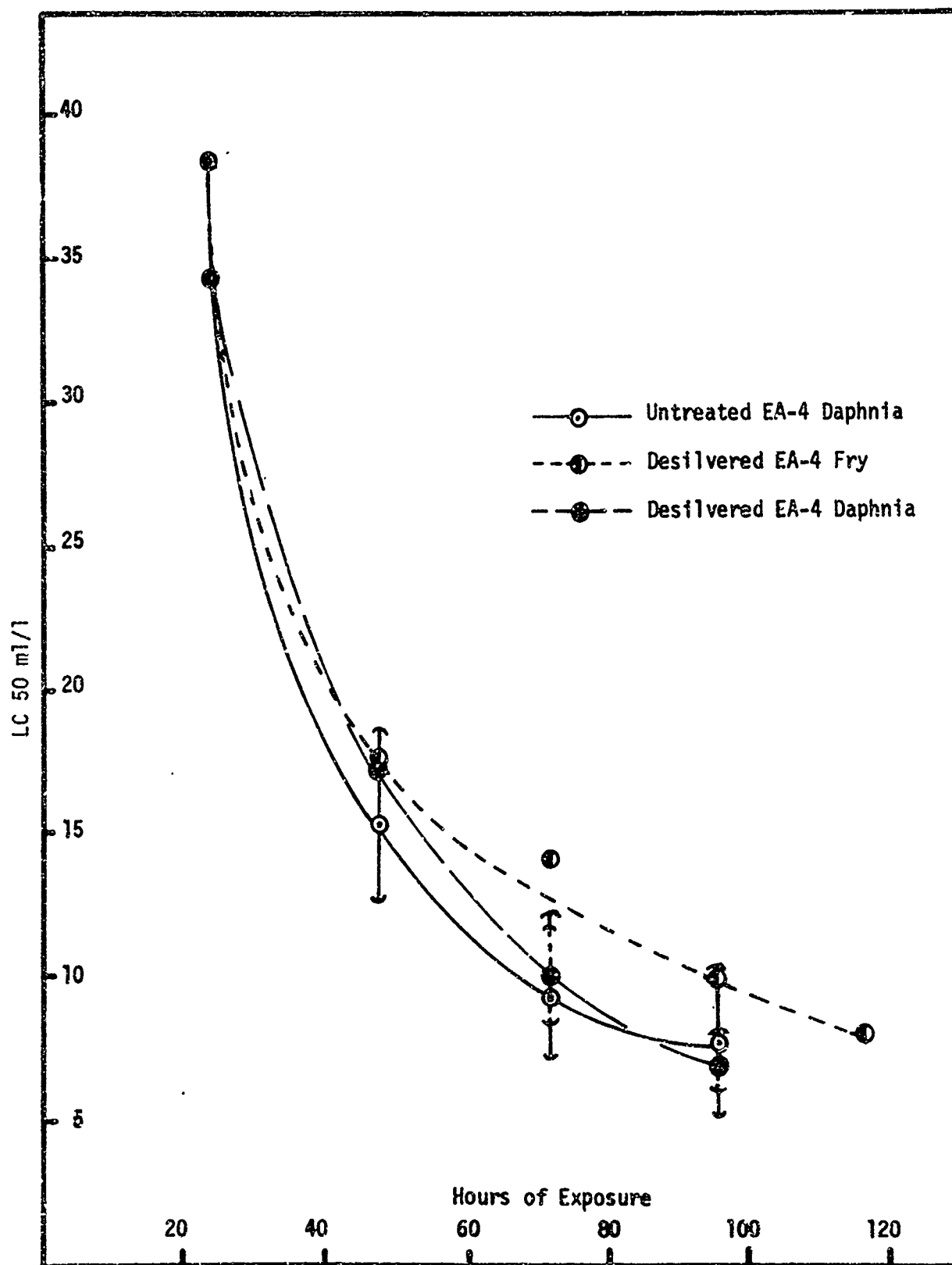


Figure 12
35

LC(50) of this untreated EA-4 waste is between 5 and 10.1 ml/l for adult D. magna regardless of whether the fixer is desilvered or not. Fish fry and daphnia lived in concentrations of 4 ml/l and lower for 96 hours with no mortality.

c. A variable which would grossly affect the acute toxicity of EA-4 photowaste in nature was not tested in these laboratory bioassays. As previously mentioned in this report, the EA-4 process utilizes a cyanide bleach. Table 2 indicates that the combined effluent of this process contains 414 mg/l ferrocyanide and 450 mg/l thiocyanate ion. The following is a review of the complicated problems disposal of such bleaches pose.

(1) Cyanide ions in aqueous solutions dissociate according to the reaction, $\frac{(\text{CN}^-)}{(\text{HCN})} = \frac{7.2 \times 10^{-9(9)}}{(\text{H}^+)}$. Therefore, at pH 8 <93% of the cyanide ion is in the form of HCN: at pH 7 <99% is HCN. Hydrogen cyanide is more rapidly absorbed through the fish and invertebrate gill and is therefore more toxic than cyanide ion. The LC(50) of HCN is less than 0.05 mg/l for some fish and 3.4 mg/l for daphnia.⁽¹⁸⁹⁾ Raising the pH above 8.5 decreases the toxicity of cyanide many fold.

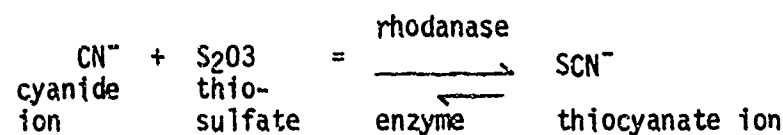
(a) Cyanide is a respiratory poison which inhibits most metalloproteins containing copper or iron by forming stable complexes with these metals. Other enzymes not involved in metal catalysis are also cyanide-sensitive, this chemical combining with carbonyl groups in enzymes, cofactors, prosthetic groups, or substrate. Cyanide also acts as a reducing agent to break disulfide links.⁽¹⁰⁾

(b) The specific mechanism of cyanide ion toxicity to cytochrome oxidase is well known. Although oxygen is the ultimate

biological oxidant, most cellular oxidation processes are the consequence of electron transfers between oxidized substrates (electron donors) and coenzymes (electron transferring agents). Electrons are donated by oxidized substrate (food) and passed from coenzyme to coenzyme of the electron transport system until they reach cytochrome oxidase. Cytochrome oxidase reduces oxygen thus disposing of the passed electron. Energy released by the transferred electron is chemically trapped and later used by the cell. Cyanide ion binds with the ferric ion of cytochrome oxidase forming a complex that cannot accept electrons (cannot be reduced). Cyanide ion therefore blocks the entire electron transport system.⁽¹¹⁾ The electron transport system is utilized for approximately 2/3 of the overall energy metabolism of fish and almost exclusively for energy utilization within the central nervous system.

(c) The toxicological implications of the effect of this respiratory poison on the enzyme systems of animals is not fully comprehended. There is some evidence however that cyanide acts as a chronic poison as well as an acute toxin.⁽¹²⁾ This is readily understandable in light of the broad range of enzymes which are inhibited by this compound.

(2) The acute toxicity of thiocyanate ion to fish varies among animal and chemical species from 95 to 3,880 mg/l.⁽⁹⁾ This 1900-fold decrease in toxicity from HCN (95 vs 0.05 mg/l) is logical because thiocyanate is the principle cyanide excretory product. Many organs, especially the liver, detoxify cyanide by converting it to thiocyanate according to the following reaction.⁽¹³⁾



Thiocyanate ion (SCN^-) is then excreted by the kidney.

(3) The iron cyanides would also be expected to be considerably less toxic than HCN because animal gills usually absorb small ionic molecules preferentially to larger complex molecules and, secondly, the cyanide ion would first have to be released from the iron cyanide complex in order to bind with the metal prosthetic group of the enzyme or coenzyme attached. Therefore, it is not too surprising that ferro and ferric cyanide salts are only slightly toxic to fish, trout showing no effects in concentrations as high as 8725 mg/l for one hour.⁽⁹⁾

(4) Sunlight decomposes ferro and ferri-cyanide solutions to HCN, cyanogen and cyanides.⁽¹⁴⁾ Obviously, it is important to know the rate at which the moderate to slightly toxic cyanides and cyanates of iron and sulfur convert to the highly toxic free cyanide ion in sunlight. This information was unavailable in the literature or from the Kodak Chemical Company. The following experiment was performed to estimate the maximum rate this conversion could be expected to occur in a stream receiving photographic waste.

(a) Composite solutions of EA-4 waste as described above were diluted to 32, 16, 8 and 4 ml/l samples and the total cyanide content of an aliquot of each was determined using the colorimetric method of Standard Methods.⁽³⁾ Each solution was placed in a white evaporating dish in direct sunlight (8,000 to 10,000 foot candles) at a temperature range of

80-85°F, for 1, 2, and 6 hours. The solutions were then rigorously aerated for one hour to release all HCN and the total cyanide determination repeated. Generation of HCN was taken to equal the pre-exposure total cyanide minus the post-exposure aeration total cyanide. This value may represent cyanide species other than HCN and is therefore a maximal HCN value. The results are presented in Table 9 and Figure 13.

(b) The above data suggest some interesting aspects of the kinetics of free cyanide generation in sunlight. The rate of total cyanide conversion is evidently inversely related to EA-4 concentration at the end of 6 hours. The highest concentration of photowaste apparently reached equilibrium after 30.2% conversion to apparent HCN whereas the lowest concentration did not reach equilibrium after 77.7% conversion to volatile cyanide. This suggests that the conversion of complex cyanide to volatile cyanide (HCN) is reversible and product limited. Further experiments are needed to verify these findings, to determine the actual cyanide species involved in the conversion, and to describe the kinetics of these reactions more fully.

(c) The results of this preliminary experiment indicate the conversion of complex cyanides to highly toxic HCN occurs rapidly and is of great toxicological significance when disposing of untreated photographic waste. An EA-4 solution of 4 ml/l (a concentration which killed no fish in 96 hours without sunlight present) generated over 220 times the LC(50) of free cyanide (0.05 mg/l⁽⁹⁾) in 6 hours when exposed to sunlight. Obviously, the cyanide bleach cannot be discharged untreated without the risk of a major fish kill. Disposal of untreated bleach under

Table 9
VOLATILE CYANIDES (HCN) GENERATED BY PHOTOLYSIS OF
EA-4 WASTE

Concentration of EA-4 Waste ml/l	Exposure Time/Hrs				% Conversion 6-hour
	0	1	2	6	
32	0	18.5	33.0	35.5	30.2
16	0	13.0	17.0	28.0	47.4
8	0	7.0	8.0	18.0	62.0
4	0	3.4	7.0	11.2	77.7

VOLATILE CYANIDES GENERATED BY PHOTOLYSIS OF EA-4 WASTE

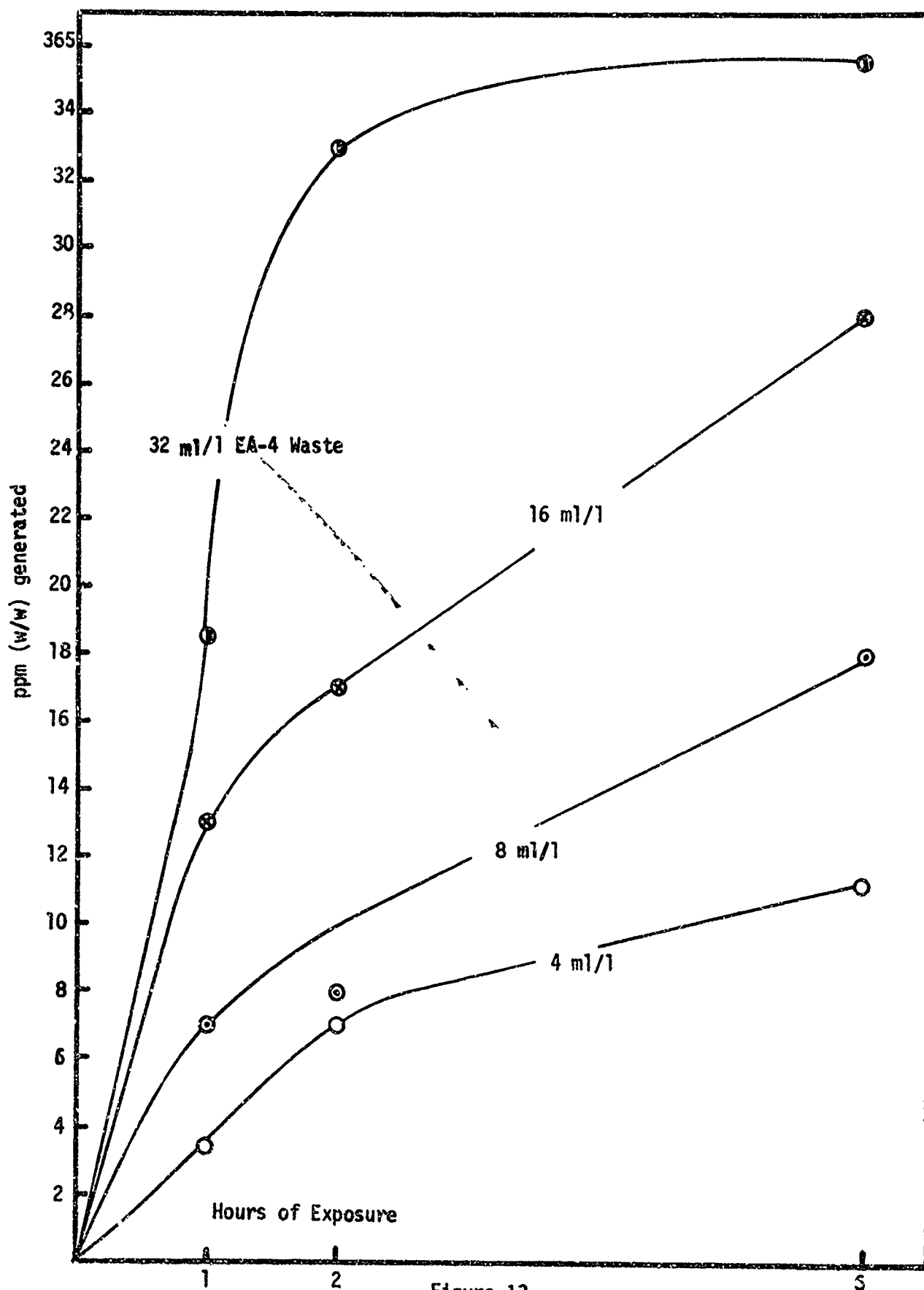


Figure 13

any circumstances is not recommended. Therefore, mobile processing units must be equipped with holding tanks capable of storing all bleach expended during field operations. Recommendations are given in Section IV concerning the disposal of this bleach.

(d) These bioassay data indicate that desilvered EA-4 photowaste, bleach absent, can be released into streams at a concentration not exceeding 0.4% photowaste to stream water, for a maximum of 5 days, in any one water basin provided: organisms more sensitive than the Fathead Minnow and D. magna are not present, and the BOD loading does not result in dissolved oxygen depletion and asphyxiation of oxygen dependent organisms. Since organisms more sensitive than those tested here may be present, an application factor of 0.125 is recommended lowering the 0.4% concentration to 0.05%. This is a tenfold dilution of the lowest 95% LC(50) confidence interval measured (Table 8 and Figure 12) above and is therefore a very conservative figure.

1 The following test was performed to determine the maximum initial rate of dissolved oxygen uptake likely to be generated by the presence of EA-4 photowaste in aquatic environments. EA-4 waste was placed in two 500 ml Erlenmeyer flasks at a concentration of 0.2% and saturated with oxygen. To one flask 1000 mg/l benzalkonium chloride (a bacteriostat) was added. Both flasks were then seeded with 10 ml of mixed liquor suspended solids from the local municipal sewage plant. The flasks were sealed with rubber stoppers, through which dissolved oxygen probes were inserted. The water solutions were continuously agitated by magnetic stirrers at room temperature (20-22°C) and the dissolved oxygen read periodically.

2 The data presented in Figure 14 indicate that under these conditions EA-4 waste exerts an initial oxygen demand of 0.038 mg/l per minute. The data also indicate that the benzalkonium chloride completely inhibits this oxygen demand thereby confirming that the oxygen demand is a true biological demand, and is not caused by chemical utilization of oxygen by the photowaste itself. Therefore, untreated EA-4 waste cannot be disposed of in streams or waterways that are not certain to be reoxygenated at least at a rate of 0.04 mg/l/min oxygen. This reoxygenation rate limits disposal of untreated EA-4 waste to swift streams only, and provides a 4-fold safety factor, necessary when applying laboratory data to natural conditions.

3 Streams inevitably flow to standing (lentic) waters. If waters which have previously received untreated EA-4 photowaste cease being reoxygenated at a rate of at least 0.04 mg/l/min before the nearly complete degradation of the EA-4 BOD, the dissolved oxygen concentration may well be lowered to a pollutional level. Therefore, personnel discharging untreated photowaste must determine that the receiving stream is adequately aerated for the period of time necessary to degrade the discharged BOD loading.

4 The Protocol in Appendix 5 has been prepared to act as a guideline in determining whether a given reach of a stream can safely accept the EA-4 BOD loadings without an excessive loss of D.O. The equations yield data practical laboratory experience indicate are realistic for EA-4 BOD depletion in streams. However, these are strictly practical formulas and have all the limitations inherent in purely practical

expressions. No claim is made concerning theoretical validity, the equations have practical applicability only.

3. The Acute Effluent Toxicity of Activated Sludge Treatment Plants Fed EA-4 Waste:

a. The Effluent Toxicity of Plants Fed EA-4 Waste Containing High Concentrations of Silver.

(1) Table 10 tabulates the toxicity of the effluents of activated sludge bench plants fed 0.01-5.0 ml/l EA-4 waste. As shown above this lower dose is 500-fold below the acute LC(50) of untreated EA-4 waste for both D. magna and P. promelas fry. Such low concentrations were necessary because, as seen in the bench-top treatment plant data, higher concentrations of non-desilvered photowaste were toxic to the sludge organisms. Microorganisms are obvious many times more sensitive to EA-4 waste than are daphnia and fathead minnow fry.

(2) Acute toxicity would not be expected in a plant effluent, the influent of which was receiving .2% of an acutely toxic dose. Table 10 indicates that statistically significant acute toxicity did occur in one of two such tests. Tukey's W procedure⁽⁸⁾ is a statistic which permits decisions as to which differences between groups of means are statistically significant from each other and which are not. Using this test, the error rate applies on an experiment-wise rather than a per comparison basis; therefore, this test can be used to make confidence interval statements concerning the differences between means.

(3) Such range test comparisons of the mean mortality of the control and dilutions of the effluent of an activated sludge plant

DISSOLVED OXYGEN UPTAKE OF 2% EA-11 SOLUTION SEEDED WITH ACTIVATED SLUDGE

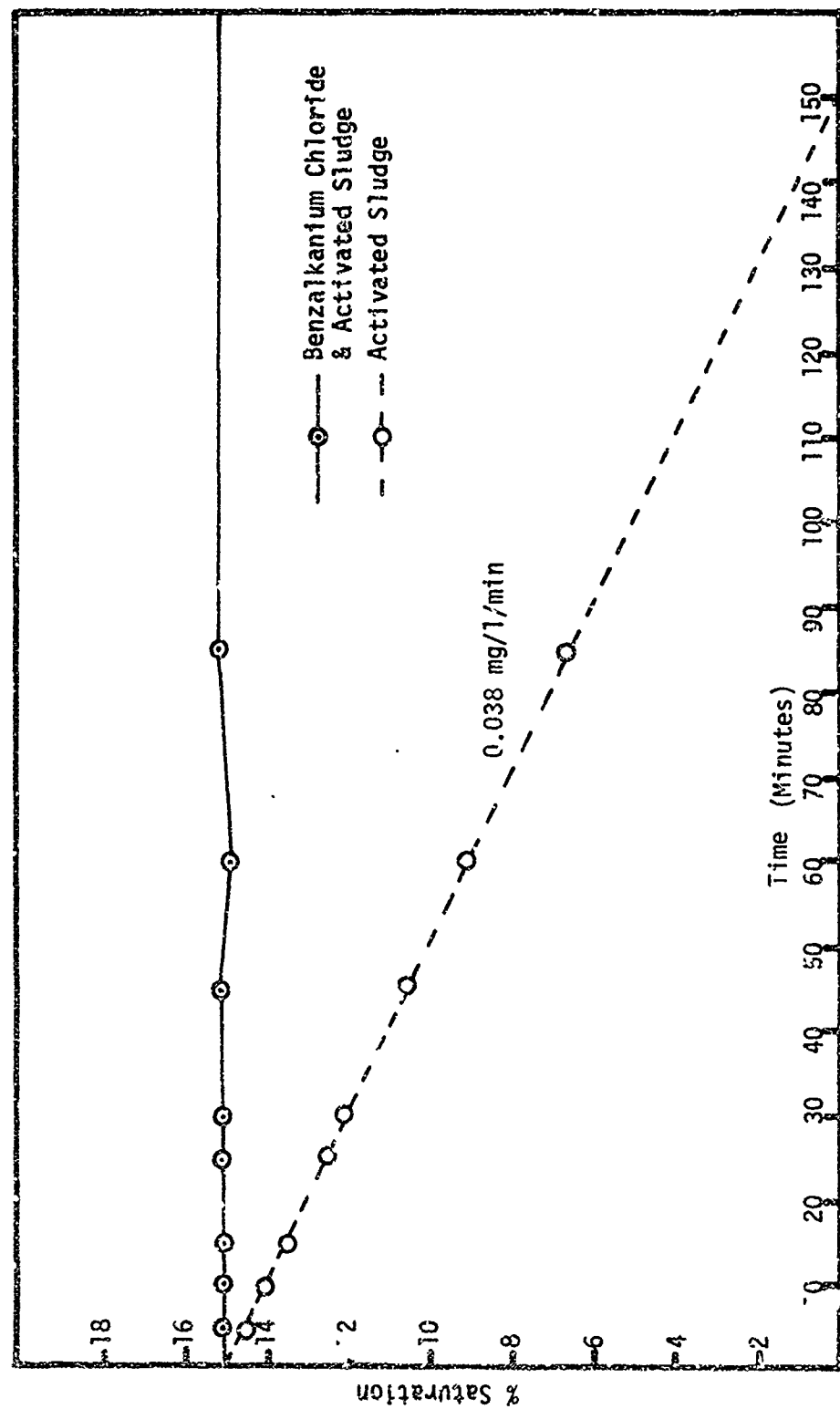


Figure 14

Table 10

THE TOXICITY OF ACTIVATED SLUDGE PLANT EFFLUENTS FED EA-4 WASTES
TO DAPHNIA MAGNA AND PIMEPHALES PROMELAS FRY

Dates Activated Sludge Plants Run	Species	ml/l EA-4 Influent	Silver Content of Waste Water**	% Mortality* EA-4 Conc.	Time (Hrs)	Statistical Significance F = (0.05)
	<u>D. magna</u>	5.0	+	50%/3.02 ml/l	96	+
	" "	0.01	+	33.3/0.01 ml/l	"	+
	" "	0.01	+	0.6/0.01 ml/l	"	-
	" "	2.0	-	0.0/2.0 ml/l	"	-
	" "	2.0	-	0.0/2.0 ml/l	"	-

*Corrected for control mortality after Finney⁽⁷⁾

** +Silver present

-Desilvered as described above

being fed 0.01 ml/l EA-4 photowaste indicate that no statistically significant (0.05 level) differences between control and treated mortality occurred at 24 or 48 hours but did occur at 72 and 96 hours. These results therefore indicate:

(a) Treatment plants fed 5 ml/l EA-4 waste produce effluents more toxic to D. magna than untreated waste;

(b) The effluents of plants fed EA-4 waste as low as .01 ml/l may cause significant mortality in treated animals.

(4) A review of these tests showed that sludge which normally settles out of the water in the settling chamber of the bench-top plant was carried over to the proportional diluter system. The mortality of daphnia in the effluent of the treatment plant fed 0.01 ml/l EA-4 waste was therefore caused by something in the sludge floc or by a solute. Chemical analysis of the sludge revealed it contained a very high concentration of silver. Table 17 (Appendix III) illustrates the silver influent versus the effluent of an activated sludge unit obtained in two grab samples on two separate days. Table 18 (Appendix III) depicts the silver found in the washed sludge versus the supernatant of the same plant. This plant was receiving 0.2% desilvered waste. Silver obviously accumulates in the sludge of treatment plants. Unfortunately, this Laboratory experienced analytical problems quantifying silver throughout the course of this study. These results are therefore only indicative of substantial silver accumulation in the plant.

b. The Effluent Toxicity of Plants Fed Desilvered EA-4 Waste.

(1) As mentioned above (para C,3(a)(8)) the silver in the EA-4 composite waste is derived from the fixer solution. The fixing solution

was therefore desilvered using the iron replacement technique described by Kodak.⁽¹⁵⁾ Desilvered photowaste proved to be less toxic to treatment plants allowing 2.0 ml/l desilvered EA-4 waste to be successfully treated (para C, 3 above). Both daphnia and fish fry exhibited no mortality when placed in this effluent for 6 days (Table 10).

(2) Substantial bound cyanides were discharged in the effluent of these plants (Appendix 3, Tables 17 & 18). Considering the unknown chronic effect of cyanide complexes and the conversion of bound cyanides to highly toxic free cyanides (see para D, 2, C above) at least a tenfold dilution factor is recommended for the effluents of plants routinely receiving EA-4 wastes.

(3) Table 17 (Appendix 3) quantitates the metals present in the effluent of a plant fed 0.2% desilvered EA-4 waste. Most of these metals are known to be chronic toxins to aquatic life at extremely low concentrations (0.03 mg/l for Cd⁽¹⁶⁾). The fact that these materials are not biodegradable and therefore become a permanent part of the ecosystem after release increases their potential hazard. However, the data indicate that a tenfold dilution of these metals will lower the concentrations to levels where the risk is minimal and will conform to present state and federal laws. Significantly most of the metals in the effluent evidently did not come from the photowaste but from the nutrient portion of the feed. This is very relevant in the case of Zn.

(4) The data cited above indicate that:

(a) Activated sludge organisms are more sensitive to EA-4 waste than D. magna or fish fry.

(b) Effluents from treatment plants fed EA-4 waste containing high silver concentrations appear to be more toxic than untreated wastes.

(c) Effluents from treatment plants fed 0.2% desilvered EA-4 waste exhibit no acute toxicity to D. magna and P. promelas over a 96 hour period.

1 Effluents from such plants contain potentially toxic complexed cyanides, necessitating at least a tenfold dilution factor in the stream receiving such wastes to prevent cyanide poisoning.

2 Such a dilution factor will lower the metals concentrations contributed by the EA-4 waste to acceptable levels.

IV. CONCLUSIONS

A. Biodegradation Studies:

1. Individual chemical baths of the EA-4 process individually inhibit microorganism respiration at concentrations of 0.01 to 1.0% by volume as measured in the Warburg apparatus. The toxicity data of the individual baths was used to predict the highest concentration of combined waste that would be non-toxic to microorganisms. The data indicated this value to be 0.05 percent.

2. Composite Waste:

a. Warburg studies of the composite waste indicated it was forty times less acutely toxic than the toxicity data of the individual baths predicted it would be. Concentrations of 2.0 percent by volume caused no respiratory repression over a 27 hour period. Therefore combining the individual chemical baths has a forty fold net detoxification effect on the acute toxicity of the EA-4 process to microorganisms.

b. Activated sludge bench plant failed at a concentration of 0.005 percent composite EA-4 waste when the sludge was not wasted from the plant. Bioassay data indicated the sludge was highly toxic to daphnia. Desilvering the fixing baths allowed 0.2% composited EA-4 waste to be successfully treated by activated sludge plants.

(1) The extreme toxicity of non-desilvered EA-4 waste to activated sludge organisms is caused by the accumulation of silver in the sludge.

(2) Silver removal is a mandatory requirement for photowaste being introduced into a biological treatment system.

(3) Desilvered EA-4 waste should cause no damage to activated sludge treatment plants at concentrations of 0.05 percent (wash water excluded).

B. The Toxicity of EA-4 Wastes to Aquatic Organisms:

1. The Disposal of Untreated EA-4 Waste.

a. Untreated EA-4 waste may be released only when the national interest justifies such action as defined in Executive Order 11507 and 11514.

b. Under no circumstances may the untreated EA-4 bleach be safely released into any stream. During field operations this bleach must be pumped into a holding tank within the processing complex and disposed of as outlined in Paragraph V, Recommendations.

c. The temperature of the receiving stream must be 4°C or above.

d. The receiving stream must be swift flowing over a reach long enough to safely lower the biological oxygen demand (BOD) of the EA-4 discharge to a non-pollutional level without seriously lowering the dissolved oxygen content of the stream. A procedure for approximating this distance is outlined in Appendix 5.

e. EA-4 waste must be desilvered prior to stream disposal. Disposal of wastes containing substantial silver content, even for a short period, will result in serious pollution.

f. Data presented in this report is inadequate to predict the safety of releasing EA-4 waste into a stream for a prolonged period of time. The data does indicate however, that provided all of the above criteria are satisfied, untreated EA-4 waste may safely be released into streams for a period of 5 to 10 days at a concentration of 0.5 milliliter

EA-4 waste per liter of stream water after complete mixing.

2. The Toxicity of Sewage Plant Effluent Fed EA-4 Waste.

a. The effluents of plants fed EA-4 waste (silver present) are more toxic to aquatic organisms than untreated waste.

b. The effluents from plants fed 0.2% desilvered EA-4 waste were not acutely toxic to Fathead Minnow Fry or to daphnia during a 96 hour period

c. Treatment plants discharging effluents to the environment must receive only desilvered photowaste.

d. An unknown amount of iron cyanides and thiocyanates (less than 3.5 mg/l assuming good plant performance) will be present in the effluent. Subsequent chlorination and the action of sunlight may result in substantial conversion of these chemicals to highly toxic HCN and CNO^- compounds. For these reasons, at least a ten fold dilution of the treatment plant effluent is necessary for any treatment plant the influent of which routinely contains EA-4 waste. A 100 fold dilution is preferable.

C. Solutions of complex problems usually do not progress simplistically to conclusions. Rather the partial solution of such problems often illuminates other areas of ignorance. This study has uncovered the following additional questions, the answers to which are necessary for the completely safe disposal of photowaste.

1. The behavior and toxicology of the various cyanide species in activated sludge plants.

2. The same information concerning cyanides in anaerobic digestors.

3. The chronic toxicity of photowaste to biological treatment systems.

4. The cyanide species present in activated sludge treatment plant effluents and their transformation to new chemical species once released into the environment.

5. The chronic toxicity to aquatic organisms of effluents from treatment plants receiving this waste.

6. The toxicity to aquatic organisms of a single 3 to 4 week exposure to untreated EA-4 waste when disposed of as recommended in this report.

7. The biodegradability and toxicology of the similar EA-5 process. The EA-5 process has been introduced since the inception of this study and is rapidly replacing the EA-4 process studied here.

V. RECOMMENDATIONS

A. Silver removal is a mandatory prerequisite for photowaste prior to release directly to the environment or indirectly via a sewage treatment plant. Desilvering of photowaste is simple and economically profitable using the iron replacement cartridge manufactured by Eastman Kodak⁽¹⁵⁾.

E. Desilvered EA-4 photowaste can best be disposed of by feeding it into an activated sludge plant or a trickling filter at a concentration not exceeding 0.05 percent of the total waste influent.

1. Plants receiving such wastes should be located on streams supplying a 10-100 fold dilution of the effluent.

C. Desilvered EA-4 photowaste can be disposed of untreated only:

1. When the national interest requires such action as described in Executive Orders 11507 and 11514.

2. When the bleach bath has been excluded from the total waste. Under no circumstances can untreated bleach be released to the environment.

a. The bleach waste should be pumped to a holding tank during field operations and disposed of at a later date.

b. Subsequently the tanked bleach waste may be disposed of by pretreatment in a cyanide destruction facility and then introduction into a sewage treatment plant at an influent concentration not exceeding 0.005 percent.

(1) Assuming cyanide destruction facilities are unavailable, bleach waste may be introduced directly into the treatment plant at or below the above concentration.

3. When the receiving stream is suitable for such disposal:

a. The waste (excluding wash water) is diluted to a concentration of 0.5 per cent or lower after mixing with the stream water.

b. The stream is reoxygenated at a rate which will preclude pollutional oxygen depletion for a period of time necessary to lower the biological oxygen demand (BOD) of the waste to a nonpollutional level. The type and length of reach necessary for such BOD depletion may be estimated from the protocol contained in Appendix 5.

c. The temperature of the stream is 4°C or higher.

4. When the untreated waste is to be discharged into a given stream for no longer than 10 days.

D. Mobile field operations of film processing laboratories therefore necessitate the selection of suitable stream reaches well in advance of field deployment. Failure to carefully preselect such areas will often result in serious pollution and major fish kills.

E. The following studies on the toxicity of photowastes are recommended to insure their safe and lawful disposal:

1. The toxicology, chemical transformations and ultimate fate of various cyanide species in activated sludge and trickling filter treatment plants.

2. The same cyanide studies concerning anaerobic digestors.

3. The chronic toxicity of photowastes to biological treatment systems.

4. The effects of a single 6-8 week exposure of untreated photowaste to *Daphnia* and fish.

5. The cyanide species discharged as a consequence of photowaste disposal and their degradation products as a result of photolysis.

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APPENDIX 1
DESCRIPTION OF KODAK EKTACHROME RT PROCESSOR

SECTION II

THE KODAK EKTACHROME RT PROCESSOR

A. DESCRIPTION

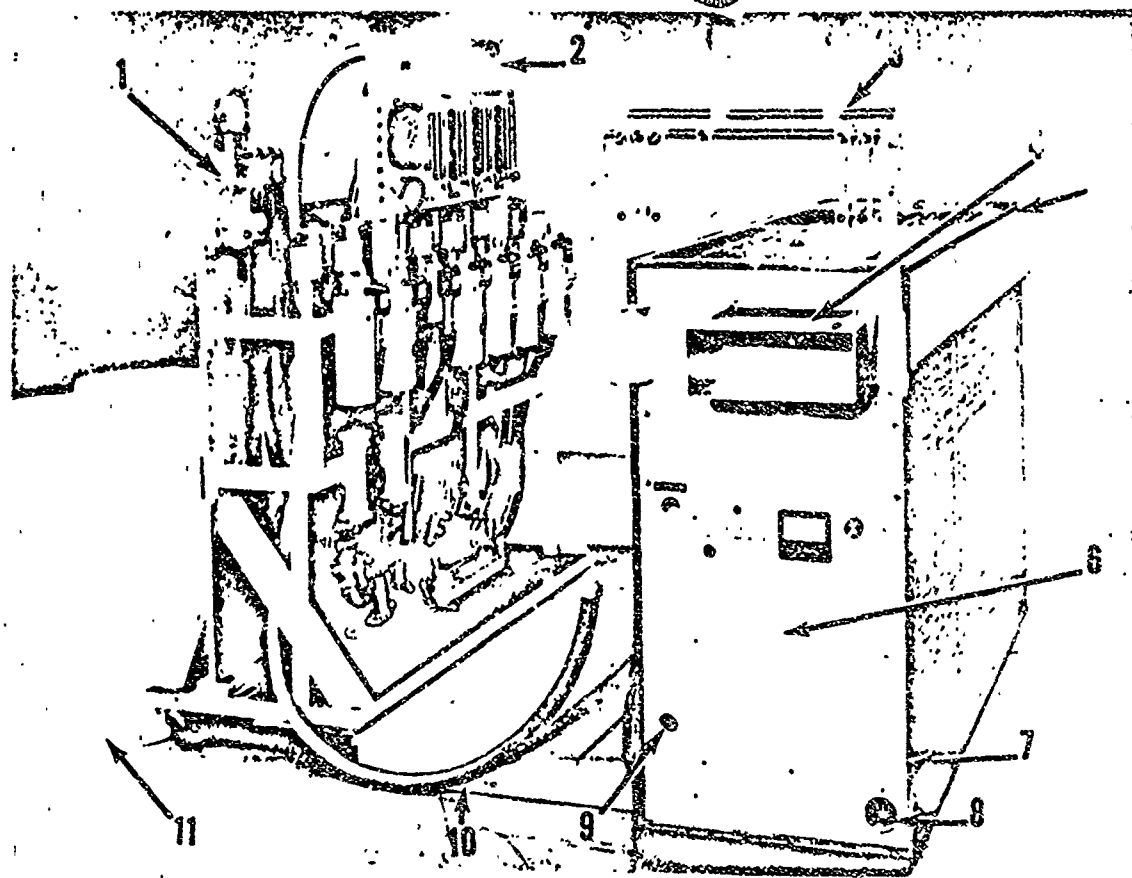
The Kodak Ektachrome RT Processor, model 1411-M, is a roller transport processor designed for continuous processing and drying of reconnaissance-type Ektachrome aerial roll films. The equipment has the same basic design as the Kodak Versamat Film Processor, model 11C, but the system has been expanded to provide the controls and processing stages required for processing color material. The processing system (Figure 1) consists of three main components: (1) the processor; (2) the chemical control panel assembly; and (3) the chemical storage tanks.

The processor consists of two seven-tank wet sections from the Versamat, model 11C, assembled with a common drive to form the necessary fourteen-tank arrangement. The standard model 11 dryer, roll feed adapter, and roll take-up adapter complete the main processor component. Since the reversal operation is accomplished by a chemical reversal agent in the color developer, there is no need for a reexposure stage. A schematic diagram of the tank and chemical arrangement is shown in Figure 2.

The chemical control panel assembly (Figure 3) contains those components that relate to recirculation, temperature control, filtration, and replenishment. All solutions are replenished; and all, excepting the neutralizer, are recirculated and temperature controlled. All solutions, excepting the neutralizer and first stop bath, are filtered. Heat wells with adjustable thermostatic controls fulfill the normal heat requirements since all chemicals, excepting the prehardener and neutralizer, operate at a temperature of 100 °F or higher. Heat exchangers, fed by the 90 °F wash water, are built into the prehardener and first developer recirculation system to provide cooling when this requirement exists. Additional booster heaters are incorporated in the recirculation system of the first and color developers and can be actuated manually when it is desirable to raise the temperature of these solutions quickly. This permits a considerable reduction in machine warmup time because these solutions are double-volume, two-tank solutions which are operated at relatively high temperatures. Replenishment is accomplished by actuating the appropriate eight toggle switches on the panel and adjusting the rate of flow, as indicated by the flowmeter. Seven additional switches control the recirculation pumps and heaters. (Neutralizer is not recirculated nor heated.) All power, solution, and water connections between the control panel and the processor are protected by a walk platform between the units, as shown in Figure 1.

The chemical storage tank farm, shown in Figure 4, consists of eight 30-gallon plastic storage tanks having floating lids and dust covers. The arrangement of the tanks is flexible and can be adjusted to suit the installation. The support rack shown in the photograph is not supplied with the processor. When tanks are stacked as shown, or when the tops of the tanks are 40 inches or more above the processor floor level, suitable shut-off valves must be provided to prevent gravity feed into the processor.

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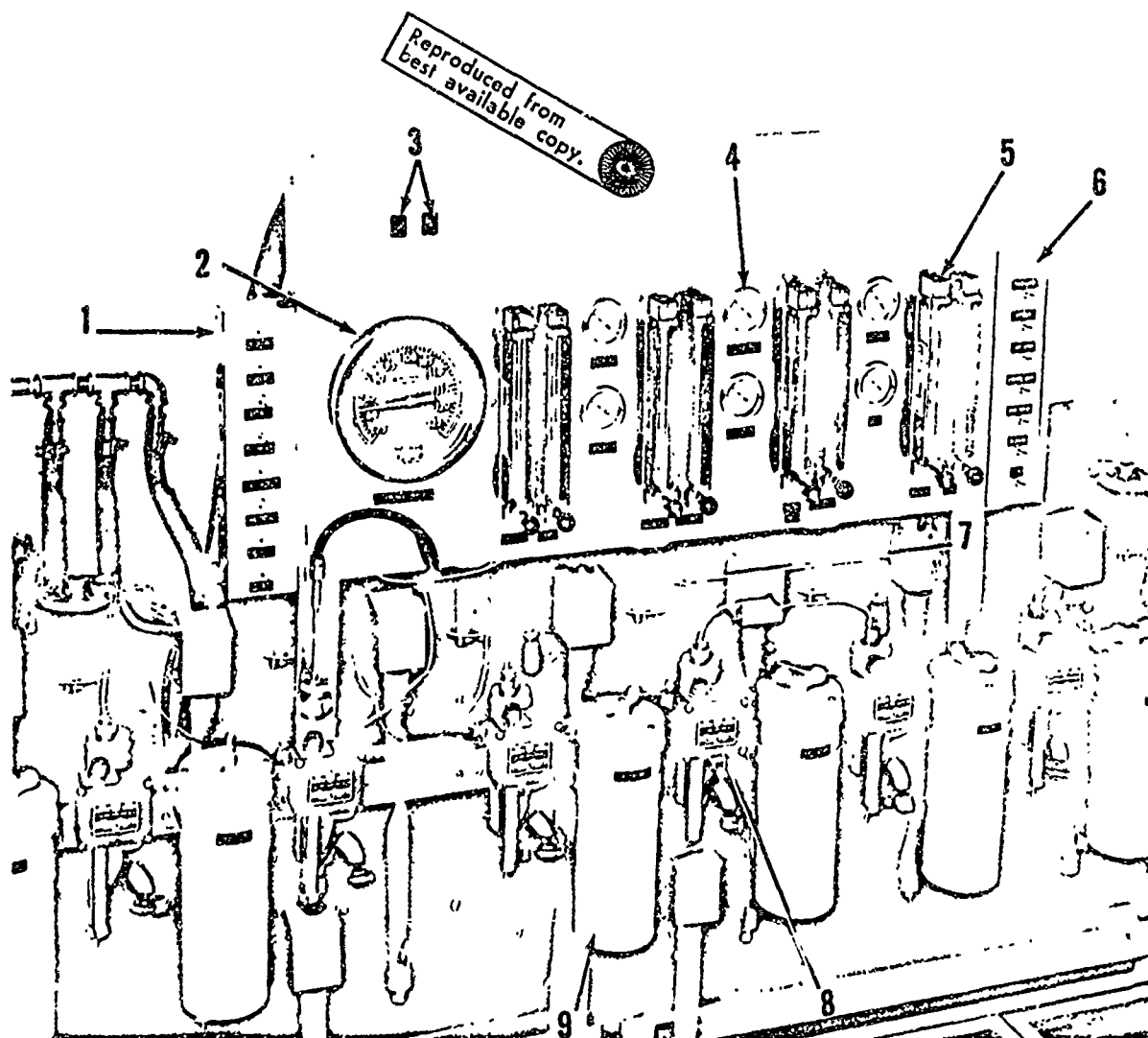


- | | | |
|------------------------------|-----------------------------|-----------------------------|
| 1. Mixing Valve | 5. Covers | 9. Drain |
| 2. Chemical Control Assembly | 6. Electrical Control Panel | 10. Platform (not supplied) |
| 3. Roll Feed Adapter | 7. Side Panels | 11. Chemical Storage Tanks |
| 4. Feed Tray | 8. Air Exhaust | |

Figure 1. The Kodak Ektachrome RT Processor, Model 1411-M

<div style="text-align: center;"> <div style="border-bottom: 1px solid black; width: 50px; margin: 0 auto;"></div> <div style="text-align: center;">FEED</div> </div>	PREHARDENER		NEUTRALIZER		FIRST DEVELOPER		FIRST STOP WASH		COLOR DEVELOPER		SECOND STOP WASH		BLEACH FIX		WASH		DRYER	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14				

Figure 2. Tank and Chemical Arrangement



- | | |
|---|---|
| 1. Replenisher Pump Switch Panel (8 switches) | 6. Recirculation Pump Switch Panel (7 switches) |
| 2. First Developer Thermometer | 7. Recirculation Pumps (7) |
| 3. Booster Heater Switches (2) | 8. Solution Thermostat (7) |
| 4. Solution Thermometer (6) | 9. Filter (6) |
| 5. Flowmeter (8) | |

Figure 3. Control Panel Assembly

1. Size, Weight, and Space Requirements: The dimensions of the main processor section are:

Length	85-5/16 inches
Width	25-3/8 inches
Height	52-3/16 inches

The addition of the model 11 Versamat roll feed adapter and roll take-up adapter adds approximately 32.5 inches to the length. The weight of the empty processor is approximately 1,500 pounds.

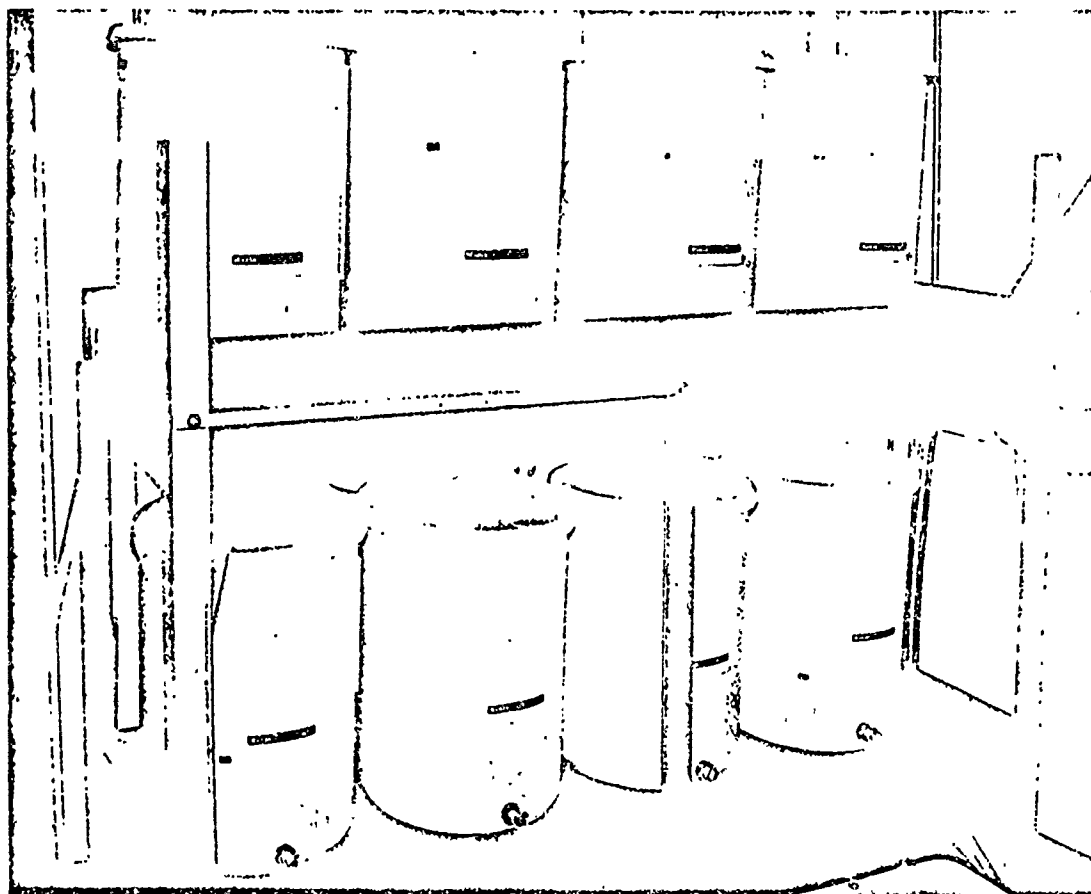


Figure 4. Replenisher Solution Storage Tank Farm

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The chemical control panel assembly, which must be close to the processor, has the following dimensions:

Length	72 inches
Width	26 inches
Height	74 inches

For accuracy and consistency in control and ease of operation, it is recommended that this panel be positioned so that it faces the plumbing side of the processor, with approximately 2.5 to 3 feet between the units. Wider separation could present problems in controlling temperature and obtaining the volume of solutions required. The space requirements, as specified by Eastman Kodak Company in the processor installation manual, are quoted in the following paragraph:

"The layout of the area in which the processor is to be used will vary from one installation to another, depending upon the needs of the particular department. The processor (processing and drying sections) occupies approximately

•16 square feet of floor space. Service clearance (approximately 3 feet) must be provided on all four sides of the processor. The feed tray extends approximately 12 inches into the darkroom. The roll feed adapter for multiroll processing extends 20 inches. The processor and dryer sections extend 87 inches from the darkroom wall; to this must be added 13 inches to accommodate either the processed film receiving bin or the roll take-up adapter. Space provision must be made for eight 30-gallon plastic replenisher tanks, to be located as near to the chemical control panel assembly as possible. The tops of the replenisher tanks must be between 35 and 40 inches from the floor level of the processor. They may be higher if suitable shut-off valves are provided and installed between the chemical control panel and the chemical replenisher tanks. Do not use the flowmeters on the chemical control panel as shut-off valves."

2. Power Requirements: The required electrical service is 208-volt, 3-phase, 4-wire, 60-cycle (67 amps per leg, 24 KVA). A thermomagnetic circuit breaker (100-ampere) must be supplied and installed by the customer. If the processor must be installed in a facility that has only 230-volt, 3-phase, 3-wire, 60-cycle (delta) service, a special transformer must be used. In the evaluation installation, three 10-KVA General Electric transformers (No. OM 9T 21 B 1003) were wired in proper phase to supply the required service.

3. Water and Drain: The processor requires six gallons of tempered water (90° F) per minute. To provide proper temperature regulation, a minimum pressure of 45 pounds per square inch (psi) must be applied to both sides of the mixing valve. The hot water temperature should not be less than 105° F, and the cold water temperature should not exceed 75° F. The thermostatic mixing valve and the visual flow regulators for the three washes are supplied with the processor, but must be installed by the customer.

4. Environmental Conditions, Venting, and Safety Precautions: The processor is designed to operate under the normal range of temperature and humidity conditions found in color processing installations. The temperature of the chemical storage tanks must be maintained between 68 and 100° F; otherwise, a change in chemical properties will occur. An additional requirement of this processor is that chemical fume and dust venting equipment must be installed. The processor has a four-inch flanged opening in the top center cover for removal of objectionable fumes from the prehardener, color developer, and fixer solutions.

Since several of the chemical agents used in this process are toxic, facilities for emergency treatment must be supplied. Eye and arm wash installations are recommended for both the mixing area and the processor room. Some method for immediate application of water must be available.

B. FILMS

1. Types: Processing cycles have been established for the following seven types of Kodak film:

- (a) Special Ektachrome MS Aerecon film, type SO-282
- (b) Special Ektachrome MS Aerographic film (Estar base), type SO-151*

- (c) Special Ektachrome MS film (Estar thin base), type SO-217
- (d) Special Ektachrome SF Aerocon film, type SO-135**
- (e) Ektachrome Color Duplicating film, type SO-271
- (f) Ektachrome Aero film, type 8442
- (g) Ektachrome Infrared film, type 8443
- (h) Aerial Ektachrome R Print, type SO-118
- (i) Special Ektachrome Infrared Aerial (Estar thin base), type SO-180
- (j) Aerial Color (Estar thin base), type SO-121

* New designation: Type 2448

** New designation: Type SO-397

More complete information is contained in film data sheets found in Appendix III.

2. Widths and Lengths: Films of all widths between 16 millimeters and 9.5 inches and with lengths greater than 5 inches, can be processed in the machine. Multiple strands of widths 5 inches or less can be processed simultaneously. Most films require the use of a short length of stiffening leader. Any Kodak black-and-white film designated as "Estar Thick Base" may be used for this purpose.

C. PROCESS PARAMETERS

1. Temperature: The process EA-4 has been designed to process all the recommended films through common chemistry. Some modification of temperature and chemistry is required for optimum results. Table I shows these conditions.

2. Transport Speed and Access Time: A constant machine speed of 3.2 feet-per-minute has been established by the manufacturer as optimum for all specified films. The only processing variable recommended by the manufacturer is the temperature of the first developer. Indications are that, with the present chemistry, an increase in machine speed would result in insufficient washing, bleaching, and fixing.

Since the film path in the machine is approximately 67 feet, the access time of the leading edge of a processed film would be approximately 20 minutes. If this were a long, continuous roll, approximately 192 feet of film would be processed every hour.

D. CHEMISTRY

Ten packaged chemicals are required to start up and maintain the EA-4 process. These chemicals, their packaged dimensions, volume, and weight are listed in Table II. The procedures for mixing and handling the EA-4 chemicals, outlined in Kodak's operating instructions, are given in Appendix I and should be followed.

TABLE I
CONDITIONS OF PROCESSING

Solution	Rack	Time (min:sec)	Temperature (degrees F)	Replenishment Rate (milliliters/sq ft)
Prehardener	1 & 2	2:30	95±0.5	60
Neutralizer	3	1:15	97±3	50
First Developer	4 & 5	2:30	*	175
First Stop	6	1:15	100±1	225
Wash	7	1:15	90+5 -2	2 gal/min
Color Developer	8 & 9	2:30	110±1	225
Second Stop	10	1:15	110±1	200
Wash	11	1:15	90+5 -2	2 gal/min
Bleach	12	1:15	110±1	60
Fix	13	1:15	110±1	60
Wash	14	1:15	90+5 -2	2 gal/min
Dryer (Set vents at 8)		2:30	125±5	

* First Developer Temperature

<u>Film</u>	<u>Temperature and Condition</u>
SO-151, 155, 217, 282, 121	100° F ± 0.5° F for normal camera speed, 106° F ± 0.5° F for double camera speed. ¹
8442, 8443 ² , SO-180	103° F ± 0.5° F.
SO-118 SO-271	95° F ± 0.5° F. 105° F ± 0.5° F.

NOTE

1. Films force-processed for double camera speed will shift somewhat in color balance and contrast and will have lower maximum densities.
2. For optimum infrared response, add 15 milligrams of Kodak Anti-Fog No. 6 per liter to prehardener tank and 20 milligrams per liter to prehardener replenisher, and adjust first developer temperature to 106° F. The modified prehardener should be used only for 8443 film. The adjusted prehardener and replenisher should be used as soon as possible after mixing.

TABLE II
EA-4 PROCESS CHEMICALS

Process EA-4 Chemical	Container Dimensions (inches)	Volume (U.S. Gallons)	Weight (pounds)
Prenardener Replenisher	11 x 14 x 17	26.5	50
Prehardener Starter Case of 24 Units	3.25 dia. x 4.5 9 x 10 x 14	10	1.33 33
Neutralizer and Replenisher	6 x 12 x 18.5	26.5	33
First Developer Case of 6 Units	6.25 dia. x 7 8 x 13 x 19	10	8 48
First Developer Replenisher	9 x 9 x 13	26.5	21
First Stop Bath and Replenisher Case of 4 Units	6 x 6 x 12 12 x 12 x 12	26.5	9 37
Color Developer	9 x 9 x 9	10	7
Color Developer Replenisher	7 x 12 x 14	26.5	18
Second Stop Bath and Replenisher Case of 4 Units	5.5 x 5.5 x 7.5 8 x 10 x 22	26.5	12 50
Bleach and Replenisher	11 x 11 x 20	26.5	45
Fixer and Replenisher	10 x 14 x 20	26.5	56

APPENDIX 2

DATA FROM BATCH ACTIVATED SLUDGE TREATMENT STUDIES ON EA-4
PHOTOGRAPHIC WASTE INCLUDING WASH WATERS FROM SHAW AFB SC

TABLE 11 FIRST BATCH ACTIVATED SLUDGE TREATMENT STUDY ON EA-4 PHOTOGRAPHIC WASTE INCLUDING WASH WATERS FROM SHAW AFB SC,

Aeration Time (hrs)	Compartments of Batch Unit				
	Control	A	B	C	D
<u>Chemical Oxygen Demand (mg/l)</u>					
0	273	284	279	301	333
2	133	139	139	183	200
4	44	39	44	105	78
6	28	67	50	78	105
24	44	49	55	71	87
<u>BOD₅ (mg/l)</u>					
0	133	120	122	124	129
6	10	6	6	10	14
24	3	0	0	3	0
<u>Total Organic Carbon (mg/l)</u>					
0	99	105	103	105	114
2	55	56	55	65	63
4	15	18	20	24	28
6	14	12	12	20	24
24	19	18	19	26	28
<u>Mixed Liquor Suspended Solids (mg/l)</u>					
0	3000	3070	3060	3030	3140
6	3100	3190	3250	3220	3280
24	2730	2720	2610	2630	2530
<u>Surfactants (as mg/l LAS)</u>					
0	3.6	5.0	4.4	4.8	5.0
6	0.6	0.4	0.6	3.4	4.6
24	0.8	0.8	0.8	1.4	1.2

TABLE 11 (cont'd)

	<u>Nitrates (mg/l)</u>				
0	8.4	3.6	1.6	3.2	3.2
6	20.8	19.2	16.4	2.4	1.2
24	46.0	46.0	36.0	38.0	32.0

	<u>Phosphates (mg/l)</u>				
0	3.2	3.2	3.2	4.0	8.0
6	2.4	2.0	2.4	4.2	8.0
24	10.8	22.4	10.0	18.4	13.4

	<u>Copper (mg/l)</u>				
0	<0.01	0.04	<0.01	0.04	0.06
6	<0.01	<0.01	<0.01	<0.01	<0.01
24	<0.01	<0.01	<0.01	<0.01	<0.01

	<u>Iron (mg/l)</u>				
0	<0.01	0.48	1.00	1.90	2.50
6	<0.01	0.21	0.64	2.21	3.28
24	<0.01	0.14	0.50	2.00	3.21

	<u>Silver (mg/l)</u>				
0	<0.01	<0.01	<0.01	<0.01	0.07
6	<0.01	<0.01	<0.01	<0.01	<0.01
24	<0.01	<0.01	<0.01	<0.01	<0.01

	<u>Zinc (mg/l)</u>				
0	<0.05	<0.05	<0.05	<0.05	0.05
6	<0.05	<0.05	<0.05	<0.05	<0.05
24	<0.05	<0.05	<0.05	<0.05	<0.05

	<u>Oils and Greases (as mg/l Heptane)</u>				
0	8.0	4.5	3.0	5.0	5.4
6	4.5	6.0	3.0	2.5	3.0
24	7.0	4.8	3.6	3.6	6.0

TABLE 11 (cont'd)

	<u>Cyanide (mg/l)</u>				
0	0.01	0.50	1.35	3.60	10.49
6	0.01	0.47	0.35	5.29	9.75
24	0.01	0.17	0.80	5.59	0.01

Lead, Manganese, Cadmium and Chromium were not detected in any units.

FIGURE 15 DISSOLVED OXYGEN UPTAKE OF SLUDGE FROM FIRST BATCH ACTIVATED
SLUDGE TREATMENT STUDY, EA-4 PHOTOGRAPHIC WASTE, FROM SHAW
AFB SC,

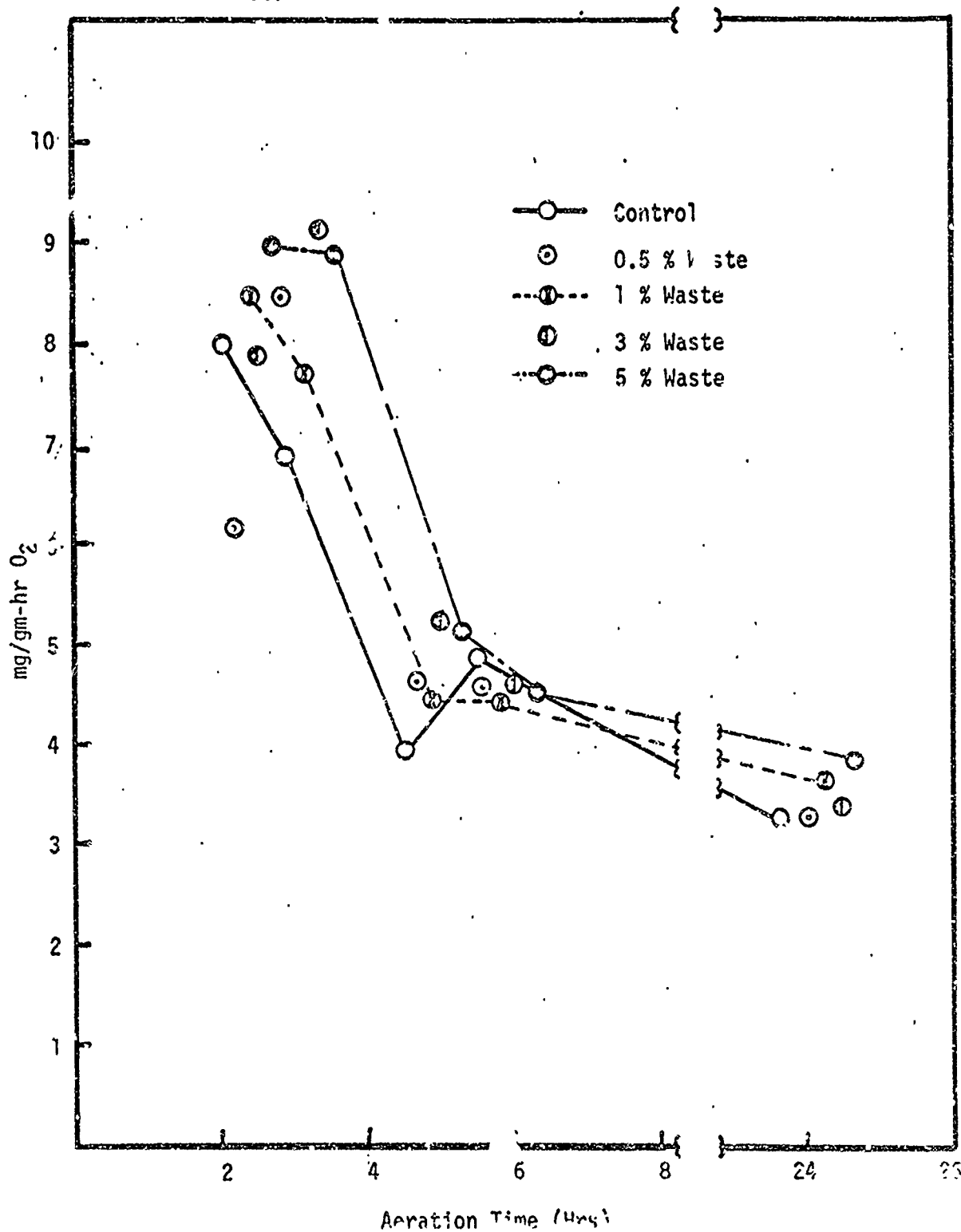


TABLE 12 SECOND BATCH ACTIVATED SLUDGE TREATMENT STUDY ON EA-4 PHOTO-GRAPHIC WASTE INCLUDING WASH WATERS FROM SHAW AFB SC,

COMPARTMENT OF BATCH UNIT

Aeration Time (hrs)	Control	A	B	C	D
<u>Chemical Oxygen Demand (mg/l)</u>					
0	257	262	262	291	328
2	131	137	153	180	208
4	22	44	44	71	82
6	27	33	44	33	93
24	60	49	65	76	87
<u>Total Organic Carbon (mg/l)</u>					
0	106	104	102	106	112
2	64	62	70	70	82
4	22	24	24	27	31
6	19	20	22	26	31
24	22	21	24	28	32
<u>Mixed Liquor Suspended Solids (mg/l)</u>					
0	2640	2710	2590	2730	2600
6	2620	2630	2630	2740	2710
24	2250	2260	2390	2150	1740
<u>Surfactants (as mg/l LAS)</u>					
0	3.6	5.6	6.4	6.4	4.6
6	0.8	0.8	0.8	4.8	4.2
24	0.6	0.6	0.6	1.0	1.2
<u>Nitrates (mg/l)</u>					
0	6.0	3.6	2.4	2.8	4.4
6	8.4	8.0	6.4	1.6	3.6
24	30.0	28.0	30.0	17.6	6.0
<u>Phosphates (mg/l)</u>					
0	5.4	16.4	15.0	22.0	5.6
6	1.1	1.2	0.8	1.4	1.0
24	5.2	3.8	0.8	2.7	4.0

TABLE 12 (cont'd)

<u>Sulfates (mg/l)</u>					
0	39	45	50	75	75
6	50	65	75	95	95
24	55	60	75	115	170

<u>Copper (mg/l)</u>					
0	0.01	0.01	<0.01	0.01	0.02
6	<0.01	<0.01	0.01	0.01	0.01
24	0.01	0.01	0.01	0.01	0.02

<u>Iron (mg/l)</u>					
0	<0.1	0.1	0.5	1.1	1.6
6	<0.1	0.1	0.2	1.2	2.1
24	<0.1	<0.1	0.1	0.8	1.8

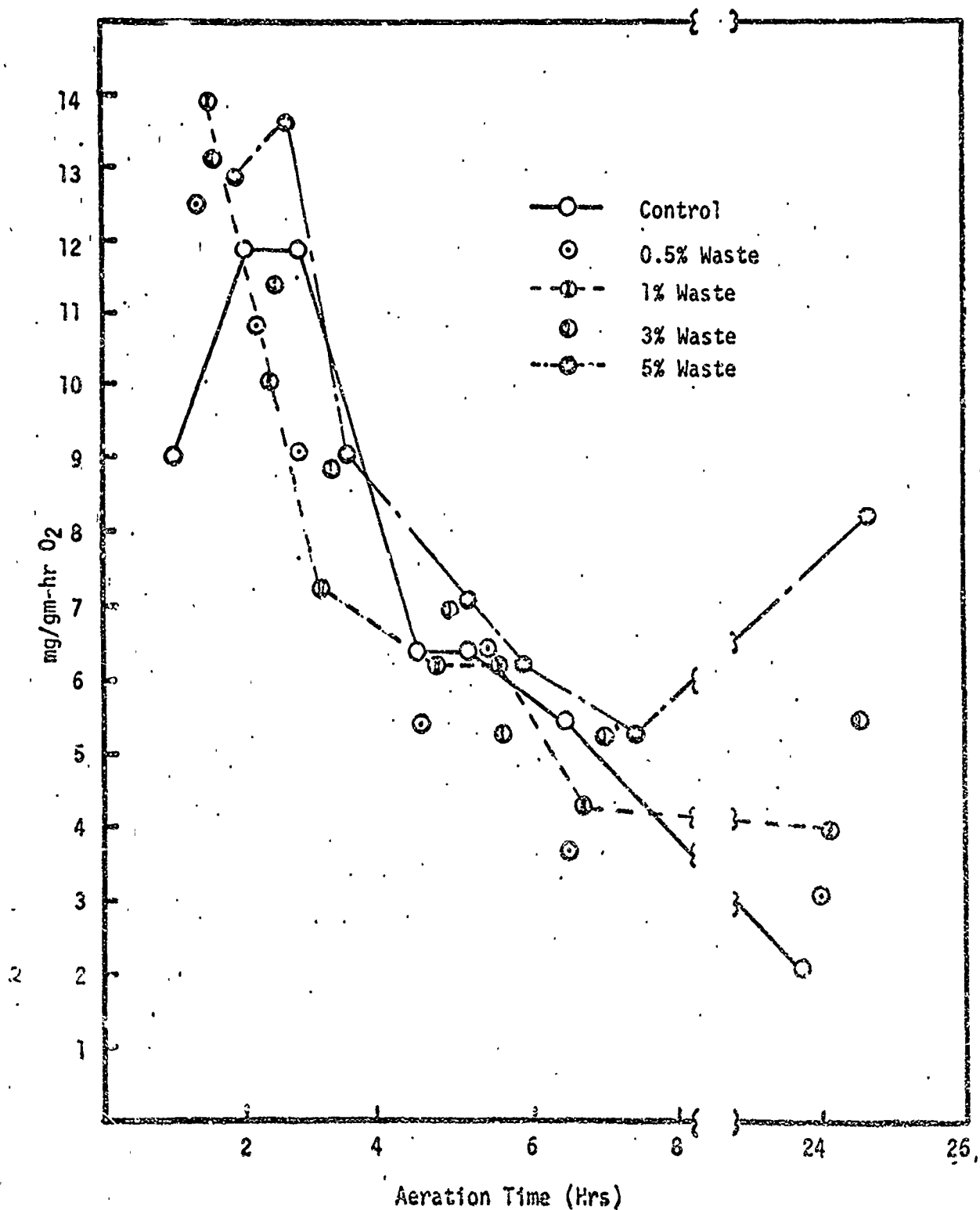
<u>Silver (mg/l)</u>					
0	<0.01	<0.01	<0.01	0.04	0.22
6	<0.01	<0.01	<0.01	<0.01	0.05
24	<0.01	<0.01	<0.01	<0.01	<0.01

<u>Zinc (mg/l)</u>					
0	<0.05	0.13	0.13	0.17	0.13
6	<0.05	<0.05	<0.05	0.13	0.13
24	<0.05	<0.05	<0.05	<0.05	<0.05

<u>Oils and Greases (as mg/l Heptane)</u>					
0	7.5	2.8	3.3	4.0	4.0
6	5.5	2.8	2.8	3.3	2.8
24	4.5	4.0	4.2	5.0	6.2

<u>Cyanide (mg/l)</u>					
0	0.06	0.08	0.87	5.50	7.24
6	0.05	0.20	0.38	4.40	6.74
24	0.02	0.05	0.06	2.60	5.51

FIGURE 16. DISSOLVED OXYGEN UPTAKE OF SLUDGE FROM SECOND BATCH ACTIVATED SLUDGE TREATMENT STUDY, EA-4 PHOTOGRAPHIC WASTE, SHAW AFB SC.



APPENDIX 3

Data from Combined EA-4 Process Waste Treatment
Studies using Bench Top Continuous Flow Activated
Sludge Plant.

TABLE 13 DATA FROM FIRST COMBINED WASTE TREATMENT STUDY IN
BENCH TOP CONTINUOUS FLOW ACTIVATED SLUDGE PLANT
(12 HOUR AERATION TIME)

<u>Date</u>	<u>% Waste</u>	<u>mg/l Suspended Solids</u>	<u>mg/l Dissolved Oxygen</u>	<u>mg/gm-hr D.O. Uptake</u>
21 Oct 69	2.0	1880		
22 Oct 69	1.5	2830		4.1
23 Oct 69	1.5	2870	1.8	3.5
24 Oct 69	1.5	2040	0.8	4.8
27 Oct 69	1.0			
28 Oct 69	0.5			
29 Oct 69	0.5	1070	1.5	4.9
31 Oct 69	0.5	1570	1.0	3.4

pH

	<u>% Waste</u>	<u>Influent</u>	<u>Effluent</u>
21 Oct 69	2.0	7.0	8.0
22 Oct 69	1.5		7.9
23 Oct 69	1.5	7.3	7.9
24 Oct 69	1.5	8.5	8.5
29 Oct 69	0.5	6.9	7.9

<u>% Waste</u>	<u>mg/l in Influent</u>	<u>mg/l in Effluent</u>
----------------	-----------------------------	-----------------------------

Total Oxygen Demand

21 Oct 69	2.0	1374	575
22 Oct 69	1.5	1020	500
23 Oct 69	1.5	805	140
24 Oct 69	1.5	960	290
27 Oct 69	1.5	1090	475
28 Oct 69	0.5	684	165
29 Oct 69	0.5	540	150
31 Oct 69	0.5	630	207
Avg		888	326

Chemical Oxygen Demand

21 Oct 69	2.0	1055	477
22 Oct 69	1.5		400
23 Oct 69	1.5	638	173
24 Oct 69	1.5	833	201
25 Oct 69	0.5	464	100
Avg		747	270

TABLE 13 (cont'd)

<u>Day</u>	<u>% Waste</u>	<u>mg/l in Influent</u>	<u>mg/l in Effluent</u>
<u>Oils & Greases</u>			
21 Oct 69	2.0	4.0	3.5
22 Oct 69	1.5		10.0
23 Oct 69	1.5	4.0	11.0
24 Oct 69	1.5	8.0	8.0
29 Oct 69	0.5	3.4	2.0
<u>Cyanide</u>			
21 Oct 69	2.0	62.4	87.4
22 Oct 69	1.5		59.9
23 Oct 69	1.5	37.5	40.5
24 Oct 69	1.5	53.0	74.9
29 Oct 69	0.5	11.0	10.0
<u>SO₃</u>			
21 Oct 69	2.0	169	46
22 Oct 69	1.5		23
23 Oct 69	1.5	45	<2
24 Oct 69	1.5	16	<2
29 Oct 69	0.5	39	<2
<u>SO₄</u>			
21 Oct 69	2.0	50	150
22 Oct 69	1.5		350
23 Oct 69	1.5	148	300
24 Oct 69	1.5	225	562
29 Oct 69	0.5	73	250
<u>NO₃</u>			
21 Oct 69	2.0	220	40
22 Oct 69	1.5		65
23 Oct 69	1.5	29	12
24 Oct 69	1.5	18	10
29 Oct 69	0.5	7	7
<u>PO₄</u>			
21 Oct 69	2.0	13	13
22 Oct 69	1.5		5
23 Oct 69	1.5	6	3
24 Oct 69	1.5	5	3
29 Oct 69	0.5	2	1

TABLE 13 (cont'd)

<u>Day</u>	<u>% Waste</u>	<u>mg/l in Influent</u>	<u>mg/l in Effluent</u>
<u>Lead</u>			
21 Oct 69	2.0	<0.05	<0.05
24 Oct 69	1.5	0.14	<0.05
29 Oct 69	0.5	<0.05	0.14
<u>Copper</u>			
21 Oct 69	2.0	0.08	0.08
24 Oct 69	1.5	0.02	0.02
29 Oct 69	0.5	0.02	<0.01
<u>Manganese</u>			
21 Oct 69	2.0	<0.05	<0.05
24 Oct 69	1.5	<0.05	<0.05
29 Oct 69	0.5	<0.05	<0.05
<u>Zinc</u>			
21 Oct 69	2.0	0.92	0.78
24 Oct 69	1.5	0.35	0.50
29 Oct 69	0.5	<0.05	0.10
<u>Cadmium</u>			
21 Oct 69	2.0	0.28	<0.01
24 Oct 69	1.5	0.01	0.01
29 Oct 69	0.5	<0.01	<0.01
<u>Silver</u>			
21 Oct 69	2.0	1.04	0.24
24 Oct 69	1.5	0.92	0.53
29 Oct 69	0.5	1.00	0.12
<u>Chromium</u>			
21 Oct 69	2.0	0.24	0.20
24 Oct 69	1.5	0.22	0.22
29 Oct 69	0.5	0.11	<0.05
<u>Iron</u>			
21 Oct 69	2.0	6.91	8.13
24 Oct 69	1.5	11.00	10.80
29 Oct 69	0.5	6.60	6.60

TABLE 14 DATA FROM SECOND COMBINED WASTE TREATMENT STUDY IN BENCH TOP
CONTINUOUS FLOW ACTIVATED SLUDGE PLANT (12 AND 9 HOUR AERATION
TIMES)

<u>Date</u>	<u>% Waste</u>	<u>Detention Time (hrs)</u>	<u>mg/l Suspended Solids</u>	<u>mg/l Dissolved Oxygen</u>	<u>mg/gm-hr D.O. Uptake</u>
19 Nov 69	0.1	12	2110	6.1	5.4
20 Nov 69	0.1	12	2250	5.2	10.2
21 Nov 69	0.1	9	2450	5.9	3.7
24 Nov 69	0.05	9	1550	5.1	10.3
25 Nov 69	0.05	9	1360	5.9	11.8
26 Nov 69	0.05	9	1660	5.8	11.0
27 Nov 69	0.05	9	-	5.1	
28 Nov 69	0.05	9	600	6.1	11.5
1 Dec 69	0.05	9	420	4.3	28.5

TABLE 15 DATA FROM THIRD COMBINED WASTE TREATMENT STUDY IN BENCH TOP
CONTINUOUS FLOW ACTIVATED SLUDGE PLANT (6 HOUR AERATION TIME)

<u>Date</u>	<u>% Waste</u>	<u>mg/l Mixed Liquor Suspended Solids</u>	<u>mg/l Dissolved Oxygen</u>	<u>mg/l DO Uptake</u>
12 Dec 69	0.005	3800	0	
16 Dec 69	0.005	1640		
17 Dec 69	0.001	2360	0.4	11.6
18 Dec 69	0.001	2270	0.6	

STARTED PLANT WITH NEW SLUDGE

22 Dec 69	0.001	2710	0.8	14.3
23 Dec 69	0.001	3190	1.3	7.9
29 Dec 69	0.001	2840	3.4	8.0
30 Dec 69	0.001	2750	1.9	12.5
31 Dec 69	0.001	3420	1.1	9.4
5 Jan 70	0.001	2960	0.6	6.9
6 Jan 70	0.001	2650	0.4	8.6
7 Jan 70	0.001	3140	0.2	12.4
8 Jan 70	0.001	-	0.4	
9 Jan 70	0.001	-	0.6	
12 Jan 70	0.5	2340	1.0	22.5
13 Jan 70	0.5	2130	2.0	29.0
14 Jan 70	0.5	2740	0.4	40.0
15 Jan 70	0.5	1870	0.4	51.3
16 Jan 70	Terminated			

<u>Date</u>	<u>% Waste</u>	<u>mg/l in Influent</u>	<u>mg/l in Effluent</u>
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Chemical Oxygen Demand

12 Dec 69	0.005	557	185
17 Dec 69	0.001	237	48

STARTED WITH NEW SLUDGE

22 Dec 69	0.001	262	128
23 Dec 69	0.001	505	33

TABLE 15 (cont'd)

<u>Date</u>	<u>% Waste</u>	<u>mg/l in Influent</u>	<u>mg/l in Effluent</u>
29 Dec 69	0.001	205	59
30 Dec 69	0.001	312	32
31 Dec 69	0.001	308	54
2 Jan 70	0.001	276	11
5 Jan 70	0.001	276	77
5 Jan 70	0.001	281	36
7 Jan 70	0.001	299	60
8 Jan 70	0.001	315	57
9 Jan 70	0.001	316	65
12 Jan 70	0.5	465	358
13 Jan 70	0.5	591	253
14 Jan 70	0.5	475	295
15 Jan 70	0.5	649	327

Oils & Greases

12 Dec 69	0.005	5.5	6.0
17 Dec 69	0.001	6.0	8.4

STARTED WITH NEW SLUDGE

30 Dec 69	0.001	2.4	4.8
31 Dec 69	0.001	8.0	3.4
5 Jan 70	0.001	5.0	5.0
7 Jan 70	0.001	3.0	4.8
9 Jan 70	0.001	2.0	4.8
12 Jan 70	0.5	4.8	8.0
14 Jan 70	0.5	1.5	4.8

Cyanide

17 Dec 69	0.001	0.06	<0.01
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STARTED WITH NEW SLUDGE

30 Dec 69	0.001	<0.01	<0.01
31 Dec 69	0.001	<0.01	0.02

TABLE 15 (cont'd)

<u>Date</u>	<u>% Waste</u>	<u>mg/l in Influent</u>	<u>mg/l Effluent</u>
<u>S0₃</u>			
17 Dec 69		None detected	None detected
<u>STARTED WITH NEW SLUDGE</u>			
30 Dec 69	0.001	None detected	None detected
31 Dec 69	0.001	None detected	None detected
5 Jan 70		None detected	None detected
7 Jan 70	0.001	None detected	None detected
9 Jan 70	0.001	None detected	None detected
12 Jan 70	0.5	34	17
14 Jan 70	0.5	31	21
<u>S0₄</u>			
17 Dec 69	0.001	47.5	30.0
<u>STARTED WITH NEW SLUDGE</u>			
30 Dec 69	0.001	28.5	17.0
31 Dec 69	0.001	25.5	22.4
5 Jan 70	0.001	31.0	27.0
7 Jan 70	0.001	35.5	28.0
9 Jan 70	0.001	38.0	28.0
12 Jan 70	0.5	100.	105.
14 Jan 70	0.5	115.	110.
<u>NO₃</u>			
12 Dec 69	0.005	2.4	0.4
17 Dec 69	0.001	<0.2	<0.2
<u>STARTED WITH NEW SLUDGE</u>			
30 Dec 69	0.001	3.8	0.3
31 Dec 69	0.001	0.4	<0.1
5 Jan 70	0.001	0.4	0.4
7 Jan 70	0.001	0.4	0.4
9 Jan 70	0.001	0.4	0.4
12 Jan 70	0.5	2.0	1.2
14 Jan 70	0.5	1.2	1.6

TABLE 15 (cont'd)

<u>Date</u>	<u>% Waste</u>	<u>mg/l in Influent</u>	<u>mg/l in Effluent</u>
<u>PO₄</u>			
12 Dec 69	0.005	110	104
17 Dec 69	0.001	85	86
<u>STARTED WITH NEW SLUDGE</u>			
30 Dec 69	0.001	74	74
31 Dec 69	0.001	104	60
5 Jan 70	0.001	86	92
7 Jan 70	0.001	84	98
9 Jan 70	0.001	108	104
12 Jan 70	0.5	100	110
14 Jan 70	0.5	105	90
<u>MBAS as LAS</u>			
12 Dec 69	0.005	38	26
17 Dec 69	0.001		3.
<u>STARTED WITH NEW SLUDGE</u>			
30 Dec 69	0.001	11.2	6.6
31 Dec 69	0.001	14.0	1.6
5 Jan 70	0.001	0.6	2.8
7 Jan 70	0.001	12.0	6.0
9 Jan 70	0.001	10.0	5.6
12 Jan 70	0.5	12.0	5.6
14 Jan 70	0.5	9.6	7.6
<u>Formaldehyde</u>			
17 Dec 69	0.001	<0.05	-
18 Dec 69	0.001	<0.05	<0.05
<u>STARTED WITH NEW SLUDGE</u>			
30 Dec 69	0.001	3.0	0.2
31 Dec 69	0.001	1.5	<0.05
5 Jan 70	0.001	0.5	0.2
7 Jan 70	0.001	0.2	<0.05
9 Jan 70	0.001	<0.05	<0.05
12 Jan 70	0.5	<0.05	<0.05
14 Jan 70	0.5	<0.05	<0.05

TABLE 16 (cont'd)

<u>Date</u>	<u>% Waste</u>	<u>mg/l in Influent</u>	<u>mg/l in Effluent</u>
<u>Total Cr</u>			
12 Dec 69	0.005	1.26	0.4
17 Dec 69	0.001	<0.05	<0.05
<u>STARTED WITH NEW SLUDGE</u>			
30 Dec 69	0.001	<0.05	<0.05
31 Dec 69	0.001	<0.05	<0.05
5 Jan 70	0.001	<0.05	<0.05
7 Jan 70	0.001	<0.05	<0.05
9 Jan 70	0.001	<0.05	<0.05
12 Jan 70	0.5	0.16	0.16
14 Jan 70	0.5	0.19	0.19
<u>Hexavalent Cr</u>			
12 Dec 69	0.005	1.25	0.4
<u>STARTED WITH NEW SLUDGE</u>			
5 Jan 70	0.005	0.005	0.005
7 Jan 70	0.001	0.005	0.005
9 Jan 70	0.001	0.005	0.005
12 Jan 70	0.5	0.005	0.005
14 Jan 70	0.5	0.005	0.005
<u>Silver</u>			
17 Dec 69	0.001	0.01	0.01
<u>STARTED WITH NEW SLUDGE</u>			
30 Dec 69	0.001	0.01	0.01
31 Dec 69	0.01	0.01	0.01
5 Jan 70	0.001	0.01	0.01
7 Jan 70	0.001	0.01	0.01
9 Jan 70	0.001	0.01	0.01
12 Jan 70	0.5	0.20	0.08
14 Jan 70	0.5	0.28	0.16

Note: No Lead, Copper, Manganese or Zinc in excess of 0.05 mg/l detected in Influent or Effluent from treatment plant.

TABLE 16 DATA FROM DESILVERED WASTE TREATMENT STUDY IN BENCH TOP CONTINUOUS FLOW ACTIVATED SLUDGE PLANTS RECEIVING 0.2 PERCENT WASTE.

DATE	MLSS	COD		NO ₃		PO ₄		Oils & Greases		SO ₄		SO ₃		MBAS as LAS	
		INF	EFF	INF	EFF	INF	EFF	INF	EFF	INF	EFF	INF	EFF	INF	EFF
24 Feb	2964	372	80												
25 Feb	*2620	408	64												
26 Feb	2760	352	78												
27 Feb	*2292	-	-												
2 Mar	2650	-	-												
3 Mar	*2250	336	45												
4 Mar	2532	397	43	1.6	0.8	34	12	2.5	3.3	40	95	6	<2	0.3	0.2
5 Mar	2690	300	36												
6 Mar	2720	321	50	2.4	3.2	34.4	27.6	4.0	4.0	50	91	13	<2	0.4	0.3
9 Mar	2750	264	45												
10 Mar	3130	216	42												

*Sludge Wasted.

TABLE 17 HEAVY METALS CONTAINED IN THE INFLUENT AND EFFLUENT OF TWO ACTIVATED SLUDGE PLANTS, ONE RECEIVING A CONTROL FEED ONLY, THE SECOND FED AN ADDITIONAL 0.2% DESILVERED EA-4 WASTE*

	CONTROL		TREATED	
	Influent	Effluent	Influent	Effluent
	March 4 6	March 4 6	March 4 6	March 4 6
Cu	<0.01	<0.01	<0.01	<0.01
Mn	<0.05	<0.05	<0.05	<0.05
Zn	0.11	<0.05	<0.05	0.11
Cd	<0.01	<0.01	<0.01	<0.01
Ag	<0.01	<0.01	0.07	<0.01
Cs	<0.05	<0.05	<0.05	<0.05
Fe	<0.01	0.03	2.6	1.9
Pb	<0.05	<0.05	<0.05	<0.05
Total CN	-	-	4.25	2.00

*Composite of waste chemicals - wash water excluded.

TABLE 18. CYANIDES AND METALS IN THE WASHED SLUDGE¹
OF ACTIVATED SLUDGE PLANTS

WASHED SLUDGE						
DATE	CONTROL			TREATED ²		
	4 Mar	6 Mar	9 Mar	4 Mar	6 Mar	9 Mar
TOTAL CN ³	<.3ug/g	<.4ug/g	<.3ug/g	1900ug/g	1300ug/g	1000ug/g
FREE CN	-	-	-	-	-	-
<u>HEAVY METALS¹</u>						
Pb	.72mg/l	.50mg/l	.68mg/l	.31mg/l	.40mg/l	.22mg/l
Cu	.82mg/l	.38mg/l	.36mg/l	.40mg/l	.25mg/l	.15mg/l
Mn	.29mg/l	.26mg/l	.26mg/l	.29mg/l	.17mg/l	.12mg/l
Zn	5.80mg/l	4.70mg/l	4.70mg/l	2.30mg/l	1.70mg/l	0.88mg/l
Cd	.05mg/l	.02mg/l	.03mg/l	.02mg/l	.01mg/l	.02mg/l
Ag	.13mg/l	.12mg/l	.12mg/l	1.10mg/l	1.60mg/l	1.30mg/l
Cr	3.00mg/l	2.30mg/l	2.30mg/l	3.00mg/l	3.00mg/l	1.60mg/l
Fe	84.00mg/l	97.0mg/l	150.00mg/l	250.00mg/l	220.00mg/l	130.00mg/l

- NOTES: 1. MLSS was centrifuged to separate sludge and supernatant. The sludge was resuspended in water and recentrifuged. The washed sludge was then resuspended in distilled water before analysis for heavy metals.
2. Treated Plant was fed a 0.2% Desilvered EA-4 waste.
3. Results reported in ug per gram dry sludge.

TABLE 19. CYANIDES AND METALS IN SOLUTION IN THE MLSS
OF ACTIVATED SLUDGE PLANTS.¹

<u>DATE</u>	<u>SUPERNATANT</u>					
	<u>4 Mar</u>	<u>CONTROL</u> <u>6 Mar</u>	<u>9 Mar</u>	<u>4 Mar</u>	<u>TREATED</u> <u>6 Mar</u>	<u>9 Mar</u>
TOTAL CN	<.01mg/l	<.09mg/l	<.01mg/l	3.50mg/l	2.75mg/l	3.25mg/l
FREE CN	<.01mg/l	<.01mg/l	<.01mg/l	.029mg/l	.228mg/l	.037mg/l
<u>HEAVY METALS</u>						
Pb	.22mg/l	.09mg/l	.09mg/l	<.05mg/l	.05mg/l	.09mg/l
Cu	.80mg/l	.07mg/l	.04mg/l	.11mg/l	.08mg/l	.05mg/l
Mn	<.05mg/l	<.05mg/l	<.05mg/l	<.05mg/l	<.05mg/l	<.05mg/l
Zn	.23mg/l	.35mg/l	.35mg/l	.29mg/l	.47mg/l	.29mg/l
Cd	.16mg/l	.02mg/l	.02mg/l	.02mg/l	.02mg/l	.02mg/l
Ag	.11mg/l	.04mg/l	.03mg/l	.02mg/l	.09mg/l	.08mg/l
Cr	.13mg/l	.10mg/l	.10mg/l	.20mg/l	.10mg/l	.10mg/l
Fe	.91mg/l	2.20mg/l	2.70mg/l	4.50mg/l	5.30mg/l	5.50mg/l

¹
MLSS was centrifuged to separate sludge and supernatant.

²
Treated plant was fed 0.2% Desilvered EA-4 Waste.

APPENDIX 4

Probit Regression Lines of Treated and Untreated EA-4 Waste
to D. magna.

PROBIT REGRESSION LINE OF UNTREATED EA-4 WASTE TO D. MAGNA 24 HOURS

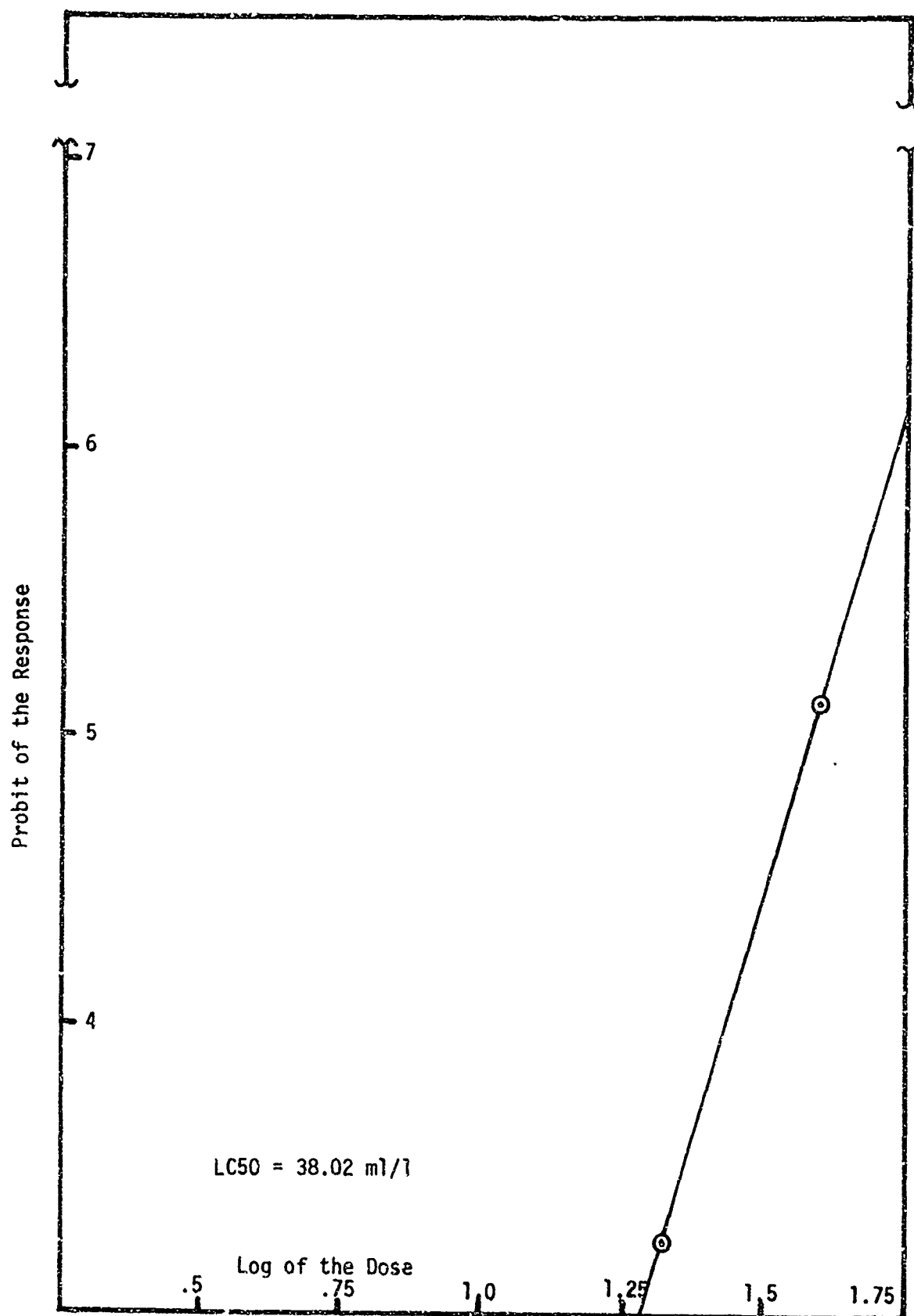


Figure 17
89

PROBIT REGRESSION LINE OF UNTREATED EA-4 WASTE TO D. MAGNA 48 HOURS

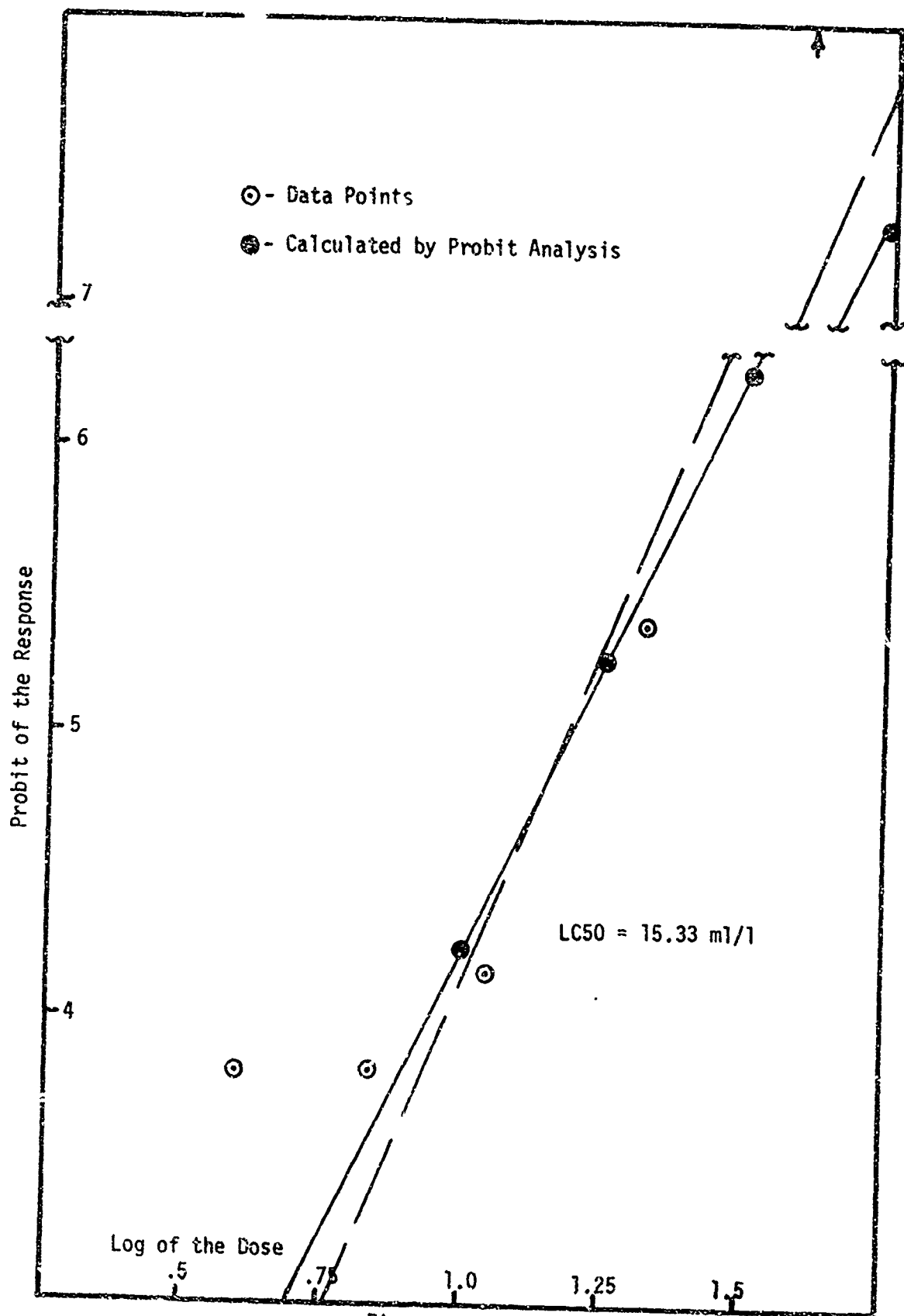


Figure 18
90

PROBIT REGRESSION LINE OF UNTREATED EA-4 WASTE TO D. magna ⁷² HOURS

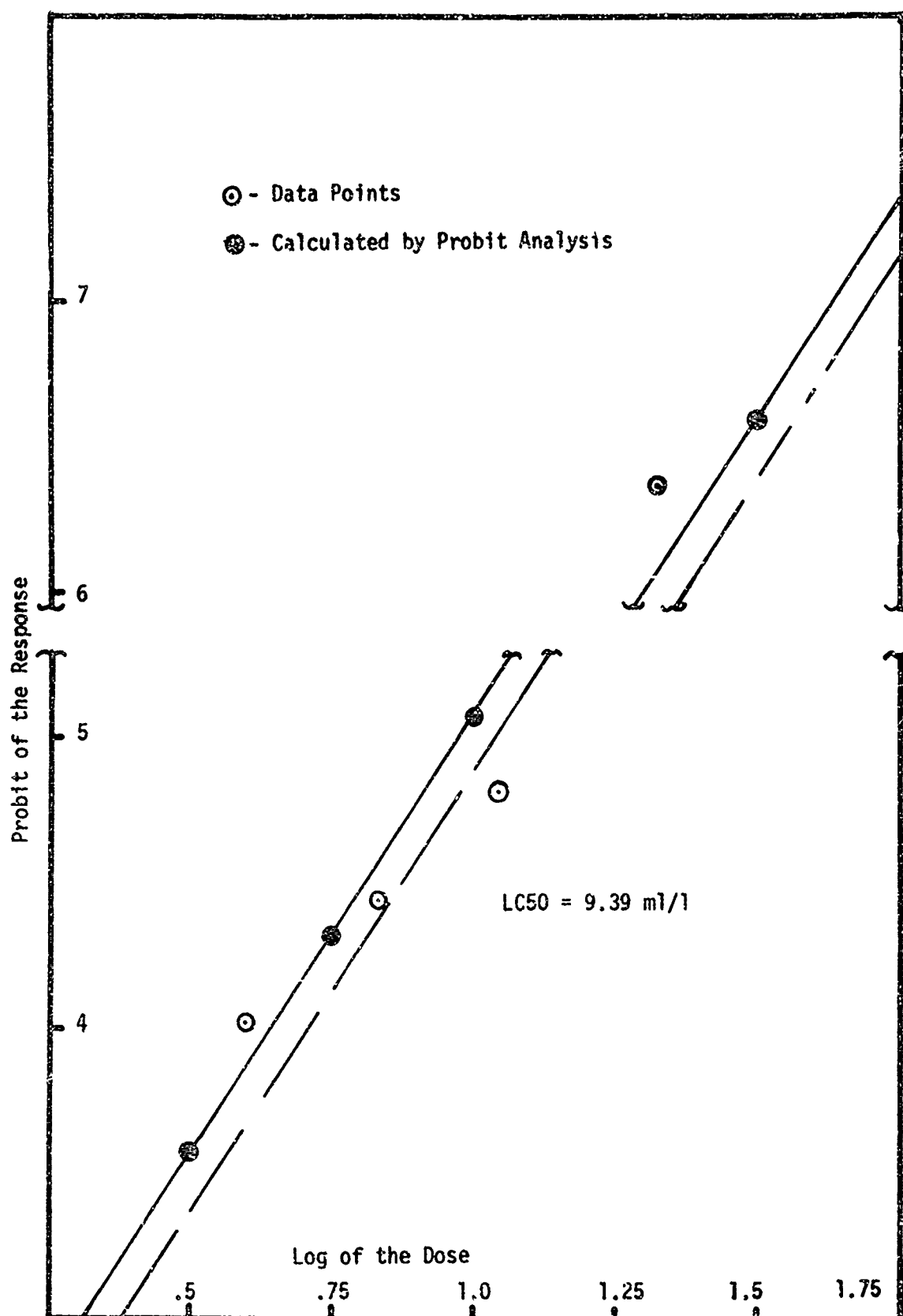


Figure 19
91

PROBIT REGRESSION LINE OF UNTREATED EA-4 WASTE TO D_L MAGNA -96 HOURS

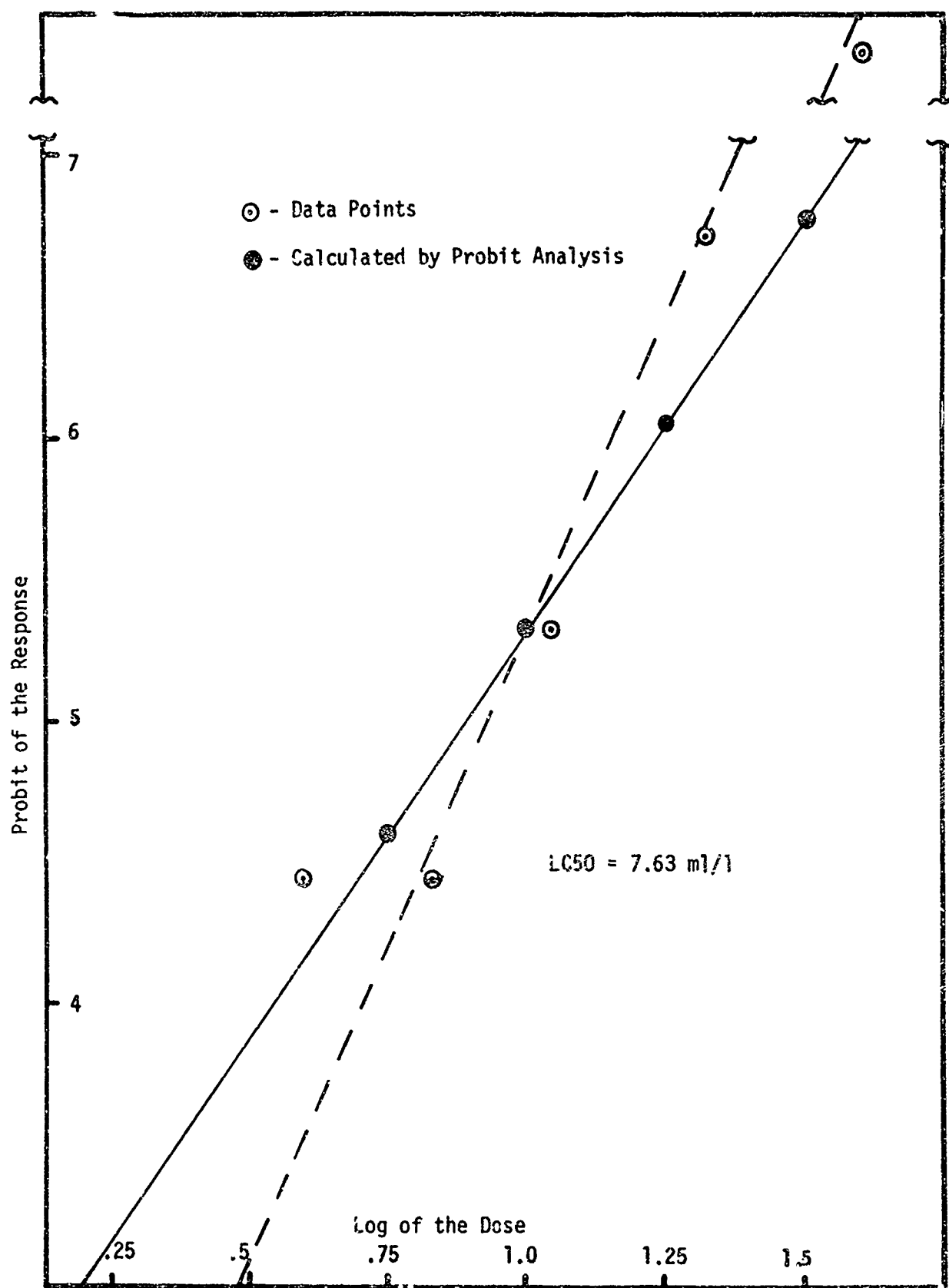


Figure 20

PROBIT REGRESSION OF DESILIVERED EA-4 PHOTOWASTE TO D. MAGNA - 24 HOURS

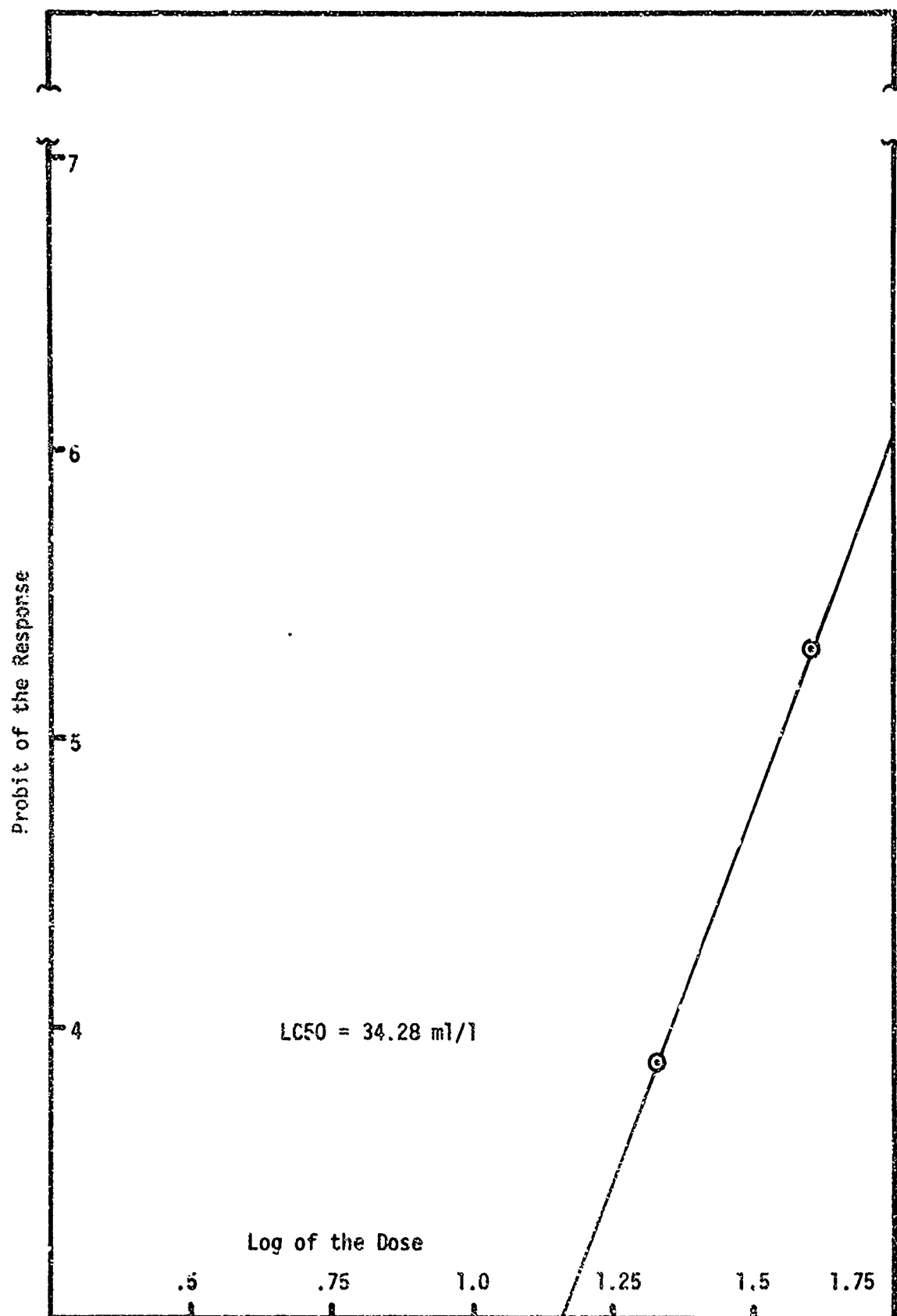


Figure 21

PROBIT REGRESSION LINE OF DESILVERED EA-4 PHOTOWASTE TO D. MAGNA 48 HOURS

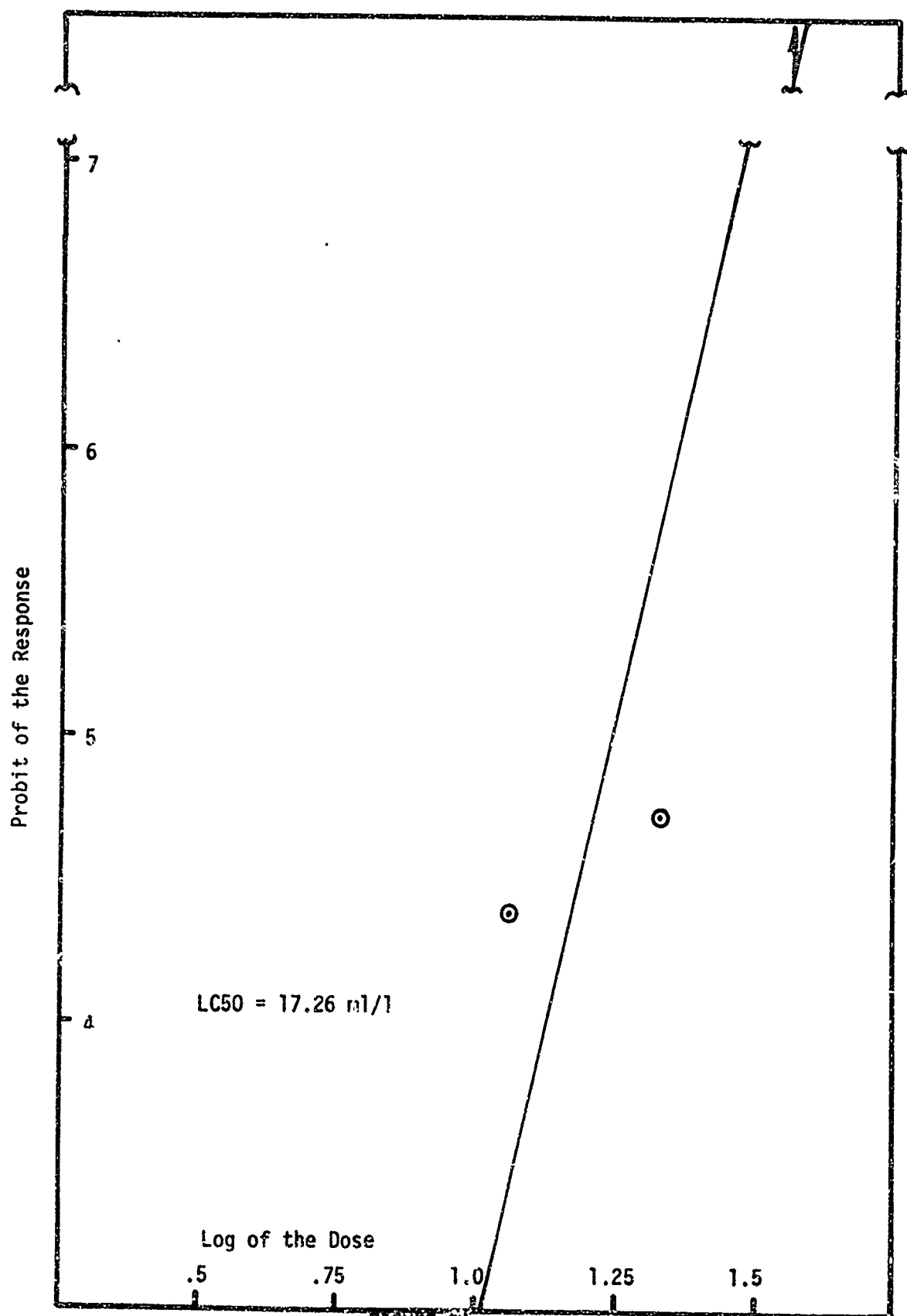


FIGURE 22

PROBIT REGRESSION LINE OF DESILVERED EA-4 WASTE TO D. MAGNA 72 HOURS

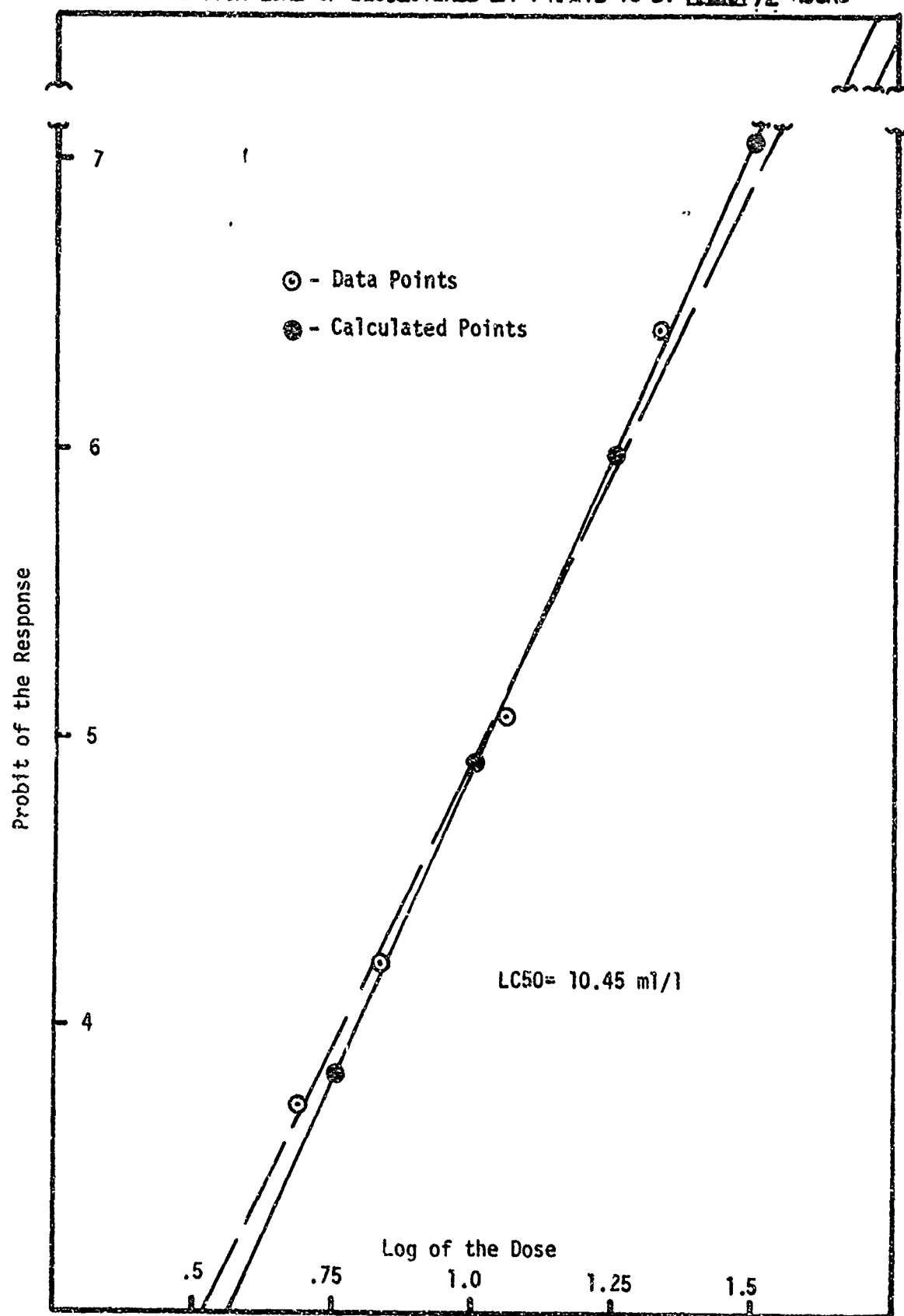


Figure 23
95

PROBIT REGRESSION LINE OF DESILIVERED EA-4 PHOTOWASTE TO D. MAGNA - 96 HOURS

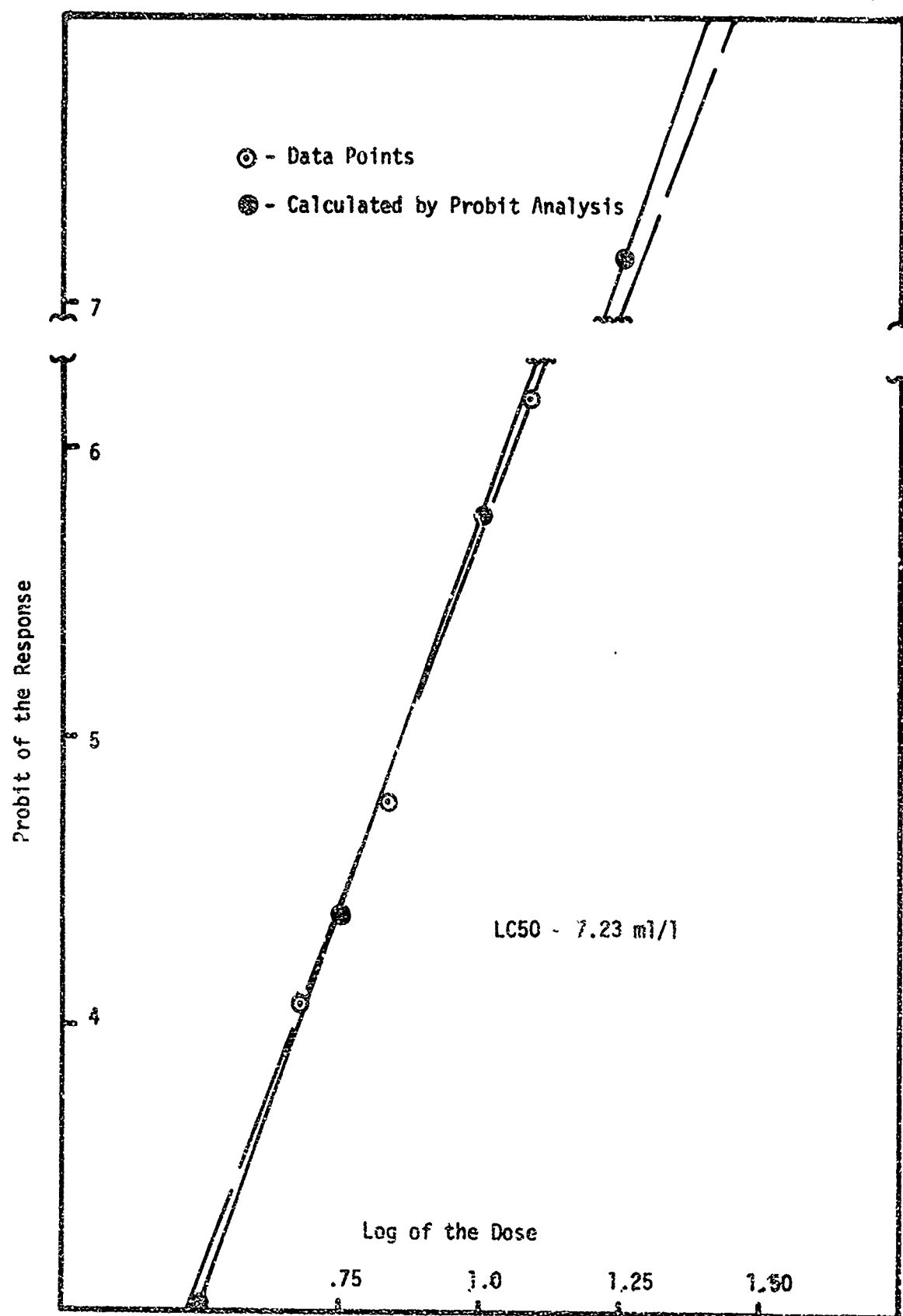


Figure 24
96

PROBIT REGRESSION LINE OF THE EFFLUENT OF AN ACTIVATED SLUDGE PLANT
FED 0.5% EA-4 WASTE TO D. MAGNA - 96 HOURS

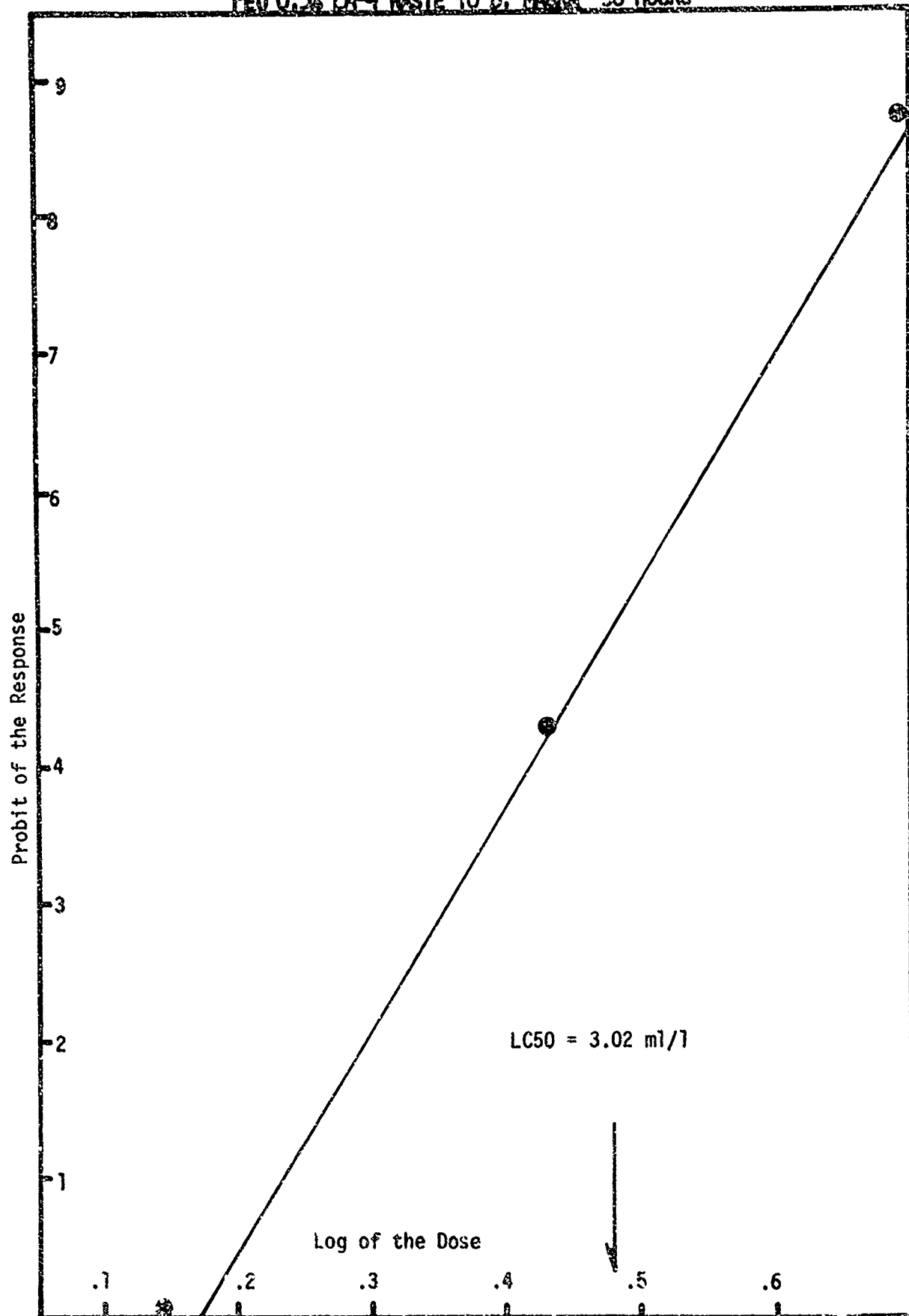


FIGURE 25

APPENDIX 5

PROTOCOL FOR ASSESSING THE ABILITY OF A STREAM REACH TO
ACCEPT THE BOD LOADING OF UNTREATED DESILIVERED EA-4
WASTE - BLEACH EXCLUDED.

APPENDIX 5

Protocol for Assessing the Ability of a Stream Reach to Accept the BOD Loading of Untreated Desilvered EA-4 Waste - Bleach Excluded.

1. Laboratory experience indicates that the following protocol will yield realistic guidelines concerning the ability of a given reach of a stream to accept the BOD loading of untreated, desilvered EA-4 waste generated by the Kodak Ektachrome RT Processor for the period of time necessary for endemic stream organisms to lower the BOD to safe levels. This is a strictly empirical method and has all the limitations inherent in such purely practical procedures. No claim is made concerning theoretical validity; the equations have practical applicability only.

2. The requirement to temporarily dispose of untreated waste must meet the criteria outlined in Executive Order 11507 and 11514. Untreated waste cannot be ordinarily introduced into streams.

3. EA-4 waste must be desilvered and the bleach bath excluded as described in Section III, paragraph c.

4. Aerial photographs of candidate streams and approximate data concerning the volume of flow and the flow rates of the stream reaches must be available prior to site selection.

5. The selected stream must have a total flow of at least 3.4 cubic feet per second (CFS).

6. Classify the stream reach as to rapidity of flow using aerial photographs and the following Table.

TABLE 20
Classification of Swift Flowing Streams

<u>Classification Symbol</u>	<u>Calculation Constant</u>	<u>Description</u>
X	1	Stream consisting of at least 10% riffles or falls. Stream never without riffles for more than 1 hour of flow.
Y	2	Swift stream averaging at least 2.0 feet/sec flow. Surface often broken.
Z	4	Moderately flowing stream with occasionally broken surface. Averaging not less than 1.0 feet/second flow.

Streams with flows less than 1.0 foot/second cannot be safely used for disposal purposes.

7. Using Equation (1) Calculate A - the miles necessary to satisfactorily degrade concentrations up to 0.05% EA-4 waste in the selected stream

Equation 1

$$\text{Miles} = \frac{(\text{ml/min EA-4 chemicals}) (\text{stream flow ft/sec}) (0.1604)}{(\text{CFS of stream flow}) (\text{Temp of stream } ^\circ\text{C})}$$

8. Recheck aerial photo to confirm stream flow characteristics equal to Z persist for at least the distance calculated in paragraph 7. If these stream conditions do persist, disposal of EA-4 waste should be safe for a period of 5-10 days.

a. If the lower reach has a flow of less than 1.0 foot/second, another stream should be selected. If this stream must be used and the

area of lower flow is at least 5 miles below discharge point, the ml/min of EA-4 waste that can be safely discharged into this stream can be calculated by Equation II.

$$\text{Equation II ml/min} = \frac{(67 \times \text{stream CFS}) (T^{\circ}\text{C}) (B/A)}{\text{Stream Classification Constant}}$$

Where A = Value calculated in Paragraph 7.

B = Miles of stream from disposal point to area of less than 1.0 CFS flow (must be at least 5 mi.).

Stream
Classification Constant = Calculation Constant applicable from point of discharge to point B.

9. If two acceptable streams are available, the larger stream should be selected.

10. During operation of the mobile unit, monitor the DO and stream conditions above and 1 and 5 miles below the processing laboratory. Dissolved oxygen in trout and salmon streams must remain 7 ppm or above at all times (low 24 hour reading usually occurs between 0100 and 0500 hours). Most other streams can stand depressions to 5 ppm for short periods. Slime growths on stream bottom indicate pollution and the unit should be moved.