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DEVELOPMENT OF TECHNIQUES FOR DETECTION OF LOW MOLECULAR WEIGHT--ETC(U)

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DEVELOPMENT OF TECHNIQUES FOR DETECTION OF LOW MOLECULAR WEIGHT  
CONTAMINANTS IN PRODUCT WATER FROM WATER PURIFICATION  
OR WATER RE-USE SYSTEMS

FINAL COMPREHENSIVE REPORT

Thomas W. Mix  
Hans Scharen

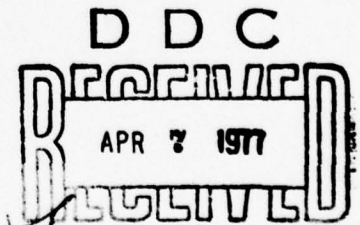
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U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND  
Washington, D. C. 20315

Contract No. DADA17-72-C-2169

Amicon Corporation  
25 Hartwell Avenue  
Lexington, Massachusetts 02173



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TOC	Wastewater	
Total Organic Carbon	Permanganate	
MUST	Carbon Adsorption	
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A permanganate colorimeter instrument to monitor the quality of MUST product water has been developed and successfully tested at the breadboard level. During the program it was demonstrated that (1) aldehydes are the last of the constituents of MUST RO permeate to be ozonated, (2) residual MUST aldehydes (principally acetaldehyde) rapidly reduce permanganate solutions, and (3) the degree of permanganate reduction may be easily quantitated colorimetrically and is directly proportional to residual MUST water contamination. The colorimeter and required hardware is judged low-cost, rugged, simple, and reliable.		

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I. SUMMARY

For three years Amicon Corporation has been under contract to the U. S. Army Medical Research and Development Command for the Development of Techniques for Detection of Low Molecular Weight Contaminants in Product Water from Water Purification or Water Reuse Systems.

Principal emphasis during the latter portion of the program has centered on the development of a permanganate colorimeter instrument to monitor the quality of MUST product water which has been processed through both reverse osmosis and ozonation. The selection of the permanganate colorimeter was based on a number of factors:

1. The rate limiting step in the ozonation of the MUST RO permeate appears to be the ozonation of aldehydes (acetaldehyde, in particular). These aldehydes may therefore be expected to accumulate and to represent an appreciable fraction of the TOC in the product water;
2. Aldehydes are rapidly oxidized by basic permanganate solutions (as are alcohols and many other organic compounds);
3. Permanganate and manganate ions have high extinction coefficients and are rapidly detectable in low concentration spectrophotometrically; and
4. A colorimeter is compatible with the requirements for low cost, ruggedness, simplicity, reliability, and field operation.

In addition, the technique offers the fail-safe backup of a simple color comparator.

Initial testing of a breadboard colorimeter with a MUST pilot unit tends to confirm the suitability of the technique for MUST product quality monitoring but is insufficient in scope to establish it with the requisite certainty. Additional work with MUST pilot plant samples and with known or suspected contaminants is therefore recommended.

Additional work done under the program deals with the following subjects:

1. A preliminary investigation of a spectrophotometer technique to monitor the rate of decay of ozone concentration as a measure of product water purity.

2. Carbon adsorption experiments related to monitoring of carbon column adsorption when this was a processing step under consideration for the MUST; and
3. A preliminary study of the monitoring of the combination of reverse osmosis and ozonation and/or carbon adsorption as tertiary treatment steps for the output from a municipal treatment plant.

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## II. OZONATION STUDIES

### A. Ozonation Equipment

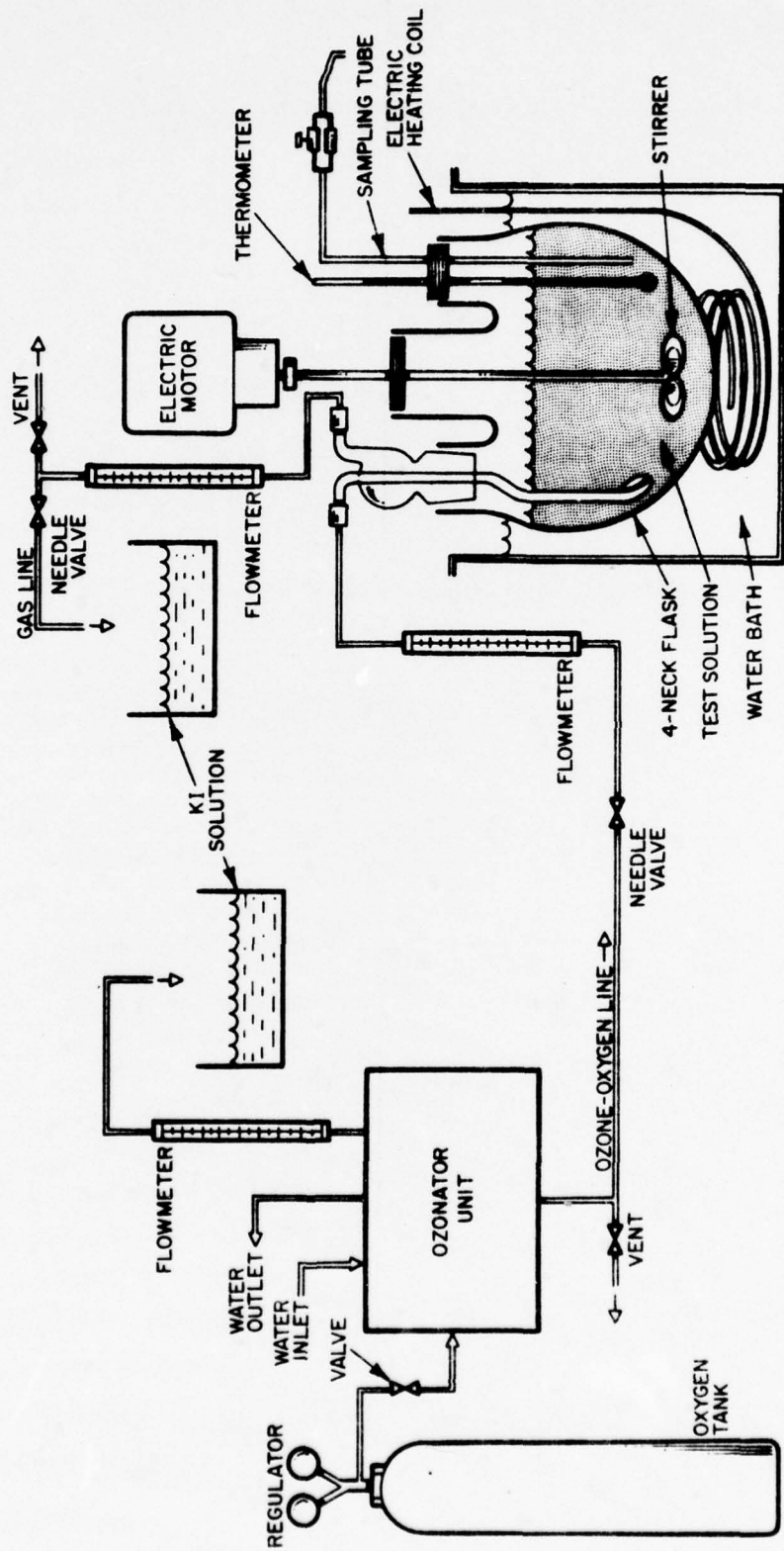
The apparatus used for the ozonation studies is shown in Figure 1 and consists of a four-necked reaction flask containing a high shear stirrer, a gas dispersion tube, a sample withdrawal tube, and a thermometer. An automatically-controlled temperature bath was used to keep the temperature within  $\pm 1^{\circ}\text{C}$  of the reaction temperature. The ozone was generated by a Welsbach Ozonator (Model T-816) with an ozone production rate of 1.7% by weight or 16 g/hour using oxygen. In order to make the system airtight, all the joints were fitted with Teflon sleeves. A special shaft of stainless steel with a Teflon bearing was machined for the high shear dispersator disc. Stainless steel, glass and Teflon were used as piping material since they are all resistant to attack by ozone.

### B. Experimental Procedures

#### Ethanol Ozonation

A 100 ppm solution of ethanol was added to the reaction flask and ozonated for three hours. Samples for TOC analysis and ethanol determination were withdrawn periodically every 30 minutes; the last sample being taken at 180 minutes. All TOC analysis was performed at Fram Corporation, Pawtucket, Rhode Island. For TOC analysis, a Beckman TOC Analyzer was used. Ethanol concentrations were determined by oxidizing with acidified dichromate and measuring the disappearance of the characteristic dichromate color at 549 nm with a spectrophotometer. The O.D. values obtained were then compared to a previously prepared standard reference curve from which the actual concentration in mg/liter was read<sup>(1)</sup>. Ozonations of acetic acid, acetaldehyde, quinone, oxalic acid, formaldehyde, methanol, glycine, and MUST RO permeate were performed in a similar manner. A 100 ppm solution of each compound was prepared. They were ozonated for three hours each and samples were withdrawn for TOC analysis. A portion of the acetic acid sample was used for titration with sodium hydroxide and a portion of the quinone sample was used for the spectrophotometric determination of quinone (Figure 2). The ozonation conditions typically used were: the ozone concentration, 38 mg/liter; gas flow, 0.5 liters/minute; and the reaction temperature,  $60^{\circ}\text{C}$ .

FIGURE 1



OZONATION TEST SET-UP



$\lambda$  max. 245 nm

● Standard Curve

▼ Quinone samples after treatment with ozone

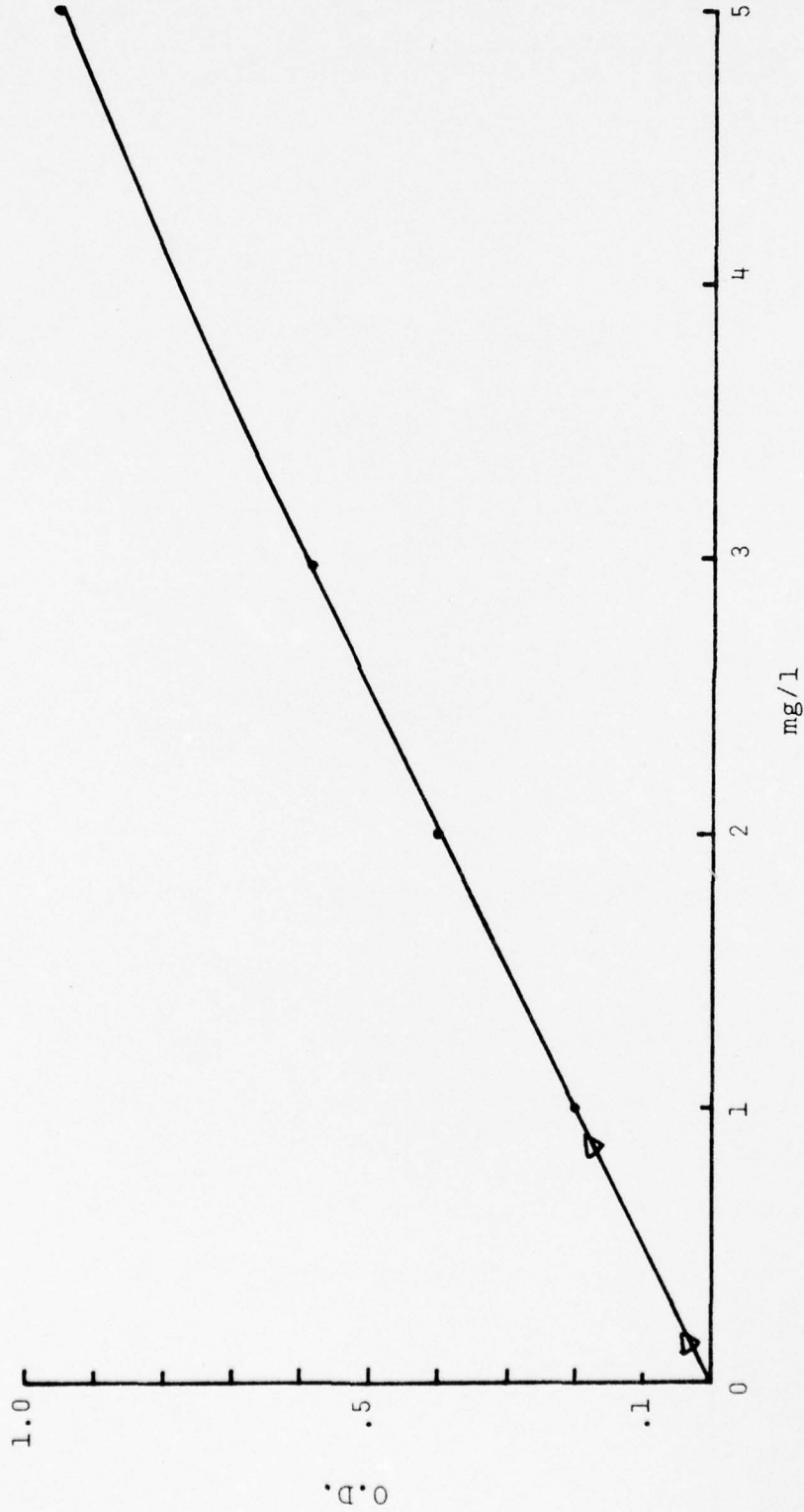


FIGURE 2  
DETERMINATION OF QUINONE

C. Interpretation of Data

Figure 3 presents curves for the disappearance of TOC with time for a number of chemicals which were selected as candidate tracers for a variety of reasons.

Ethanol and methanol were selected because they have been identified as principal contaminants in typical MUST reverse osmosis permeate<sup>(2,3)</sup>. Acetaldehyde, acetic acid, and oxalic acid were selected because they are potential compounds formed in the progressive oxidation of ethanol and possibly other alcohols.

Formaldehyde was selected because it is likely to be formed in the ozonation of methanol.

Acetic acid was also selected because Professor Wiberg of Yale University<sup>(4)</sup> pointed out that it is frequently part of the oxidation pathway for aliphatic compounds (and aromatic compounds where ring opening occurs) and is likely to be the most oxidation resistant step in the pathway. Similarly, quinone was selected because it is frequently the rate limiting step in the oxidation of many aromatic compounds<sup>(4)</sup>.

Glycine was selected because amino acids can be detected in very small concentrations through use of fluorescent dye indicators, such as Roche's Fluram<sup>(5)</sup>. The rapid oxidation of both glycine and quinone makes them unsuitable as tracers. The normally oxidation-resistant quinone is probably susceptible to attack by ozone at its double bonds. Acetic acid is also not useful as a tracer but for a different reason: it is essentially impervious to attack by ozone. Since MUST reverse osmosis permeate is susceptible to oxidation by ozone and does not show a sufficient lowering of pH during ozonation to indicate appreciable accumulation of acid, acetic acid is not formed to any significant extent during MUST permeate ozonation at neutral pHs. Because of acetic acid's inertness, it can be tolerated by the body in fairly high concentration, making its removal from the MUST water to be recycled of limited importance.

Oxalic acid, which is a likely intermediate in many of the oxidation sequences, is relatively rapidly ozonated, which is also consistent with the slight change in pH as ozonation proceeds. Methanol and formaldehyde also disappear relatively rapidly under ozonation conditions. The broad scatter in the formaldehyde data (Figure 4) is not understood but may perhaps be attributable to some polymeric material or particulate impurities in the formaldehyde solution used.

OZONATION STUDIES

FIGURE 3

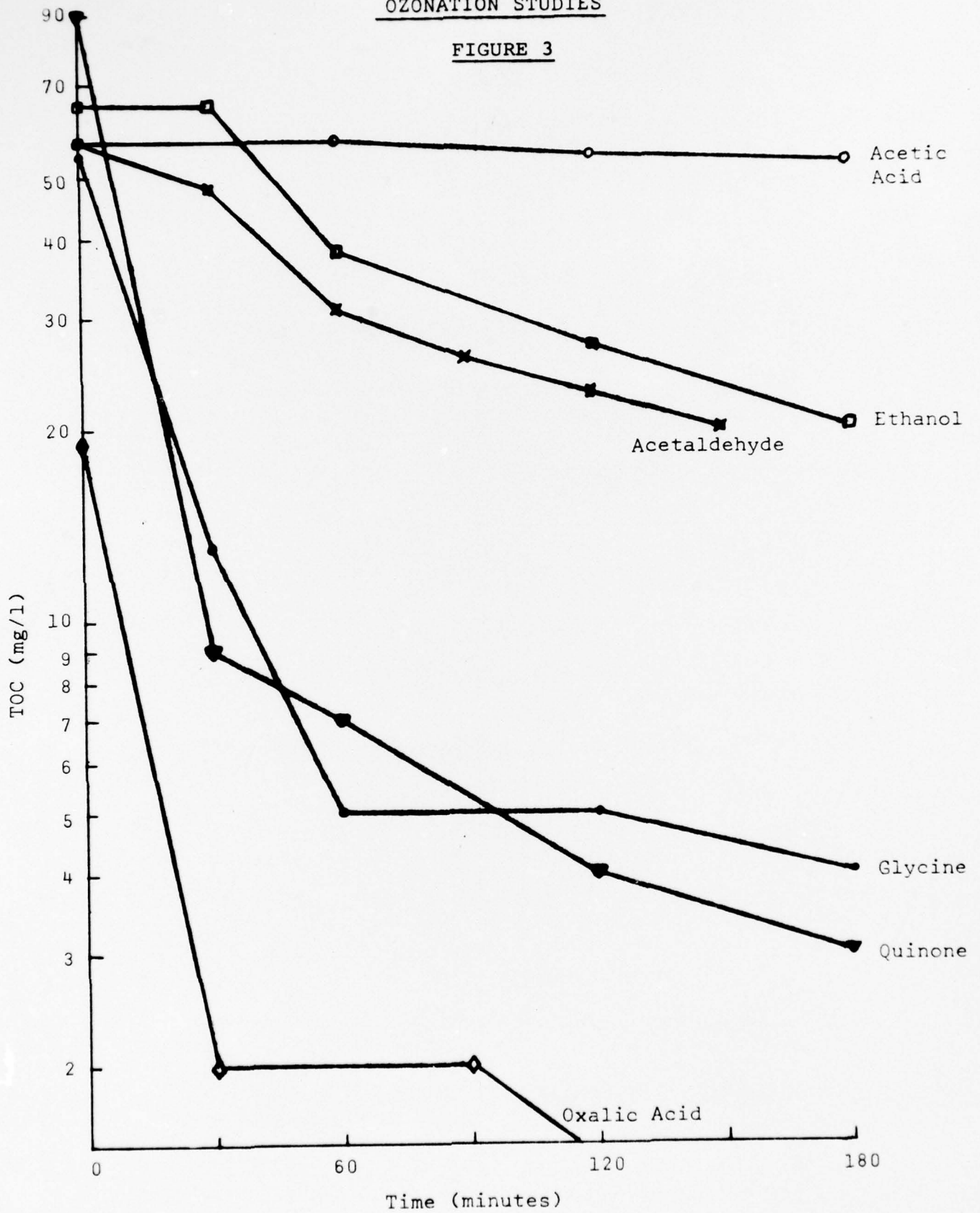




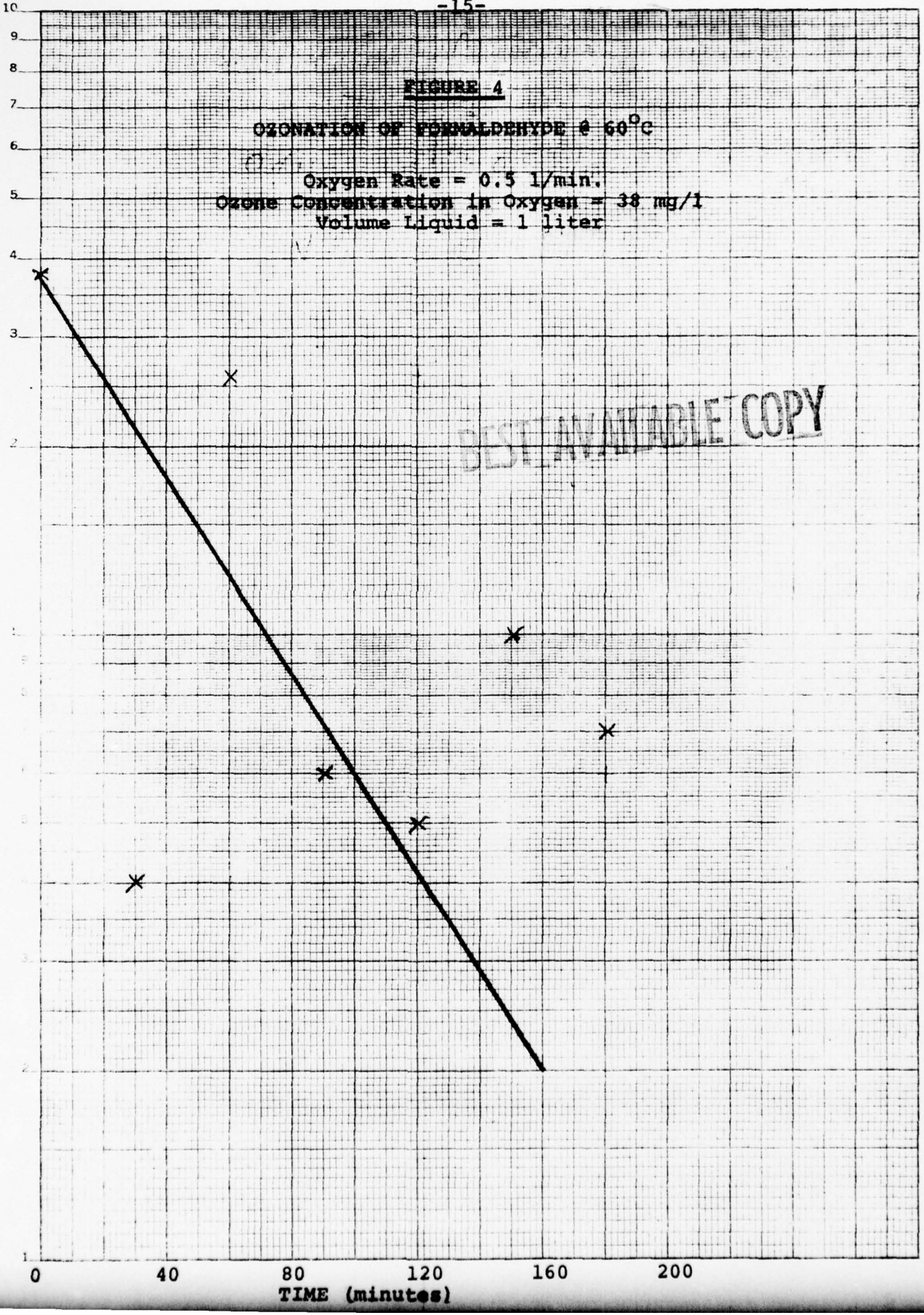
FIGURE 4

OZONATION OF FORMALDEHYDE @ 60°C

Oxygen Rate = 0.5 l/min.  
Ozone Concentration in Oxygen = 38 mg/l  
Volume Liquid = 1 liter

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2 CYCLES X 100 DIVISIONS  
RUFFEL & LINDNER CO.





Both ethanol and acetaldehyde, however, have TOC disappearance characteristics quite similar to those of the MUST RO permeate (Figure 5). The similarity among the three TOC disappearance curves suggests that acetaldehyde disappearance is the rate limiting step for all three. This is confirmed by studies of the rate of ethanol disappearance using potassium dichromate which is specific in the time allotted for reaction<sup>(6)</sup>. The rate of disappearance of ethyl alcohol during ozonation, as measured by dichromate disappearance, shown in Figure 6, is much more rapid than the rate of intermediary oxidation product of ethanol which is relatively resistant to ozonation. There are two possible pathways for ethanol oxidation: one is through acetaldehyde to oxalic acid, which is favored by basic conditions, and the other to acetic acid, which is favored by acidic conditions. The measured pH of the ethanol solution before and after ozonation and the known dissociation constants for acetic and oxalic acids indicate that after ozonation, these acids, if present, should be completely ionized. Their concentration may, therefore, be estimated from the pH since electrical neutrality requires that the anion concentration equal the difference between the hydrogen ion concentration and the hydroxyl ion concentration. This difference is small enough to indicate that there are only negligible levels of either acetic acid or oxalic acid present. Acetaldehyde does, therefore, appear to be the rate limiting step in the ozonation of ethyl alcohol to CO<sub>2</sub> and may, therefore, be an appropriate monitor through which the effectiveness of the ozonation step may be followed provided a sensitive enough method of detection can be developed.

The rate of volatilization (gas stripping) of acetaldehyde may be estimated from its known activity coefficient at infinite dilution<sup>(7)</sup> and vapor pressure<sup>(7)</sup> using the equation:

$$\ln (x_i/x_t) = \frac{G\alpha P^0}{V\pi} \quad (1)$$

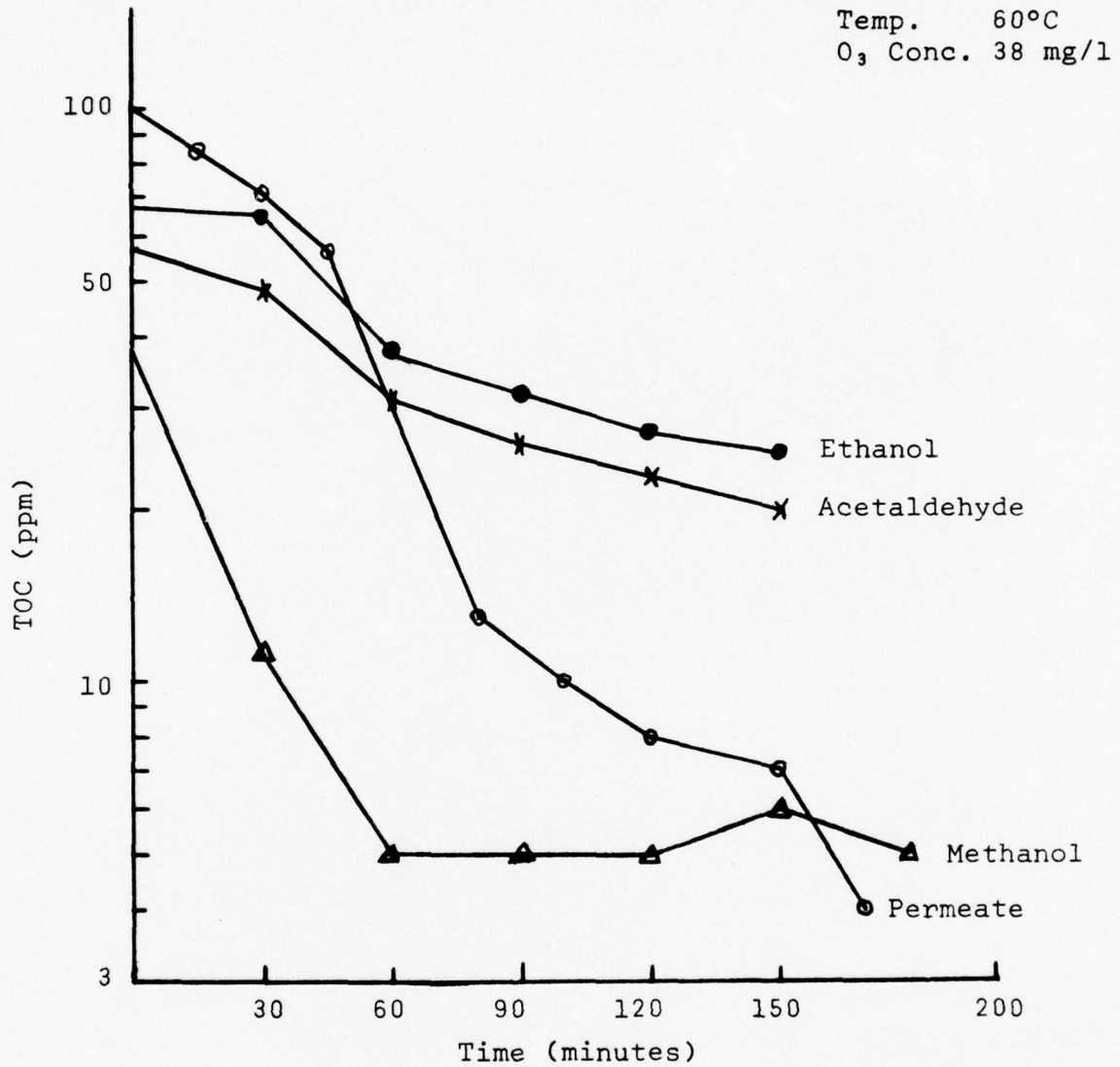
where  $x_t$  = concentration of acetaldehyde in water at time,  $t$

$x_i$  = initial acetaldehyde concentration

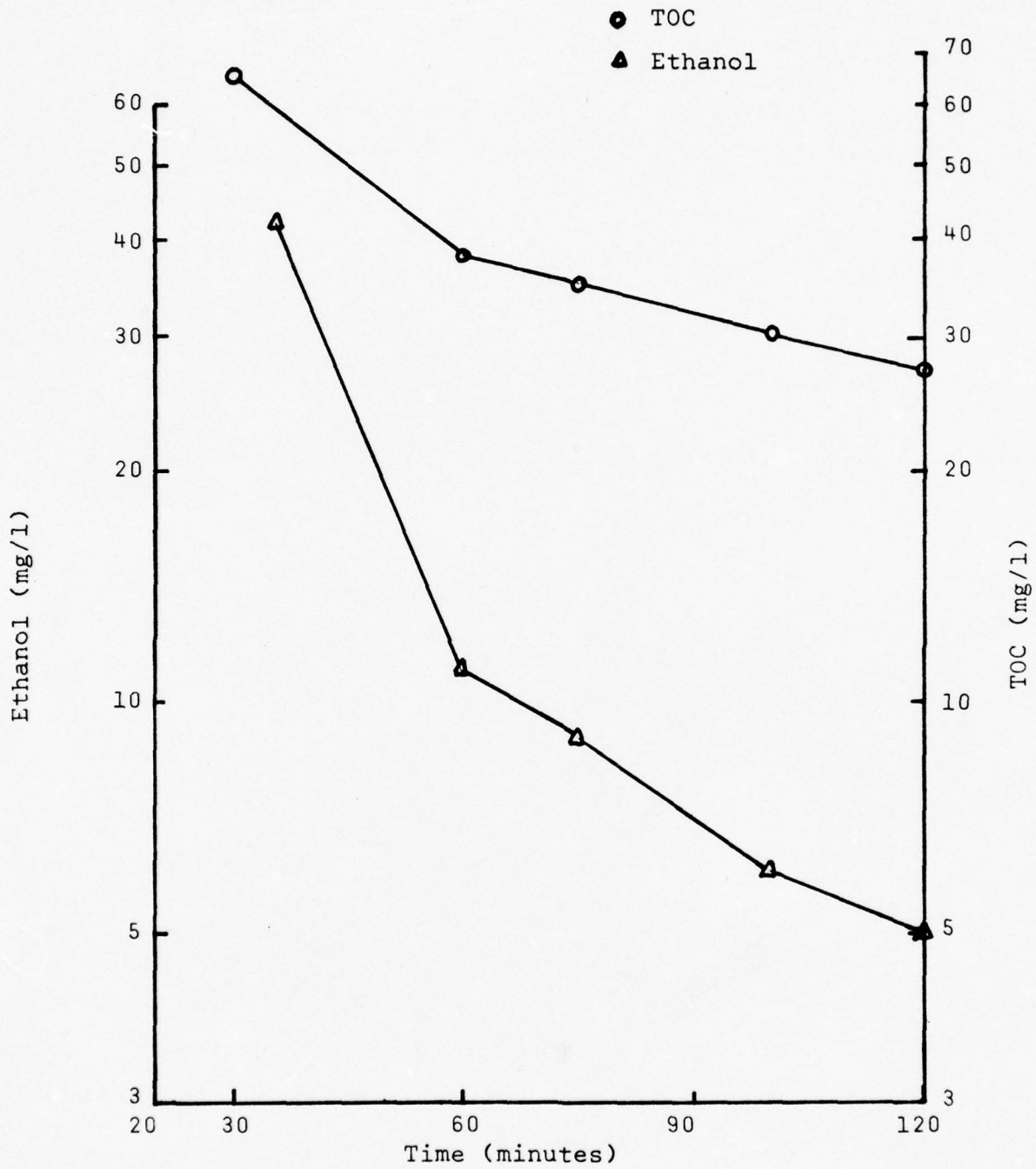
$G$  = oxygen supply rate, g moles/min

$V$  = liquid reservoir holdup, g moles

FIGURE 5



TOC REDUCTION OF MUST PERMEATE (X-RAY WASTE)  
AT pH 6.5 AND A 100 PPM ACETALDEHYDE SOLUTION,  
A 100 PPM ETHANOL SOLUTION  
AND A 100 PPM METHANOL SOLUTION



**FIGURE 6**  
DETERMINATION OF RESIDUAL ETHANOL WITH DICHROMATE  
METHOD AFTER OZONATION

$\alpha$  = activity coefficient for acetaldehyde  
in water at infinite dilution and 60°C

$P^{\circ}$  = vapor pressure of acetaldehyde at 60°C,  
atm

$\pi$  = atmospheric pressure, atm

$t$  = time, minutes

For the acetaldehyde ozonation,  $G \approx 0.021$  g/moles/  
min.,  $V = 55.5$  g moles,  $\alpha \approx 4.75 \frac{P^{\circ}}{\pi} = 4.05$ , and  $\ln$   
 $(x_i/x_t) = .0073t$ .

As may be seen from Figure 7, the disappearance of  
acetaldehyde may be accounted for entirely by  
stripping.

For ethyl alcohol, however, the volatilization (gas  
stripping) rate is given by the equation:

$$\ln x_i/x_t = .0076t$$

As may be seen in Figure 8, gas stripping makes only  
a very minor contribution to the disappearance of  
ethanol.

For formaldehyde, the very low activity coefficient  
in aqueous solution<sup>(8)</sup> more than compensates for  
the high vapor pressure of the pure material, so  
that gas stripping contributes negligibly to its  
loss during ozonation.

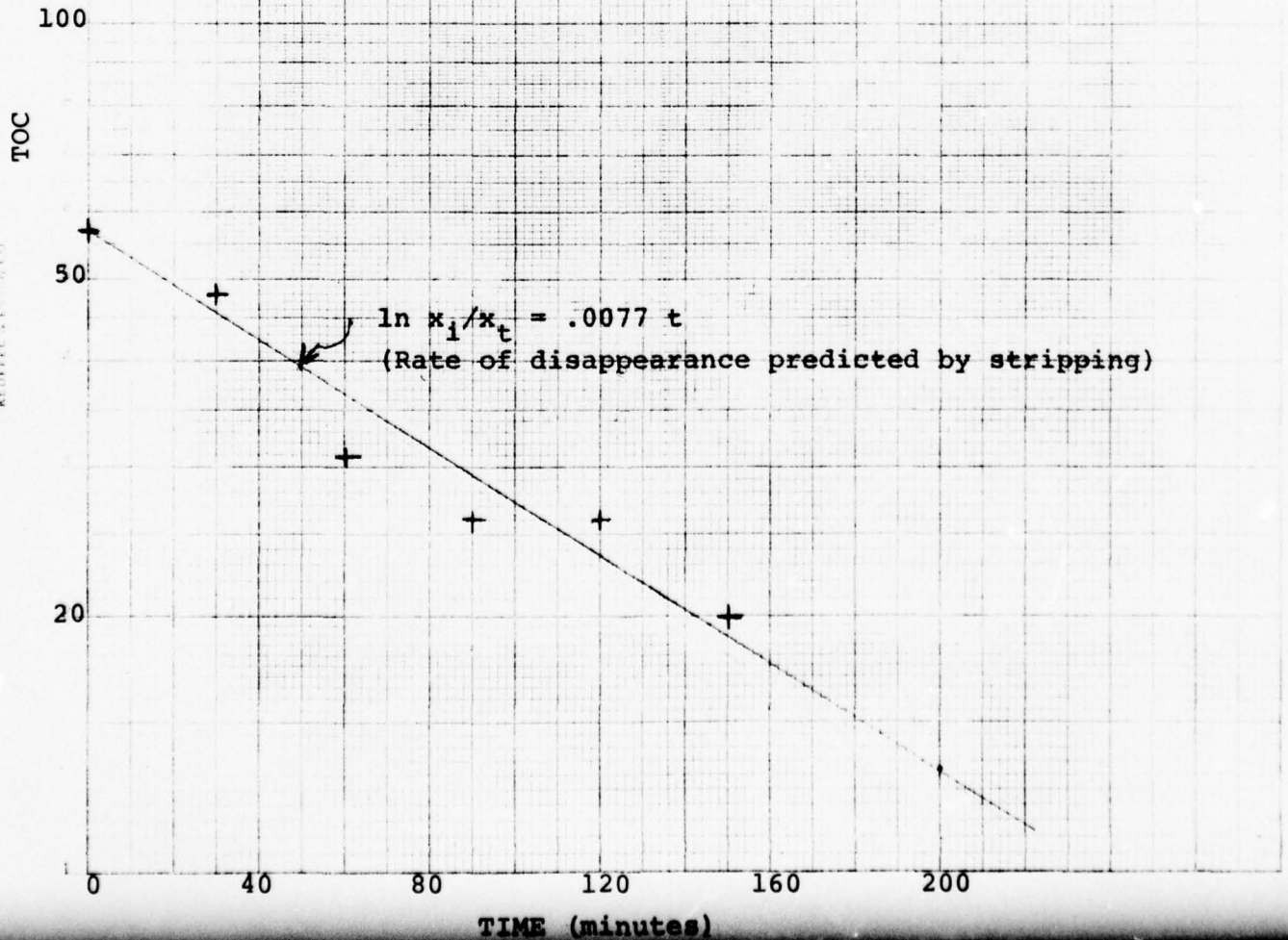
Potassium permanganate is a strong oxidizing agent  
affecting many organic compounds in acid, neutral,  
or basic solution. During preliminary investigations,  
it was found that raw and treated MUST waste water  
when added to a roughly 100 ppm basic potassium  
permanganate solution effected a noticeable change  
in the deeply purple color. Aldehydes are known to  
be oxidized in basic potassium permanganate and when  
roughly stoichiometric amounts of potassium  
permanganate and acetaldehyde were allowed to react  
in basic solution at room temperature, a noticeable  
color change occurred in less than ten minutes.  
The results of these preliminary experiments were  
encouraging enough to warrant investigation into a  
colorimeter monitor for ozonated MUST product water  
based on permanganate oxidation of residual con-  
taminants.

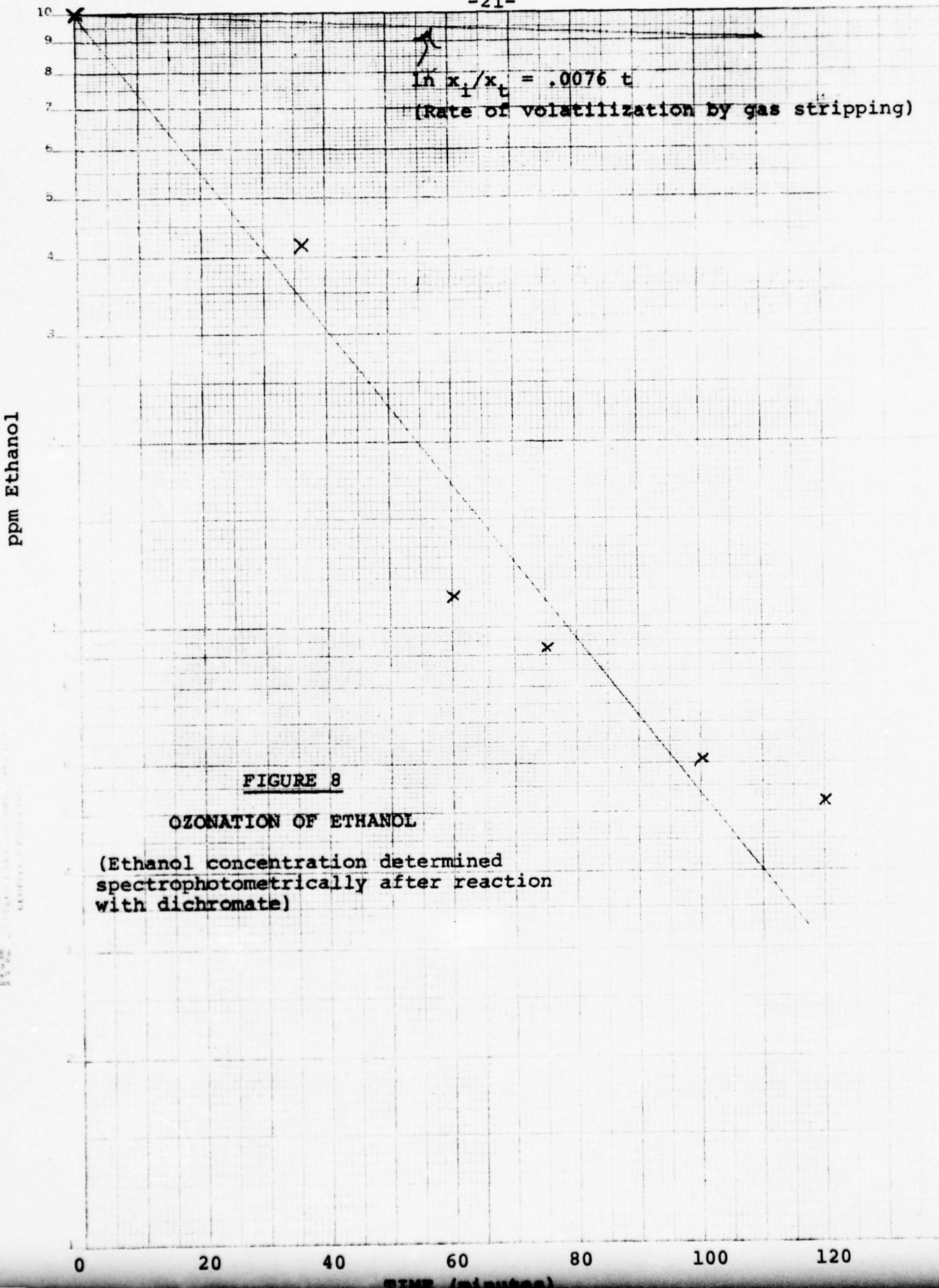


FIGURE 7

OZONATION OF ACETALDEHYDE AT 60°C

Liquid Volume = 1 liter  
Oxygen Flow Rate = 0.5 l/min.  
Ozone Concentration in Oxygen = 38 mg/l





### III. MONITORING TECHNIQUES

#### A. Development of Acetaldehyde Assay Using Potassium Permanganate in Basic Solution

A stock solution of 10,000 ppm acetaldehyde in distilled water was prepared. Appropriate dilutions were made and samples of 5, 10, and 20 ppm were prepared. A slight excess of basic potassium permanganate was added to the reaction flasks which were allowed to stand at room temperature for 20 minutes. The total reaction volume of each flask was 5 ml and the pH was between 12 and 12.5. A blank was prepared in the same way using distilled water. The spectral absorption curve of each solution was then determined using a Beckman 505 Scanning Spectrophotometer. For all measurements, the reference cell contained a solution of potassium hydroxide with a pH of approximately 12. The solutions were scanned from 200 nm to 600 nm. Figure 9 shows the absorption spectrum of the various samples. From the spectra, it is obvious that suitable wavelengths for measurements of permanganate and manganate concentrations in a solution are 522 and 426 nm, consistent with literature findings<sup>(6)</sup>. The absorption at the former wavelength is due mainly to permanganate and at the latter mainly due to manganate.

If permanganate ion is reduced no further than manganate ion, the ratio of the decrease in optical density at 522 nm to the increase in optical density at 426 nm may be shown to be:

$$\frac{(\Delta OD)_{522}}{(\Delta OD)_{426}} = 11.54$$

From Figure 9 it is clear that the  $\Delta OD$  ratio experimentally observed is less. For 5 ppm acetaldehyde, the experimental ratio is 1.28; for 10 ppm, it is 1.23; and for 20 ppm, it is 1.12. Since acetaldehyde and its oxidation products should have negligible absorption at 522 nm and 426 nm, and since reduction of permanganate to manganese dioxide is likely to occur, the observed discrepancy is doubtless attributable to the production of colloidal manganese dioxide. Typically the size of colloidal manganese dioxide particles produced will be of the order of the wavelength of light<sup>(4)</sup>. The scattering effect is likely to be greater at the shorter wavelength



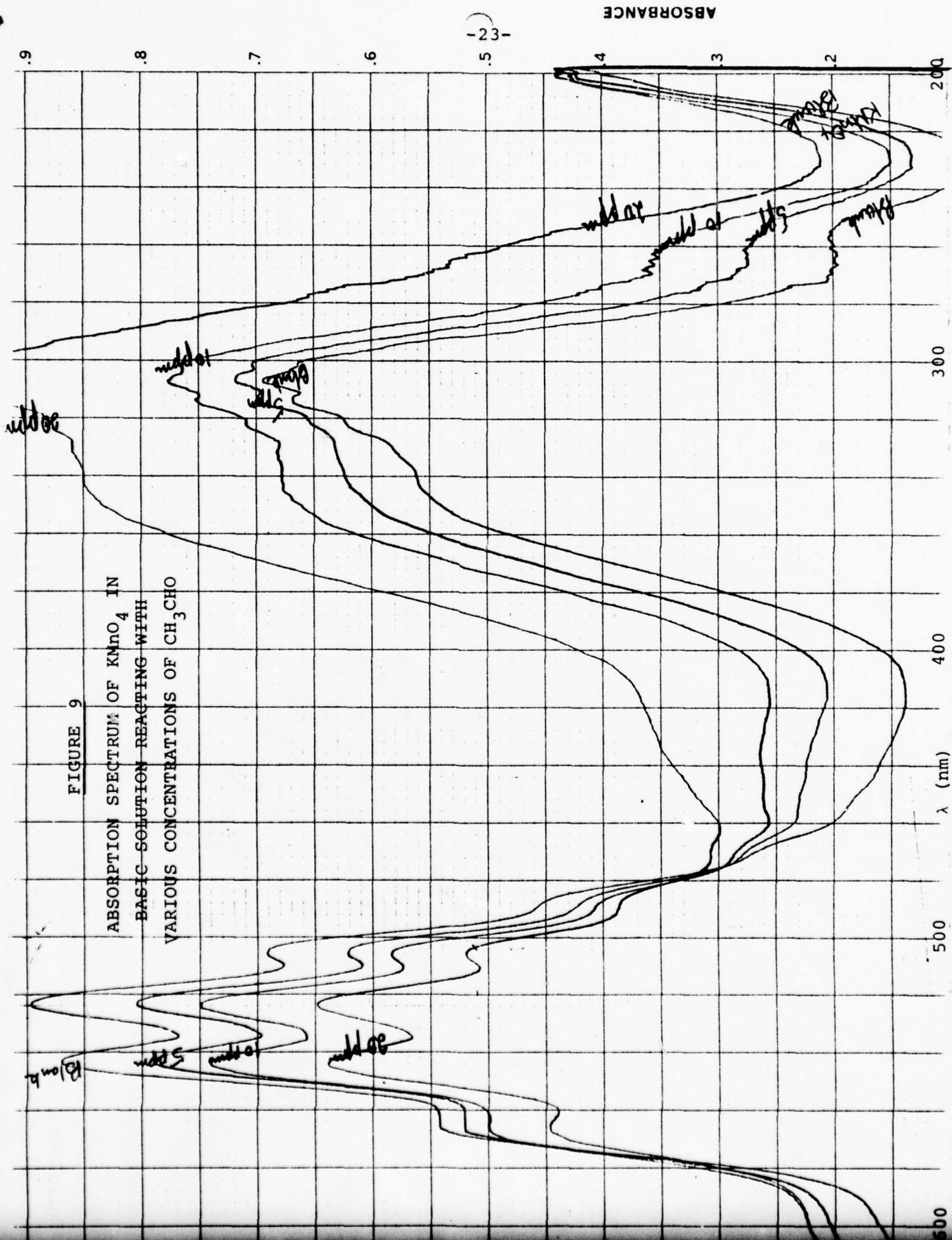


FIGURE 9

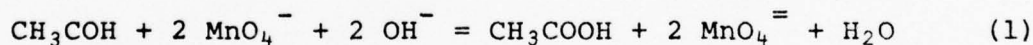
ABSORPTION SPECTRUM OF  $KMnO_4$  IN  
 BASIC SOLUTION REACTING WITH  
 VARIOUS CONCENTRATIONS OF  $CH_3CHO$



so that a relatively small ratio of manganese dioxide to manganate ion could account for the discrepancy in  $\Delta$  OD ratios. The formation of manganese dioxide can be suppressed by increasing the concentration of base and maintaining a sufficient excess of permanganate ion (see later discussion and Figures 13, 14, and 15).

Calibration curves, which show the disappearance of permanganate at 522 nm or the appearance of manganate at 426 nm for a given temperature as a function of ppm of acetaldehyde, should be adequate for estimation of acetaldehyde concentration in solution provided adequate time is allowed for completion of the reaction. Thus, the next step was to investigate the reaction at 522 nm and 426 nm and to determine optimum time and temperature for the reaction.

Stoichiometric requirements for permanganate oxidation of aldehydes in alkaline solution are not clear because oxidation to the corresponding carboxylic acid competes with carbon-carbon bond scission<sup>(6)</sup>. Oxidation to the corresponding carboxylic acid in alkaline solution requires 2 moles of permanganate per mole of aldehyde, as indicated in Equation 1, while carbon-carbon bond cleavage can consume many more moles of permanganate per mole of aldehyde<sup>(6)</sup>.



The U. S. Army Medical Research and Development Command has established as an interim standard, a TOC level of 5 ppm as the maximum acceptable for treated MUST waste water reuse. The acetaldehyde concentration in the treated MUST waste water must, therefore, be less than 10 ppm since this corresponds to a TOC of 5 ppm, presuming no other compounds present. As treatment processes are improved and optimized, the acceptable TOC level will eventually be reduced further. The range of the calibration curve for an acetaldehyde assay was therefore selected as from 1-10 ppm. Based upon reaction (1) above, the stoichiometric amount of  $\text{KMnO}_4$  to react with 10 ppm of  $\text{CH}_3\text{COH}$  is 72 ppm. A solution A was prepared in the following way: 1 ml of ( $\text{KMnO}_4$ ) solution containing 7200 mg/liter plus 4 ml distilled water plus 5 ml 1 MKOH solution were added to a reagent flask. The final  $\text{KMnO}_4$  concentration of this solution is 720 mg/l. Since  $\text{KMnO}_4$  undergoes slight decomposition in basic solution, reagent A has to be prepared freshly before each test. To

3 ml of distilled water (for blank) 0.3 ml of solution A was added. This gave a final  $\text{KMnO}_4$  reaction concentration of 65.4 mg/liter and a pH of 12.2. The reaction was followed spectrophotometrically at 522 nm and OD readings were recorded at two-minute intervals. This procedure was repeated with 1, 5, and 10 ppm acetaldehyde solutions replacing the distilled water. As mentioned above, at 522 nm the disappearance of permanganate is measured. The entire procedure was then repeated but this time the measuring wavelength of the spectrophotometer was set at 426 nm and the appearance of manganese dioxide is determined. The results of these experiments are shown in Figures 10 and 11. The reactions at both wavelengths were followed over a period of one hour. In Figures 10 and 11, the results were plotted up to 20 minutes since the curves were fairly straight from that point onwards after the blank values were subtracted. It is also evident from the two figures that the curves reach a near maximum level at different times; when observed at 522 nm, it is about six minutes and at 426 nm, it is about ten minutes. The longer time to reach equilibrium at 426 nm is probably due to the kinetics of formation and growth of colloidal manganese dioxide particles. These particles are likely to scatter light more at 426 nm than at 522 nm. As short as possible a reaction time is essential so that variations of acetaldehyde levels in the processed effluent stream can be detected quickly.

Advantages of monitoring the 522 nm wavelength are the shorter time to a constant reading and the higher extinction coefficient for the permanganate ion. Advantages of monitoring the 426 nm wavelength are the possibly higher sensitivity of the colorimeter in the low OD range and the additional  $\Delta$  O.D. resulting from manganese dioxide production, provided the effect is reproducible.

Standard curves were obtained at both 522 nm and at 426 nm, with the 522 nm readings taken after six minutes at room temperature for reaction, and those at 426 nm taken after 20 minutes. These curves are presented in Figure 12. Additional data were obtained using a Cary 14 Recording Spectrophotometer to study the effect of base concentration on the OD readings and on permanganate decomposition. An increase in base level should make manganese dioxide less likely to form but should accelerate the slow

FIGURE 10: REACTION BETWEEN  $\text{KMnO}_4$  AND  $\text{CH}_3\text{COH}$  IN BASIC SOLUTION

Final  $[\text{KMnO}_4] = 65.4 \text{ mg/l}$

Final pH 12.2

$\lambda$  522 nm

O.D. values corrected for blanks (Blank - Reading)

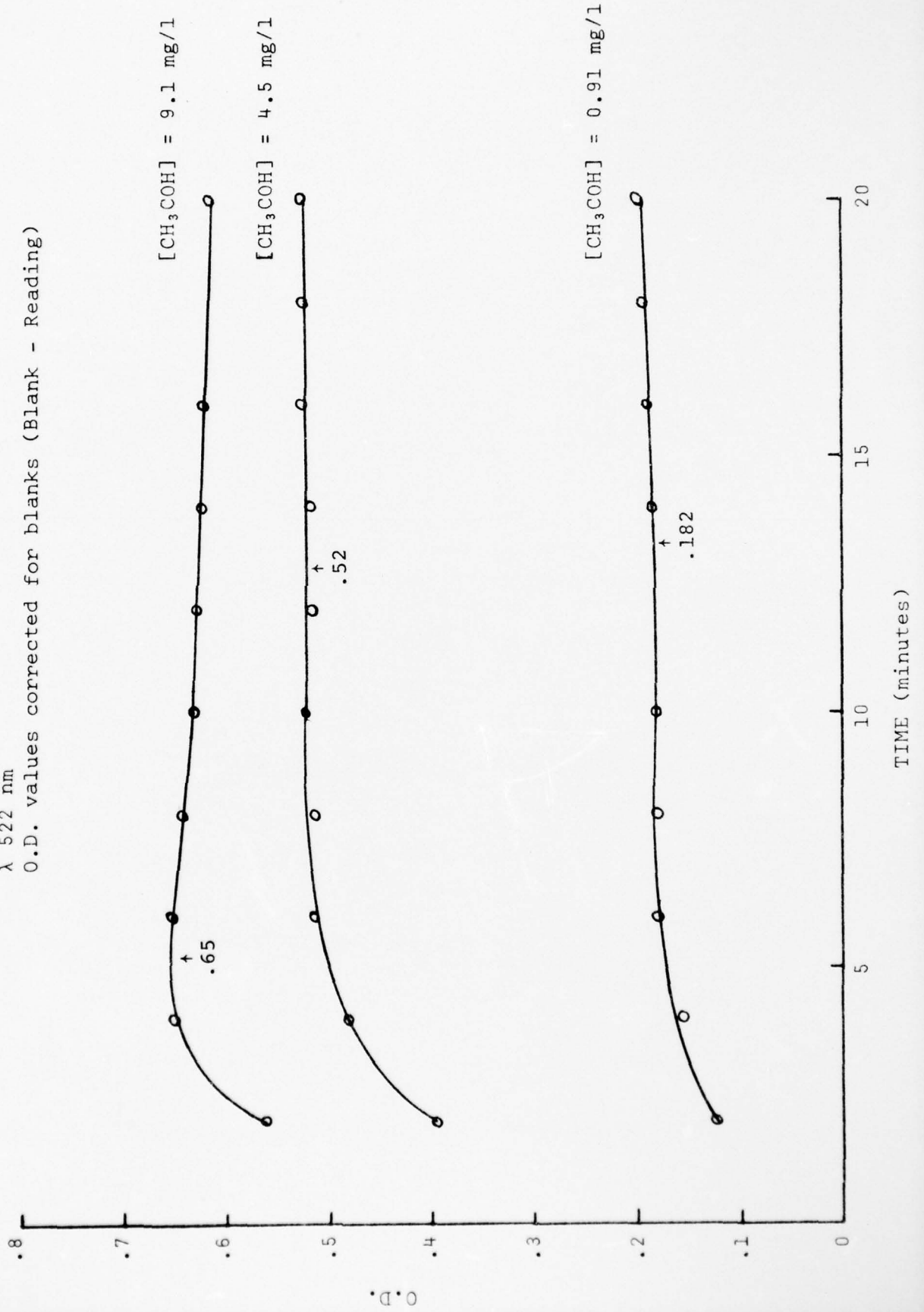


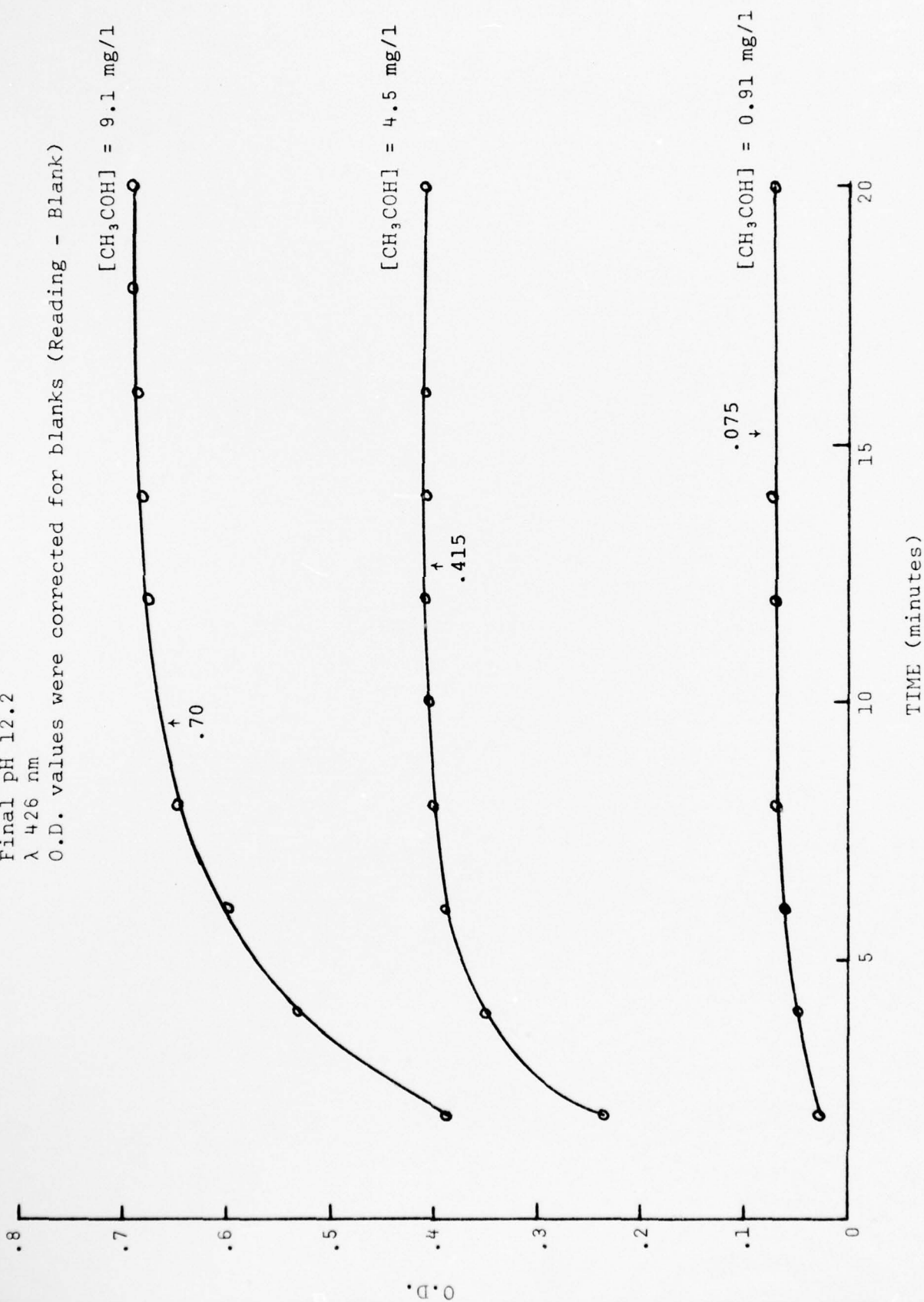
FIGURE 11: REACTION BETWEEN  $\text{KMnO}_4$  AND  $\text{CH}_3\text{COH}$  IN BASIC SOLUTION

Final  $[\text{KMnO}_4] = 65.4 \text{ mg/l}$

Final pH 12.2

$\lambda = 426 \text{ nm}$

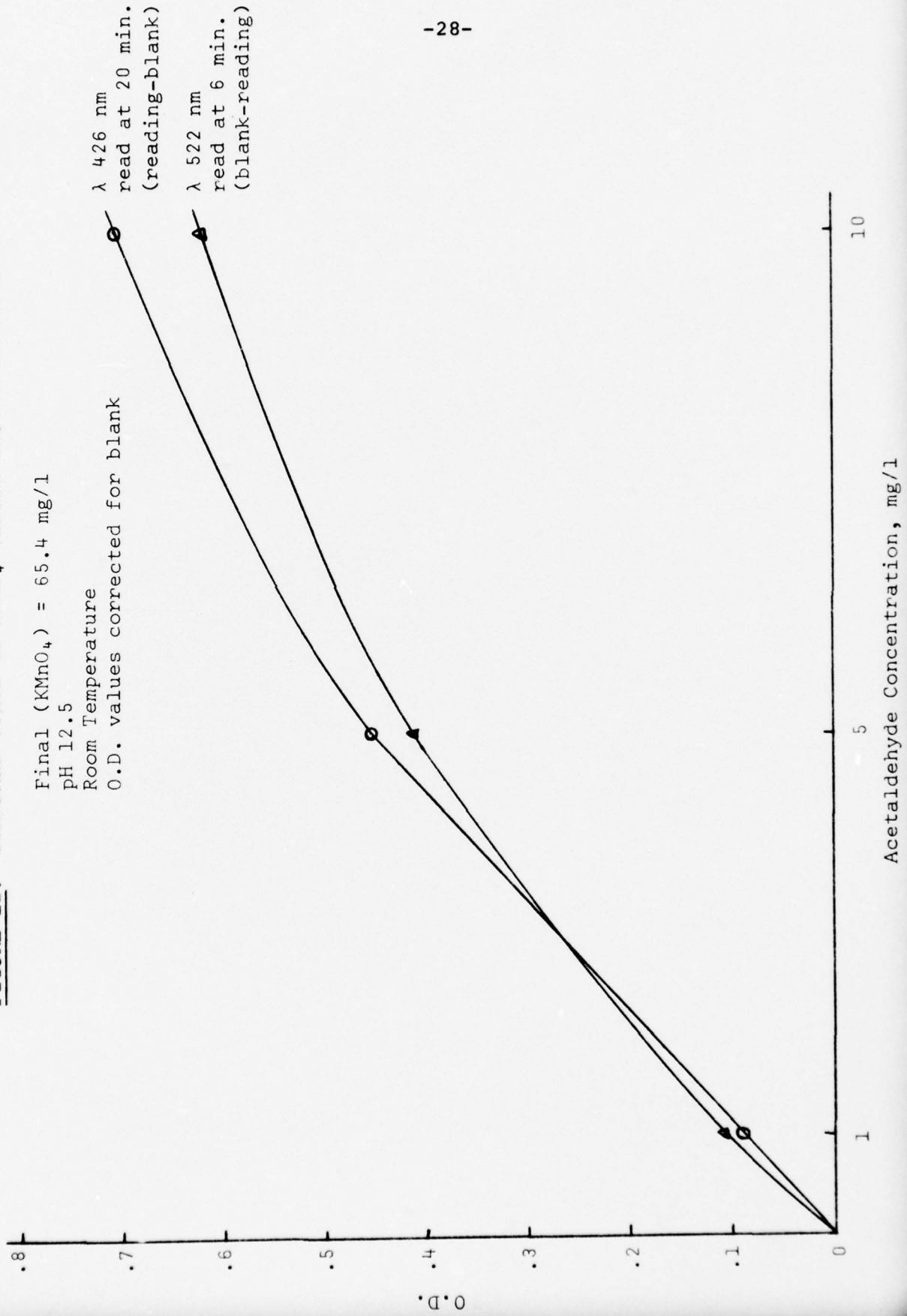
O.D. values were corrected for blanks (Reading - Blank)





**FIGURE 12:** STANDARD CURVE OF  $\text{KMnO}_4$  VERSUS  $\text{CH}_3\text{CHO}$  IN BASIC SOLUTION

Final ( $\text{KMnO}_4$ ) = 65.4 mg/l  
pH 12.5  
Room Temperature  
O.D. values corrected for blank



autodecomposition of permanganate. Results are presented in Figures 13, 14, and 15 and Table 0. A higher base concentration does result in slightly more reaction and in a higher  $\Delta OD_{522}/\Delta OD_{426}$  ratio and is, therefore, helpful in suppressing manganese dioxide formation. It has negligible effect on permanganate decomposition kinetics for the time scale of interest. A higher base concentration is therefore desirable.

From Figure 14 the moles of permanganate which react with a mole of acetaldehyde may be estimated to be at least 2.8. The true number is somewhat higher because the manganese dioxide scattering at 522 nm raises the OD and therefore makes the permanganate disappearance appear to be smaller than it is.

B. Preliminary Design Work on a Continuous Flow Monitoring Technique

Permanganate oxidation of acetaldehyde appears to meet the requirements for a continuous monitoring technique. If necessary, ethanol or acetaldehyde may be added continuously into the process stream upstream of the ozonation reactor in an appropriate concentration and acetaldehyde monitored continuously in the effluent stream. Permanganate will also oxidize ethanol, although more slowly; if ethanol is added as a tracer, the amount of tracer utilized and the permanganate oxidation conditions must be selected so as to guarantee tripping of the system alarm should the ozonation reactor be malfunctioning so as not even to oxidize ethanol to acetaldehyde.

One schematic for a permanganate colorimeter monitor is shown in Figure 16.  $KMnO_4$  and  $KOH$  are stored in separate tanks. Originally distilled water and RO permeate are also stored in tanks but once the system is on line, RO permeate is fed to the monitor via a direct line from the processed effluent stream and distilled water is produced by an appropriate unit on a continuous basis. The reagents are fed into two Vortex mixers with volumes of about one ml and tangential inlets into the mixing chambers. From the Vortex mixers the reaction mixture enters static mixers and coils of appropriate holdup to give the desired residence time for reaction. The length of the coils is chosen to allow adequate reaction time; from Figure 10, a residence time of about six minutes is desirable. From the coils, the reaction mixture enters flow-through cells of a double beam colorimeter where the difference in optical density between the two streams is determined. The reaction mixture of the sample stream consists

**FIGURE 13:**  $\text{KMnO}_4$  REACTION WITH  $\text{CH}_3\text{CHO}$  IN BASIC SOLUTION FOR 10 MINUTES @  $21^\circ\text{C}$  AS A FUNCTION OF WAVELENGTH AND  $\{\text{OH}^-\}$  CONCENTRATION

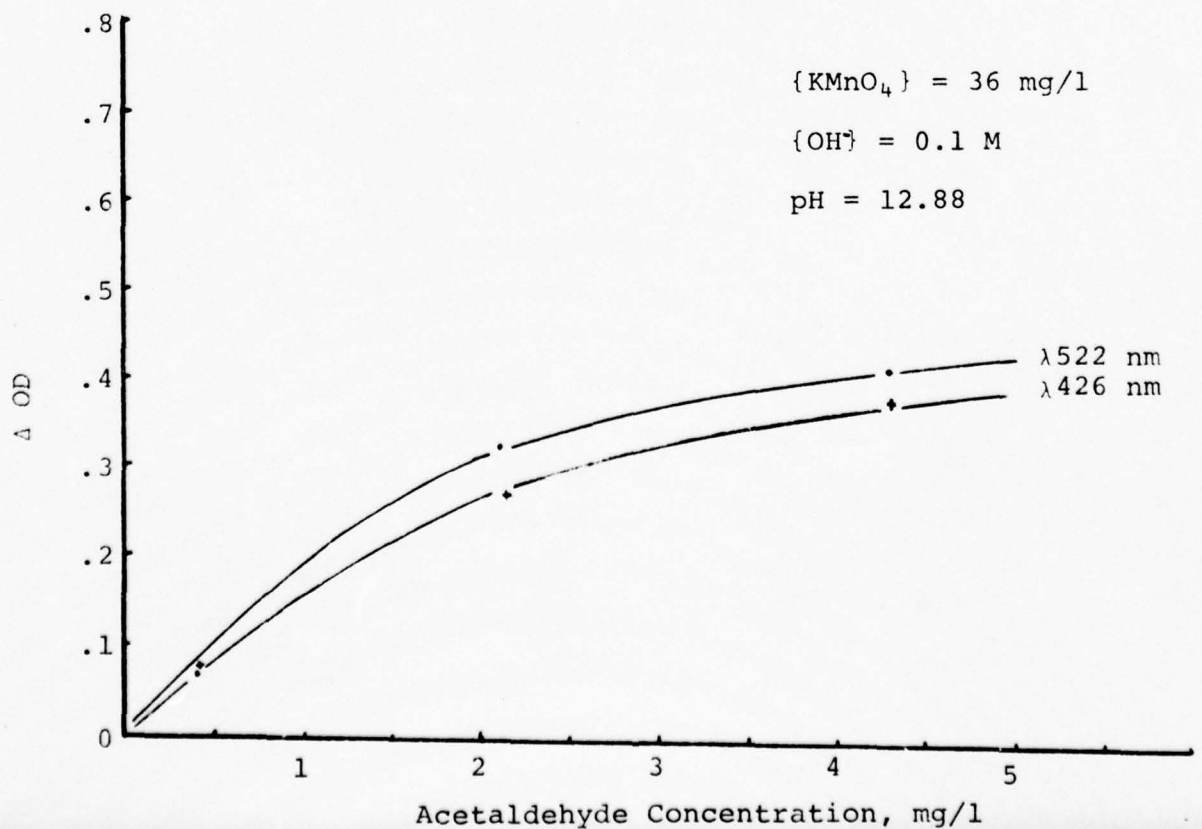
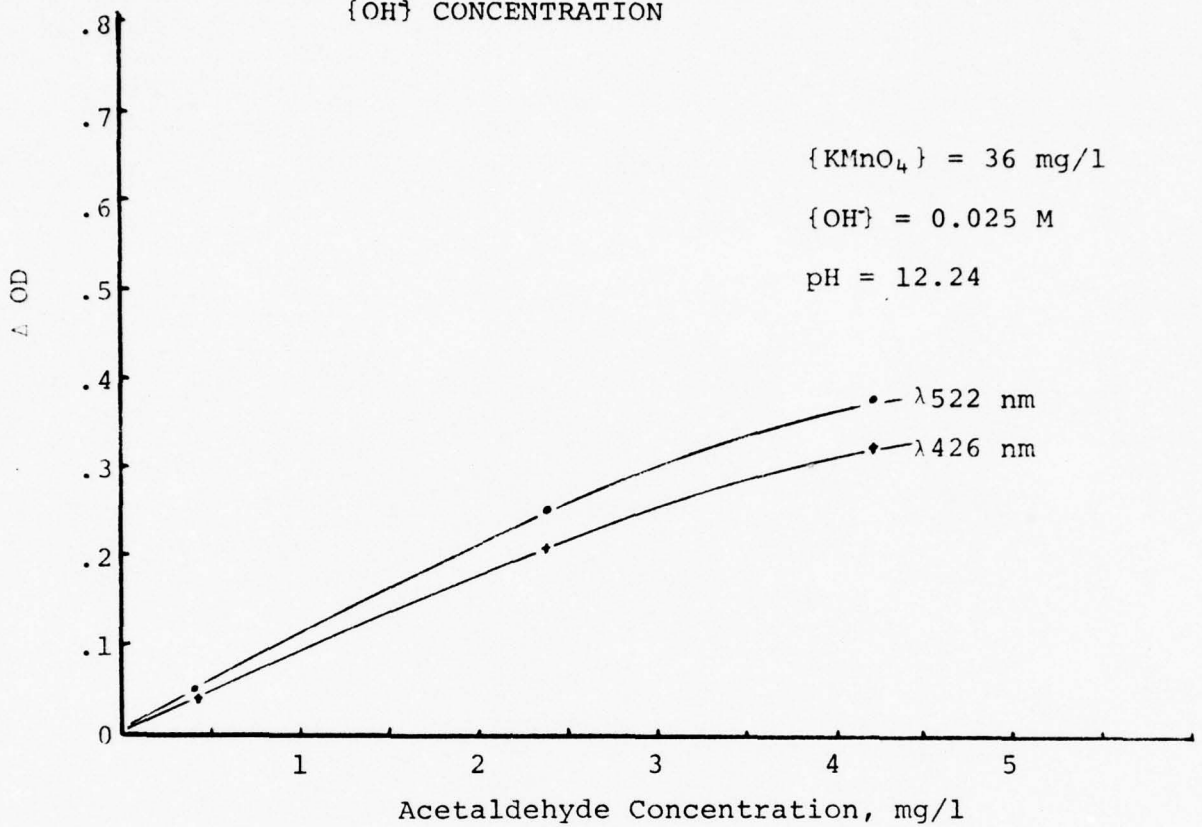


FIGURE 14:  $\text{KMnO}_4$  REACTION WITH  $\text{CH}_3\text{CHO}$  IN BASIC SOLUTION FOR 10 MINUTES AT  $21^\circ\text{C}$  AS A FUNCTION OF WAVELENGTH AND  $\{\text{OH}^-\}$  CONCENTRATION

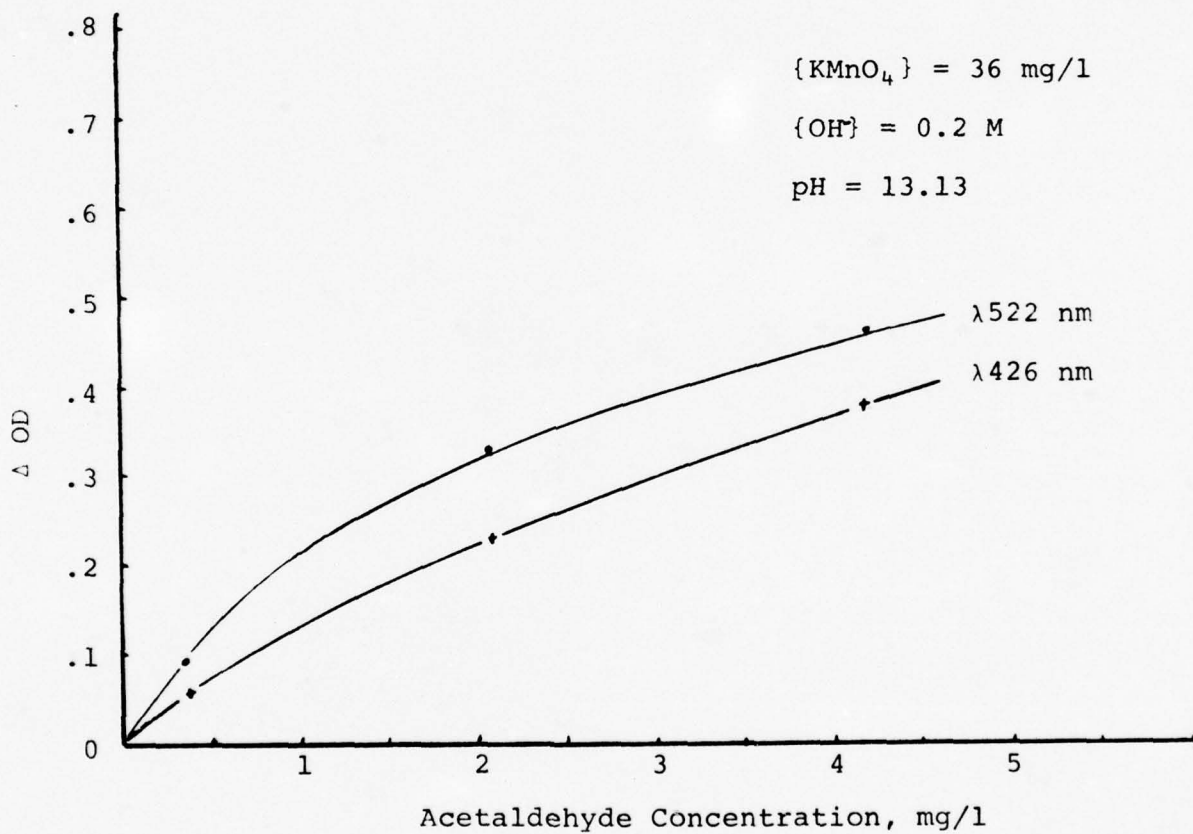




FIGURE 15:  $\text{KMnO}_4$  DECOMPOSITION IN BASIC SOLUTION AT ROOM TEMPERATURE

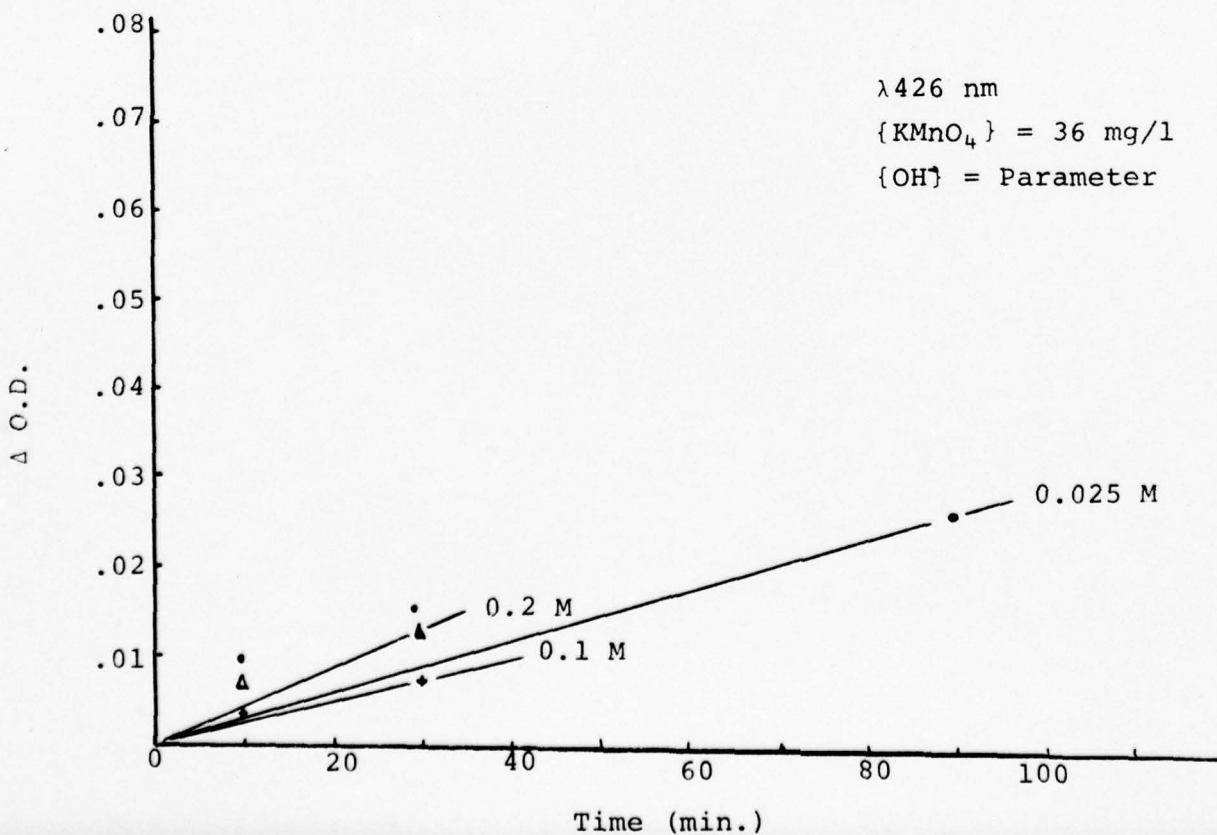
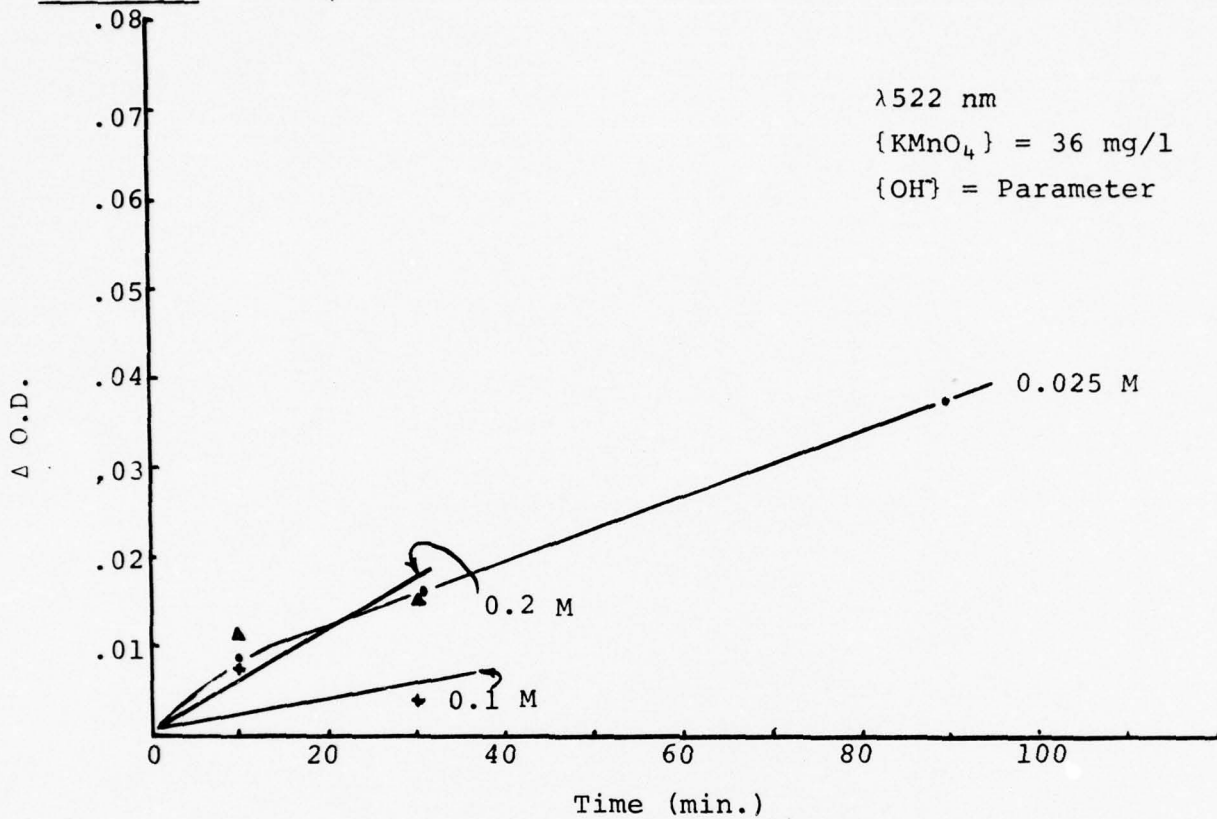
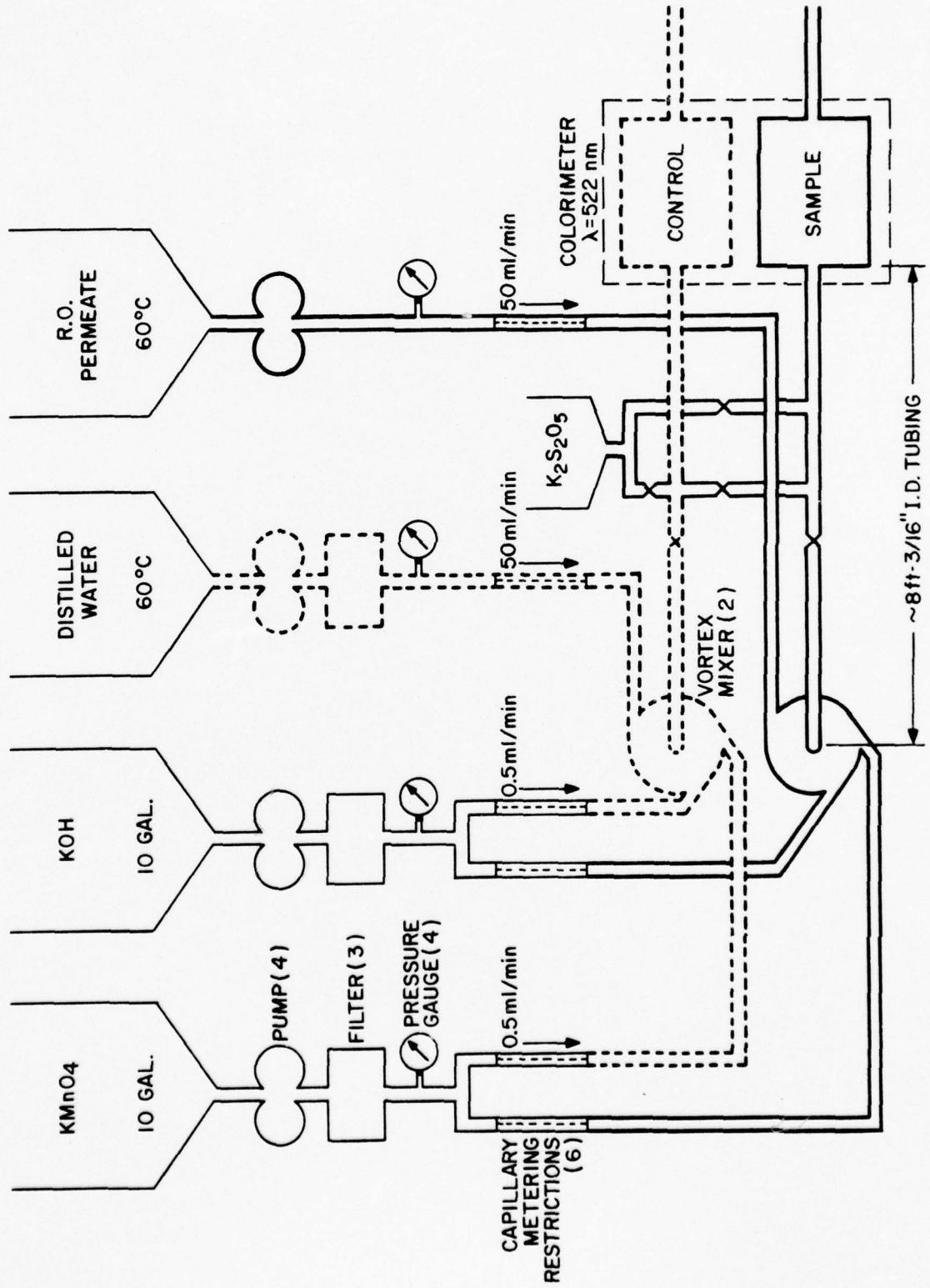


TABLE 0

20 HOUR  $\Delta$  OD OF  $\text{KMnO}_4$  DECOMPOSITION AS A  
FUNCTION OF  $\{\text{OH}\}$  AT WAVELENGTHS OF 426 AND 522 nm

<u><math>\{\text{OH}\}</math></u>	<u><math>\lambda 426</math> nm</u>	<u><math>\lambda 522</math> nm</u>
0.0 M	0.026	0.006
0.025 M	0.120	0.025

FIGURE 16  
**SCHEMATIC OF PERMANGANATE COLORIMETER MONITOR**



of  $\text{KMnO}_4$ , KOH and RO effluent whereas the reference stream contains  $\text{KMnO}_4$ , KOH, and distilled water.

The colorimeter compares the disappearance of permanganate ion in ozonated MUST RO permeate, to which potassium permanganate has been added, with the permanganate ion concentration in a distilled water sample, to which an identical quantity of permanganate solution has been added.

A second schematic for a permanganate colorimeter monitor is shown in Figure 17. MUST product water to which permanganate and base have been added is fed to the colorimeter cells in series. The mixture is fed to the first cell immediately after mixing; then flows through a coil of suitable holdup to allow time for the permanganate oxidation to occur; and then flows through the second colorimeter cell. The residence time between the mixing of the permanganate and base with the product water and the flow of this solution through the first colorimeter cell is kept sufficiently short that relatively little reaction occurs during this time. This first cell can then serve as a reference cell and indicate the concentration of permanganate prior to reaction while the second cell indicates the permanganate concentration after reaction.

A third schematic for a permanganate colorimeter is shown in Figure 18. A colorimeter with a single cell is used and the absorbance at two wavelengths is monitored. MUST Product water to which permanganate and base have been added and which has flowed through a delay coil which provides the requisite residence time for reaction to occur, flows through the cell. One of the monitoring wavelengths is 522 nm to monitor the disappearance of permanganate as a result of reaction. The second wavelength may be chosen at an isosbestic point where the absorbance of permanganate and manganate ions are equal; the absorbance of the cell at this wavelength will then be independent of the relative concentrations of these two ions but will vary directly as the sum of their concentrations. The absorbance at this second wavelength then provides the requisite information on the concentration of permanganate added which is provided by the reference cell in the two previously discussed colorimeter schematics.

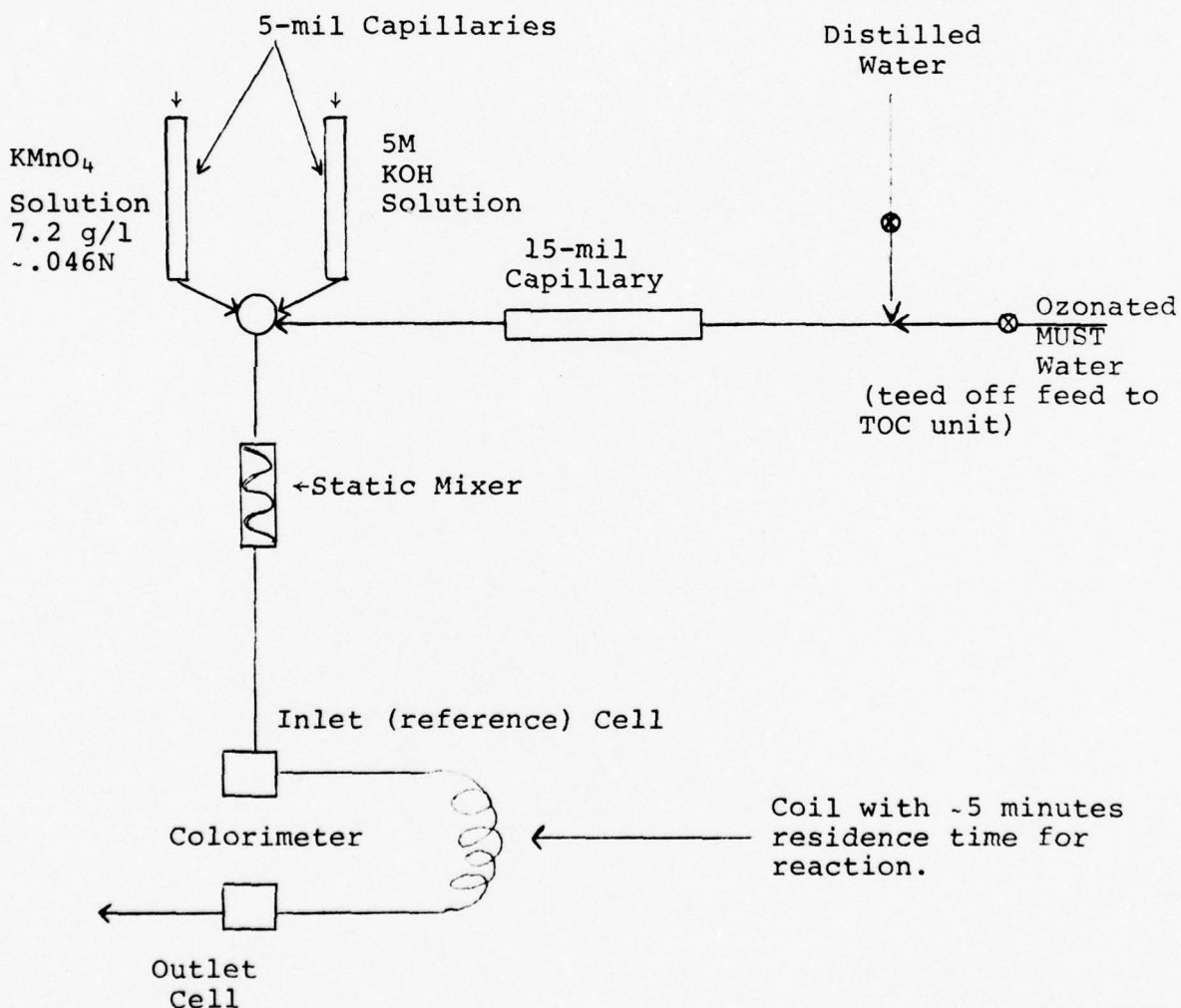
Alternatively, the two wavelengths may be chosen to be 522 nm and 426 nm, with the ratio of transmittances at these wavelengths the monitoring output. For low contaminant levels, the ratio  $\frac{\text{OD}_{426}}{\text{OD}_{522}}$  will be



FIGURE 17

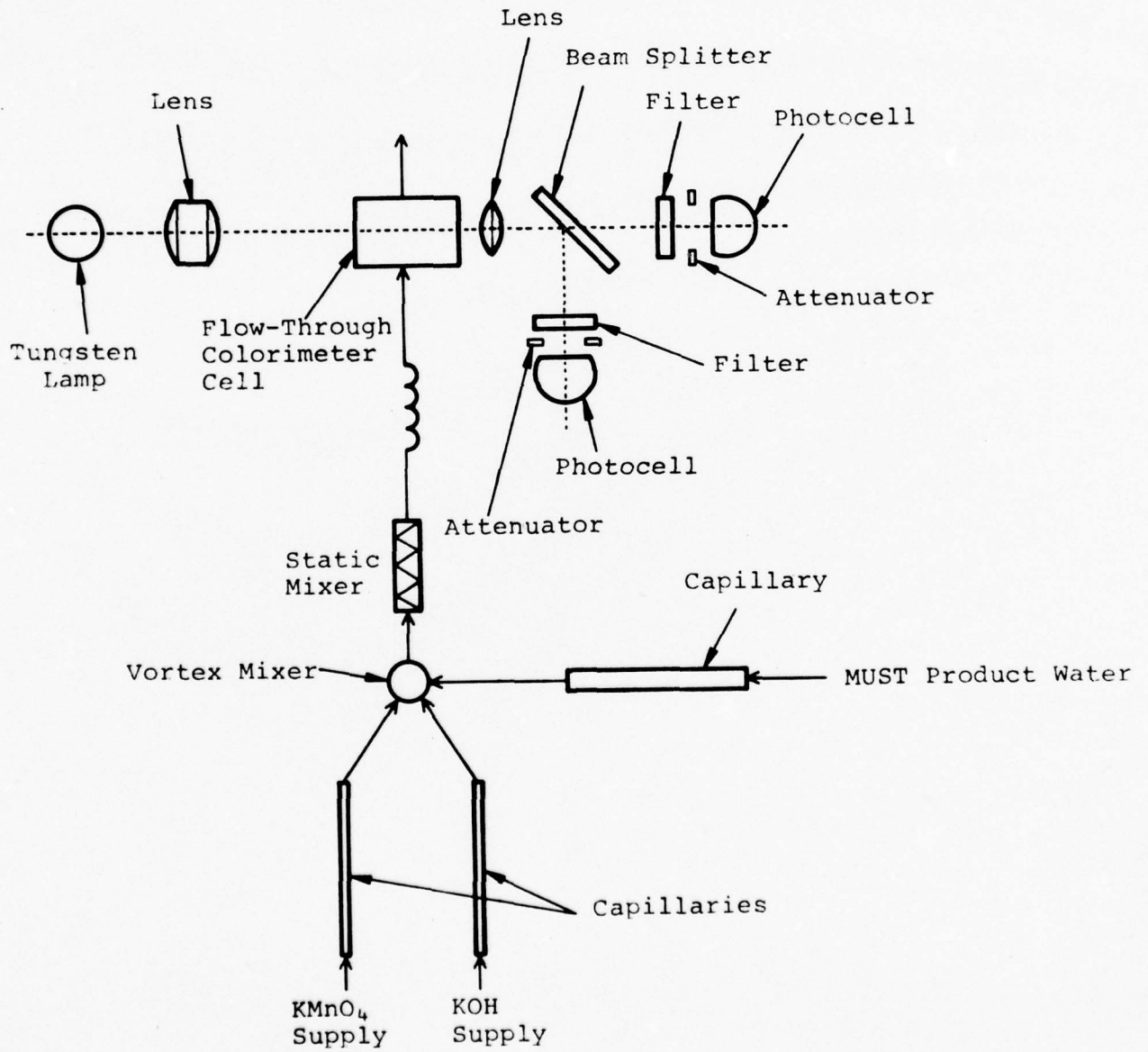
MONITOR SCHEMATIC

The  $\text{KMnO}_4$  and KOH solutions and the distilled water were nitrogen pressurized at -14.2 psi. The pressure on the MUST water feed was ~13.0 psi.



Colorimeter monitoring transmission at 522 nm

FIGURE 18  
DUAL WAVELENGTH MODE OF OPERATION



low and for high contaminant ratios, it will be high. One advantage of using these two wavelengths is that for a given contaminant level, they will produce a larger instrument reading than the other approaches. A second advantage is that the ratio will be relatively insensitive to fluctuations in permanganate concentration at low contaminant levels since these will have little effect on the numerator ( $OD_{426}$ ).

The response of the monitor as the concentration of impurities which are oxidizable by permanganate varies may be analyzed as follows:

$$D_{522} = 2370 \{MnO_4^-\} + 387 \{MnO_4^{2-}\}$$

$$D_{426} = 77 \{MnO_4^-\} + 1370 \{MnO_4^{2-}\}$$

$$D_{\text{isosbestic}} = c (\{MnO_4^-\} + \{MnO_4^{2-}\})$$

where

$D_{522}$  = optical density at 522 nanometers

$D_{\text{isosbestic}}$  = optical density at an isobestic point

$D_{426}$  = optical density at 426 nanometers

$\{MnO_4^-\}$  = molarity of permanganate ion

$\{MnO_4^{2-}\}$  = molarity of manganate ion

and the coefficients are the extinction coefficients for the respective ions and wavelengths.

From the definition of optical density

$$I_{522} = I_{O_{522}} e^{-D_{522}}$$

$$I_{426} = I_{O_{426}} e^{-D_{426}}$$

where  $I_0$  = light intensity incident on the colorimeter  
 $I$  = transmitted light intensity.

For the two cell mode of operation, the colorimeter output is the log of the ratio of the transmitted light intensities through the two cells:

$$S_1 = \ln \left[ \frac{I_{522, \text{DW}, 5 \text{ min}}}{I_{522, \text{WW}, 5 \text{ min}}} \right] = D_{522, \text{DW}, 5 \text{ min}} - D_{522, \text{WW}, 5 \text{ min}}$$

$$\text{and } S_2 = \ln \left[ \frac{I_{522, \text{WW}, \sim 30 \text{ sec}}}{I_{522, \text{WW}, \sim 5 \text{ min}}} \right] = D_{522, \text{WW}, 30 \text{ sec}} - D_{522, \text{WW}, 5 \text{ min}}$$

where the subscript DW refers to distilled water;

the subscript WW refers to waste water;

the subscripts 30 sec and 5 min refer to the time allowed for permanganate reaction before monitoring transmittance;

$S_1$  refers to the colorimeter signal output with the mode of operation depicted in Figure 16;

$S_2$  refers to the colorimeter signal output with the mode of operation depicted in Figure 17.

Similarly for the single cell, dual wavelength mode of operation, the colorimeter output is the log of the ratio of the transmitted light intensities at the two wavelengths:



$$S_3 = \ln \left[ \frac{I_{522} \text{ 5 min}}{I_{\text{Isosbestic}} \text{ 5 min}} \right] = D_{522 \text{ 5 min}} - D_{\text{Isosbestic 5 min}}$$

$$\text{and } S_4 = \ln \left[ \frac{I_{522} \text{ 5 min}}{I_{426} \text{ 5 min}} \right] = D_{522 \text{ 5 min}} - D_{426 \text{ 5 min}}$$

$\text{KMnO}_4$  has a very high extinction coefficient and this reagent has to be added very accurately. Suitable micropumps are very expensive and of questionable accuracy and reliability and pose maintenance problems. For this reason, reagent dispensing is accomplished by the use of capillary metering restrictions with a pressure head to force the fluid through the capillaries. Using Poiseuille's Law, the dimensions of the capillaries to deliver a predetermined volume with a known pressure head can be calculated. To generate the necessary pressure, a separate pump for each line could be used as shown in Figure 10. A probably less-expensive method (also fewer moving parts) is to use a single nitrogen tank to pressurize the reagent dispensers and this approach was selected for initial development. The pressure necessary to force the liquid through the capillaries and deliver the required volume was kept relatively low, between 10 and 20 psi, so as to minimize problems generated by the dissolving of gas in the reagents. At higher pressures diaphragms would have to be used to separate the two media and prevent the dissolving of gas.

The diameters of the capillaries are very small and proper precautions must be taken to prevent blocking. An inexpensive method is to use fine filters to remove small particulate impurities. The filter material has to be inert to chemical attack by the reagents, i.e.,  $\text{KMnO}_4$  and  $\text{KOH}$ . Very fine mesh stainless steel cloth is used for this purpose. Pressure gauges indicate the proper flow of reagents through the system. The gauges are protected from chemical corrosion by stainless steel diaphragms. Eventually all tubing containing reagents as well as the Vortex mixers should be made of stainless steel.

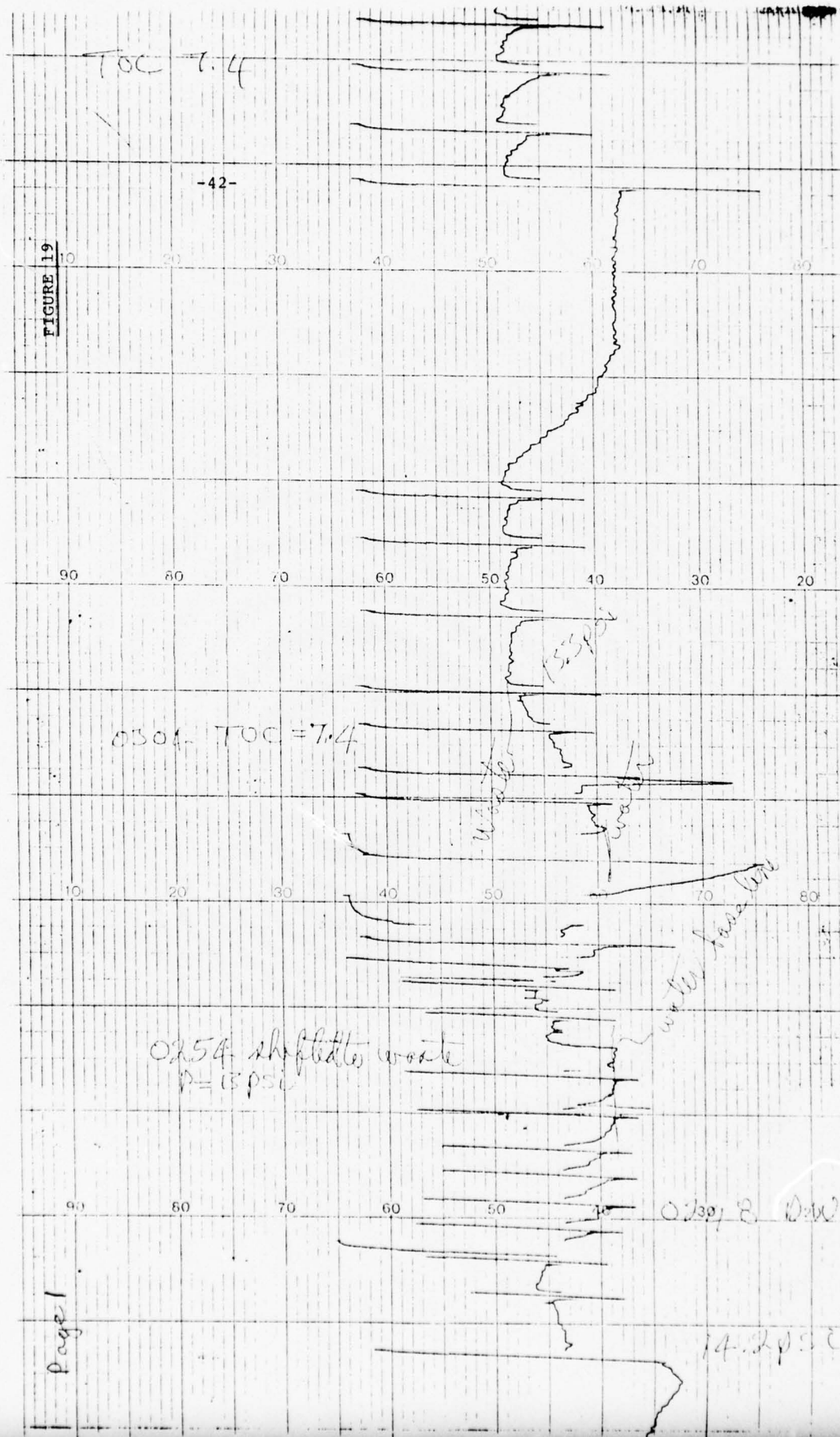
Slow decomposition of  $\text{KMnO}_4$  occurs, especially after the Vortex mixer where the solution is made basic by the addition of  $\text{KOH}$ . A fine, dark-brown film of manganese dioxide deposits gradually on the surface of the materials in contact with the reaction mixture. The stainless steel tubing and the flow-through cell of the colorimeter therefore require periodic cleaning, particularly since the decomposition reaction is autocatalytic, i.e., is catalyzed by manganese dioxide. A 1% solution of sodium or potassium bisulphite can remove all  $\text{MnO}_2$  rapidly by chemical reaction<sup>(4)</sup>. A reservoir containing  $\text{K}_2\text{S}_2\text{O}_5$  is connected to the monitor so the parts in question may be flushed periodically whenever the need arises as determined experimentally.

C. Abcor Pilot Run

The permanganate colorimeter monitor was set up at the Abcor pilot plant late in August of 1974 to operate in parallel with the Ionics TOC instrument so as to determine its suitability for monitoring the quality of MUST product water. The colorimeter was set up to operate as shown in Figure 17; the product water with permanganate and base added flowed through the two instrument cells in series with a delay loop in between. The instrument baseline was periodically established using a distilled water feed. Early instrument malfunction was traced to improper electrical grounding of the ground wire in the power line. This was corrected by separate grounding of the instrument and recorder cases. Unfortunately, the instrument became operational only in time for the last pilot run. Although good data were obtained over a significant portion of this run, a number of instrument defects were apparent which need correction before the instrument can qualify for field use.

These defects and their correction will be discussed later. The Abcor run started at about 1:00 P.M. on Thursday, August 28, and was completed at about 8:00 A.M. the following morning. The bulk of the useful Amicon data was obtained between about 10:30 P.M. Thursday evening and 3:30 A.M. Friday morning. Xerox copies of the recorder traces for these data are presented in Figure 19. Tabulations of recorder readings and " $\Delta$  OD" numbers derived from these recorder traces are presented in Table I along with TOC readings from the Ionics monitor and TOC data obtained subsequently at Amicon using a Technicon/Phase Separations Tocsin I Analyzer. Recorder readings for the stream, W, refer to operation with

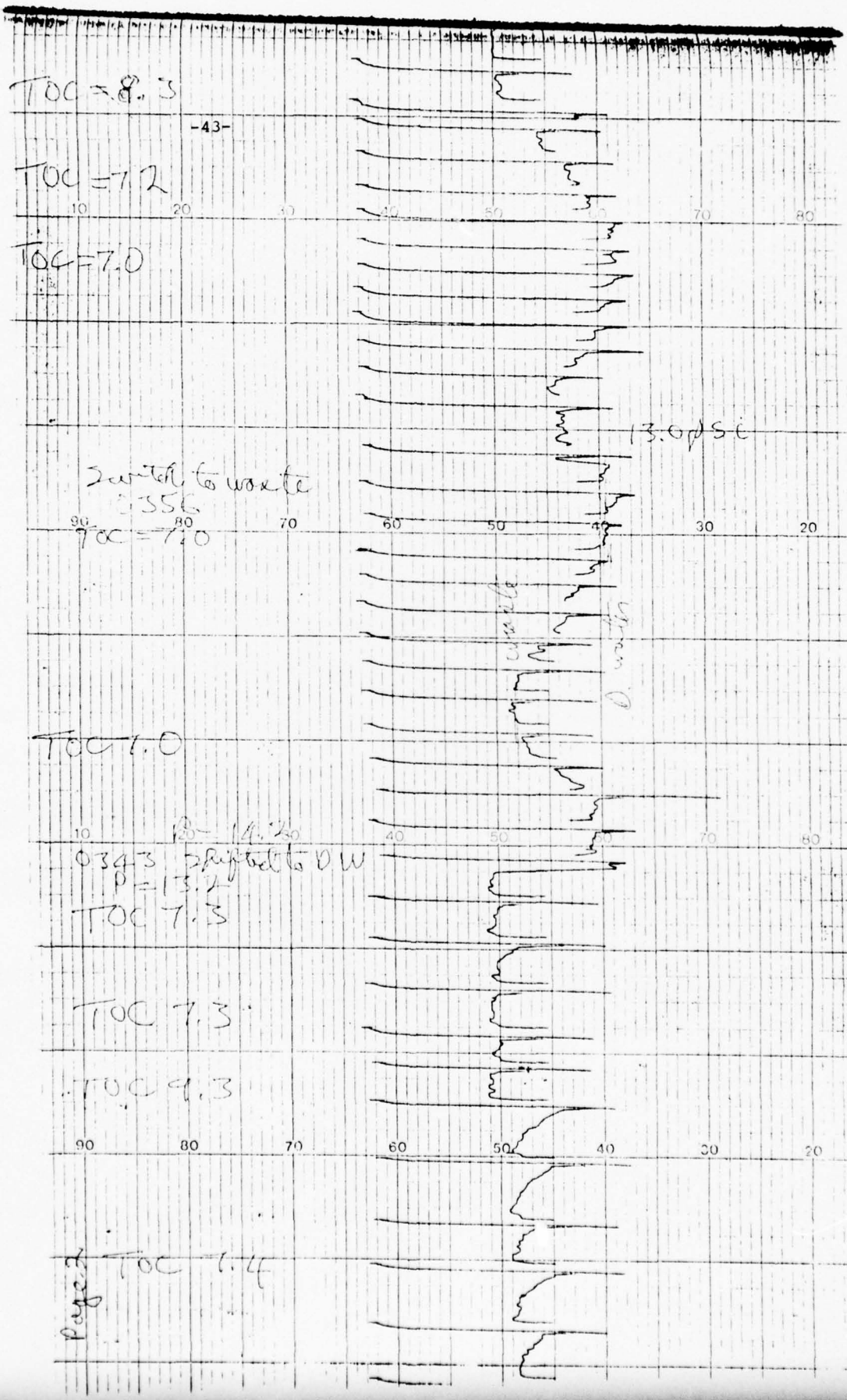
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Page 1

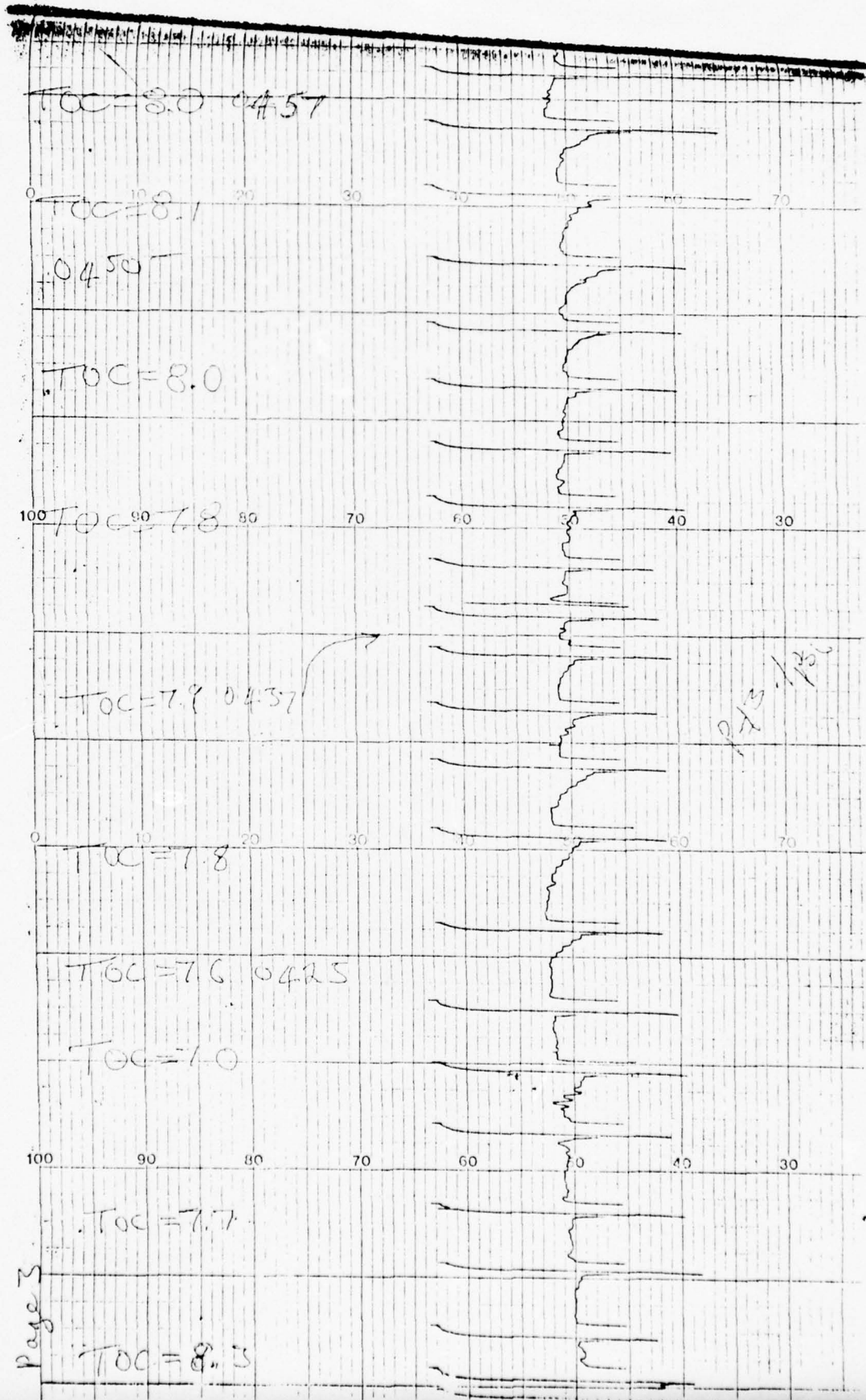


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Page 3

OC = 8.9

90 80 70 60 50 40 30 20

OC = 8.4

OC = 8.8

10 20 30 40 50 60 70 80

OC = 8.5

OC = 8.6

OC = 8.3

90 80 70 60 50 40 30 20

OC = 8.4 0502

OC = 8.0 0457

10 20 30 40 50 60 70 80

0450

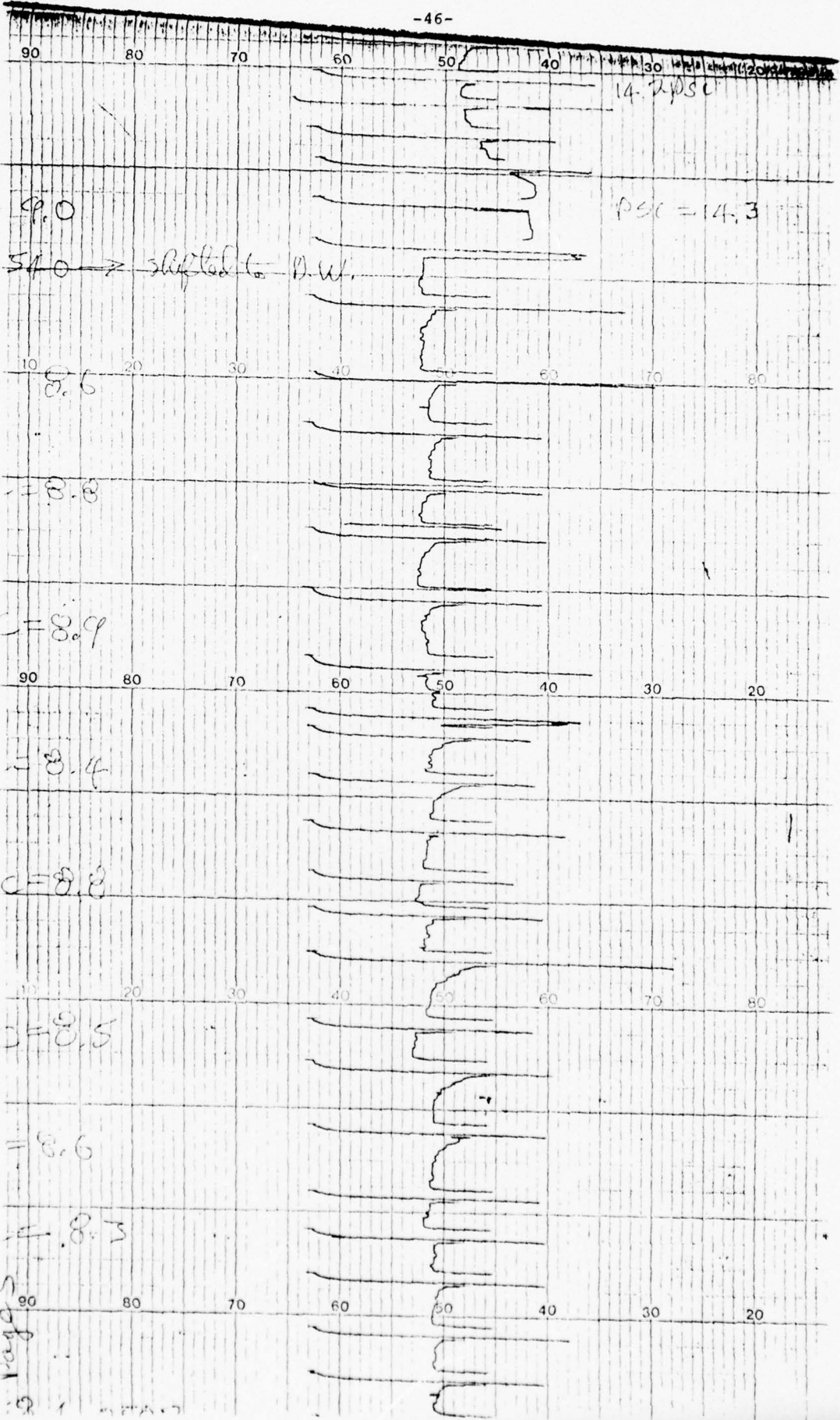
OC = 8.0

90 80 70 60 50 40 30 20

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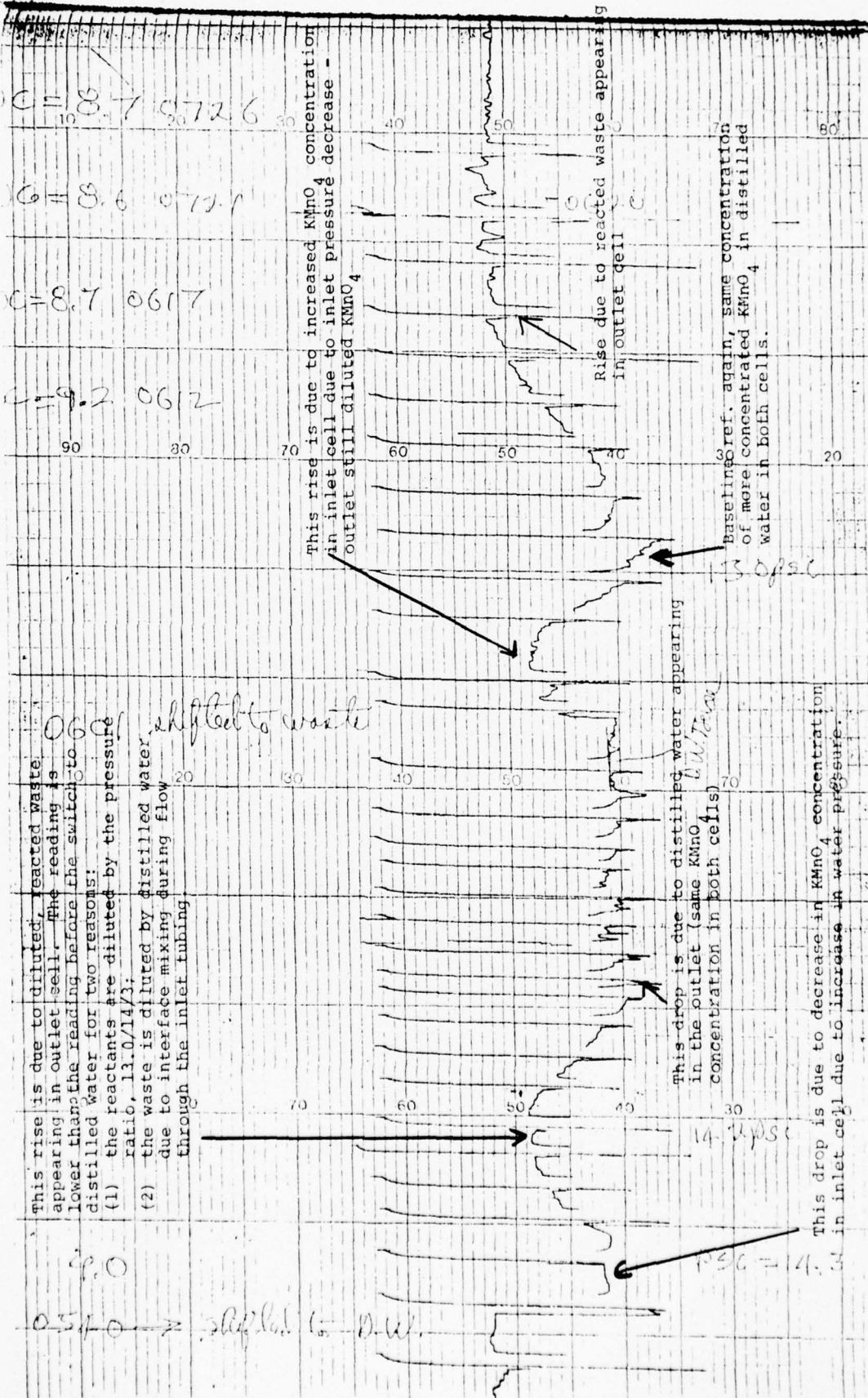
0507

0507



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C = 8.8 0726

C = 8.6 0721

C = 8.7 0617

C = 9.2 0612

This rise is due to diluted, reacted waste appearing in outlet cell. The reading is lower than the reading before the switch to distilled water for two reasons:  
 (1) the reactants are diluted by the pressure ratio, 13.0/14.3;  
 (2) the waste is diluted by distilled water due to interface mixing during flow through the inlet tubing

shifted to waste

This rise is due to increased  $KMnO_4$  concentration in inlet cell due to inlet pressure decrease - outlet still diluted  $KMnO_4$

Rise due to reacted waste appearing in outlet cell

Baseline ref. again, same concentration of more concentrated  $KMnO_4$  in distilled water in both cells.

This drop is due to distilled water appearing in the outlet (same  $KMnO_4$  concentration in both cells)

This drop is due to decrease in  $KMnO_4$  concentration in inlet cell due to increase in water pressure.

9.0

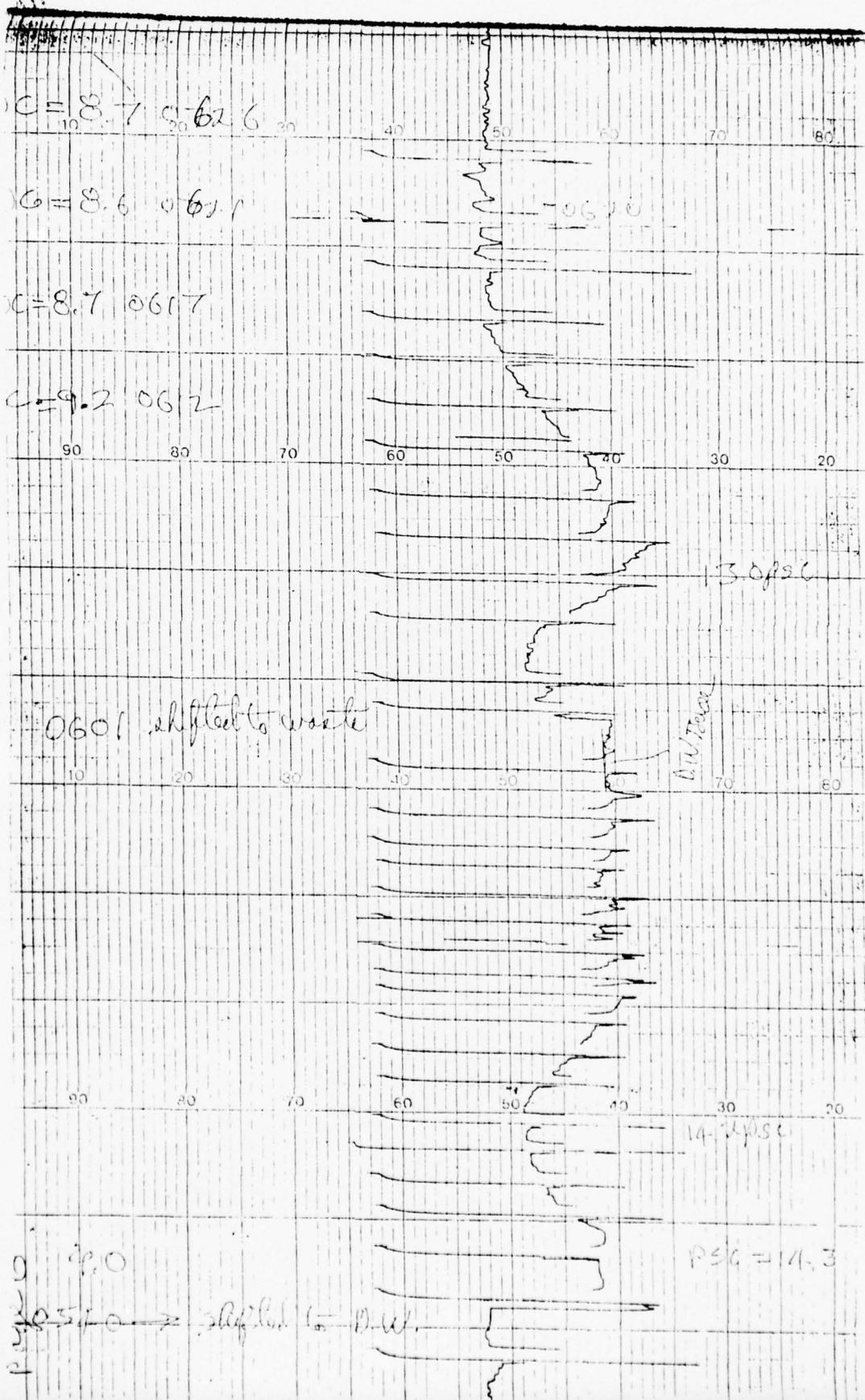
0.540 -> shifted to D.W.

14.3 PSI

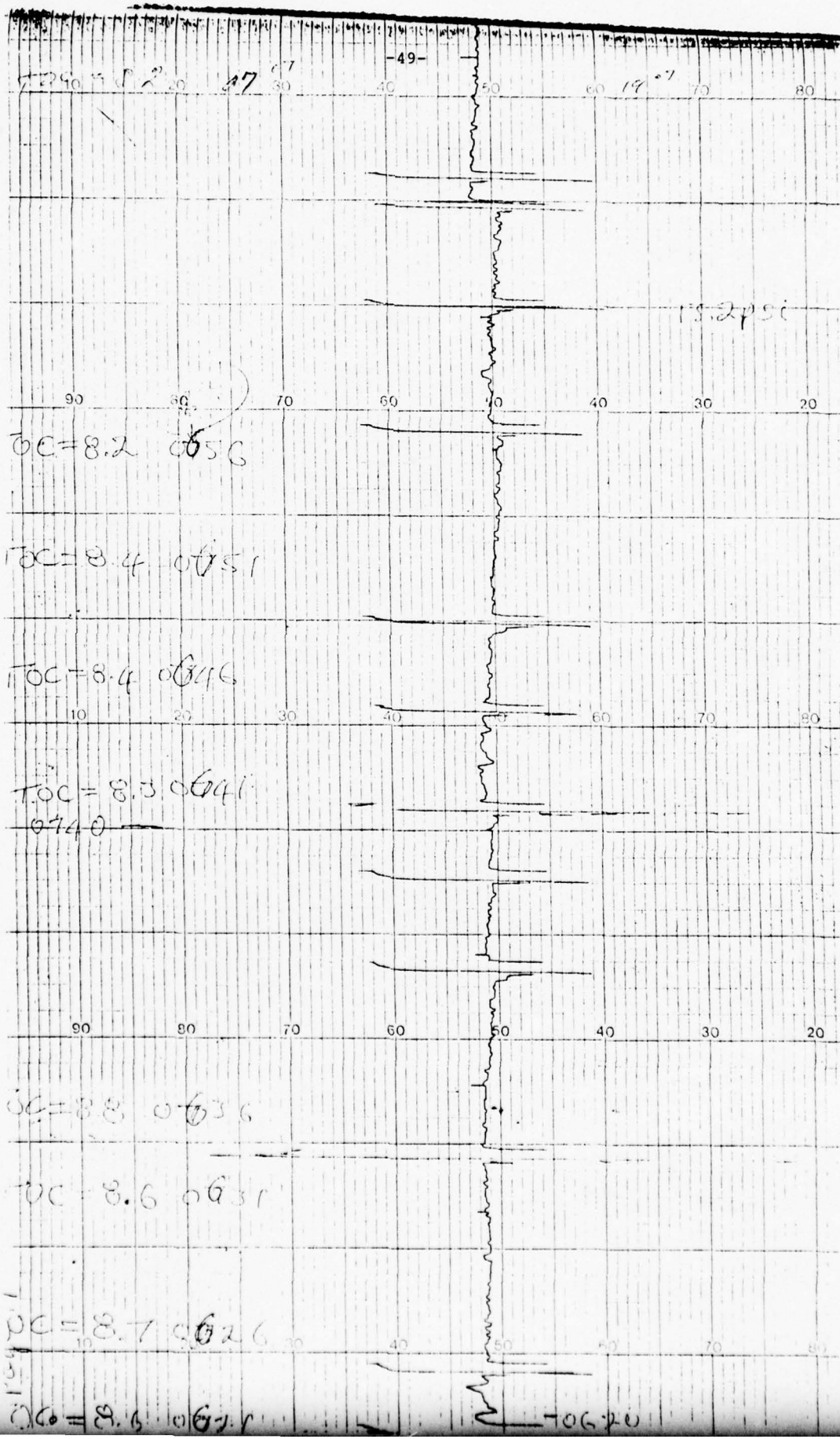
PSI = 14.3

30 PSI

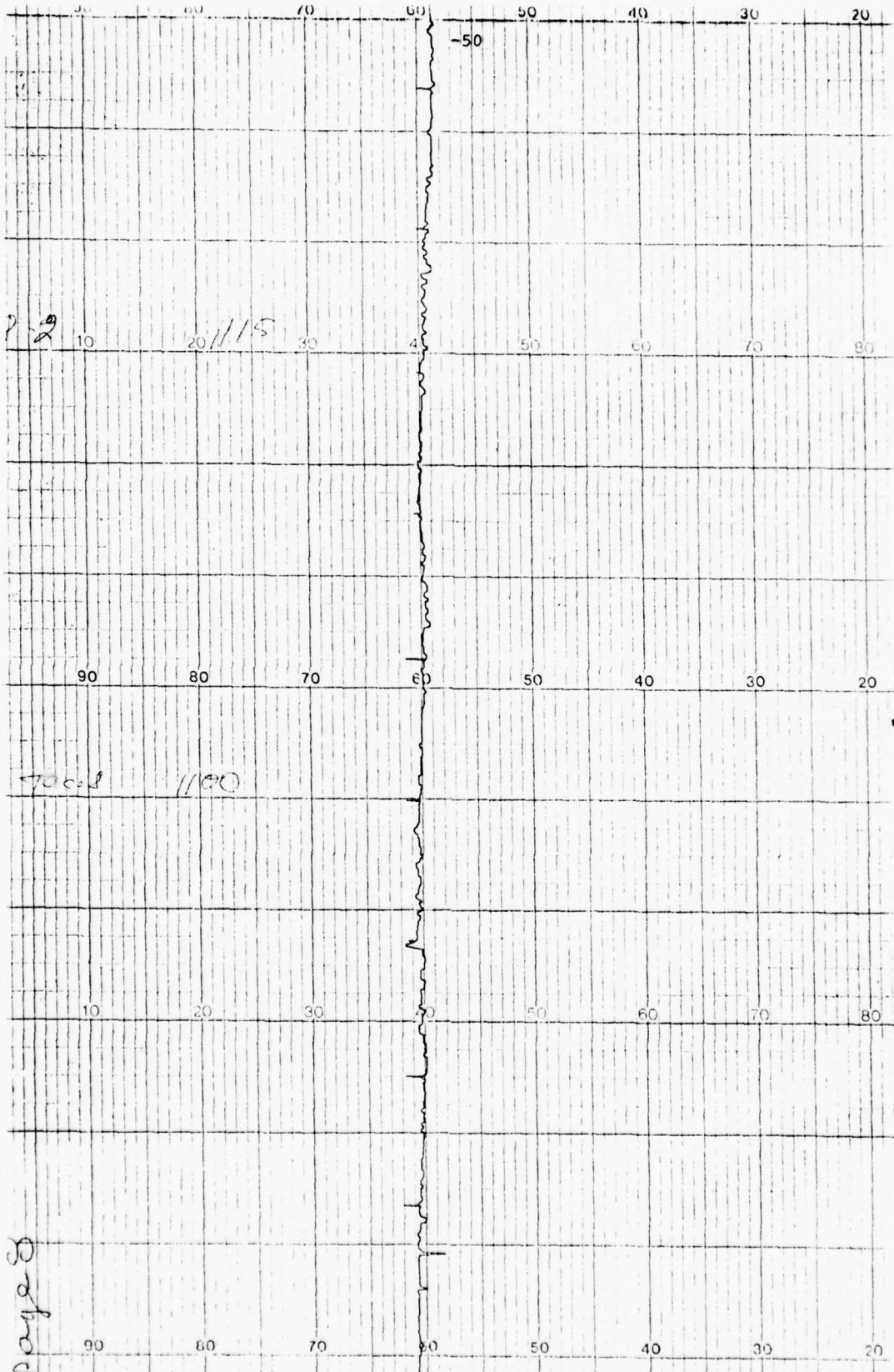




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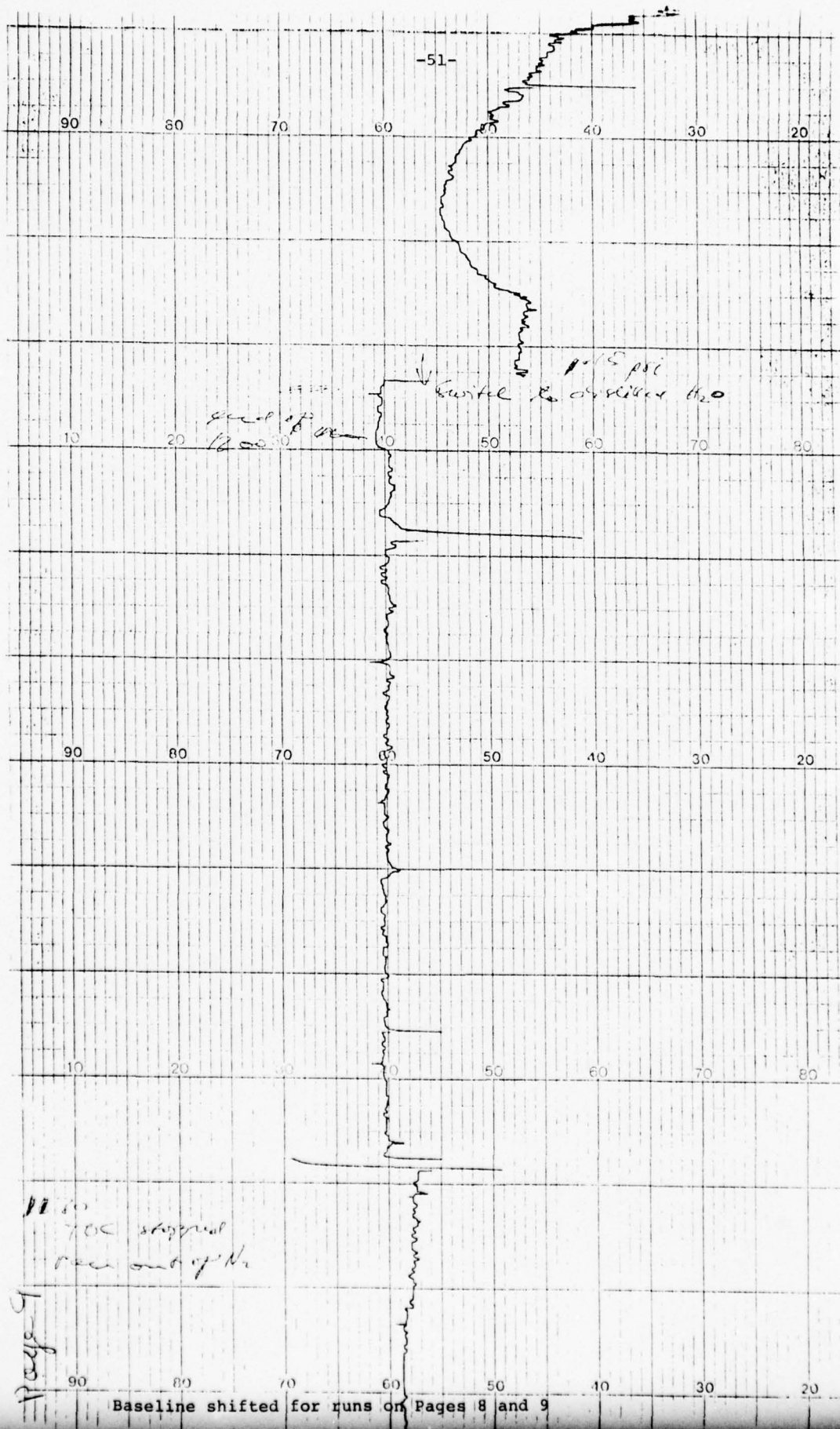
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Baseline shifted from runs on pages 8 and 9.

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TABLE I

RECORDER OUTPUT READINGS

$\Delta$  OD = 1.0 = 10 ppm acetaldehyde

<u>Time</u>	<u>Stream</u>	<u>TOC</u>	<u>Monitor Reading</u>	<u>(<math>\Delta</math> OD)</u>	<u>Time</u>	<u>TOC</u>
1200						
0230	W	7.2	.48	.092		
0240	W	7.2	.475	.087		
0240	DW		.388			
0254	W					
0304	W	7.4	.488	0.100		
0325	W	7.4	.49	0.102		
					1530	6.1
0334	W	9.3	.51	0.113		
0343	W	7.3	.51	0.115		
0343	DW		.395			
0356	W					
0400	W	7.0	.50	0.105		
0405	W	7.2	.510	0.115		
0410	W	8.3	.525	0.130		
0415	W	7.7	.520	0.125		
0420	W	7.0	.51	0.112		
0425	W	7.6	.51	0.112		
0430	W	7.8	.51	0.112		
0435	W	7.9	.51	0.112		
0440	W	7.8	.51	0.112		
0445	W	8.0	.515	0.117		
0450	W	8.1	.510	0.108		
0455	W	8.0	.515	0.113		
0500	W	8.4	.520	0.118		
0505	W	8.3	.520	0.118		
0510	W	8.6	.520	0.118		
0515	W	8.5	.517	0.117		
0520	W	8.8	.521	0.121		
0525	W	8.4	0.318	0.118		
0530	W	8.9	0.320	0.120	1730	6.0, 6.5
0535	W	8.8	0.520	0.120		
0540	W	8.6				
0545	W	9.0				
0550						
0555						
0600	DW		0.400			
0610	W	9.2	0.518	0.118		
0615	W	8.7	0.511	0.111		
0620	W	8.6	0.514	0.114		
0625	W	8.7	0.510	0.110		
0630	W	8.6	0.510	0.110		

TABLE I (continued)

<u>Time</u>	<u>Stream</u>	<u>TOC</u>	<u>Monitor Reading</u>	<u>(Δ OD)</u>	<u>Time</u>	<u>TOC</u>
0635	W	8.8	0.511	0.111		
0640	W	8.3	0.502	0.102		
0645	W	8.4	0.502	0.102		
0650	W	8.4	0.500	0.100		
0655	W	8.2	0.520	0.120		
0700	W					
0705	W	8.2	0.510	0.110		
0710	W					
0715	W	7.9	0.511	0.111		
0720	W	7.9				
0725	W	7.5	0.500	0.100		
	W	7.3	0.492	0.092	1930	5.8

MUST product water (to which permanganate and base have been added) flowing through the two cells in series. Recorder readings for the stream, DW, are obtained with distilled water (to which permanganate and base have been added) flowing through the two cells in series. These latter readings represent the instrument baseline--the output with no permanganate oxidation occurring. The  $\Delta$  OD column represents the difference between the readings with the product water flowing through the distilled water baseline. Since a 10 ppm acetaldehyde solution gives a  $\Delta$  OD of about 1.0, the  $\Delta$  OD of about 0.1 consistently obtained is equivalent to about a one ppm concentration of acetaldehyde. In order to obtain a uniform mixture entering the first cell of the colorimeter, it was, however, necessary to use a Kenics Static Mixer following the Vortex Mixer. This introduced a time delay so that the solution had about 30 seconds to react before entering this first colorimeter cell. From Figure 11, the rate of acetaldehyde oxidation by permanganate is such that with a solution of about one ppm acetaldehyde, the oxidation would have gone about 25% towards completion in 30 seconds. Thus, the readings are really equivalent to an acetaldehyde concentration of about 1.5 ppm. Of course, if higher aldehydes are being oxidized only to the corresponding acid, the permanganate readings correspond to a higher ppm. One important conclusion from these tests is that it does not appear necessary to use a tracer with the permanganate colorimeter to monitor the ozonation. Aldehydes appear to be produced and to accumulate naturally during ozonation.

From the rate of flow through the permanganate monitor and the holdup in the tubing between the tee into the TOC monitor supply and the second flow cell in the colorimeter, a delay may be calculated to determine what TOC monitor reading to compare with the permanganate monitor reading. This delay is equivalent to about 13 minutes; a permanganate colorimeter reading should therefore be compared with a TOC reading taken 13 minutes earlier. In Table II data for the Ionics TOC monitor, the permanganate colorimeter, and the Phase Separations Tocsin I TOC Analyzer are compared for the three samples in this time period for which Tocsin data are available. Although there are data for the permanganate monitor at close to the desired times (10 minutes after the TOC readings) for comparative evaluation, the data are not always available at precisely corresponding times. From the trends of the Ionics and permanganate monitor readings, however, the changes which are apt to occur in the

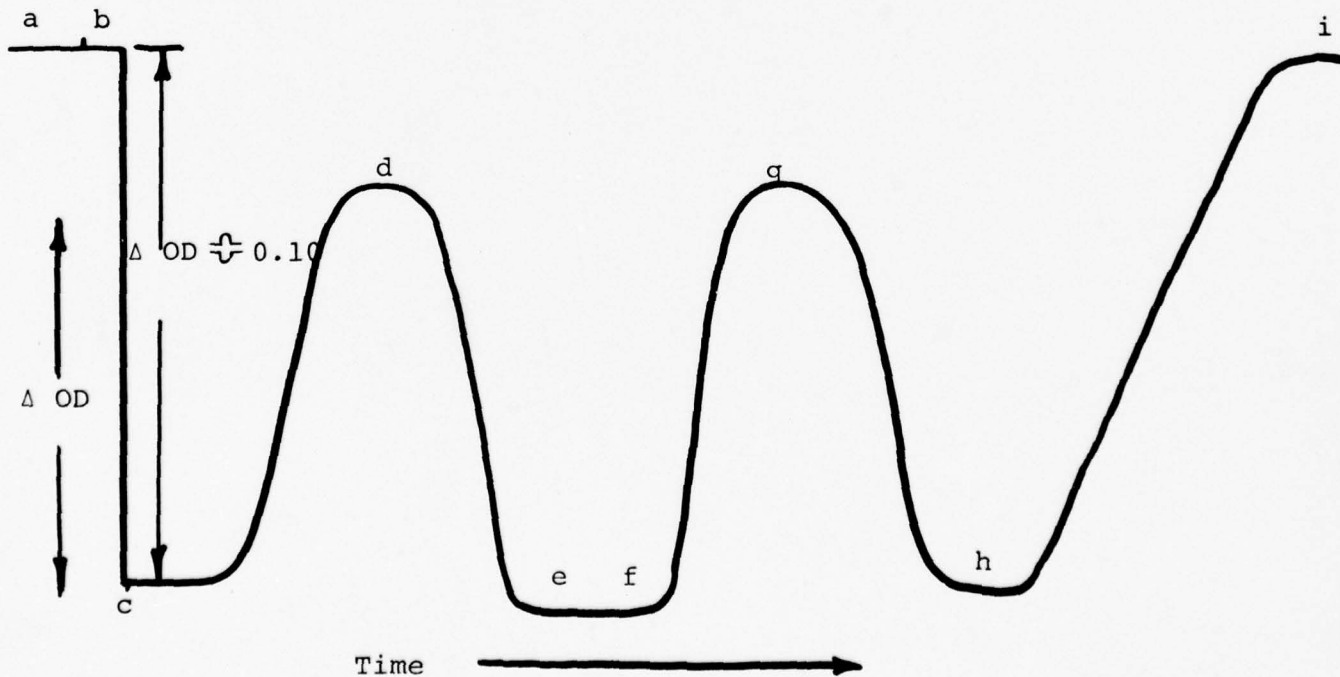
TABLE II

<u>Run Time</u>	<u>Ionics TOC Reading</u>	<u>Technicon Phase Separations Tocsin I Reading</u>	<u>Permanganate Colorimeter Monitor Reading</u>
1525	7.4		
1530		6.1	
1543			0.115
1725	8.4		
1730	8.9	6.2	
1735			0.120
1915	7.9		
1925	7.5		0.100
1930		5.8	



short time differences from direct correspondence are small. From Table II it is apparent that there is not enough variation in any of the data to establish whether a correspondence between TOC and the permanganate colorimeter readings exists or not. It is at least clear that such a correspondence is not ruled out for MUST product water by these data. The instrument does appear to have the required sensitivity, particularly since the noise, once micro-bubbles are eliminated, appears to be less than .01 OD which corresponds to about 0.1 ppm of acetaldehyde and from Table II assuming the Phase Separations Tocsin I measurements to be more accurate, to be equivalent to about 0.6 ppm of TOC.

The response characteristics of the instrument may be deduced from the recorder data by analyzing the response when the feed is shifted from the MUST product water to distilled water and then back again to the MUST product water. A typical recorder trace for this sequence together with an explanation for the changes observed is shown in Figure 19. A typical response is sketched below:



a = recorder reading with wastewater feed to colorimeter. Gas pressure on  $\text{KMnO}_4$  and KOH feed streams  $\approx 14.3$  psig; pump pressure on wastewater feed stream  $\approx 13.0$  psi.  $\text{KMnO}_4$  feed stream concentration and capillary diameters and lengths are chosen to give a potassium permanganate concentration of 72 mg/liter = 0.455 millimolar with the same pressure upstream of all capillaries. With the pressure on the wastewater being less than that on the permanganate stream upstream of the capillaries, the permanganate concentration before any oxidation/reduction reaction will be

$$\frac{14.3}{13.0} \times .455 = 0.500 \text{ millimolar.}$$

b = feed shifted from wastewater at 13.0 psi to distilled water at 14.3 psi.

c = the diluted distilled water appears in the inlet cell of the colorimeter. This generates a drop in  $\Delta$  (OD) of about 0.10. The calculated drop, assuming no reaction in either the distilled water or wastewater before flow through the inlet cell:

$$\Delta (\text{OD}) = \epsilon \Delta \{\text{MnO}_4^-\}$$

where  $\epsilon$  = extinction coefficient for permanganate ion at 522 nm.

$$\begin{aligned} \Delta (\text{OD}) &= 2370 \Delta \{\text{MnO}_4^-\} \\ &= 2370 \times .0455 \times 10^{-3} \\ &= 0.108 \end{aligned}$$

The observed  $\Delta$  (OD) of 0.100 is quite close to this, but the agreement is good in part because of two cancelling factors: (1) the wastewater is partially oxidized and the permanganate stream reduced when the wastewater permanganate stream flows through the inlet colorimeter cell; and (2) the distilled water contains some organics which are apt to be oxidized prior to flow through the inlet colorimeter cell.

- d = diluted reacted waste appears in the outlet cell. Because of axial mixing, the rise is lower than would be expected with distilled water in the inlet cell and reacted waste in the outlet cell. The solution flowing through the outlet cell is a mixture of reacted waste and distilled water.
- e = distilled water-permanganate solution appears in the outlet cell. This produces the distilled water baseline reference.
- f = the feed is shifted from distilled water to wastewater.
- g = This peak results from an increased concentration of permanganate ion in the inlet cell due to the decreased pressure on the wastewater stream. As the more concentrated wastewater stream enters the inlet cell, the rise in  $\Delta OD$  is less than expected from the straight dilution effect due to reaction of permanganate with the wastewater prior to entering the inlet colorimeter cell.
- h = concentrated distilled water in the outlet cell, concentrated wastewater in the inlet cell.
- i = concentrated wastewater in the inlet and outlet cells.

Since the recorder paper speed is inches/minute, the time from shifting the feed to its appearance in full concentration in the outlet cell is seen to be about 13 minutes, while it first begins to affect the outlet cell reading in about 7 minutes. Back-mixing due to laminar flow pipeline mixing therefore gives a time spread of about 6 minutes from first appearance of the feed in the outlet cell to its passing through the outlet cell in full concentration. These times can be significantly reduced by shortening lines, but the delay line between the cells is of course required to ensure time for reaction. This delay line is coiled which generates a stable secondary flow which reduces axial dispersion<sup>(9)</sup>. Tighter coiling of a larger diameter tube can be utilized to increase the Dean number and thereby further minimize the axial dispersion in this delay line. Elevating the fluid temperature in this delay line will increase the reaction rate and decrease the required residence time in the delay line but will also increase the rate of decomposition of permanganate under the alkaline conditions in this delay loop.

## 1. Gas Evolution and Entrapment

A number of design modifications to the permanganate colorimeter monitor appear desirable in light of the operational experience obtained with it thus far. The principal design change called for is one to reduce gas evolution and entrapment in the colorimeter cells, primarily in the cell following the delay loop. The gas probably resulted from a combination of: permanganate oxidation; the slow decomposition of permanganate under alkaline conditions<sup>(6)</sup>; dissolution of nitrogen used for pressurization of the distilled water, permanganate and base streams; and dissolved ozone and air evolution from the ozonated MUST stream. The pressure drop through the capillary flow restrictions will clearly lead to some gas bubble formation if the liquid is saturated with nitrogen at the same temperature upstream of the capillaries. The delay loop between colorimeter flow cells appears to be a source of bubbles, probably both due to nucleation and growth of bubbles from a supersaturated solution, due to permanganate oxidation and due to the slow breakdown of permanganate under strongly alkaline conditions<sup>(6)</sup>. Buildup of manganese dioxide in the delay loop or in other parts of the system will, of course, aggravate the gas evolution problem because of the autocatalytic nature of the decomposition reaction. The flow cell configurations, with leads into and out of the top of the cells, compounds the problem because these cells are effective bubble traps. A cell with flow inlet at its base and flow outlet at its top should do much to alleviate the entrapment of bubbles in the cell.

## 2. Mode of Operation

Use of the single cell, two wavelength mode of colorimeter operation discussed above would appear to introduce substantial improvements:

- a. the noise level in the output signal should be significantly reduced since most of the factors generating noise will affect both wavelength cancelling out. Problems due to microbubbles, manganese dioxide deposition on the windows or scattering of the light beam and fluctuations in flow rates should be markedly diminished.



- b. The operation is simpler and involves less equipment than the other possible modes of operation. There is no need for rapid mixing since the flow enters the colorimeter only after a suitable delay time for oxidation to occur.
- c. Operation with 522 nm and 426 nm as the two wavelengths monitored produces a higher signal than with operation at one of these wavelengths and an isosbestic point or with either of the single frequency modes of operation. Experimentally, about 4 moles of permanganate are found to react with each mole of acetaldehyde when permanganate is in excess and the concentration is sufficiently basic. Oxidation of acetaldehyde to acetic acid requires only two moles of permanganate per mole of acetaldehyde, so some carbon-carbon bond scission is occurring as well. The calculated changes in permanganate colorimeter OD with single cell operation at 522 nm and 426 nm and reaction with 1 ppm of acetaldehyde is compared in Table III with the  $\Delta$  OD obtained monitoring either at 522 nm or at 426 nm with either a dual cell, single-wavelength mode of operation or a single cell, dual wavelength mode of operation where the second wavelength is at an isosbestic point.

The colorimeter was subsequently modified at Amicon to convert it to the dual wavelength mode of operation, with 522 nm and 460 nm (an isosbestic point) chosen as the two wavelengths. A flow-through cell with positive flushing was introduced. These modifications essentially eliminated the gas bubble entrapment problem and reduced baseline noise to a small fraction of 0.01 OD as may be seen from the recorder tracing reproduced in Figure 20. The data show that, even after the Kenics Mixer, small concentration fluctuations due to incomplete mixing are present. These are eliminated by flow through the delay coil.

a. Instrument response

Experiments were carried out to determine the instrument response as a function of the level of base concentration and the permanganate acetaldehyde ratio. Results are presented in Table IV. The calculated

TABLE III  
CALCULATED  $\Delta$  OD FOR 1 PPM ACETALDEHYDE

$\Delta$ $\left[ \begin{array}{l} -D_{522} \\ +D_{426} \end{array} \right]$	$\Delta D_{522}$	$\Delta D_{426}$
0.298	0.180	0.118

FIGURE 20: TCS DUAL WAVELENGTH SPECTROGRAM OF { $\text{KMnO}_4$ }  
72 mg/l AT ROOM TEMPERATURE IN BASIC SOLUTION

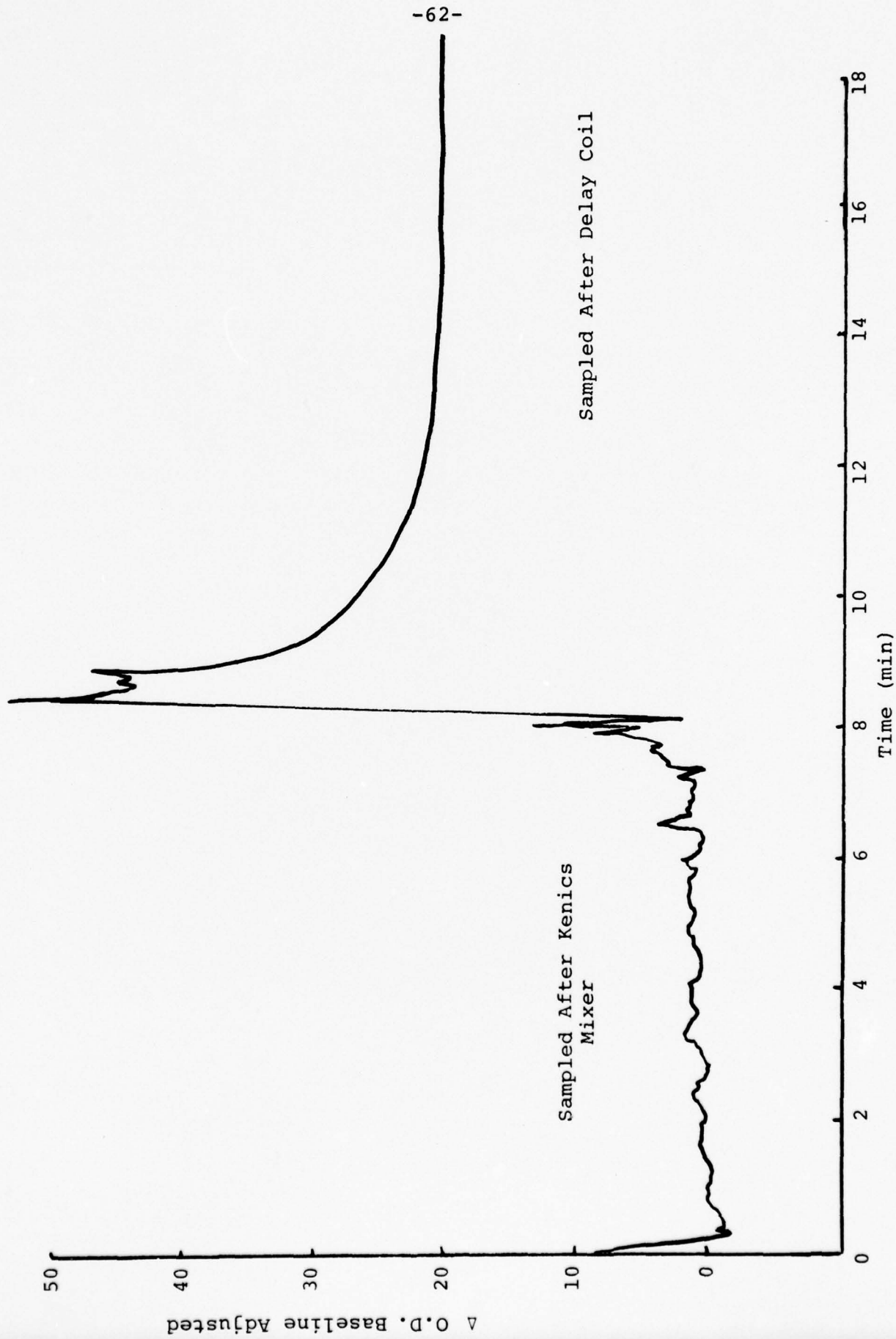




TABLE IV

Initial  $\{\text{MnO}_4^-\} = 36 \text{ mg/l} = 0.228 \times 10^{-3}\text{M}$

$\oplus$  2.5 ppm  $\text{CH}_3\text{COH}$  if 4 mols  $\text{MnO}_4^-$  react with 1 mol  $\text{CH}_3\text{COH}$

Calculated $\Delta$ OD			Experimental $\Delta$ OD			
ppm $\text{CH}_3\text{COH}$	$-D_{522}$ $+D_{426}$	$\Delta$ OD	$-D_{522}$ $+D_{426}$	0.1M $\{\text{OH}^-\}$	$-D_{522}$ $+D_{426}$	0.2M $\{\text{OH}^-\}$
0	-0.523		-0.522		-0.527	
0.42		0.126		0.127		0.131
1.00		0.298				
2.12		0.632		0.582		0.540
2.5		0.747				
4.24				0.812		0.775

and experimental agreement is good when only enough acetaldehyde is present to react with one-sixth of the permanganate, but is not as good when the acetaldehyde concentration is high enough to react with 80% of the permanganate. In Table V the range of optical densities are presented which would be observed with permanganate concentration sufficient to react with three different levels of acetaldehyde and a one cm path length cell. Optical densities above one become increasingly difficult to measure because of stray light, interference with the low levels of transmitted light. As the table indicates, if permanganate utilization is kept below 40%, and the correspondence between ozonated MUST TOC and permanganate is that observed in the limited experiments to date where one ppm of TOC reacts with about  $0.2 \times 10^{-4}$  moles of permanganate, then from 0 to 10 ppm of TOC can be monitored by noise, which in the dual wavelength mode of operation appears to be less than .002 OD by baseline drift which can be limited by frequent calibration and by permanganate decomposition which can be factored out. Conservatively, with baseline calibration every few hours, a sensitivity of .01 OD equivalent to 0.2 ppm of TOC should be readily attainable.

b. Instrument calibration

In the dual wavelength mode of operation, after flushing with bisulfite and rinsing with distilled water, the instrument baseline may be calibrated by introducing a neutral filter of known absorbance.

3. Flow Capillaries

The use of capillaries of selected diameters and lengths to control the flow ratios of the reactants appears sound, but the diameter of the capillary used to feed the permanganate should be enlarged. Its length should probably also be increased so as to maintain the same hydraulic resistance and it should either be folded back and forth or coiled to keep dimensions small. A larger diameter capillary will show less tendency to plug due to permanganate decomposition and will be easier to clean by flow or bisulfite through the system.

TABLE V

ABSORBANCE RANGE WITH A 1 CM PATH LENGTH AND 4 MOLS  $\text{MnO}_4^-$  PER MOL  $\text{CH}_3\text{COH}$

Range of acetaldehyde concentrations to be monitored

Lower Limit	Upper Limit	$D_{522}$	$D_{426}$
ppm- $\text{CH}_3\text{COH}$			
0	2.5	.540 - .072	.018 - .296
0	5.0	1.080 - .144	.036 - .592
0	10.0	2.16 - .288	.072 - 1.184

$$\frac{\text{ppm CH}_3\text{COH}}{\text{ppm TOC}} \approx \frac{1}{5}$$

$$\frac{\Delta \text{OD}}{\text{ppm TOC}} \approx \frac{0.3}{6} = .05$$

If  $\text{MnO}_4^-$  utilization is kept to 40% to prevent  $\text{MnO}_2$  formation, a high enough  $\text{MnO}_4^-$  concentration to react with 5 ppm  $\text{CH}_3\text{COH}$  will permit determination of  $0.4 \times 5 \times 5 = 10$  ppm TOC with a 1 cm path length and a sensitivity of about 0.2 ppm TOC.



Precise control of the permanganate concentration in the monitoring stream is a prerequisite for reliable monitoring. This requirement is considerably alleviated by operation in the dual wavelength mode with 426 nm and 522 nm, the two wavelengths monitored, since the absorbance at 426 nm results almost entirely from reaction with contaminant and is essentially proportional to contaminant level (for contaminants of a given reactivity level).

To control the permanganate/sample ratio more accurately, it may be desirable to pump the sample into a container which is pressurized by the same gas pressure used to drive the permanganate through its flow capillary. Limit switches would be used to control the liquid level in the container, and the container volume would be kept small to minimize the time lag it introduces.

#### 4. Pressure Measurement

Replacement of the present Bourdon tube-type pressure gauges by electromechanical (piezoelectric or semiconductor) gauges will eliminate dead spot regions where permanganate can slowly decompose and release manganese dioxide into the system. Measurement of pressure after the metallic filters may prove unnecessary, particularly if a periodic bisulfite cleaning flush schedule is set up.

#### 5. Instrument Simplification and Cost Reduction

Considerable simplification and ruggedization of the permanganate colorimeter is desirable and should be feasible once the desired characteristics have been pinned down.

#### D. Rate of Decay of Ozone

An alternate technique for monitoring the ozonation reactor is to monitor the rate of decay of ozone concentration in the effluent from the reactor. This can be done spectrophotometrically since ozone has a molar absorptivity of 2500 to 3000 (10) at 360 m $\mu$  using a long (10 cm) path cell to obtain the desired sensitivity. The rate of decay of ozone concentration may be represented approximately by the equation:

(1)

$$\frac{-dO_3}{dt} = k_2(O_3)(TOC) + k_d e^{-\frac{14.6}{RT}} (O_3)^{3/2}$$

The first term on the right represents the rate of oxidation of TOC and is a reasonable empirical approximation for typical waste streams, particularly for intermediate ozonation times (1, 11, 12). The rate constant,  $k_2$ , is of course a function, both of the organic material present, the pH, and catalyst (e.g., UV) concentration. The second term on the right represents the rate of auto-decomposition of dissolved ozone as given by Li et al (13). The rate constant,  $k_d$ , is also a function of pH, catalyst concentration, and ionic strength. For product water which has been treated with both reverse osmosis and ozonation, however,  $k_d$  should be essentially constant since the pH will be close to neutrality and since the impurity levels are quite low.

For very low impurity concentrations, the rate of decay of ozone concentration will be determined solely by the rate of autodecomposition; as impurity levels are increased, the rate of decay of ozone concentration will increase due to the first term on the right-hand side of equation (1), provided the impurities react with ozone. Measurement of the rate of decay of ozone concentration will then provide a measure of whether material which is oxidizable by ozone remains in the system.

To provide a preliminary indication of the utility of this concept, experiments were conducted with both distilled water and secondary effluent RO permeate, monitoring the rate of decay of ozone concentration in a long path (10 cm) cell at 254 nm and at room temperature ( $\approx 25^\circ\text{C}$ ) as a function of ozonation time. Results are presented in Table VI and Figures 21, 22, and 23. As may be seen, the ozone rate of decomposition in distilled water shows the three-halves dependency on ozone concentration found by Li (13) and the zero time extrapolated intercept agrees with the solubility data of Rawson (14). The relatively low OD readings at early times are probably attributable to Beer's Law deviations at high concentrations due to stray light interference in the Coleman 139 Spectrophotometer. The two different intercepts are probably partially attributable to a difference in temperature, but the data for the sample ozonated one hour (circular data points, Figure 1) are believed more accurate.

TABLE VI - PART A

DECOMPOSITION OF OZONE IN DISTILLED WATER

Absorbance monitored at 254 nm in a 10 cm path length cell

500 ml of water ozonated 30 minutes at room temperature with oxygen containing 38 mg/l ozone

<u>TIME</u>	<u>OD</u>	<u>(OD)<sup>-1/2</sup></u>
7	0.23	
10	0.25	2.0
20	0.22	2.13
40	0.21	2.18
55	0.18	2.35
120	0.076	3.63
130	0.070	3.78
145	0.060	4.08
175	0.040	5.00
205	0.035	5.35
265	0.025	6.33

TABLE VI - PART B

DECOMPOSITION OF OZONE IN DISTILLED WATER

500 ml of water ozonated one hour at room temperature (~25°C) with oxygen containing ~38 mg/l ozone

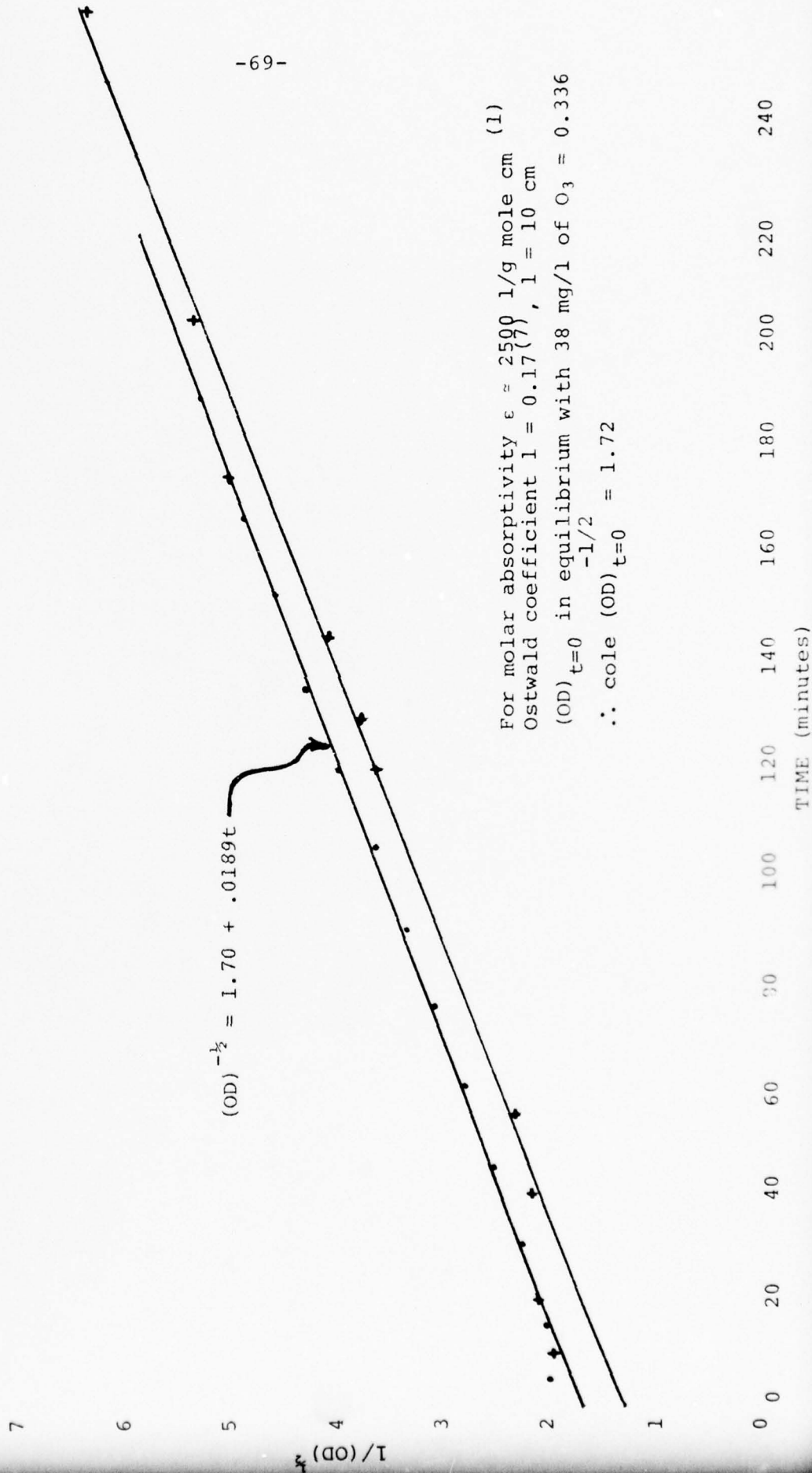
Absorbance monitored at 254 nm

<u>TIME</u>	<u>OD</u>	<u>(OD)<sup>-1/2</sup></u>
5	0.242	2.03
15	0.232	2.07
30	0.195	2.27
45	0.153	2.56
60	0.128	2.80
75	0.105	3.09
90	0.088	3.38
105	0.075	3.65
120	0.062	4.01
135	0.054	4.31
153	0.047	4.60
167	0.042	4.88
190	0.036	5.27

FIGURE 21

OZONE AUTODECOMPOSITION IN DISTILLED WATER AT ROOM TEMPERATURE (25°C)

- + ozonated 30 minutes with gas containing 38 mg/l O<sub>3</sub> at room temperature
- 0 Ozonated 1 hour with gas containing 38 mg/l O<sub>3</sub> at room temperature



For molar absorptivity  $\epsilon = 2500$  l/g mole cm (1)  
 Ostwald coefficient  $l = 0.17$ ,  $l = 10$  cm  
 $(OD)_{t=0}$  in equilibrium with 38 mg/l of O<sub>3</sub> = 0.336  
 $\therefore$  slope  $(OD)_{t=0}^{-1/2} = 1.72$



FIGURE 22

DECOMPOSITION OF OZONE IN SECONDARY EFFLUENT

Ozonated one hour at room temperature with oxygen containing 38 mg/l ozone

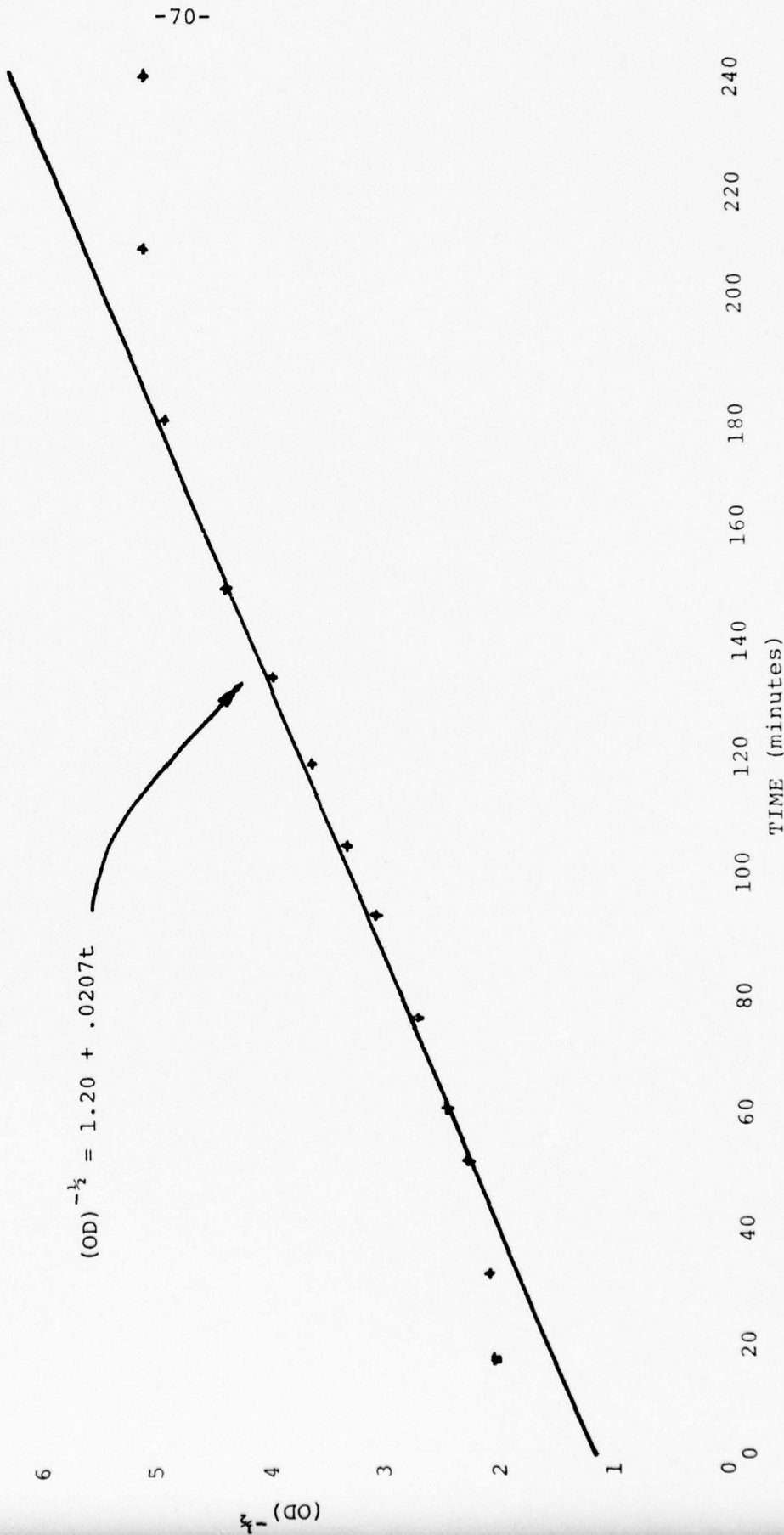
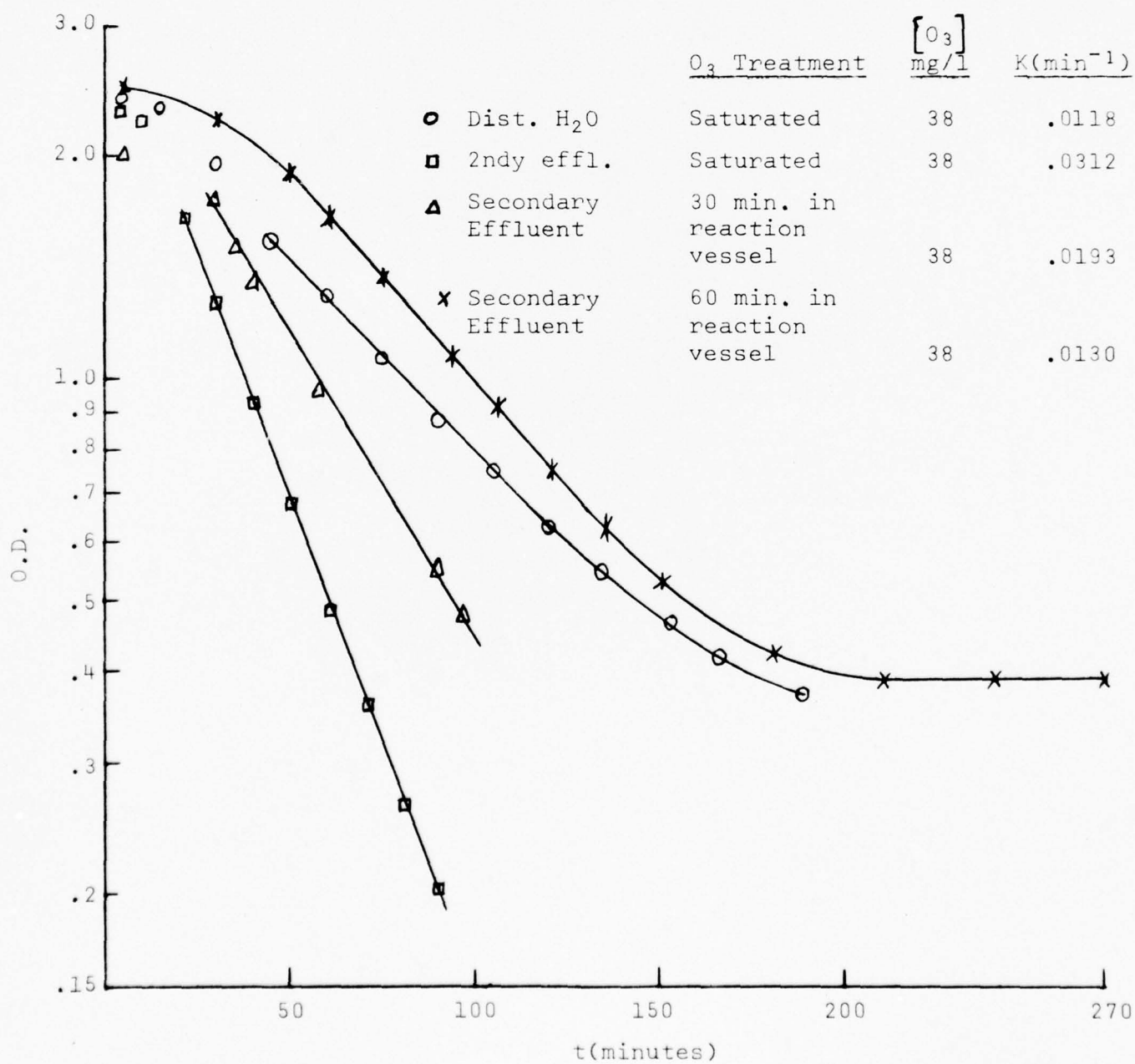


FIGURE 23

RATE OF DECAY OF OZONE IN DISTILLED WATER  
AND SECONDARY EFFLUENT RO PERMEATE AT  
ROOM TEMPERATURE

$$2.303 \log \frac{OD_1}{OD_2} = K \Delta t$$



With the secondary effluent, the rate of decay of ozone concentration is clearly higher than with distilled water, particularly for material ozonated for less than one hour. The effluent contacted with ozone for a few minutes to saturate it and that ozonated for 30 minutes both show rates of decay dominated by the rate of oxidation of TOC (first right-hand term in Equation 1). The zero time intercepts for these data are again in approximate agreement with the Rawson solubility data<sup>(14)</sup>. For secondary effluent ozonated at room temperature for one hour, the rate of decay of ozone (Figures 2 and 3) is only slightly greater than in distilled water and the further purification achievable with room temperature ozonation in a reasonable time period is therefore small.

To evaluate the true potential of this monitoring technique, low holdup flow cells should be utilized and measurements at higher temperatures, where reaction rates are faster, should be investigated. The technique appears to hold promise.

#### IV. CARBON ADSORPTION EXPERIMENTS

Three primary processing steps presently contemplated for the purification of MUST water are RO treatment, ozonation and adsorption by activated carbon. In order to investigate the adsorption characteristics of activated carbon relative to MUST RO permeate, adsorption isotherms were studied for both ethanol and acetaldehyde. Ethanol was selected as a known principal impurity in the MUST RO permeate. Acetaldehyde was selected as a principal contaminant in ozonated MUST RO permeate.

##### A. Experimental Procedures

A 790 ppm solution of ethanol was prepared by adding 1 ml of ethanol to 1,000 ml of distilled water. This solution was added to a reaction flask. One hundred grams of previously-washed Pittsburgh Charcoal 20/50 mesh was then added to the reaction flask. This solution was then agitated overnight on a rotary mill. The following day the charcoal was removed by using a Buchner Funnel with suction and Whatman #1 Filter Paper. A sample of the filtrate was then analyzed and the ethanol concentration determined as usual by the acidified dichromate method. This entire experiment was carried out at room temperature. The same experiment was repeated at 60°C. The solution was stirred overnight in a reaction vessel at 60°C and filtered hot before being analyzed for ethanol concentration. A third experiment was carried out at room temperature with a 800 ppm solution of acetaldehyde. The acetaldehyde concentration was determined by reacting it with basic potassium permanganate as described previously in this report. The results are represented in Table VII.

Two more carbon adsorption experiments were performed and both times a Pyrex glass column was used since this setup is more in line with the actual processing step than batch-type experiments. In the first column experiment 114 g of activated carbon were added to a 1" I.D. x 2' long Pyrex column with a fritted glass base. The carbon filled approximately 10" of the column. The column was filled with distilled water and then four liters of a 79 ppm ethanol solution were passed through the column at room temperature at a flow rate of 20 ml/minute. Small samples of about 20 ml were collected every 250 ml, analyzed for ethanol using an acidified potassium dichromate colorimeter test. A second



TABLE VII

DECOMPOSITION OF OZONE IN SECONDARY EFFLUENT RO PERMEATE

700 ml of secondary effluent (Brockton) RO permeate was ozonated for one hour at room temperature with oxygen containing 38 mg/l of ozone, and the absorbance then monitored at 254 nm in a 10 cm path length cell

<u>Time</u>	<u>OD</u>	<u>1/(OD)</u> <sup>1/2</sup>
0	~0.25	
15	0.235	2.06
30	0.225	2.11
50	0.192	2.28
60	0.165	2.47
75	0.137	2.71
93	0.107	3.06
105	0.091	3.31
120	0.075	3.65
135	0.063	3.98
150	0.053	4.35
180	0.042	4.88
210	0.039	5.06
240	0.039	5.06
285	0.039	5.06

identical experiment was performed with slightly less activated carbon, i.e., only 73 grams of activated carbon were used. The results are presented in Figure 24.

B. Discussion of Results

From the effluent curves, the total alcohol adsorption on the activated carbon may be estimated and a distribution coefficient for alcohol between the carbon and the solution calculated and compared with those derived from batch experiments. These data are presented in Table VIII.

The adsorption experiments indicate (Table IX and Figure 25 and 26) that the batch equilibrium data fit Freundlich adsorption isotherms. The slight effect of temperature on ethanol distribution indicates a low heat of adsorption which is consistent with the relatively weak adsorption of the alcohol.

Acetaldehyde is somewhat more strongly adsorbed than the ethyl alcohol, which is consistent with the higher hydrogen bonding potential of the alcohol and its consequent greater affinity for water. The data indicate both ethyl alcohol and acetaldehyde can be adsorbed from MUST RO permeate using activated carbon columns but the low distribution coefficients indicate that the carbon would have to be regenerated frequently. With a distribution coefficient of  $\alpha$ , the weight of carbon is at a minimum  $W/\alpha$ . Thus, to process 3500 gallons of water with an alcohol distribution coefficient of 30, approximately 18 ft.<sup>3</sup> of carbon would be required. With a volume of 18 ft.<sup>3</sup> of carbon to process 3500 gallons of water, the carbon would have to be regenerated on a daily basis.

From the standpoint of monitoring, neither alcohol nor acetaldehyde is strongly adsorbed and either might be a suitable tracer material depending on the location of the activated carbon and the impurities which were to be removed by it. For example, if it were located after the ozonation step and were intended to remove substantially all residual impurities, then acetaldehyde might again prove to be a suitable tracer compound, both because it is likely to be the principal residual impurity and because it is not strongly adsorbed.

FIGURE 24: COLUMN ADSORPTION EXPERIMENTS

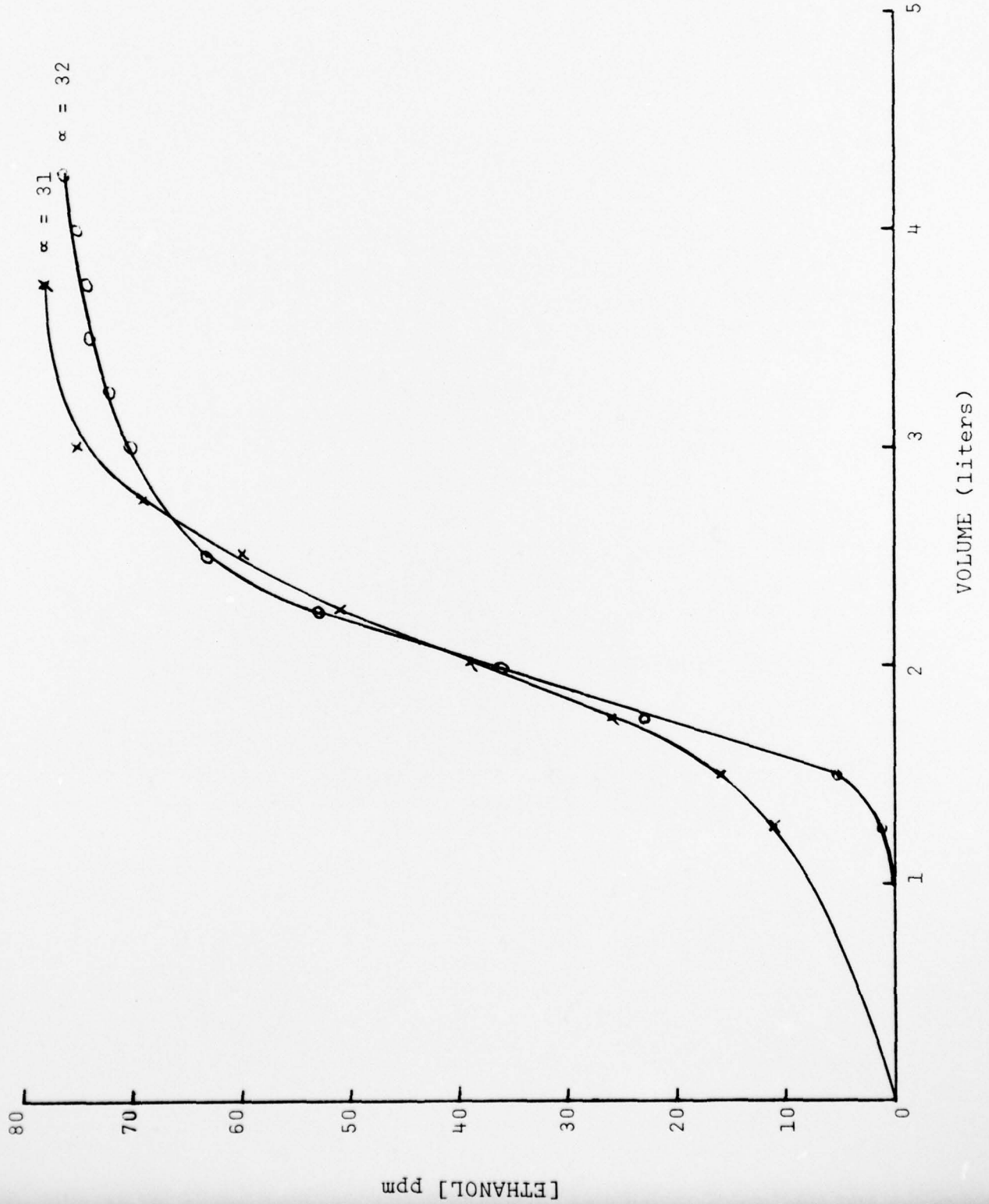


TABLE VIII

DECOMPOSITION OF OZONE IN SECONDARY EFFLUENT RO PERMEATE

One liter of permeate ozonated at room temperature  
for 30 minutes with oxygen containing 38 mg/l ozone

Absorbance monitored at 254 nm in a 10 cm path  
length cell using a Coleman 139 Spectrophotometer

<u>Time (minutes)</u>	<u>OD</u>	<u>pH</u>
5	>0.20	
20	0.175	
25	0.150	
30	0.135	
47	0.092	
80	0.055	
87	0.048	
~24 hours	0.0146	4.8

One liter of permeate contacted with gas containing  
38 mg/l ozone for a few minutes to saturate it

Absorbance monitored as above

<u>Time (minutes)</u>	<u>OD</u>
5	0.020
20	0.0166
30	0.0126
40	0.092
50	0.068
60	0.048
70	0.036
80	0.020
90	0.020



TABLE IX

BATCH TYPE CARBON ADSORPTION EXPERIMENTS

<u>Substance</u>	<u>Volume of H<sub>2</sub>O (liters)</u>	<u>Amount of Carbon (gms)</u>	<u>Temp. (°C)</u>	<u>Before Adsorption [ppm]</u>	<u>After Adsorption [ppm]</u>	
C <sub>2</sub> H <sub>5</sub> OH	1	100	25	740	240	α = 21
C <sub>2</sub> H <sub>5</sub> OH	1	100	60	760	230	α = 23
C <sub>2</sub> H <sub>5</sub> OH	1	100	25	50	13	α = 28
C <sub>2</sub> H <sub>5</sub> OH	1	100	25	96	72	α = 30
CH <sub>3</sub> COH	1	100	25	800	170	β = 37
CH <sub>3</sub> COH	1	100	25	51	8.5	β = 50
CH <sub>3</sub> COH	1	100	25	100	18.5	β = 44

Equilibration Time ~17 hours

Column Adsorption Experiments

<u>Substance</u>	<u>Temp. (°C)</u>	<u>Solution Concentration [ppm]</u>	
C <sub>2</sub> H <sub>5</sub> OH	25	79	α = 32
CH <sub>3</sub> COH	25	~ 2	β = 250

Distribution Coefficient: α =  $\frac{\text{gms alcohol adsorbed/gms carbon}}{\text{gms alcohol in solution/gms water}}$

β =  $\frac{\text{gms acetaldehyde absorbed/gms carbon}}{\text{gms acetaldehyde in solution/gms water}}$

FIGURE 25

FREUNDLICH ADSORPTION ISOTHERM FOR ETHANOL

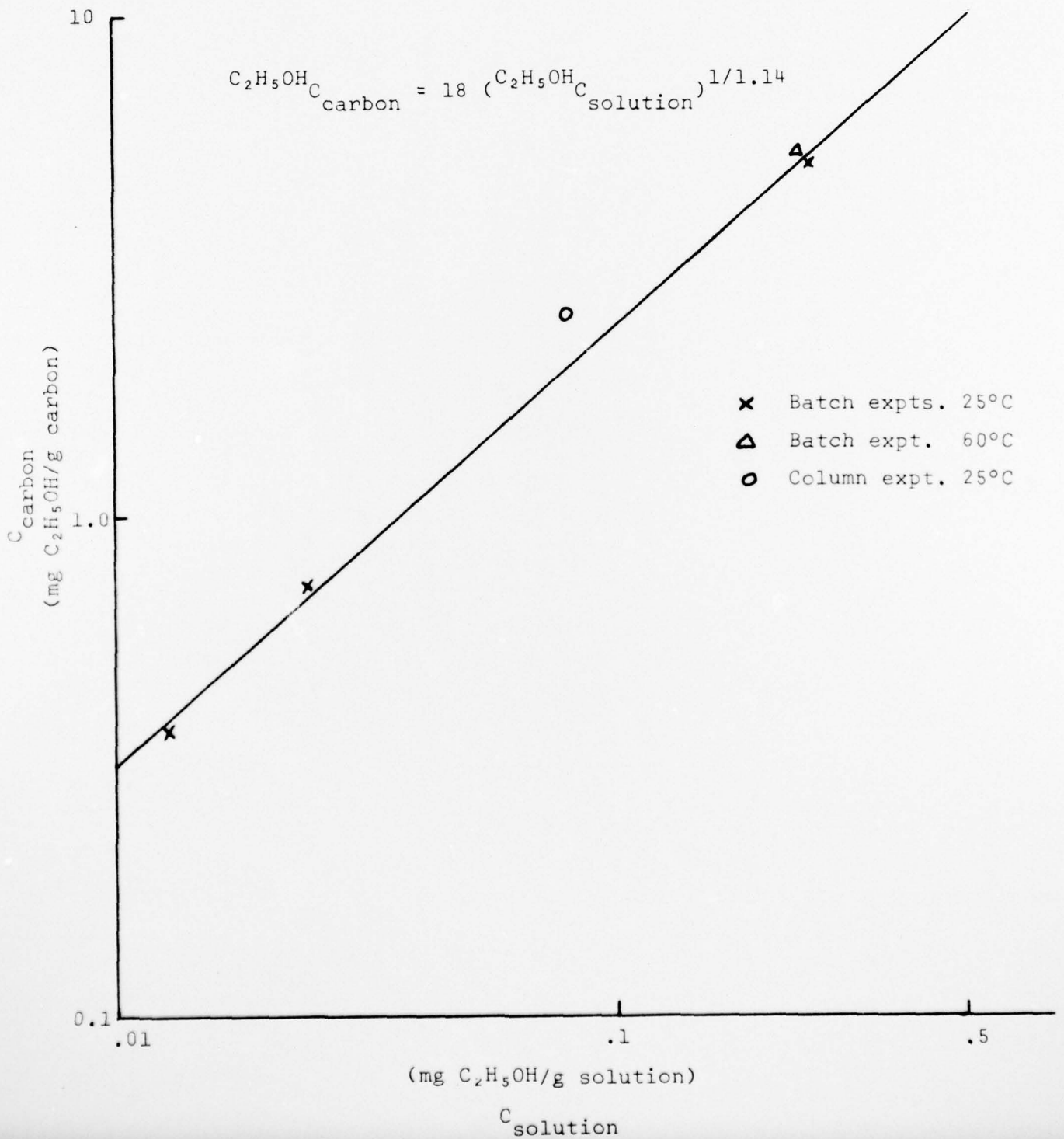
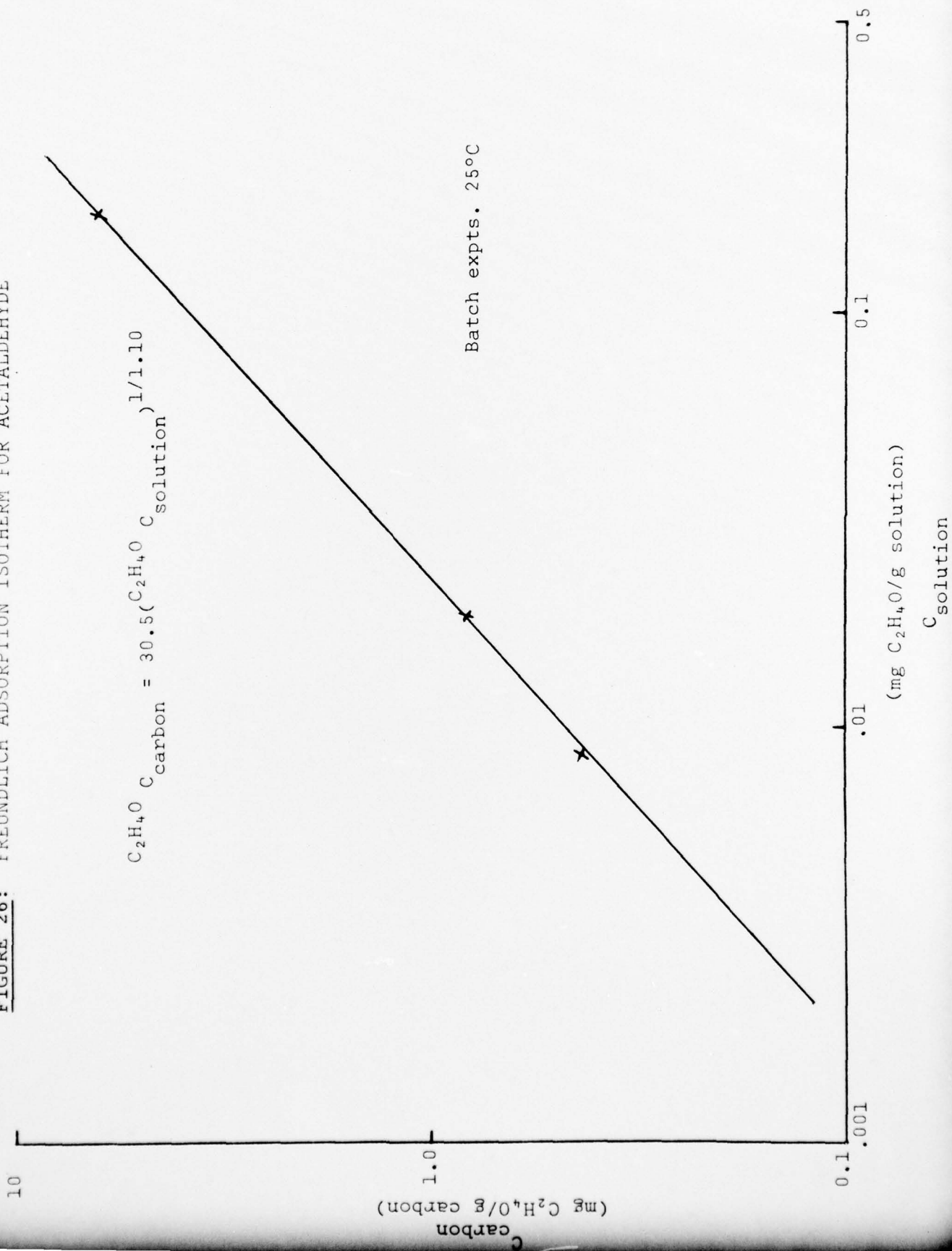


FIGURE 26: FREUNDLICH ADSORPTION ISOTHERM FOR ACETALDEHYDE



V. SECONDARY EFFLUENT WASTE WATER STUDIES

Amicon has initiated studies for the monitoring of reverse osmosis, ozonation, and activated carbon treatment steps in various combinations for the processing of secondary effluent of municipal waste water to upgrade it to tertiary quality. Amicon arranged to receive secondary effluent waste water from the municipal waste treatment plant in Brockton, Massachusetts.

A. Pilot Plant - Construction and Operation

A pilot plant for the treatment of secondary effluent waste water was constructed as shown in Figure 27. The ten-gallon, stainless steel reservoir is filled with secondary effluent waste water. With the appropriate valves open and shut, the untreated effluent is transferred from the reservoir to the accumulator by pressurizing the reservoir with the aid of the nitrogen tank. Once the accumulator is filled, the reservoir is isolated from the system by closing the valves leading to it. The whole system is then pressurized to operating pressure via the nitrogen tank. The tubing used to build the plant consists of 1/2" stainless steel tubing except for the cooling coil which is 5/8" stainless steel acting as a simple heat exchanger. The pump used in this system is a sealless magnet drive pump bought from the Kontro Co., Inc. Since the recirculating pump has a capacity of 20 gpm, which is considerably in excess of that required by the RO unit, most of the waste water is recirculated through the bypass loop, i.e., the cooling coil. The cooling coil is situated in a large vessel which is filled with ice before each run since an appreciable rise in temperature occurs during the course of an experiment. The RO unit was received from Universal Oil Products Company. It is a spiral-wound, 620 mini-module with 1.0 sq. ft. membrane area, producing 10.5 gfd with 96.6% sodium chloride rejection at 600 psi, 25°C and 5,000 ppm NaCl solution. The recommended flow rate through the module is 2.0 gpm.

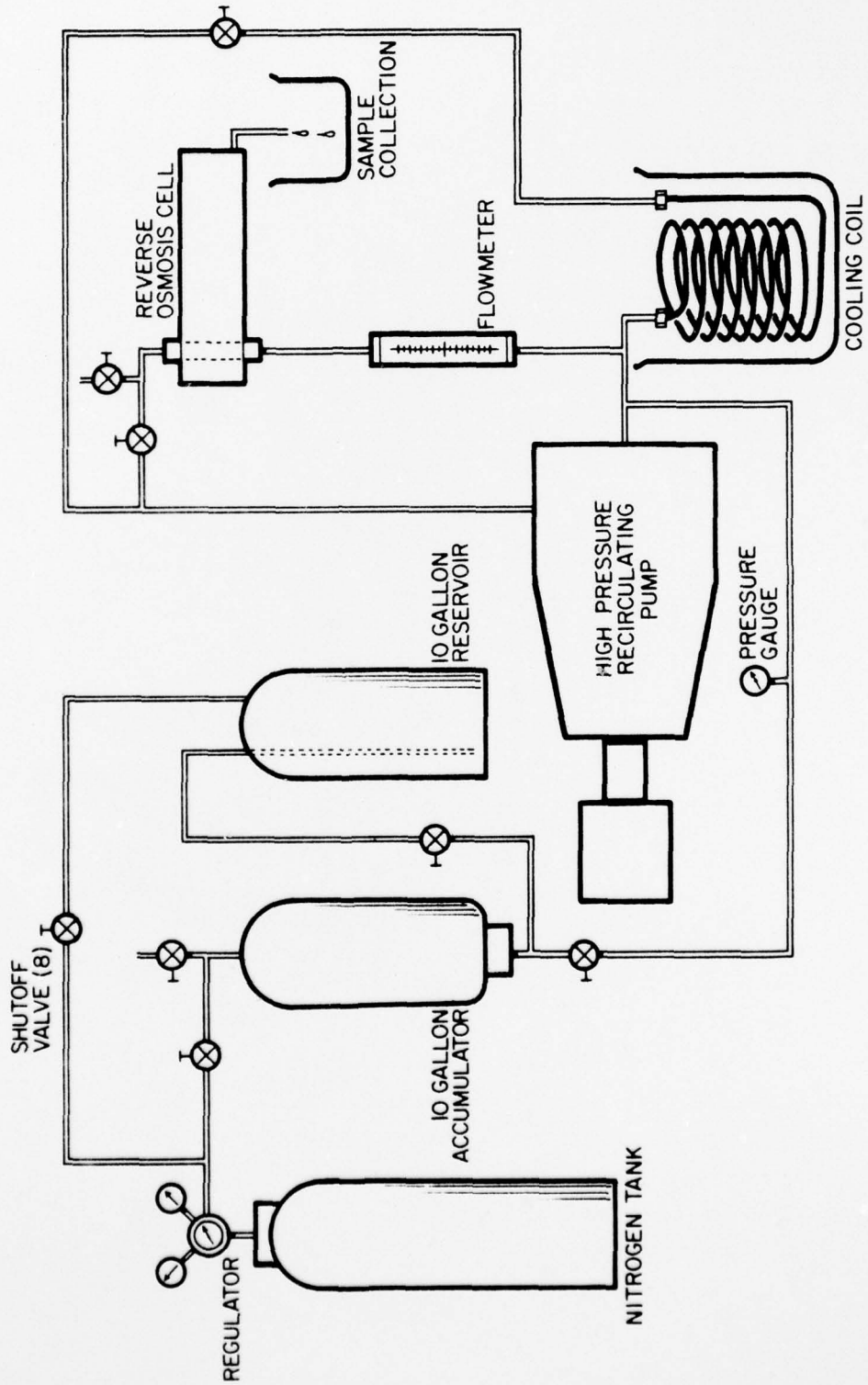
B. Experimental Procedure

To five gallons of waste water enough sodium chloride was added to make a 5,000 ppm solution. This solution was added to the reservoir and then transferred to the accumulator and pressurized at 600 psi. Ice was added to the cooling coil container and the pump switched on. The flow through the RO unit was adjusted to 2 gpm and samples of approximately 20 ml



FIGURE 27

PILOT PLANT FOR SECONDARY EFFLUENT  
REVERSE OSMOSIS TREATMENT



were collected for TOC analysis at two-liter intervals. A total volume of eight liters was collected. The results of this experiment are represented in Figure 28.

In a subsequent experiment, water from the Brockton waste treatment plant was again processed through the VOP RO module as before, and the RO permeate was then divided into three parts. The first was ozonated for 30 minutes at room temperature with oxygen containing 38 mg/l of ozone using the apparatus shown in Figure 1; the second was ozonated under the same conditions for 60 minutes; and the third was not subjected to further treatment. All three samples were then reacted with alkaline permanganate to determine whether a detectable change in OD would occur and all three samples were analyzed for TOC. Results are presented in Table X.

FIGURE 28: RO TREATMENT OF SECONDARY EFFLUENT WASTE WATER

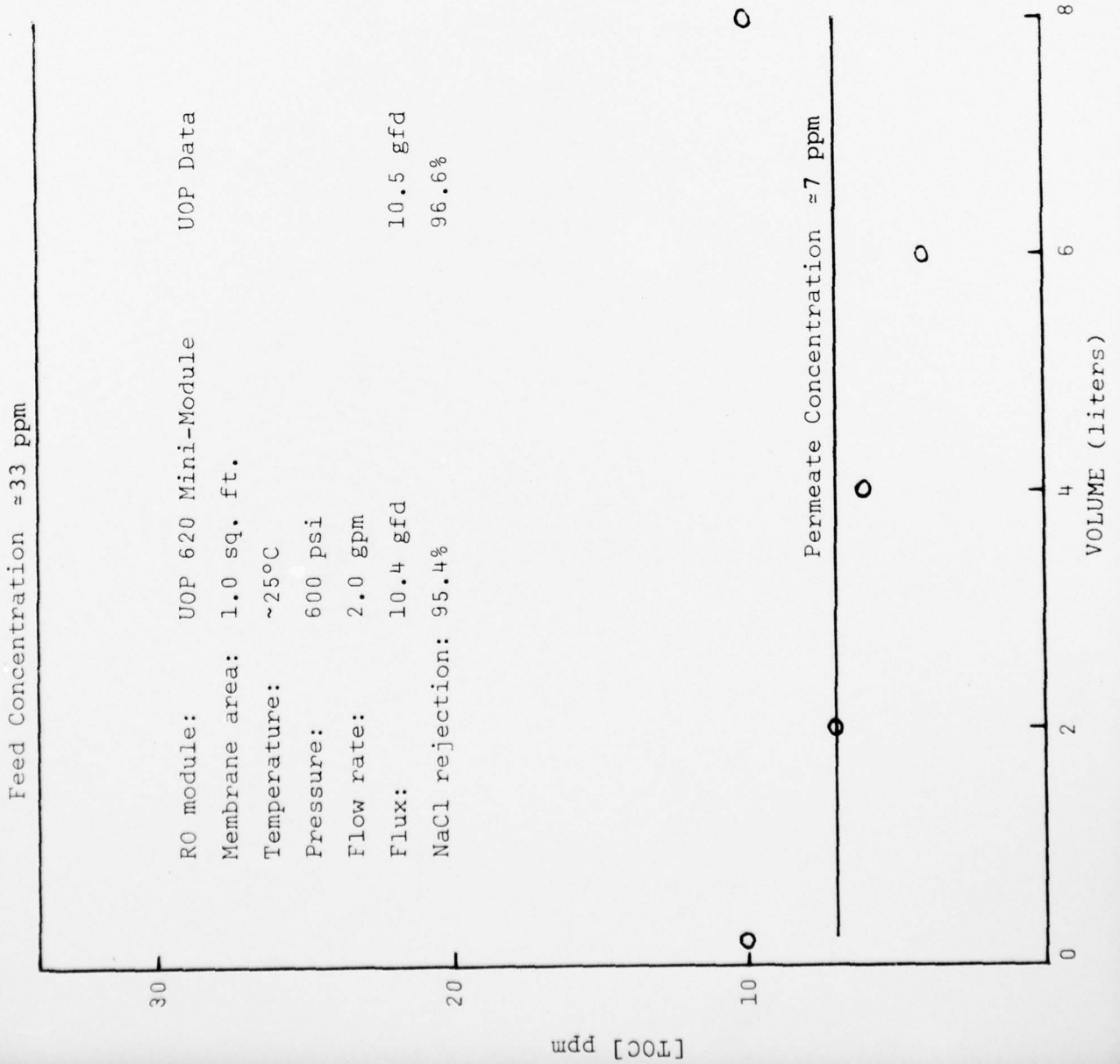


TABLE X

OZONATION OF RO PERMEATE OF SECONDARY EFFLUENT  
FROM THE BROCKTON, MASSACHUSETTS, MUNICIPAL  
WASTEWATER TREATMENT FACILITY

<u>Sample</u>	<u>Ozonation Time (minutes)</u>	<u>Ozonation Temperature (°C)</u>	<u>TOC</u>
RO permeate	0	--	6.5
RO permeate	30	25	2.7
RO permeate	60	25	2.5
RO permeate	30	40	1.6
RO permeate	60	40	1.5



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