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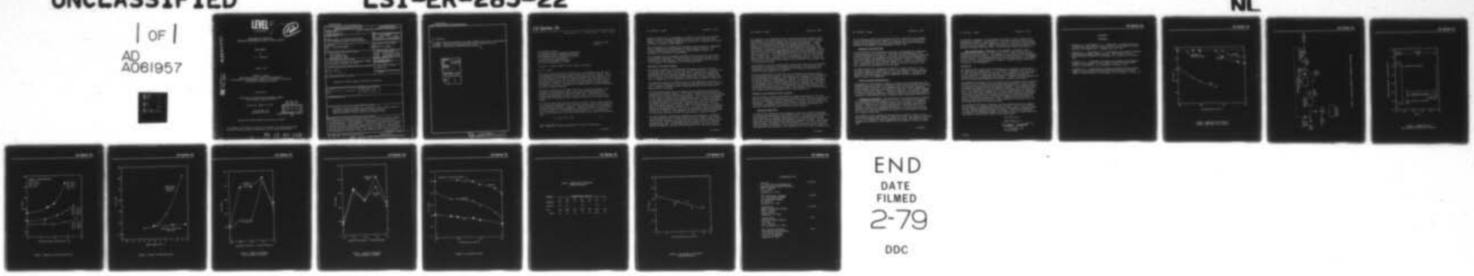

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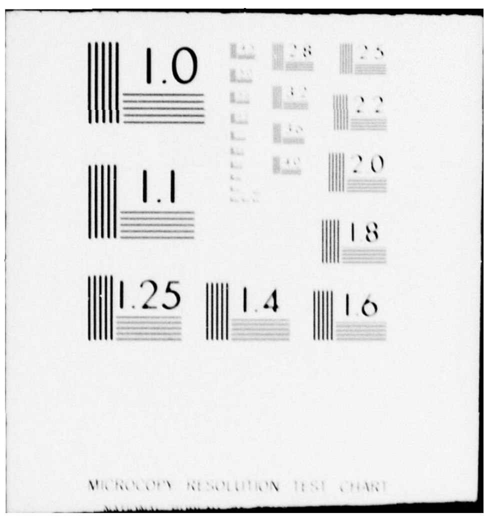
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DEVELOPMENT AND TESTING OF BREADBOARD ELECTROCHEMICAL ORGANIC CONTENT ANALYZER

FINAL REPORT

by

R. J. Davenport

October, 1978

William J. Cooper
Contracting Officer's Technical Representative
US Army Medical Bioengineering Research and Development Laboratory
Fort Detrick, Frederick, MD 21701

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A Breadboard Electrochemical Organic Content (EOC) Analyzer has been designed and developed for on-line monitoring of organic solute concentrations in ozonated effluents. The performance of the Analyzer has been improved through the addition of the intermittent flow accessory that employs in situ electrochemical reduction of dissolved oxygen in order to measure EOC values without interference from dissolved oxygen. The accessory allows accurate and precise EOC measurements to be made at electrode potentials where the EOC response

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to organic solutes is sensitive, but which normally are subject to interference by oxygen. The operation of the accessory and its checkout tests are described. Results and conclusions are presented.

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October 27, 1978
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Mr. William J. Cooper
Contracting Officer's Technical Representative
Environmental Research Requirements Division
Environmental Protection Research Department
U.S. Army Medical Bioengineering
Research and Development Laboratory
Ft. Detrick, Frederick, MD 21701

Reference: Contract DAMD17-75-C-5070, Letter Final Report

Dear Mr. Cooper:

This is the Letter Final Report (ER-285-22) of the Development and Testing of the Breadboard Electrochemical Organic Content (EOC) Analyzer Program. This report summarizes the program activities performed since the submission of the two Annual Reports.(1,2) Also, an Interim Report(3) has been submitted as a summary of work performed for the Naval Civil Engineering Laboratory (CEL) at Port Huenene, CA 93043. This work involved the evaluation of the Breadboard EOC Analyzer as a monitor of aqueous film forming foams in wastewaters generated during fire fighting training.

The efforts reported in this Letter Final Report involve development of the intermittent flow accessory, which is used in the Breadboard Analyzer to eliminate interferences from dissolved oxygen (O_2). Development of the accessory was undertaken in order to permit operation of the Analyzer with organic adsorption potentials that increased its sensitivity to many organic solutes.

Prior efforts have shown that the electrode potential used for organic adsorption and the EOC measurement is an important variable affecting the sensitivity of the Analyzer's response to organics. During development of the Breadboard Analyzer it was shown that operation at adsorption potentials between 0.0 and -0.8 V was subject to an interference from dissolved O_2. The interference is due to the reaction of O_2 at the indicating electrode during the EOC measurement:

$$O_2 + 2H_2O + 4e^- = 4OH^- \quad (1)$$

Note: References cited in parentheses are listed in Attachment 1.

continued -

Operation without the O_2 interference is possible at potentials more positive than 0.0 V because at these potentials O_2 does not react at the electrode. However, at 0.0 V the Analyzer exhibits low sensitivity to methanol and acetone, with better response to urea (Figure 1).

The intermittent flow accessory is a relatively simple approach to eliminating the O_2 interference at the potentials of optimum organic response. The accessory employs the approach of in situ electrochemical reduction of dissolved O_2 to eliminate its interference.

This technique has the advantages of simple, automated operation and requires few mechanical components. Few modifications to existing EOC hardware were required to add the accessory. The function of the accessory and the results of the checkout tests performed on it are described below.

Operation of the Flow Accessory

The hardware schematic of the Breadboard EOC Analyzer is shown in Figure 2. The solenoid valve, which with the logic required to operate it constitutes the intermittent flow accessory, directs the flow of sample/electrolyte mixture through the EOC cell or through a bypass loop around the cell. Whenever the flow of solution is directed through the bypass loop, the solution within the cell is stagnant and O_2 is eliminated by electrochemical reduction (Equation 1).

The temperature sensor for feedback control of the temperature controller is located at the intersection of the bypass loop and the solution path in the EOC cell. Therefore, feedback control is maintained whether the solution flows through cell or the bypass.

The relationship between the flow sequence and the indicating electrode preconditioning is shown in Figure 3. This figure illustrates that solution flows through EOC cell during the electrode oxidation. This results in the introduction into the cell of a fresh batch of sample solution prior to the EOC measurement. It also permits oxidation products generated during the oxidative cleaning of the indicating electrode to be flushed from the cell. The electrode reduction step begins as soon as the solution is bypassed around the cell. The very negative potential applied to reduce oxides on the indicating electrode also aids in the electrochemical reduction of O_2. The bypass sequence is maintained through the adsorption stage so that the EOC measurement is made after several seconds of O_2 reduction. This sequence was selected for effective elimination of the high O_2 concentrations that are experienced in ozonated effluents.

The logic required to operate the intermittent flow accessory is integrated with the Analyzer's logic through a single electrical connector that brings power from the Analyzer to the accessory and returns operator commands to the solenoid valve. The accessory logic package includes controls for automatic and manual operation. In the MANUAL mode, the operator can select FLOW or BYPASS conditions for checkout or experimentation with other flow sequences.

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The operation of the intermittent flow accessory requires the operator to be knowledgeable of two special conditions. The first is startup of the Analyzer after it has been stored, cleaned or flushed with distilled water. Initial startup of the Analyzer must be made in the MANUAL FLOW position. In this position the cell will be filled with the sample/electrolyte mixture. The conductivity of the solution in the cell will therefore be sufficiently high that automatic sequencing of the electrode preconditioning is possible. If the Analyzer is started in the MANUAL BYPASS position or in the AUTOMATIC position when it happens to be in the BYPASS Mode, the cell will be dry or will contain only distilled water. In either case, the resistance of the cell will be too high to permit normal operation of the preconditioning sequence. Without the operation of the preconditioning sequence, the intermittent flow accessory will not automatically operate.

Proper startup of the EOC Analyzer after storage should begin with approximately five minutes of operation in the MANUAL FLOW position. Following that, the intermittent flow accessory can be placed in the AUTOMATIC position and the normal startup procedures can be used.[4]

The second consideration is operation of the Breadboard EOC Analyzer without the intermittent flow accessory. The accessory logic package can be disconnected and the Breadboard EOC Analyzer can be operated in a continuous flowing mode for special scientific investigations. However, the solenoid valve will remain in the position it is in when the accessory logic is disconnected. Therefore, if the solenoid valve is in the BYPASS position, the accessory should be put in the MANUAL FLOW position prior to disconnecting the electrical interface connector which attaches the accessory logic to the Analyzer. The solution/electrolyte mixture will then continuously flow through the EOC cell.

Checkout of the Intermittent Flow Accessory

Tests performed to check out the accessory included optimization of the flow sequence to eliminate the dissolved O_2 interference and a checkout of the effectiveness of the temperature control components with the bypass loop incorporated in the Analyzer. Optimum potentials for response to acetone, methanol and urea were identified, and response of the Analyzer to those organics was measured for solutions containing individual solutes and solute mixtures.

Dissolved Oxygen Test

In Figure 4 the response of the EOC Analyzer to solutions containing dissolved O_2 at concentrations between 0 and 18 ppm is shown. The largest O_2 concentration is determined by the expected concentration of O_2 in ozonated effluents from ozone (O_3) contactors operated with pressurized O_3/O_2 gas mixtures. Results using three flow and electrode preconditioning sequences are shown. The sequence shown in Figure 3 resulted in very little response to O_2 over the entire O_2 concentration range investigated. Other sequences that involve shorter reduction and adsorption times resulted in more significant errors at high O_2 concentrations.

continued -

For the sequence selected as the baseline with the intermittent flow accessory, no error was observed over the range 0 to 10 ppm O_2, and it is therefore concluded that this sequence will be entirely effective for normal air-saturated effluents having maximum O_2 concentrations of about 8 ppm.

Temperature Controller Test

The effectiveness of the temperature controller in maintaining the temperature of the solution and EOC cell at 25 C was tested with the intermittent flow accessory installed in the Analyzer. This test is required because the insertion of the intermittent flow accessory and solution bypass loop was considered to potentially impact the temperature control function. In order to minimize this effect, the bypass loop is an internal channel in the Teflon body of the EOC cell. Location of the bypass loop in the body of the cell was chosen to aid heat transfer from the solution to the cell body.

The effectiveness of the temperature controller is shown in Figure 5. Over the sample temperature range of 24.7 to 30.5 C the temperature controller maintained the response of the EOC Analyzer relatively constant. Response during operation of the EOC Analyzer with the temperature controller inoperative is shown in Figure 5 for comparison.

Organic Response Characteristics

Investigation of the Analyzer's response to organics with the intermittent flow accessory installed was begun by determining the electrode potential that resulted in the greatest sensitivity. Then response curves for solutions containing acetone, methanol and urea were prepared for comparison to the response obtained without the accessory (Figure 1). During the last test, the Analyzer's response to solutions containing mixtures of acetone, methanol and urea was measured for comparison to data obtained earlier during the Design Verification Test (DVT).[2]

Individual Solute Tests. The intermittent flow accessory permits operation in the adsorption potential range of 0 to -0.8 V. The first effort required was identification of the optimum potential within this range for response to organics. Figures 6 and 7 show the response of the Analyzer to methanol and acetone as a function of the adsorption potential. The sensitivity of the response is shown by the difference between the curve for distilled water and the curve for a solution containing the organic at a concentration of 100 ppm total organic carbon (TOC).

The Analyzer is more responsive to methanol than to acetone, except at -0.2 V. Even at this potential the response to acetone is small. The adsorption potential of -0.6 V was selected for use in subsequent tests since the Analyzer is very responsive to methanol at that potential and its response to acetone is acceptable.

continued -

The Analyzer's response to urea, methanol and acetone is shown in Figure 8 for concentrations between 1 and 1000 ppm TOC. With the intermittent flow accessory the detection limits for these organics are less than 1 ppm TOC for urea and methanol and 10 ppm for acetone. Without the accessory the detection limits for urea, methanol and acetone were less than 1, 50 and 100 ppm, respectively (Figure 1).

Solute Mixture Test. Measurement of the Analyzer's response to seven simulated ozonated effluents was part of the DVT.[(2)] These solutions had the compositions listed in Table 1. The response of the Analyzer to these solutions was measured with the accessory, and this data is shown in Figure 9. The response curve is similar to that obtained during the DVT and suggests that the Breadboard Analyzer with the accessory produces a response to organic mixtures that can be correlated to TOC measurements.

Conclusions

The Breadboard EOC Analyzer has been developed as an automated, on-line monitor of organic solute concentrations. It is capable of unattended operation for up to 24 hours with daily resupply of electrolyte. The reliability of the instrument and its capability for unattended operation has been improved through the incorporation of the intermittent flow accessory. Checkout tests have demonstrated that the accessory has improved the instrument's analytical performance.

The Breadboard EOC Analyzer is now a valuable tool for evaluating the EOC Analyzer concept for use in various control and monitoring applications. While it must be recognized that the Analyzer was designed specifically for monitoring ozonated effluents, measurements of other effluents are possible. These effluents should not contain particulates for proper operation of the sample pump and solenoid valve. The Analyzer was designed for a constant sample pressure and significant variations in the sample pressure during operation will necessitate adjustments to the sample pump flow rate. Operation with highly contaminated samples may result in unexpected performance of Analyzer components such as the sample or electrolyte pump and solenoid valve. These components were selected for use in monitoring high quality, ozonated effluents.

The Breadboard EOC Analyzer represents the first demonstration of an automated monitor based on a promising new analytical technique. Future efforts will be directed toward simplified hardware and operator requirements, including simpler and less frequent electrolyte resupply procedures. While these developments are underway, the Breadboard Analyzer may be used to obtain a valuable data base with which to assess the EOC concept for new applications.

Very truly yours,

LIFE SYSTEMS, INC.

Ronald J. Davenport

R. J. Davenport, PhD
Program Manager

RJD/bg

ATTACHMENT 1

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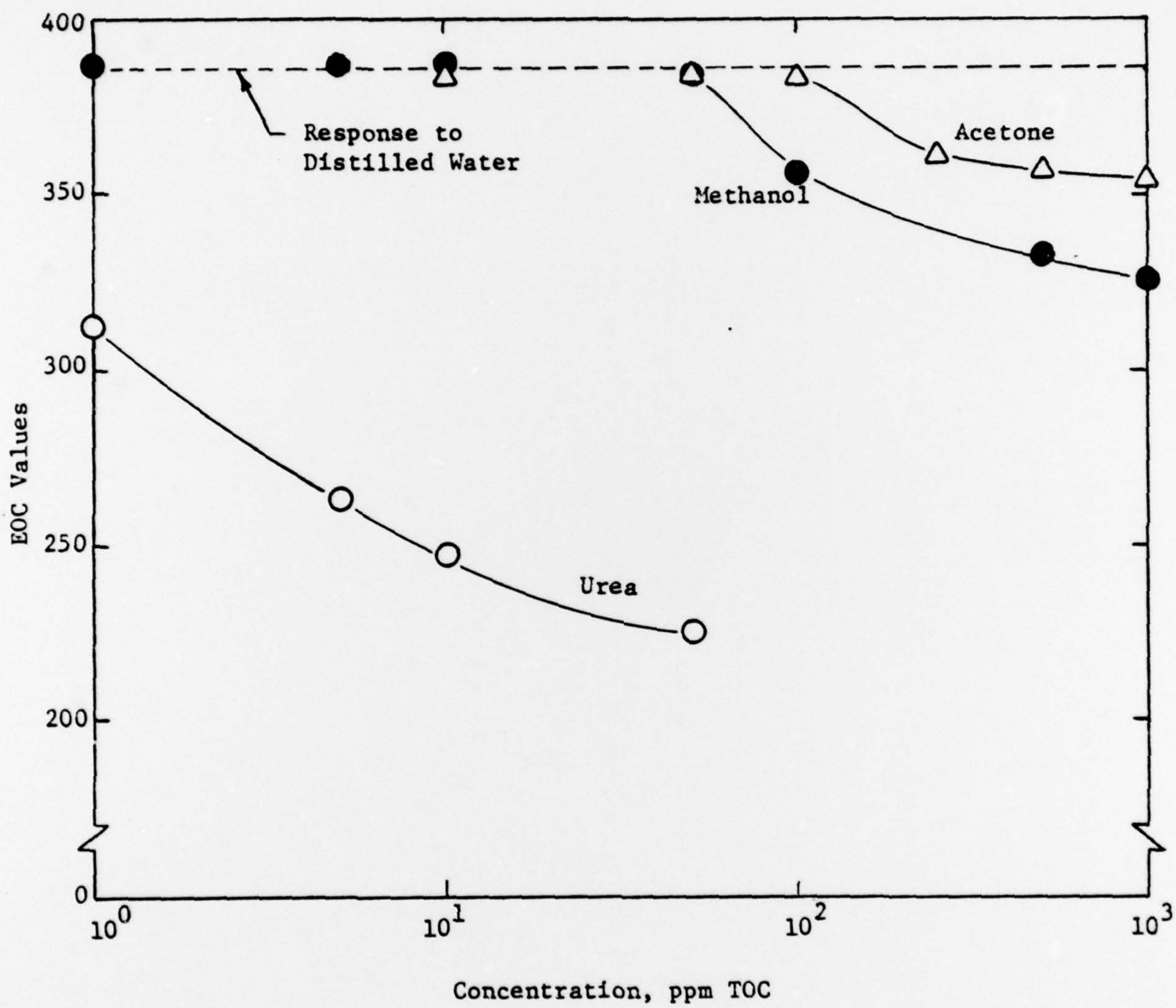

FIGURE 1 RESPONSE OF EOC ANALYZER
WITHOUT INTERMITTENT FLOW ACCESSORY

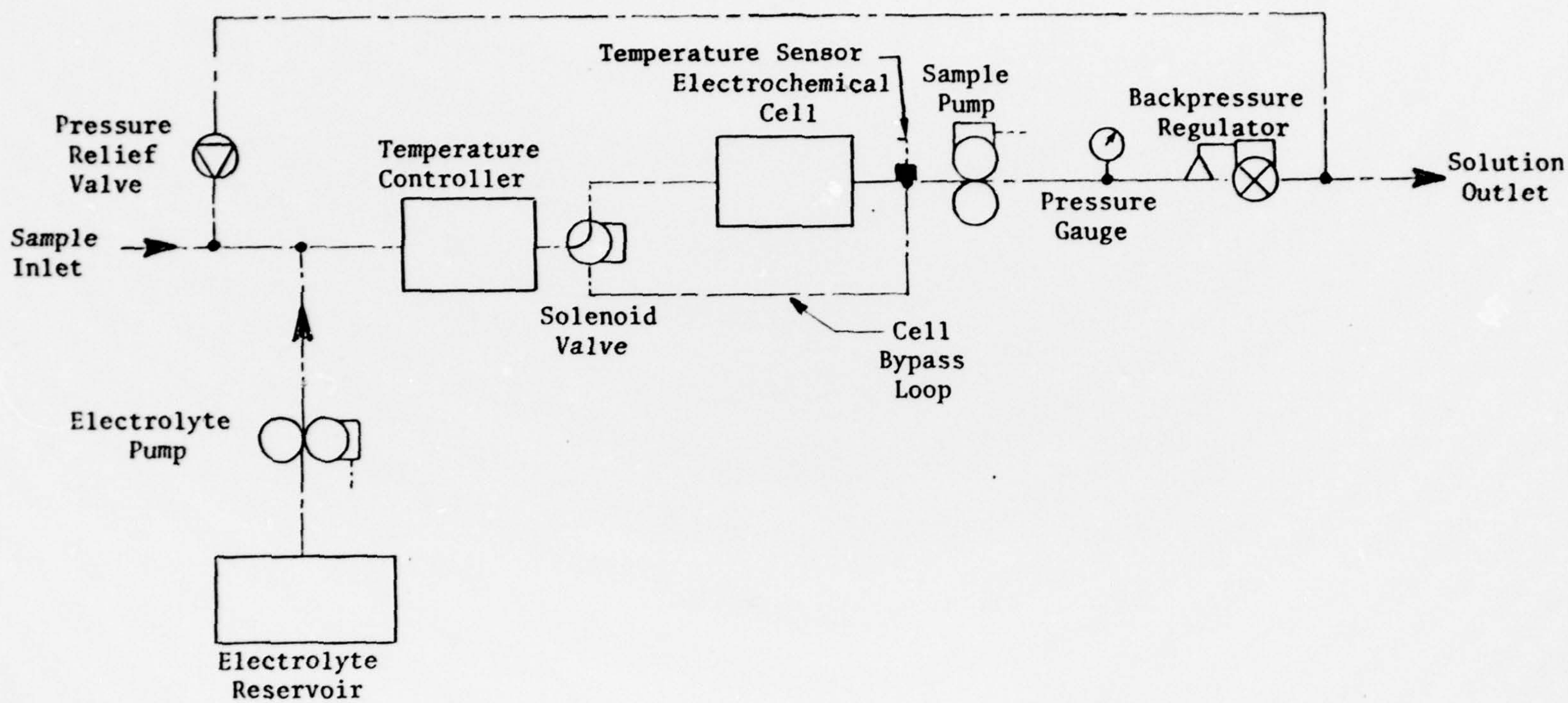

FIGURE 2 MECHANICAL SCHEMATIC OF BREADBOARD EOC ANALYZER

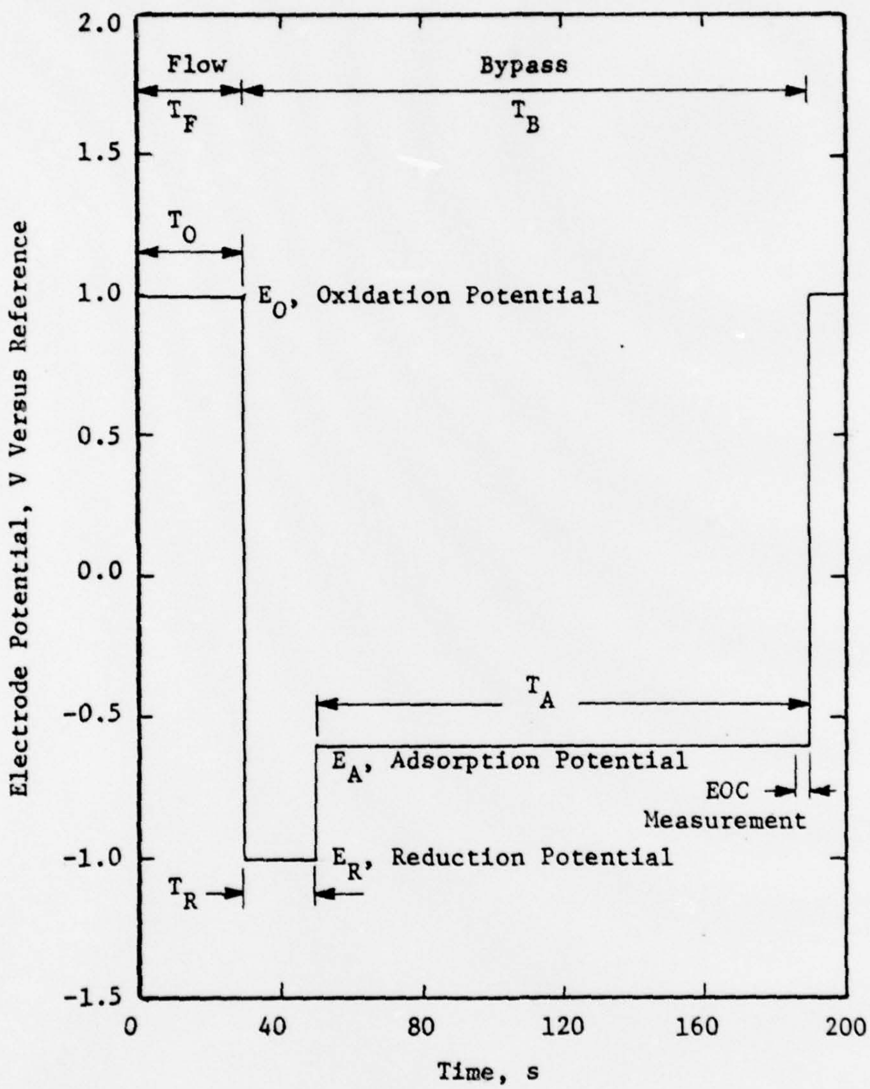

FIGURE 3 INTERMITTENT FLOW AND ELECTRODE PRECONDITIONING SEQUENCE

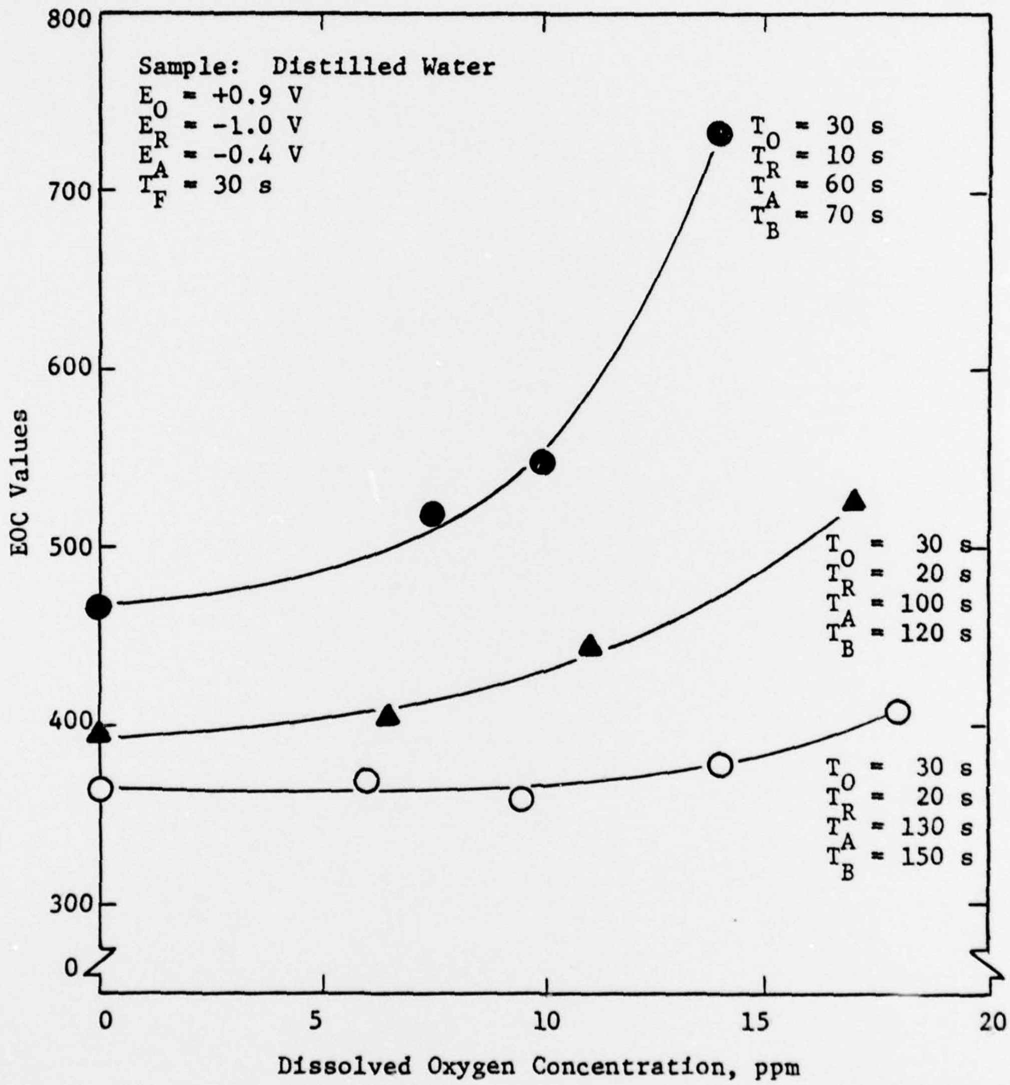

FIGURE 4 RESULTS OF DISSOLVED OXYGEN TEST

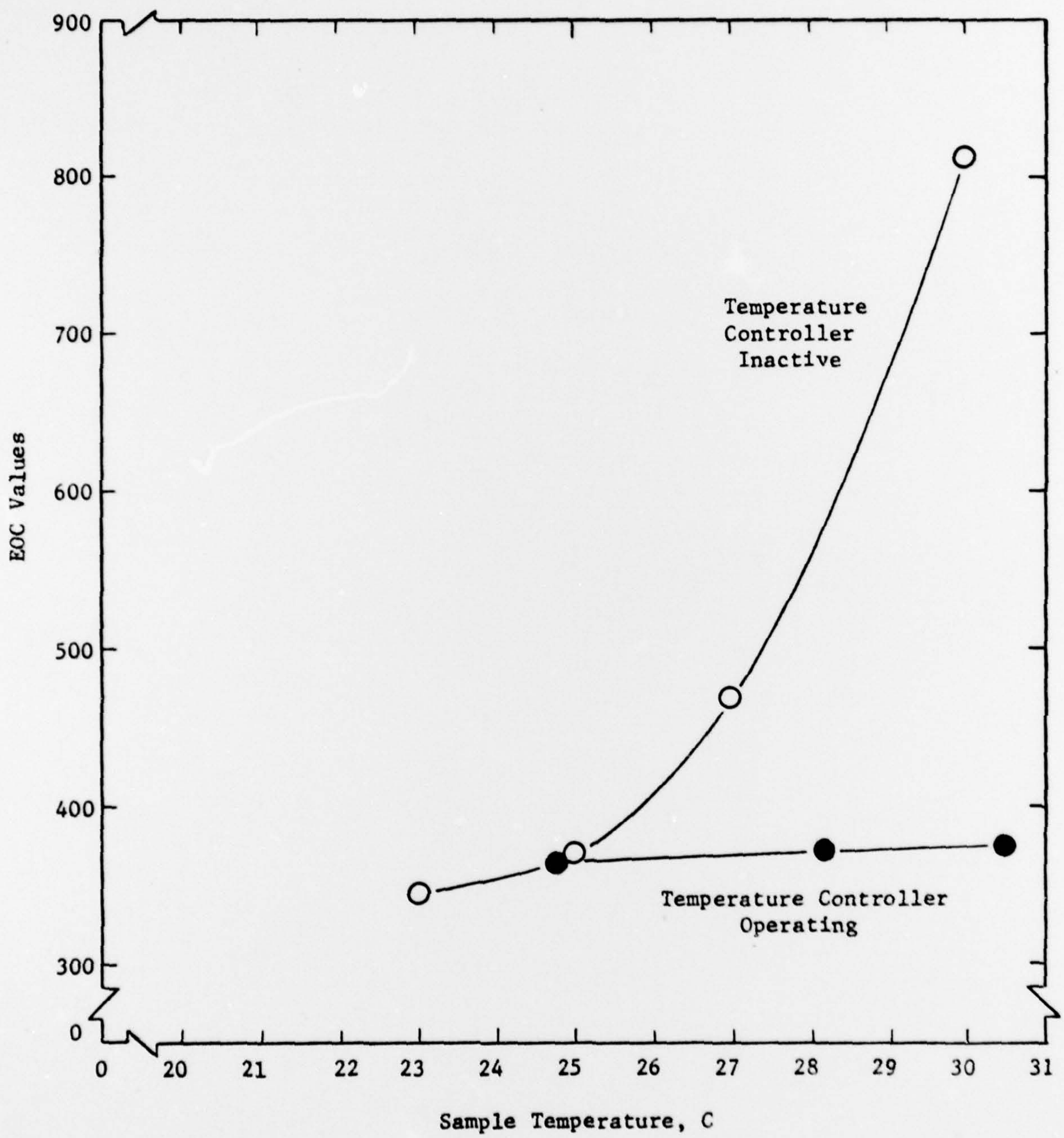

FIGURE 5 RESULTS OF TEMPERATURE STUDY

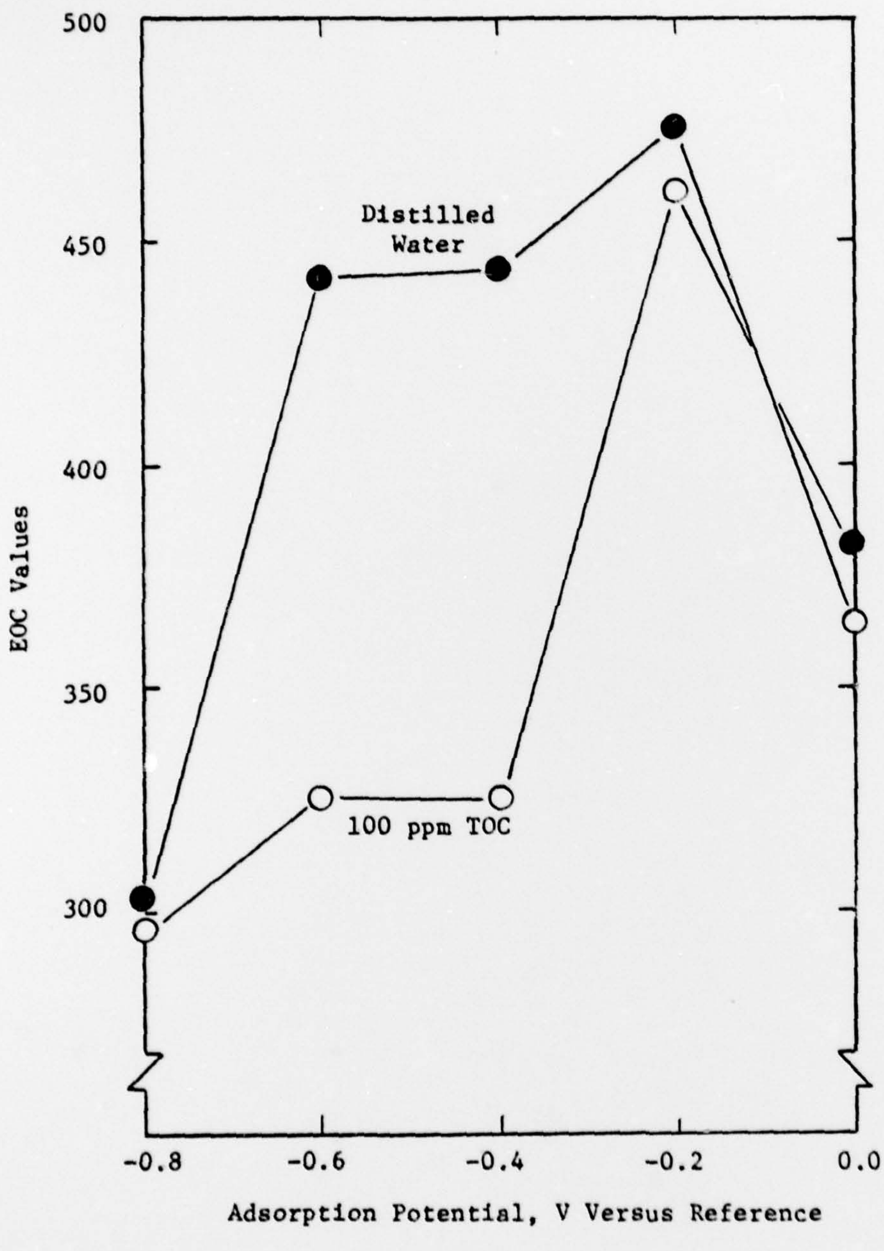

FIGURE 6 POTENTIAL DEPENDENCE
OF EOC RESPONSE TO METHANOL

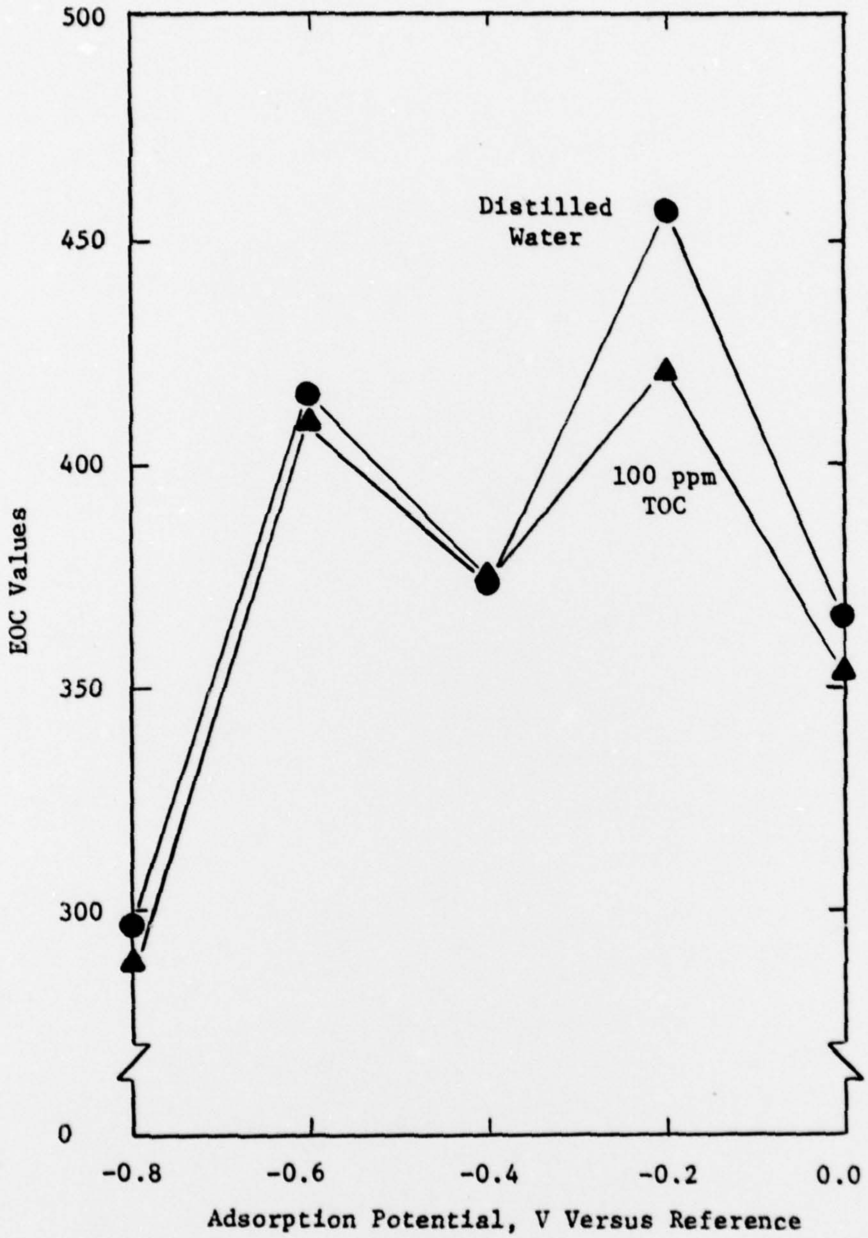

FIGURE 7 POTENTIAL DEPENDENCE
OF EOC RESPONSE TO ACETONE

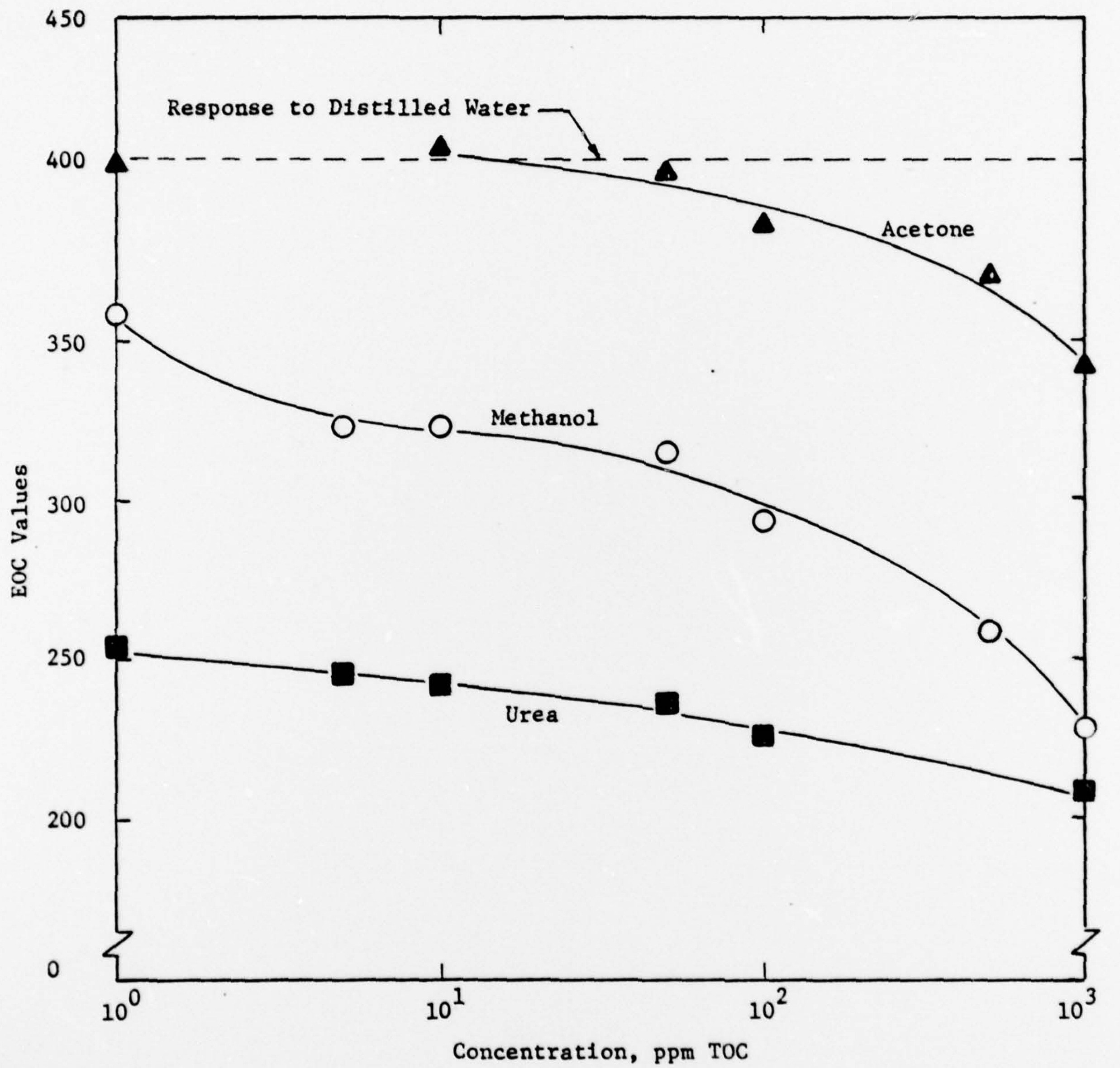

FIGURE 8 EOC RESPONSE CURVES

TABLE 1 COMPOSITION OF SIMULATED OZONATED EFFLUENTS

Solutes	Concentration, ppm TOC						
	1	2	3	4	5	6	7
Methanol	1.1	5.2	-	1.8	0.5	9.7	-
Acetone	0.4	1.6	-	2.9	-	6.2	-
Urea	2.6	2.5	3.3	2.6	2.7	2.7	1.0
Total	4.1	9.3	3.3	7.3	3.2	18.6	1.0

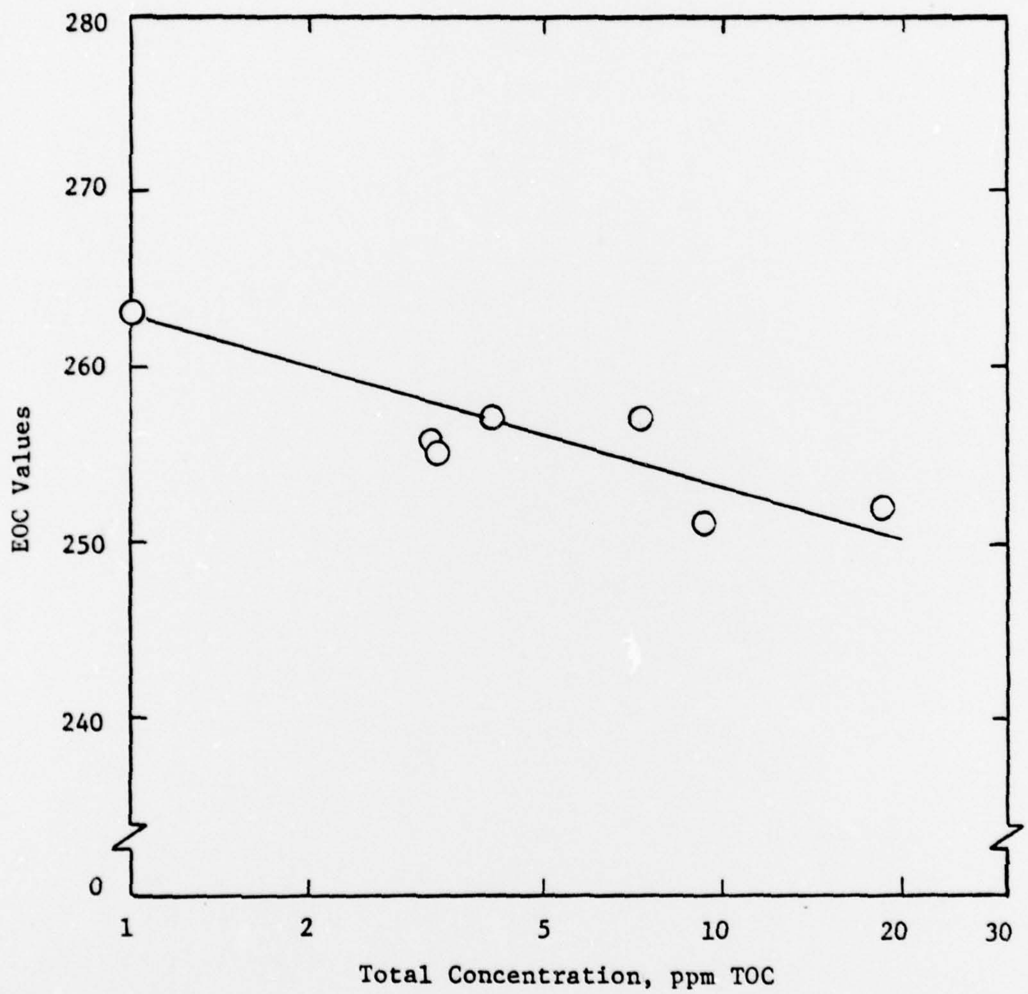

FIGURE 9 EOC RESPONSE TO SIMULATED OZONATED EFFLUENTS

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