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DEVELOPMENT AND TESTING OF BREADBOARD ELECTROCHEMICAL ORGANIC CONTENT ANALYZER (U)

ANNUAL REPORT

by

R. J. Davenport and R. A. Wynveen

October 1977

Project Officer: William J. Cooper
Environmental Protection Research Division
US Army Medical Bioengineering
Research and Development Laboratory
Ft. Detrick, MD 21701

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Cleveland, Ohio 44122

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A Breadboard Electrochemical Organic Content (EOC) Analyzer was designed and developed for on-line monitoring of organic solute concentrations in the ozonated effluent of the Water Processing Element Pilot Plant in the Medical Unit, Self-Contained, Transportable (MUST) hospital. Techniques were incorporated to eliminate various interferences. The test program included tests of the analyzer's response to organics and tests of the effectiveness of the interference eliminating components. The analyzer successfully completed → over

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Monitor
Water Processing Element
Medical Unit, Self-Contained, Transportable
Organic Adsorption
Electrode
Platinum
Breadboard
Electrolyte
Ozone Oxidation Unit Process
Ozonated Effluent
On-Line

20. continued

30 days of continuous, on-line operation without component failures. Results, conclusions and recommendations are presented.

Life Systems, Inc.

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LIFE SYSTEMS, INC.
Cleveland, Ohio 44122

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Washington, D. C. 20314

EXECUTIVE SUMMARY

The Breadboard Electrochemical Organic Content Analyzer was developed and tested during the second phase of Contract DAMD17-75-C-5070. The analyzer was developed to be interfaced with the Water Processing Element Pilot Plant and its Data Acquisition System. The analyzer is designed to monitor organic solute concentrations in the effluent of the Ozone Oxidation Unit Process. The organic concentration determination is based on adsorption of organic solutes on an indicating electrode, and measurement of the resulting decrease in the electrode's interfacial capacitance. This measurement technique was evaluated during an earlier phase of the contract and was found to be feasible for use in the Water Processing Element.

During the feasibility analysis, some chemical and physical parameters were found to affect the analyzer's response. Therefore, techniques were investigated, developed and incorporated in the Breadboard Analyzer to eliminate interferences from these parameters. The Analyzer contains a flow-through electrochemical cell for measurement of the organic solutes, which permits the analyzer to be used for on-line monitoring of the ozonated effluent. The analyzer has been designed for continuous operation, and a 0-5V DC analog output signal is available for automated data collection. The analyzer also incorporates in situ calibration of the capacitance measuring circuitry.

The test program has demonstrated that the analyzer is capable of long-term, continuous operation. During one test, the analyzer operated continuously for 30 days without any operator maintenance required other than preparation of electrolyte and sample solutions, and adjustment of the electrolyte flow rate.

Other tests have shown that the chemical and physical parameters of the ozonated effluent, other than organic concentrations, will not affect the analyzer response.

Some tests involved preliminary correlations between analyzer response and the total organic carbon concentrations for samples having mixtures of solutes. Also, initial data related to calibration methods for the analyzer were obtained.

Conclusions and recommendations are presented regarding improvements that may be made to the Breadboard Analyzer to reduce operator labor and expendables required by the analyzer. Recommendations are made to investigate means of increasing the analyzer response to some solutes, and improving the correlation between its response and total organic carbon concentrations for solute mixtures.

The possible development of advanced versions of the analyzer is discussed. If pursued, the development of the advanced analyzers may result in a low-cost, compact, reliable and simple to operate monitor of organic solute concentrations for use in field and industrial process-control applications.

FOREWORD

The analytical and experimental work described herein was performed by Life Systems, Inc. under U.S. Army Contract DAMD17-75-C-5070 during the period June 30, 1976 to October 1, 1977. The program was directed by Dr. R. J. Davenport. The technical effort was completed by Dr. R. J. Davenport, J. D. Powell, N. S. Sasso and T. S. Steenson.

The Contract Project Officer was Mr. William J. Cooper, U. S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, MD 21701.

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COD	Chemical Oxygen Demand
DVT	Design Verification Test
EOC	Electrochemical Organic Content
IRAD	Internal Research and Development
MBRDL	Medical Bioengineering Research and Development Laboratory
MUST	Medical Unit, Self-Contained, Transportable
RDE	Rotating Disk Electrode
RO	Reverse Osmosis
TOC	Total Organic Carbon
UF	Ultrafiltration
WPE	Water Processing Element

INTRODUCTION

There is a need for simple, reliable and inexpensive analyzers for monitoring low concentrations of organic solutes in effluent streams. In some applications, automated, on-line monitors are required, and if the analyzers are to be used in the field, they should operate with few consumables to minimize logistic demands.

One application of this type is the Water Processing Element (WPE) of the Medical Unit, Self-Contained, Transportable (MUST) Army Field Hospital. The WPE will purify waste water generated in the hospital for nonconsumptive reuse and discharge. For water purification, the WPE will utilize Ultrafiltration (UF), Reverse Osmosis (RO), and Ozone (O_3) Oxidation Unit Processes, as shown in Figure 1. The purpose of the O_3 Oxidation Unit Process is to destroy organic compounds dissolved in the RO permeate. The presently accepted maximum organic solute concentrations in the ozonated effluent are 5 ppm total organic carbon (TOC) and 10 ppm chemical oxygen demand (COD).(1)

An organic solute monitor located in the effluent stream of the O_3 Oxidation Unit Process, as shown in Figure 1, is necessary to detect nonoxidized organic solutes in the effluent, and to provide assurance that the concentrations are less than the maximum acceptable levels. The monitor will be capable of producing an alarm signal in case the organic solute concentrations exceed those levels. The monitor may also be used to provide continuous organic solute concentration data. The organic solute monitor might then be used in a feedback mode to control the rate of O_3 generation in the O_3 Oxidation Unit Process. The feedback control would result in the most efficient operation of the process, since the O_3 generation rate would be decreased to conserve power during periods when the waste water entering the WPE contains low organic solute concentrations. Conversely, the O_3 generation rate would be automatically increased by the organic solute monitor if the organic loading in the waste water increased.

Presently available analyzers do not meet the requirements for use in the WPE. For example, commercially available, automated TOC analyzers typically weigh 200 to 400 lbs, occupy volumes up to 25 ft^3 and consume considerable amounts of compressed gases and reagent solutions. They are usually designed to measure larger organic solute concentrations than those in the WPE effluent, and the analyzers cost $12,000 to $14,000.

To satisfy the requirements of monitoring organic solutes in the WPE, an evaluation of various approaches to organic solute monitoring was performed during an earlier stage of the present program.(2) One of the approaches evaluated was the Electrochemical Organic Content (EOC) Analyzer which had been conceptually designed previously by Life Systems, Inc. (LSI). The EOC Analyzer is based on measurement of organic solutes through their adsorption on an indicating electrode and determination of the resulting decrease in the capacitance of the electrode/solution interface.

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(1) References cited in parentheses are listed at the end of this report.

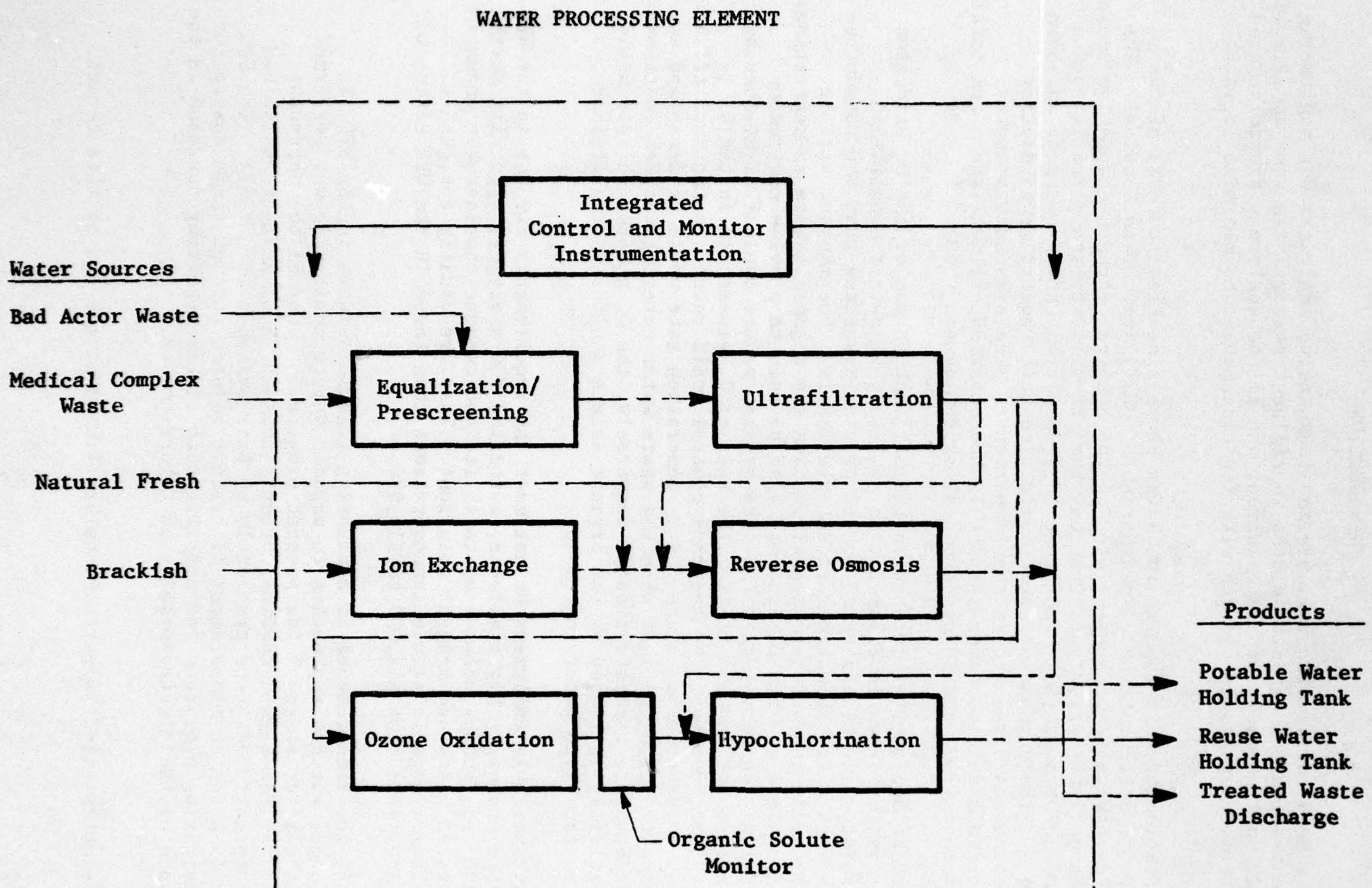

FIGURE 1 WATER PROCESSING ELEMENT BLOCK DIAGRAM

Electrochemical measurement of organic adsorption was selected for evaluation, in part, because it is a technique that is responsive to low concentrations of organic solutes. Also, it was considered to require relatively little hardware. Conceptually, only three components are required. These are the electrochemical cell that contains the indicating electrode, the logic circuitry, and the concentration readout device.

The feasibility of the EOC Analyzer concept was evaluated by designing, assembling and testing a laboratory breadboard version of the EOC Analyzer. The response of the analyzer to selected organic solutes was quantified and has been reported.(2)

These tests indicated that the EOC concept was a feasible approach to monitoring effluents of water purification processes. However, to quantify the analyzer's response and to demonstrate its performance in the WPE Pilot Plant, a more advanced version of the analyzer was required. Therefore, the present phase of Contract DAMD17-75-C-5070 was undertaken with the objective of developing and testing a Breadboard EOC Analyzer capable of continuous, on-line monitoring of the O_3 Oxidation Unit Process effluent.

Some chemical and physical parameters, other than organic solute concentrations, were found to affect the response of the Laboratory Breadboard Analyzer. Approaches were required to prevent interferences by these parameters in the Breadboard Analyzer. However, because a goal of the program was timely development of the analyzer for integration in the WPE Pilot Plant, relatively little time was available for development of the analyzer plus the interference eliminating techniques. Therefore, LSI adopted an "overkill" approach to eliminating interferences in the Breadboard EOC Analyzer. In other words, techniques that did not require extensive testing or development efforts were incorporated in the analyzer. For example, the effects of conductivity variations in the sample are masked by the addition to the sample of a highly conducting supporting electrolyte.

Initially this phase of the contract concerned only development of the Breadboard Analyzer and performing tests of the analyzer hardware. These tests demonstrated the value of automated data collection with the analyzer and other modifications to the analyzer components which would result in reliable operation in the WPE Pilot Plant for an extended period. These improvements were made during an addition to the original program. The results of both the Breadboard Analyzer development and the program addition are reported here.

Definitions

The organic solute concentration indices related to the EOC Analyzer are defined below:

1. Electrochemical Organic Content (EOC): EOC values refer to the measured response of the EOC Analyzer to organic solutes. The response of the EOC Analyzer is reported in instrument units.

2. Total Organic Carbon (TOC): TOC values represent the concentration of carbonaceous organic solutes in the sample, expressed in terms of milligrams of carbon per liter of sample.

3. Chemical Oxygen Demand (COD): COD values represent the oxygen (O_2) equivalents consumed in the chemical oxidation of oxidizable solutes (primarily organic species). The COD of the sample is determined by measuring the quantity of a strong chemical oxidizing agent consumed during oxidation of the solutes. COD is expressed as mg/l.

Summary of Prior Efforts

The original tests and evaluation of the EOC concept were performed with the Laboratory Breadboard EOC Analyzer shown in Figure 2.(2) Standard laboratory hardware was used for the electrochemical cell and platinum (Pt) indicating electrode. A rotating disk electrode (RDE) geometry was used.

Automated EOC logic and concentration readout circuitry were developed and are shown schematically in Figure 3. The logic circuitry contains two parts. One part controls the potential of the indicating electrode with respect to the potential of a reference electrode. In this way, the potential of the indicating electrode can be accurately maintained at the optimum value for organic adsorption. Also, the logic circuit contains the capacitance-measuring circuitry, which provides a signal to the concentration readout display.

The EOC Analyzer responds to organic solutes in water samples by adsorption of the solutes onto the surface of the indicating electrode. The adsorbed organic solutes on the electrode are shown graphically in Figure 4. The positive charges on the electrode surface and the layer of negatively-charged ions (anions) in the close vicinity of the electrode surface represent the two plates of a capacitor at the electrode/solution interface. In the absence of adsorbed organics, the anions are in close proximity with the electrode surface, or are separated from the surface by water molecules. When the organic solutes are adsorbed on the electrode, they displace some of the anions, and the anions are then separated from the surface by the organic molecules. Organic molecules typically have lower dielectric constants than do water molecules. Therefore, the adsorption of organic solutes decreases the interfacial capacitance because the distance between the electrode surface and the oppositely-charged ions increases and the dielectric constant at the interface decreases.

The output of the EOC Analyzer is basically a logarithmic function of the organic solute concentration. This is because the amount of organic solutes that adsorb on Pt is proportional to the logarithm of the solute concentration. This is shown in Figure 5 for ethylene glycol. The fractional coverage, Θ, is proportional to the EOC Analyzer response and is logarithmically related to the concentration of ethylene glycol over a wide range of concentrations. The logarithmic relationship exists until the concentration of the organic is sufficient to completely cover the electrode. At this point, Θ equals 1.0 and no further adsorption occurs.

Prior to each organic adsorption and capacitance measurement, previously adsorbed organics must be removed from the electrode and the electrode surface must be prepared for the subsequent adsorption step. This desorption and surface preparation is termed the electrode preconditioning sequence. The

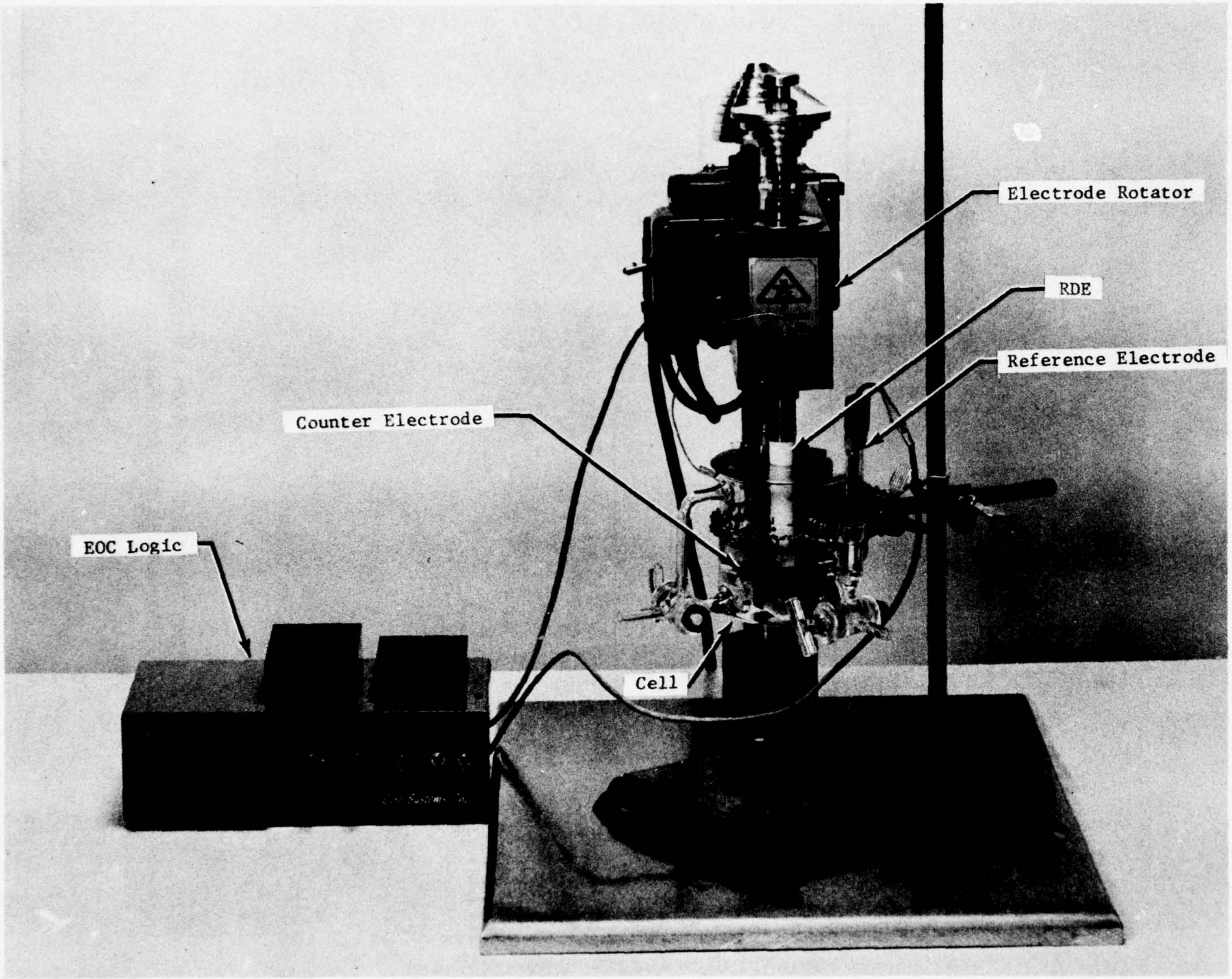

FIGURE 2 LABORATORY BREADBOARD EOC ANALYZER

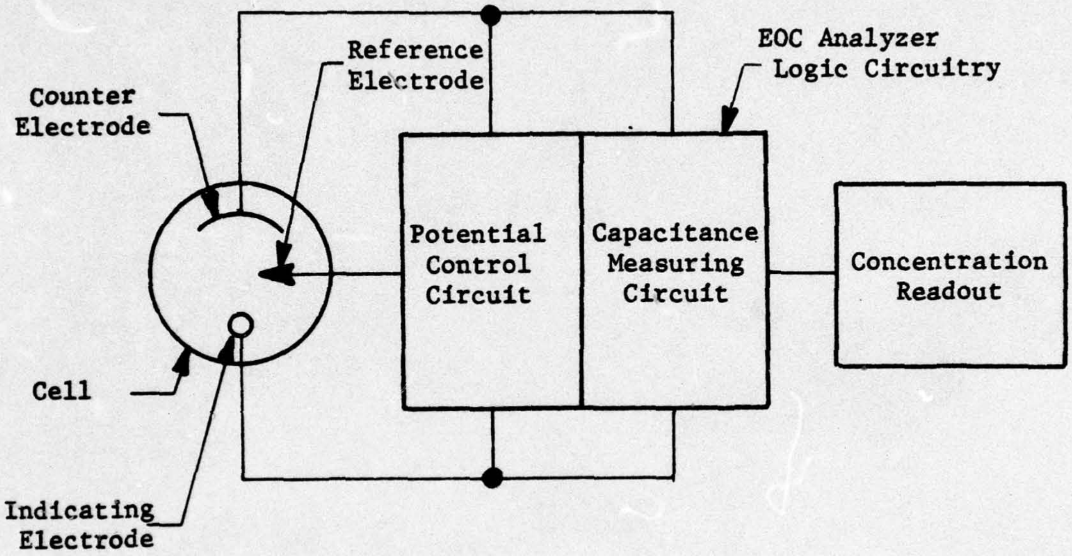

FIGURE 3 FUNCTIONAL BLOCK DIAGRAM OF LABORATORY BREADBOARD EOC ANALYZER

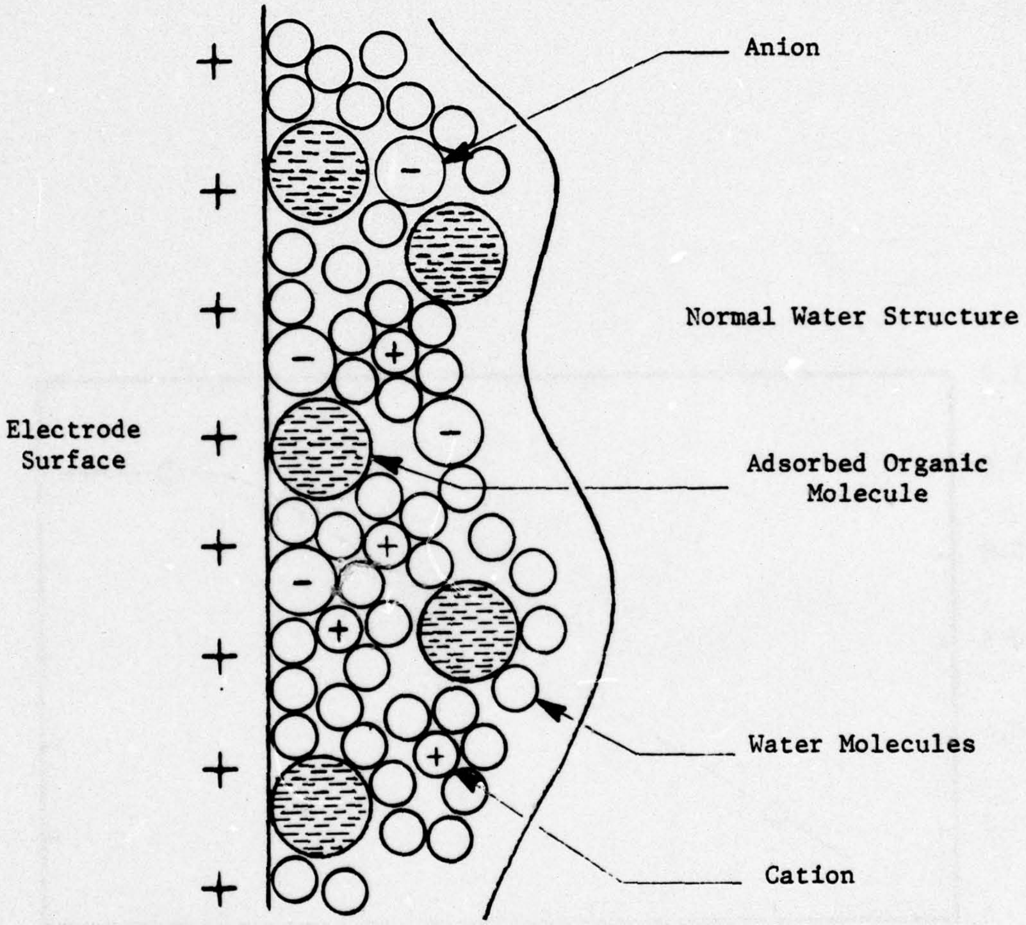

FIGURE 4 ELECTRODE/SOLUTION INTERFACE SHOWING ADSORBED ORGANIC MOLECULES

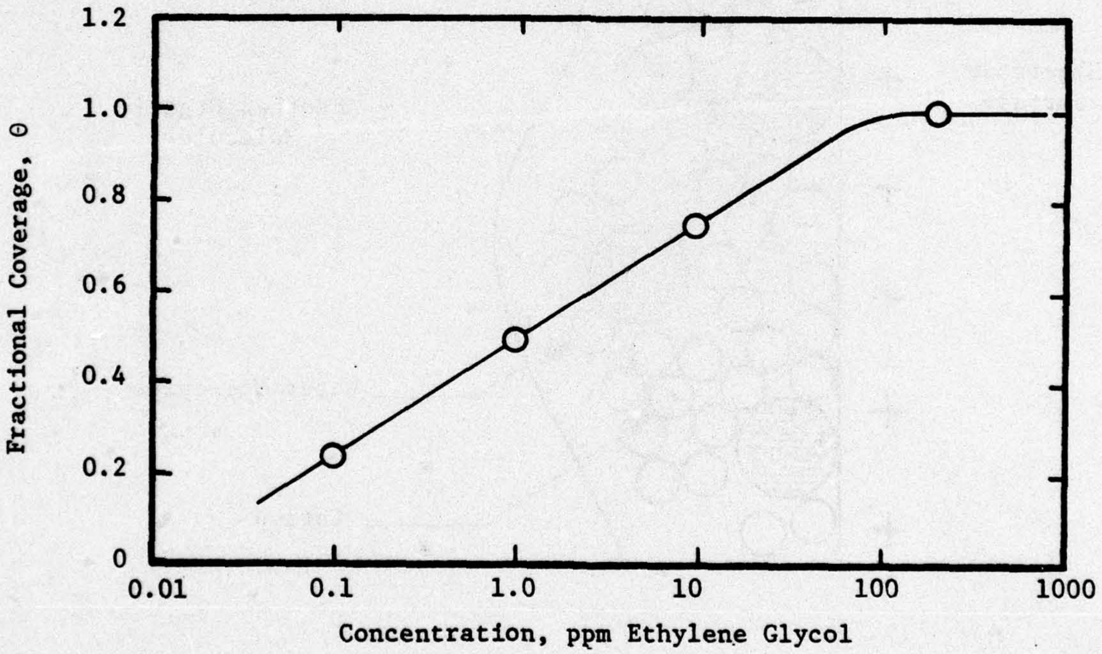

FIGURE 5 ADSORPTION ISOTHERM OF ETHYLENE GYLCOL ON PLATINUM AT 35C

potential control circuit in the logic automatically preconditions the electrode so that the organic adsorption and capacitance measurement are performed at a uniformly prepared, clean electrode surface.

The electrode preconditioning sequence used with the Breadboard EOC Analyzer is shown in Figure 6. The indicating electrode is first oxidized to remove previously adsorbed organic solutes. Then the oxidized electrode is reduced to prepare it for the next organic adsorption. The electrode potential is then automatically stepped to the potential of maximum organic adsorption, and the adsorption is allowed to continue for 80 sec. At the end of that period the interfacial capacitance is measured and the electrode preconditioning sequence is automatically repeated.

The feasibility evaluation of the Laboratory Breadboard EOC Analyzer showed that the EOC Analyzer inherently has high sensitivity to several organic solutes. The greatest sensitivity was obtained for solutes that adsorbed strongly on the indicating electrode. For instance, the response was greater to Triton X-100, a non-ionic surfactant, than to urea or acetic acid (Figure 7). The detection limits of the Laboratory Breadboard EOC Analyzer for Triton X-100 and urea were less than 0.1 mg/l TOC, while a detection limit for acetic acid was approximately 1 mg/l TOC.

The response of the EOC Analyzer to organic solutes is dependent upon the structure of the particular organic molecules in the sample. This response is analogous to the response of conductivity sensors to particular ionic solutes. Conductivity response curves are shown for several ionic solutes in Figure 8. A conductivity sensor has the same response to 90 ppm of hydrochloric acid as to 20,000 ppm of acetic acid. Yet, conductivity measurements are valuable indicators of the efficiency of water treatment processes. Furthermore, the response of a conductivity sensor can be related to the concentration of ionic solutes when the composition of the water samples is relatively constant. Likewise, the response of the EOC Analyzer may be correlated with the concentration of organic solutes, expressed in TOC units, if the composition of the organic solutes in the sample does not vary greatly.

Program Organization

The development and testing of the Breadboard EOC Analyzer was performed during the first part of this phase of the program. The tests of the analyzer involved quantifying the performance of the overkill techniques incorporated into the analyzer to eliminate interferences. Also, the ability of the analyzer to operate continuously was tested to a limited extent. This part of the program was divided into seven technical and management tasks:

1.0 Design, fabricate and assemble the Breadboard EOC Analyzer.

2.0 Design, fabricate and assemble the Test Support Accessories (TSA) required for testing the Breadboard EOC Analyzer.

3.0 Establish, implement and maintain a mini-product assurance program.

4.0 Test the Breadboard EOC Analyzer and overkill techniques.

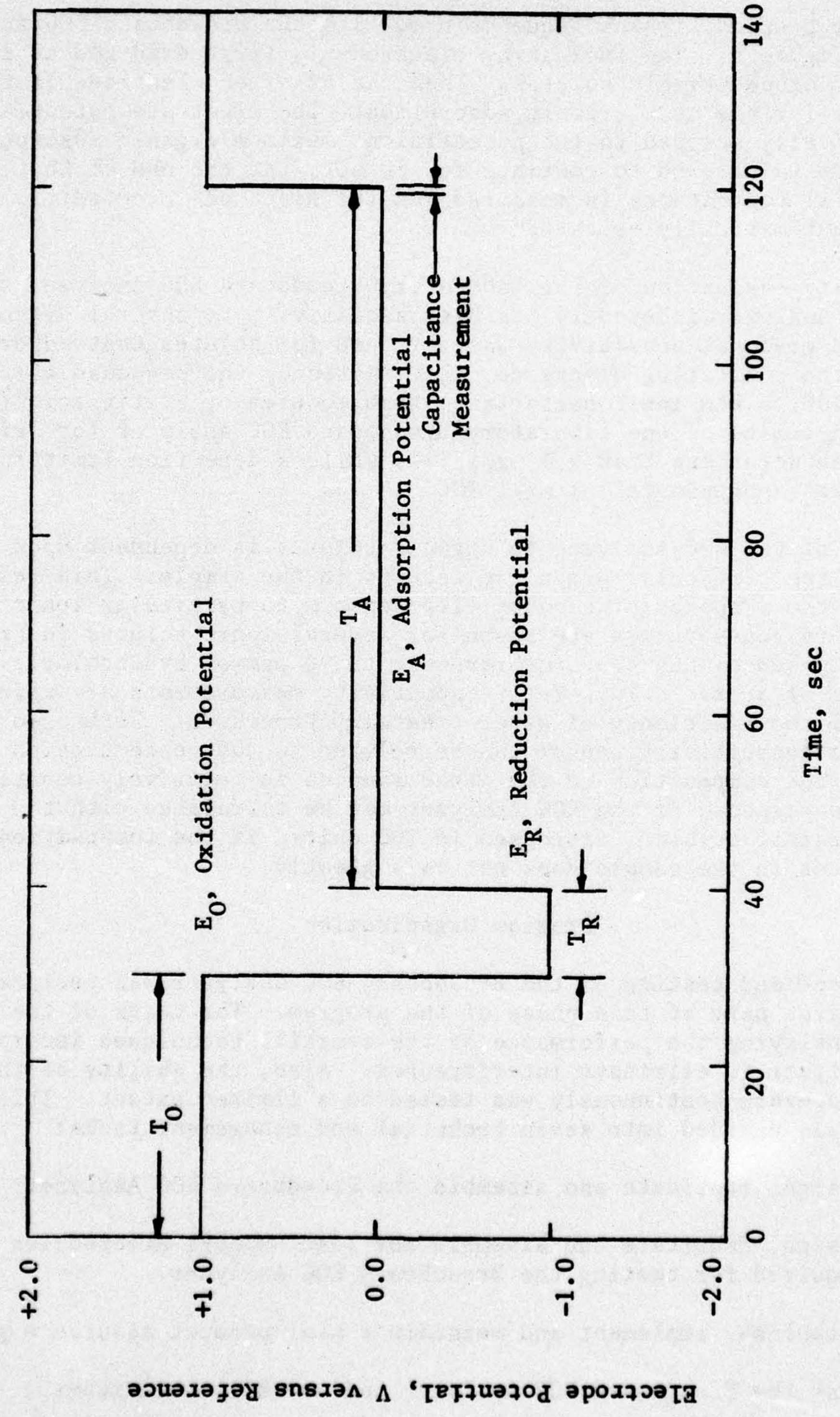

FIGURE 6 ELECTRODE PRECONDITIONING AND ADSORPTION SEQUENCE

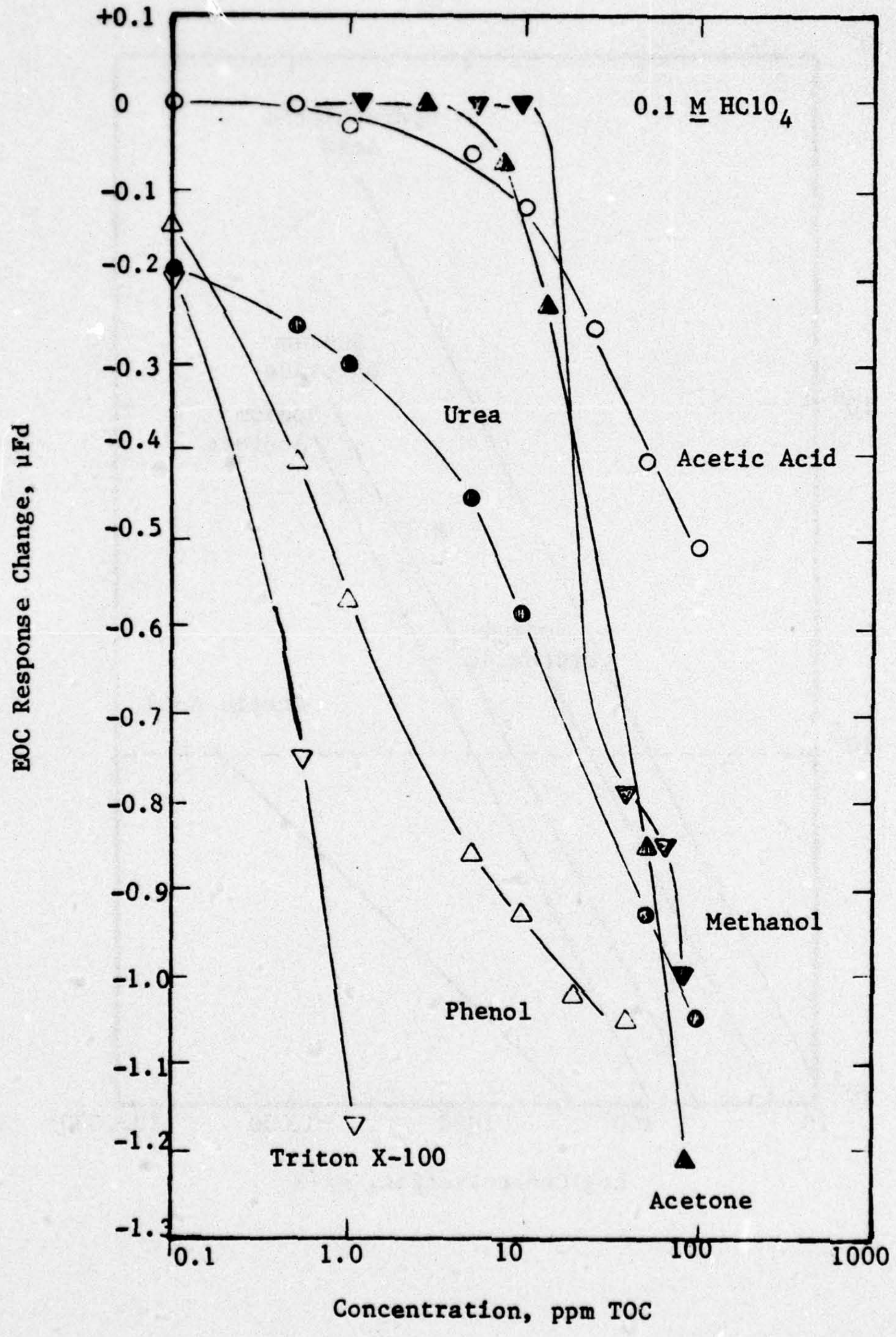

FIGURE 7 RESPONSE OF LABORATORY BREADBOARD EOC ANALYZER

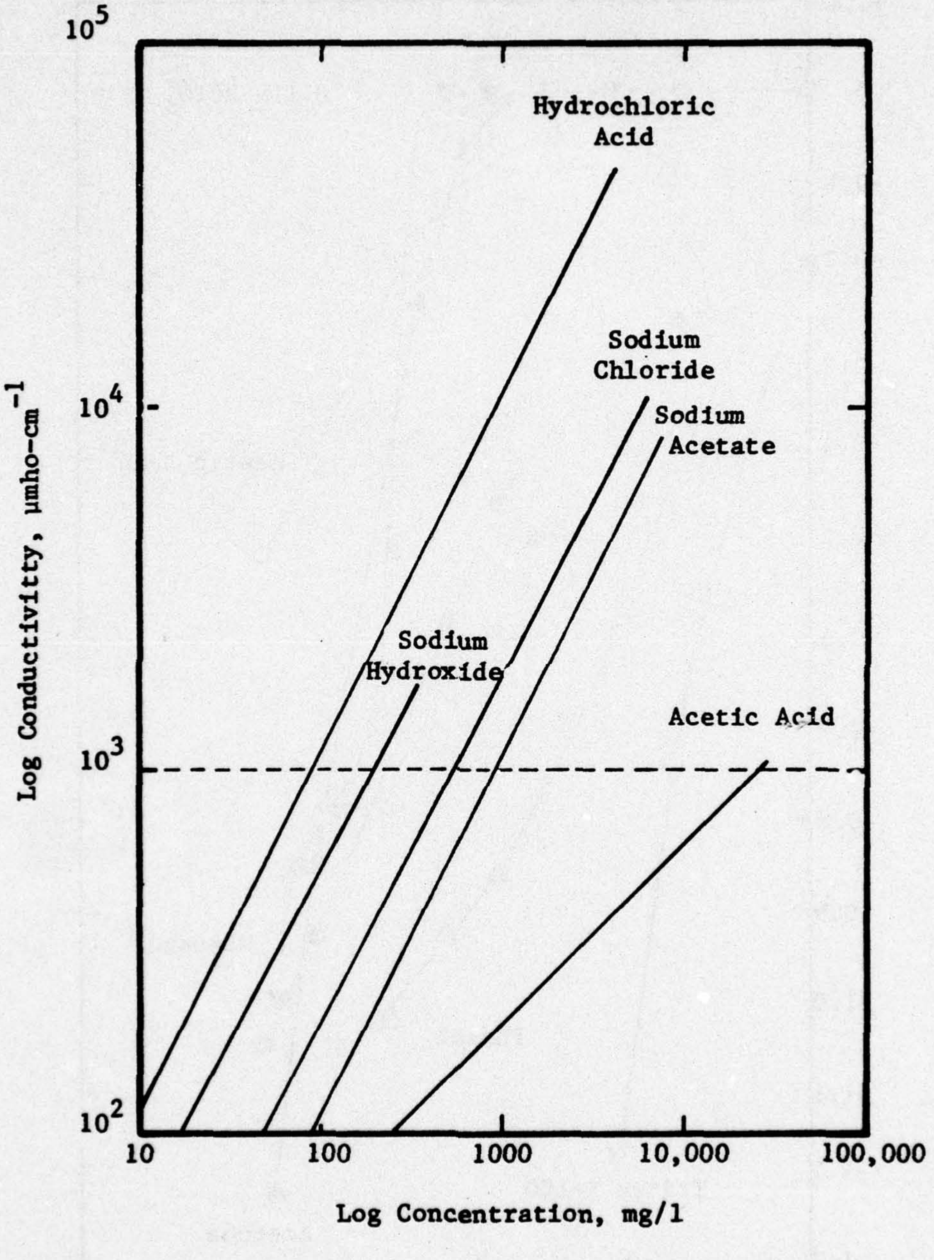

FIGURE 8 CONDUCTIVITY CALIBRATION CURVES

5.0 Perform supporting research studies to provide data necessary for the design of the Breadboard EOC Analyzer.

6.0 Prepare and submit the program's documentation and data requirements.

7.0 Perform program management needed to successfully meet the program's cost, schedule and technical performance objectives.

The second part of this phase involved interfacing the EOC Analyzer with the Data Acquisition System (DAS), and performing other tasks related to long-term testing of the analyzer in the WPE Pilot Plant. This effort was also divided into seven technical and management tasks:

1.0 Define and implement a method for incorporating the output signal from the Breadboard EOC Analyzer into the DAS.

2.0 Evaluate the performance and function of the membrane equilibrator as an overkill technique in the Breadboard EOC Analyzer.

3.0 Inspect and modify, as required, components in the analyzer to improve mechanical reliability and lower maintenance.

4.0 Perform a long-term reproducibility test of the Breadboard EOC Analyzer

5.0 Perform field service to recalibrate the Breadboard EOC Analyzer, to characterize its performance, and to generally review its operating conditions.

6.0 Prepare and submit the program's documentation and data requirements.

7.0 Perform program management needed to successfully meet the program's cost, schedule and technical performance objectives.

The field service task is to be done after delivery of the analyzer to the U. S. Army Medical Bioengineering Research and Development Laboratory (MBRDL), while the analyzer is integrated into the WPE Pilot Plant. Since this activity will extend over several months, the results of the field service task are not included here.

BREADBOARD EOC ANALYZER DESIGN STUDIES

The chemical and physical parameters that would affect the response of the EOC Analyzer were identified through tests of the Laboratory Breadboard EOC Analyzer and literature investigations covering electrochemical adsorption phenomenon. The parameters which are pertinent to monitoring organic solutes in the WPE effluent are listed in Table 1, and the specific effects of each are discussed in detail below.

Conductivity

The effect of conductivity (and its reciprocal, resistivity) on EOC response was investigated with the Laboratory Breadboard Analyzer. Data collected

TABLE 1 PARAMETERS AFFECTING EOC ANALYZER RESPONSE

A. Conductivity

B. pH

C. Temperature

D. O_2 and O_3

E. Cl^-, NO_3^-, SO_4^{-2}

during a test in which the EOC response to samples of distilled water containing various concentrations of perchloric acid ($HClO_4$) is shown in Figure 9. The EOC values generally increase with decreases in solution resistivity.

The effect of the solution and conductivity is related to the resistance between the electrodes in the EOC cell. The main effect is from the resistance between the indicating and counter electrodes, although the resistance between the reference and the indicating electrodes also affects the measured EOC values. The resistance between the electrodes is dependent upon the distance between them as well as the solution resistivity. Therefore, a baseline distance of 0.1 inches between the indicating and counter electrodes was adopted for the Laboratory Breadboard EOC cell, and this spacing was carried over to the flow-through cell design.

pH

The pH of solutions affects the degree to which organic solutes adsorb on electrodes. Therefore, pH variations can affect the response of the EOC Analyzer. Representative data is shown in Figure 10 for methanol and benzene. Both solutes are readily adsorbed at very low pH values, and methanol is also adsorbed strongly at high pH values. The degree to which these solutes are adsorbed changes markedly as the pH varies through the intermediate values.

This data suggests that the sensitivity of the EOC Analyzer may vary if the pH of test solutions changes significantly. To avoid this variation, it is necessary to maintain a constant pH value, and either a very low or a very high pH would benefit the analyzer response.

Temperature

The effect of temperature on EOC response was investigated with the Laboratory Breadboard EOC Analyzer. The temperature of the solution in the cell was varied and the response of the EOC Analyzer was monitored. The solution was 0.1 $\underline{M}$ $HClO_4$ containing no organic solutes. A generally linear curve, shown in Figure 11, was obtained with a slope of 17 EOC units/C. From this data it can be calculated that the temperature of the EOC cell must be controlled within a range of ±0.1C in order to maintain the uncertainty of the EOC measurement within ±1% at an EOC value of 200.

Dissolved Oxygen and Ozone

Dissolved O_2 was found to affect the response of the Laboratory Breadboard Analyzer. This effect was quantified and is shown in Figure 12. As indicated in the figure, increasing concentrations of dissolved O_2 produce increasing EOC response. It is probable that this effect results from reduction of O_2 at the indicating electrode according to Equation 1.

$$O_2 + 4H^+ + 4e^- = 2H_2O \qquad (1)$$

The oxidation or reduction of several species, such as O_2, has been shown to increase the interfacial capacitance of the reacting electrodes.(3)

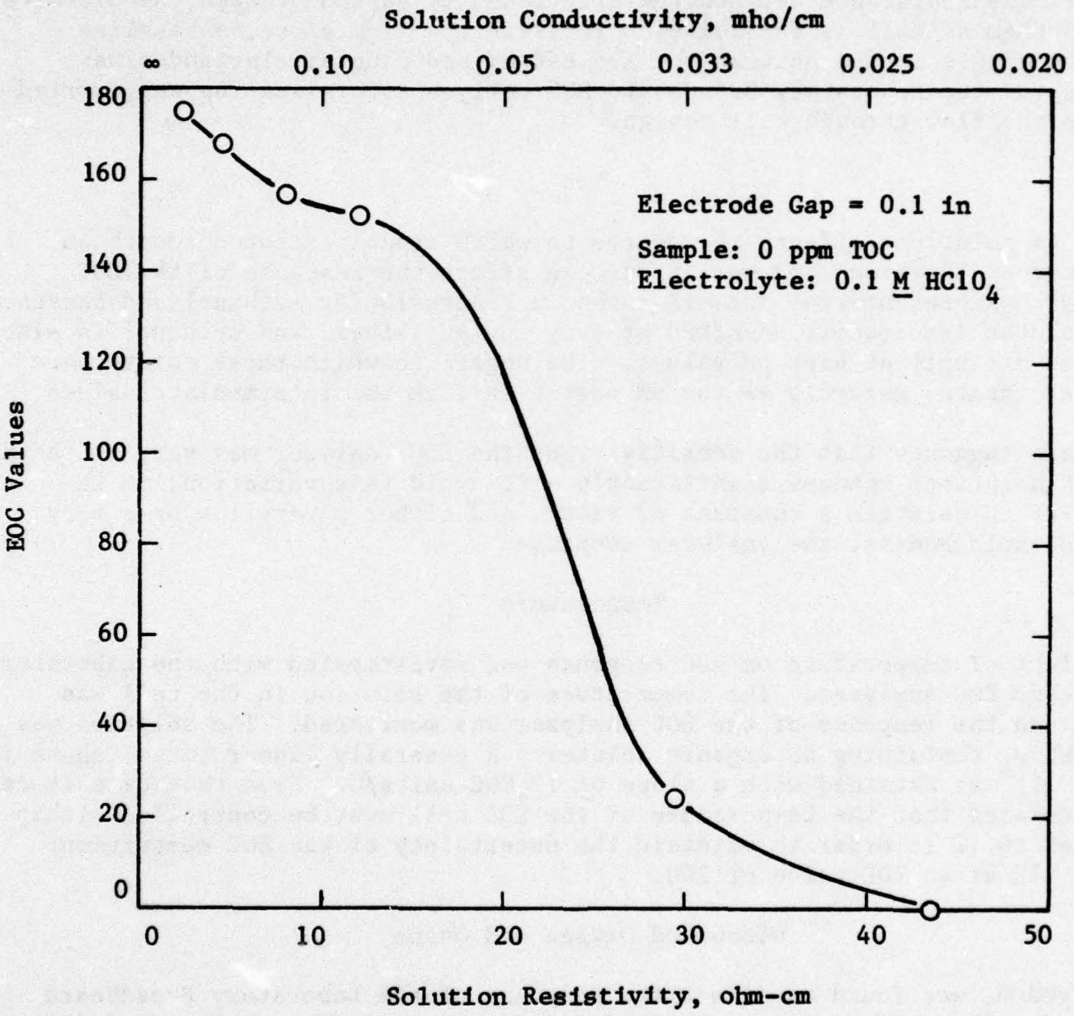

FIGURE 9 CONDUCTIVITY STUDY

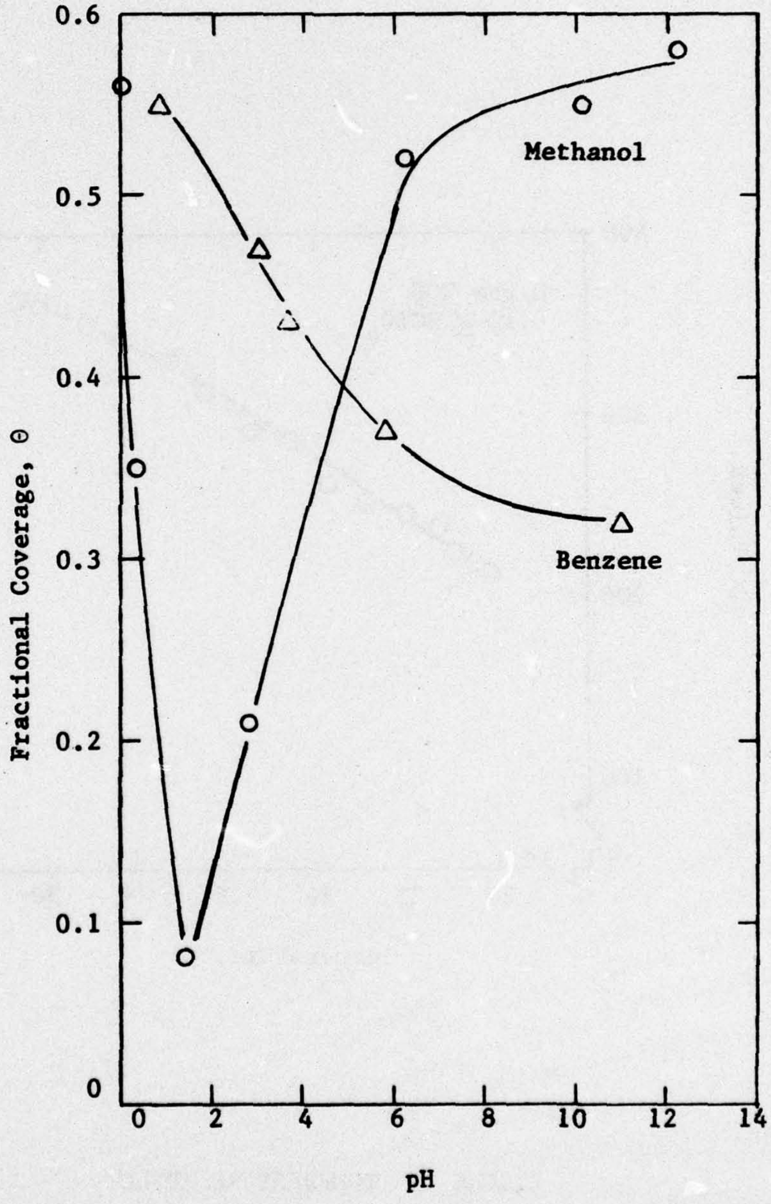

FIGURE 10 pH EFFECTS ON ORGANIC ADSORPTION

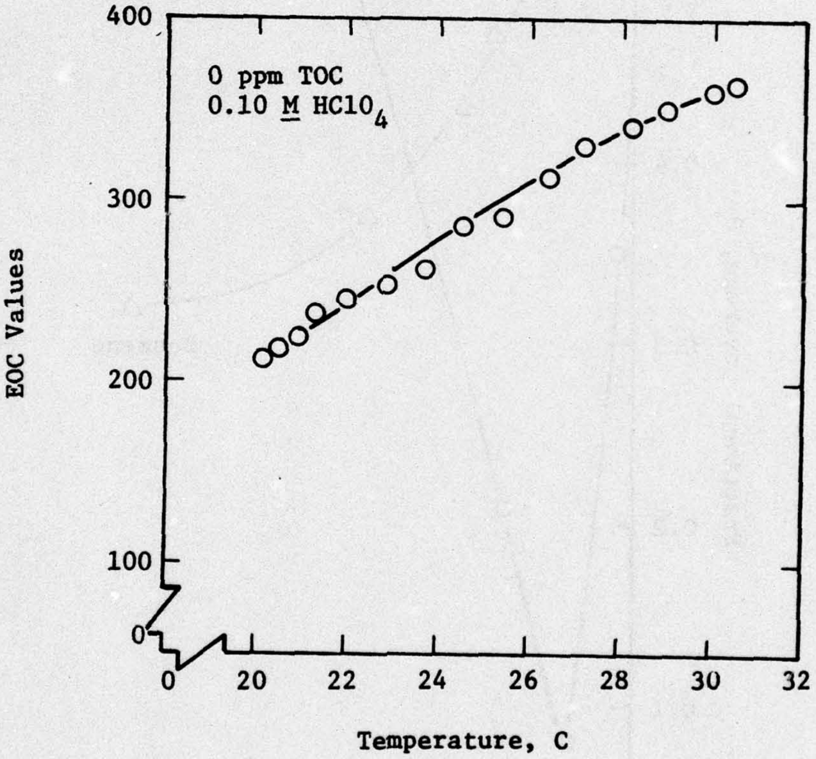

FIGURE 11 TEMPERATURE EFFECT

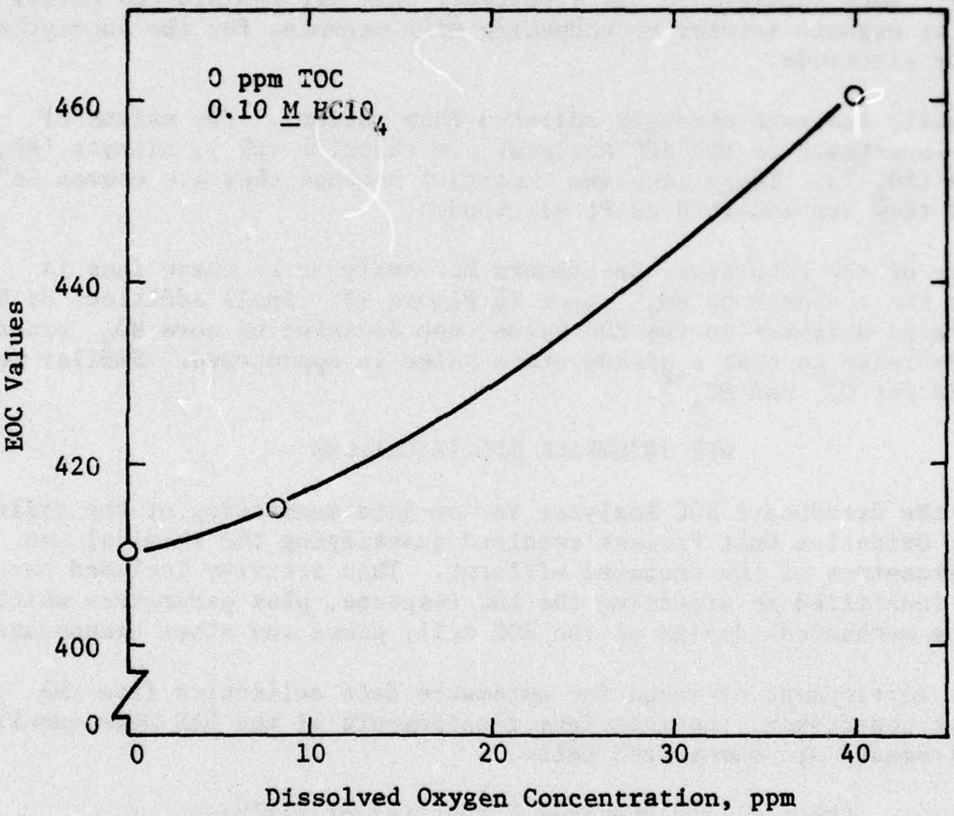

FIGURE 12 DISSOLVED OXYGEN EFFECT

Dissolved O_3 is expected to have a similar effect on the EOC response since it also is reduced at Pt electrodes. This is significant since the EOC Analyzer will be used to monitor the ozonated effluent from the O_3 Oxidation Unit Process.

Inorganic Salts

Salts sometimes affect electrochemical processes because some ions adsorb on electrode surfaces. In the case of the EOC Analyzer, ions can interfere if they adsorb on the indicating electrode because they may change its interfacial capacitance. Once adsorbed on the electrode, they may inhibit the normal adsorption of organic solutes by competing with organics for the adsorption sites on the electrode.

Anions normally are more strongly adsorbed than cations. The anions of particular importance to the EOC Analyzer are chloride (Cl^-), nitrate (NO_3^-), and sulfate (SO_4^{-2}). These ions are important because they are common in many samples and they are adsorbed on Pt electrodes.

The response of the Laboratory Breadboard EOC Analyzer to these ions is typified by its response to NO_3^- shown in Figure 13. Small additions of NO_3^- produce a large decrease in the EOC value, but addition of more NO_3^- produces less of a decrease so that a steady-state value is approached. Similar behaviour was observed for Cl^- and SO_4^{-2}.

WPE INTERFACE SPECIFICATIONS

Developing the Breadboard EOC Analyzer for on-line monitoring of the effluent from the O_3 Oxidation Unit Process required quantifying the chemical and physical parameters of the ozonated effluent. This activity included parameters which were identified as affecting the EOC response, plus parameters which affected the mechanical design of the EOC cell, pumps and other components.

Later, when development of means for automated data collection from the analyzer was undertaken, the interface requirements of the DAS were quantified. These requirements are summarized below.

Chemical and Physical Properties of Effluent

The physical properties of the ozonated effluents from the WPE Pilot Plant are listed in Table 2.(4) The effluent is heated, and the anticipated temperature range is 21 to 45C. The effluent from the O_3 Oxidation Unit Process is pressurized with compressed air and O_3 to between 8 and 13 psig.

The chemical properties of the ozonated effluent are listed in Table 3. The effluent will have pH values in the range of 5 to 9, and its conductivity is expected to be in the range of 14 to 400 µmho/cm.(4,5)

BREADBOARD EOC ANALYZER

The design goal of the Breadboard Analyzer was the capability of continuous, on-line monitoring of the ozonated effluent from the WPE Pilot Plant. The

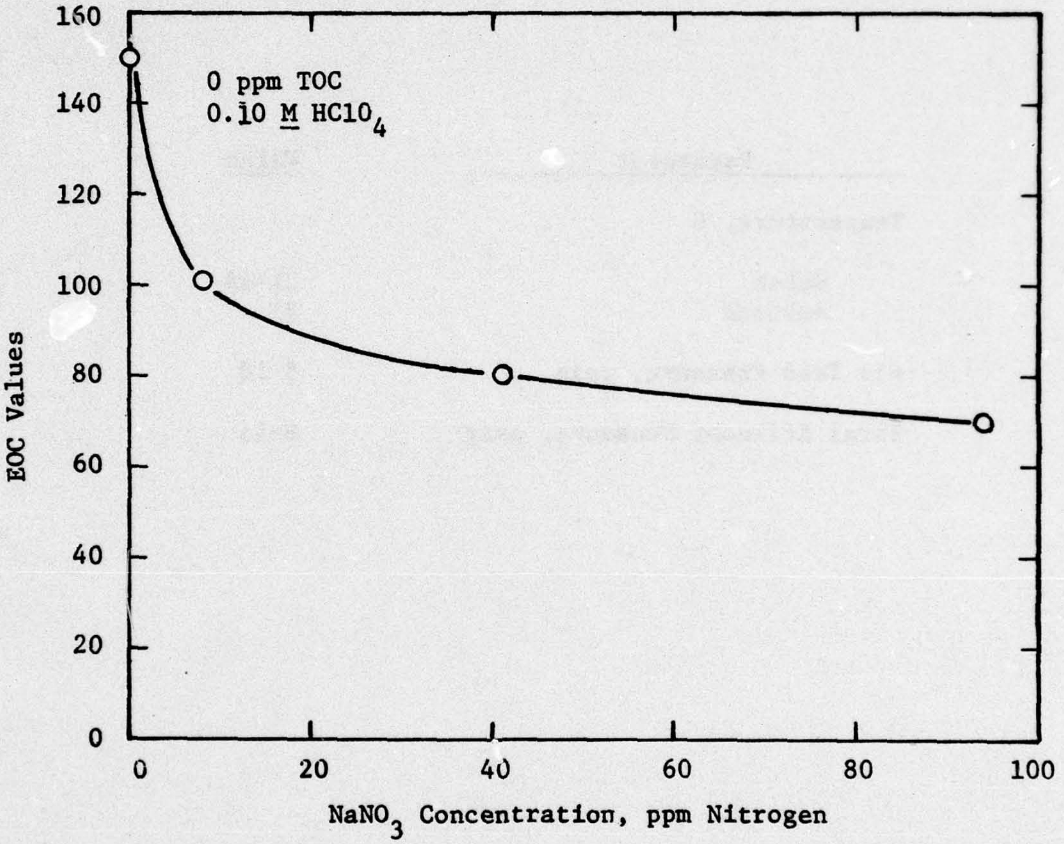

FIGURE 13 NITRATE EFFECT

TABLE 2 PHYSICAL PROPERTIES OF
OZONATED EFFLUENT

Parameter	Value
Temperature, C	
Water	21-45
Ambient	21
Air Feed Pressure, psig	5-10
Total Effluent Pressure, psig	8-13

TABLE 3 CHEMICAL PROPERTIES OF OZONATED EFFLUENT

Parameter	Value
pH	5-9
Conductivity, µmho/cm	14-400
Oxygen, ppm	9-17
Ozone, ppm	0-10
Chloride, ppm	42-150
Nitrate/Nitrogen, ppm	<2.5-10
Sulfate, ppm	16-32
Ammonia, ppm	0.6

purpose of the development was to provide an analyzer capable of providing EOC data that is not significantly affected by chemical and physical parameters other than organic solutes. This data, collected during future extended tests in the WPE Pilot Plant with a variety of ozonated samples, will provide a basis for the evaluation of the EOC Analyzer used as a go/no-go indicator of the effectiveness of the O_3 Oxidation Unit Process.

Analyzer Design

To provide data that accurately reflects the response of the analyzer to organic solutes, overkill techniques were selected for use in the analyzer to avoid interferences from the chemical and physical parameters discussed above. The selected overkill techniques and the parameters they control are listed in Table 4. An electrolyte solution is added to the sample to control the effects on the EOC response from the conductivity, pH, and the concentrations of Cl^-, NO_3^-, $SO_4^{=2}$ and O_3 in the sample. A temperature controller, which uses a heat exchanger to adjust the solution temperature, was selected to eliminate temperature effects. Finally, a membrane equilibrator was selected to equilibrate the sample/electrolyte mixture with air, thereby maintaining a constant dissolved O_2 concentration. These components are discussed in greater detail in a later section.

Breadboard Analyzer and Cell

A functional block diagram of the analyzer, including the cell and overkill components, is shown in Figure 14. The sample is drawn into the analyzer by the sample pump, and is at the pressure of the O_3 Oxidation Unit Process. Electrolyte is injected into the sample at a rate of 2.0 ml/min by the electrolyte pump. The sample pump draws the sample/electrolyte mixture through the membrane equilibrator, heat exchanger and cell. It pumps at the rate of 10.0 ml/min, and the analyzer therefore samples water at a rate of 8.0 ml/min. A pressure relief valve is included to protect the analyzer components in the event of over-pressurization, since the sample inlet is pressurized.

EOC Cell. The Breadboard Analyzer represents a significant advancement in EOC technology, as compared to the Laboratory Breadboard Analyzer. An example of the more advanced technology is the EOC cell. It is based on a flow-through design developed during one of LSI's Internal Research and Development (IRAD) programs, and is therefore capable of on-line measurements.

The cell developed for the Breadboard Analyzer is shown in Figure 15. The indicating and counter electrodes are bright Pt disks and the reference electrode is a process-style electrode, having a Teflon body and porous tip for contacting the solution. The body of the cell is also Teflon, and the Pt electrodes and cell body are sealed with Teflon-coated rubber O-rings.

Electrical contact is made directly to the reference electrode and to the indicating electrode by a stainless steel screw inserted in the electrode. A Pt lead wire extends from the back of the counter electrode to the banana jack attached to the rear of the cell.

TABLE 4 SELECTED OVERKILL TECHNIQUES

	Technique	Interference Eliminated
A.	Electrolyte Addition	Conductivity, pH, Cl^-, NO_3^-, SO_4^{-2}, O_3
B.	Temperature Control	Temperature Variations
C.	Air Equilibration	O_2

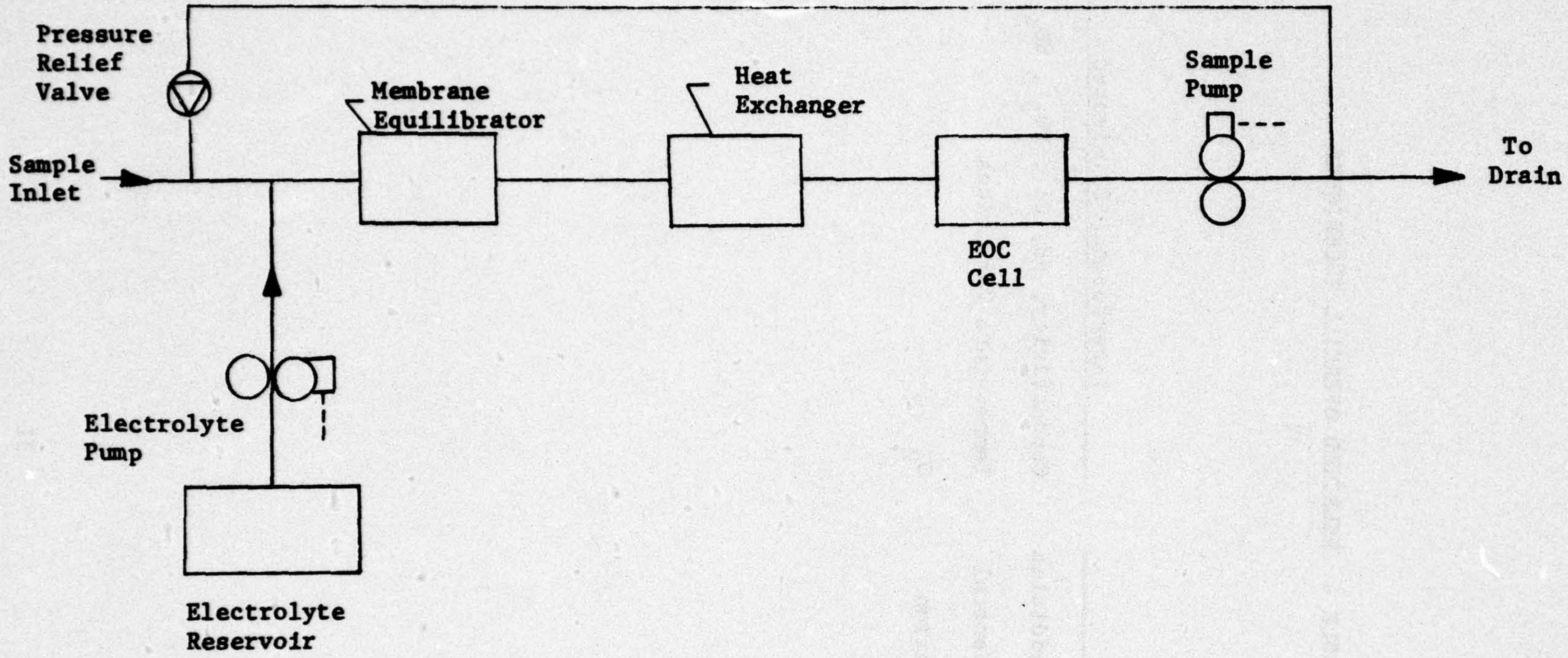

FIGURE 14 SCHEMATIC OF BREADBOARD EOC ANALYZER

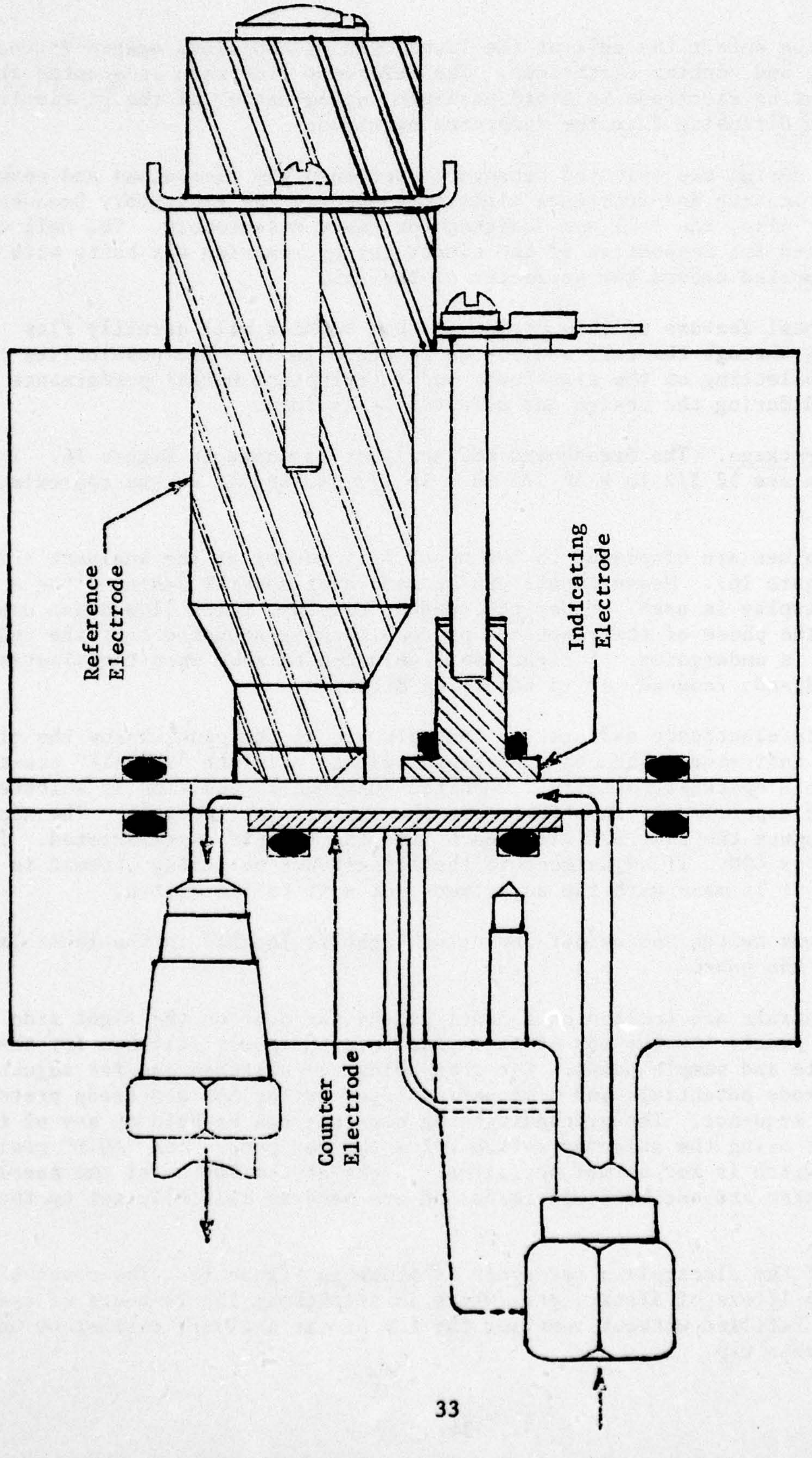

FIGURE 15 EOC CELL

The solution enters the cell at the lower opening and flows upward between the indicating and counter electrodes. The reference electrode is mounted above the indicating electrode to avoid possible contamination of the Pt electrode by species diffusing from the reference electrode.

This cell design was selected because it retained the dimensions and spacing of the indicating and reference electrodes used in the Laboratory Breadboard Analyzer. Also, the cell was designed for ready disassembly. The cell can be disassembled for inspection of the electrodes by removing six bolts with washers located around the perimeter of the cell.

An additional feature of this design is that bubbles will normally flow vertically through the cell and not be retained in it. The possibility of bubbles collecting on the electrodes and interrupting normal performance was considered during the design and effectively avoided.

Analyzer Package. The Breadboard EOC Analyzer is shown in Figure 16. Its dimensions are 12 1/2 in x 16 1/2 in x 16 1/2 in, and it weighs approximately 60 lb.

The EOC values are displayed in the upper left corner of the analyzer's front panel (Figure 16). Measurements can be made over several ranges since a 6-digit display is used. Under the readout display, three lights are used to indicate the phase of the electrode preconditioning sequence that the indicating electrode is undergoing. A light is illuminated to show when the electrode is being oxidized, reduced, or is adsorbing organics.

The in situ electronic calibration controls are on the panel below the electrode condition indicator. When the calibrate switch is in the "OPERATE" position, the EOC cell operates normally. When the "CALIBRATE" position is selected, an electronic capacitor is substituted in the circuit for the cell. The capacitor should produce the same EOC value each time the circuit is calibrated. This EOC value is 400. If adjustment to the capacitance-measuring circuit is required, it is made with the adjustment pot next to the switch.

The AC power switch and on/off indicator light is located in the lower left corner of the panel.

Manual controls are located on a panel behind the door on the right side of the front panel. At the top of this panel are the power switches for the electrolyte and sample pumps. Set pots below the switches are for adjusting the electrode potentials and time periods used during the electrode preconditioning sequence. The preconditioning sequence can be held at any of the potentials using the selector switch below the set pots. The "AUTO" position on this switch is for normal operation. Jacks at the bottom of the panel are for voltmeter and oscilloscope leads and are used to initially set up the analyzer.

The top of the electrolyte reservoir is shown in Figure 16. The reservoir contains 4 liters of electrolyte, which is sufficient for 24 hours of operation. It can be refilled without removing the top of the analyzer cabinet by unscrewing the reservoir cap.

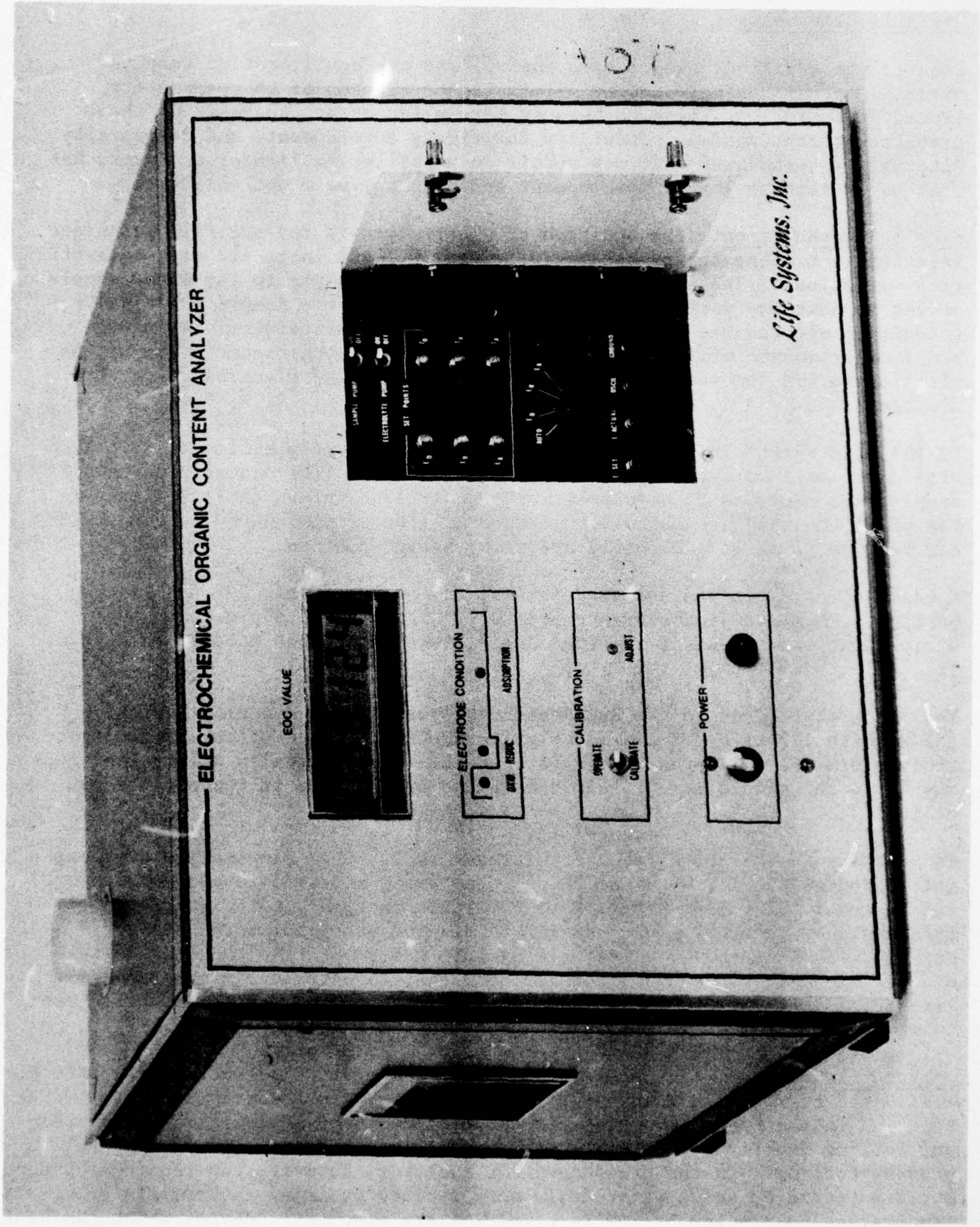

FIGURE 16 BREADBOARD EOC ANALYZER

Overkill Components

Electrolyte addition, temperature control and air equilibration were the overkill techniques selected to eliminate the effects of the parameters listed in Table 1. These techniques were selected on the basis of their predicted effectiveness, capability for timely development, and reliability. Alternative techniques that may result in a smaller or lighter analyzer, but that would require longer development and testing, were not selected.

Electrolyte Addition. The addition of electrolyte is the overkill technique selected to compensate for conductivity, pH, O_3, and inorganic salt concentration variations. The addition of supporting electrolyte to the water sample serves to mask any variation in the conductivity of the sample. A highly conducting electrolyte is effective because the final conductivity of the sample/electrolyte mixture is determined largely by the conductivity of the electrolyte and the volumetric ratio of the sample and electrolyte in the mixture.

If the electrolyte is either strongly acidic or strongly basic, then it also will mask small variations in the pH of the sample. The ozonated wastewater samples are expected to have relatively neutral pH values (5-9). Therefore, the pH of the sample/electrolyte mixture will be determined by the pH of the electrolyte if it is a strongly acidic or basic solution.

A basic electrolyte was selected for use in the Breadboard EOC Analyzer partly to eliminate interference from O_3. Ozone is rapidly decomposed in basic solutions and has a reported half-life of less than 0.5 sec at a pH of 11.(6)

The electrolyte used in the Breadboard Analyzer is 1.5 M sodium hydroxide (NaOH) with 1.7×10^{-3} M sodium chloride (NaCl). The pH of the sample/electrolyte mixture is approximately 12 when this electrolyte is used. Therefore, any O_3 in the sample is entirely decomposed by the time it reaches the EOC cell.

In addition to overcoming the interference by O_3, this electrolyte overcomes interferences by Cl^-, NO_3^- and SO_4^{-2}. The basic electrolyte was developed under one of LSI's IRAD programs to eliminate inorganic salt interferences. The previous electrolyte used during testing of the Laboratory Breadboard EOC Analyzer was 0.1 M $HClO_4$. That electrolyte was subject to the kind of salt effects shown in Figure 13. However, the basic electrolyte minimizes the effects of inorganic salts, and the small amount of NaCl added is sufficient to mask variations in salt concentrations in the sample.

Temperature Control. The effects of sample temperature variations are directly eliminated by use of a temperature controller to adjust the temperature of the solution in the EOC cell. Accurate temperature control requires both heating and cooling functions. Often, systems use filament heaters plus tap water to provide cooling. In the Breadboard EOC Analyzer, however, the requirement for a tap water inlet and a water drain were avoided by using a thermoelectric temperature controller. This is a solid-state electronic device which can be used to heat and cool by controlling the magnitude and polarity of the current flowing through it. Current flowing in one direction provides heating, while current in the other direction results in cooling.

The thermoelectric temperature controller was selected as part of the temperature control system in the analyzer. A heat exchanger technique was selected for interfacing the sample/electrolyte mixture with the temperature controller. The heat exchanger is shown schematically in Figure 17. The solution enters the center of the heat exchanger and flows radially over a circular portion of the metal plate in contact with the temperature controller. The solution then flows into a circular, recessed ring around the active area of the temperature controller, and flows to the exit port of the heat exchanger. The temperature of the solution is monitored by a thermistor in the EOC cell, and the current flowing through the temperature controller is adjusted by a feedback circuit to maintain the temperature of the solution and cell at 25C.

The heat exchanger is sealed with a Teflon-coated O-ring, and is attached to the temperature controller with four mounting screws. A metal endplate between the screw heads and Teflon body of the heat exchanger distributes the load to minimize cold-flow in the Teflon body. These parts are shown in Figure 18.

Air Equilibration. Equilibration of the sample/electrolyte mixture with air was selected as the overkill technique to avoid fluctuations in the EOC Analyzer output resulting from changes in the concentration of dissolved O_2 in the sample. To equilibrate the solution with air, the membrane equilibrator shown schematically in Figure 19 was used. The solution enters the equilibrator through a hole shown at the right side of the equilibrator, where it flows to the center and is split into two streams. Each stream flows to one side of the equilibrator, where it flows radially under a circular, porous Teflon membrane. The membrane is sealed at the edges by Teflon gasket material. When the solution reaches the edges in the membrane, it flows into a recessed circular groove which leads to the exit port of the equilibrator. The equilibrator is shown disassembled in Figure 20.

The solution is equilibrated with air on the other side of the membrane since it flows in a thin film (typically 0.004 in thick) under the membrane which is about 80% porous. Oxygen flows through the membrane until the partial pressure of O_2 on each side is equal. Also, if bubbles are in the solution they will escape from it when the solution is pressurized.

Test Program

The test program was designed to test the effectiveness of the overkill techniques and the response of the flow-through EOC cell. Most tests were done under conditions similar to those the analyzer will experience in the WPE Pilot Plant. To simulate these conditions, the TSA shown schematically in Figure 21 was used. The water storage tank holds 12 liters of water, which is sufficient for 24 hours of operation. The tank can be pressurized with air, as in the O_3 Oxidation Unit Process. Also, compressed air can be bubbled through the tank if required, for rapid air saturation.

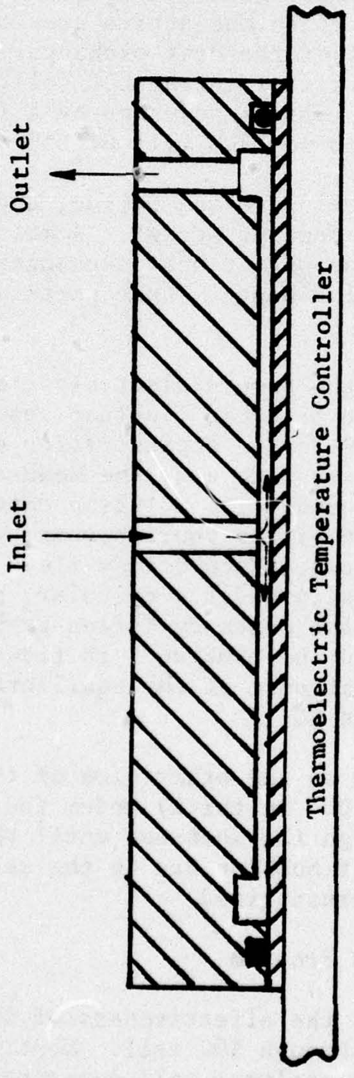

FIGURE 17 HEAT EXCHANGER SCHEMATIC

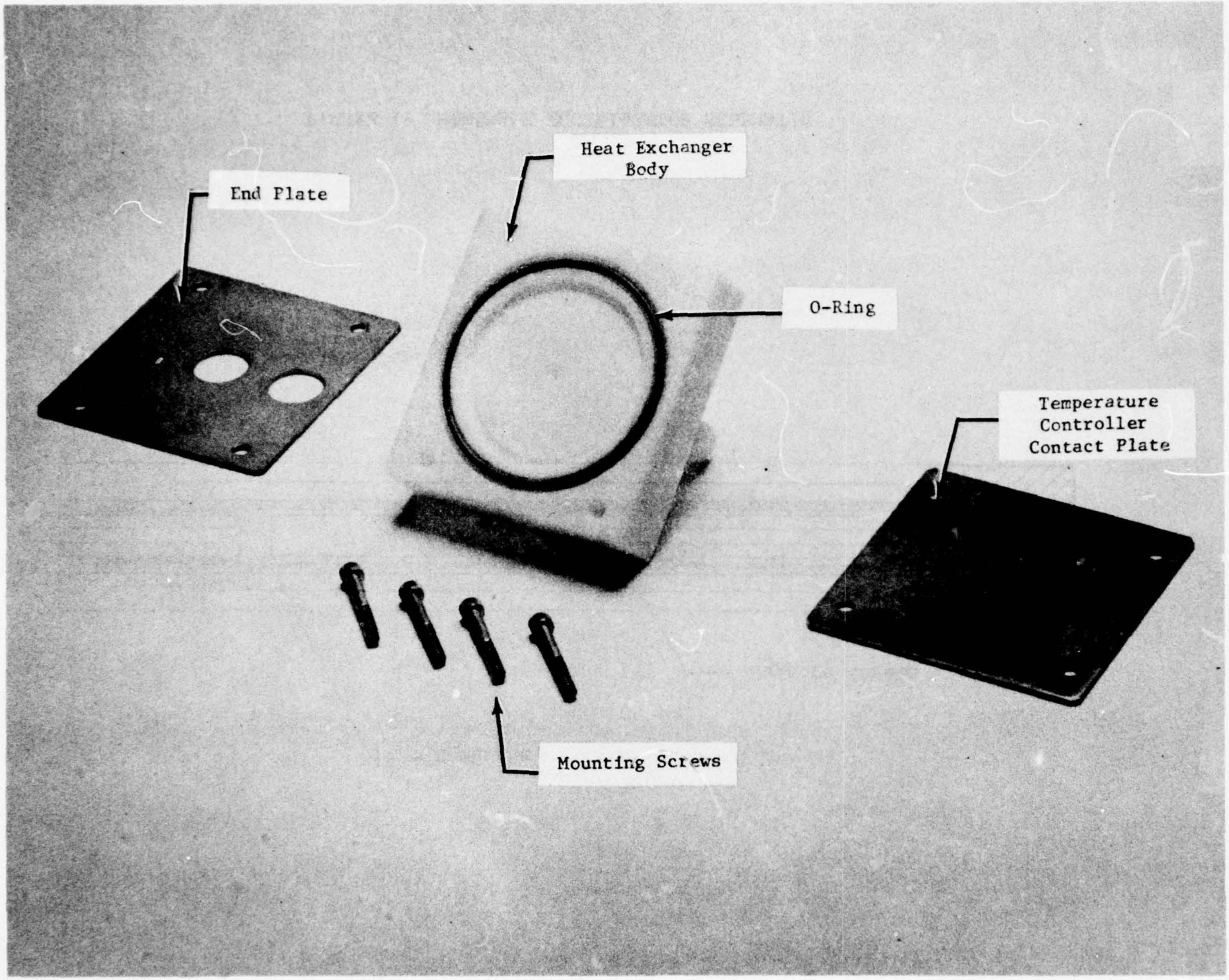

FIGURE 18 HEAT EXCHANGER

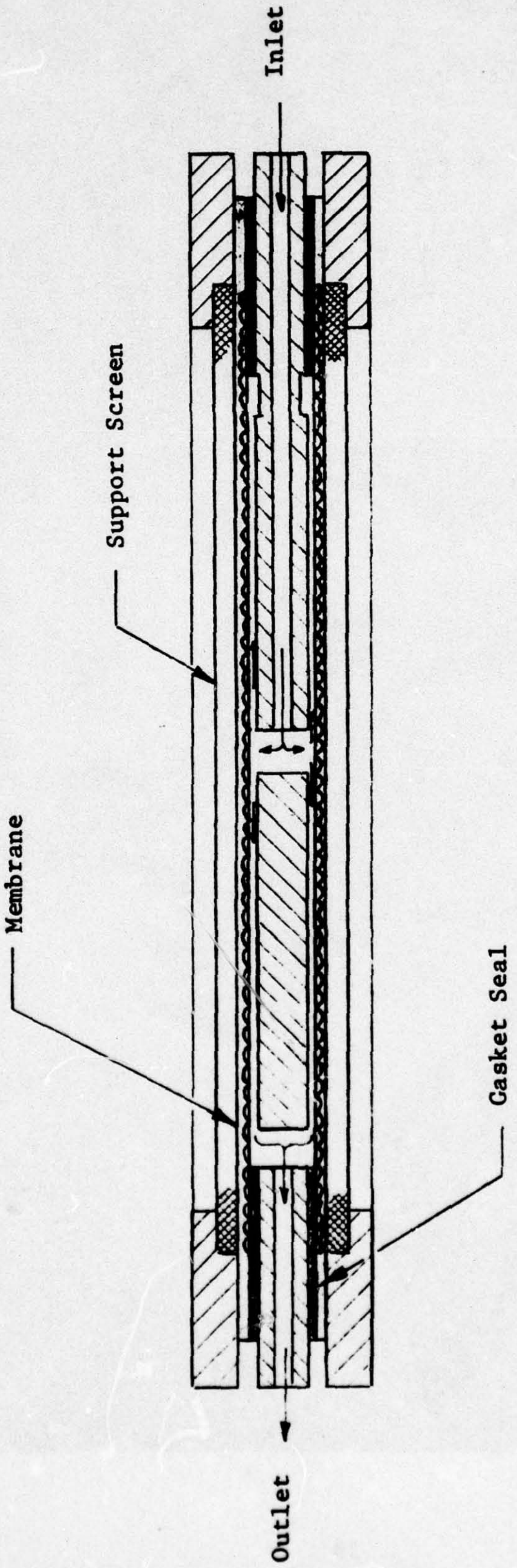

FIGURE 19 MEMBRANE EQUILIBRATOR SCHEMATIC

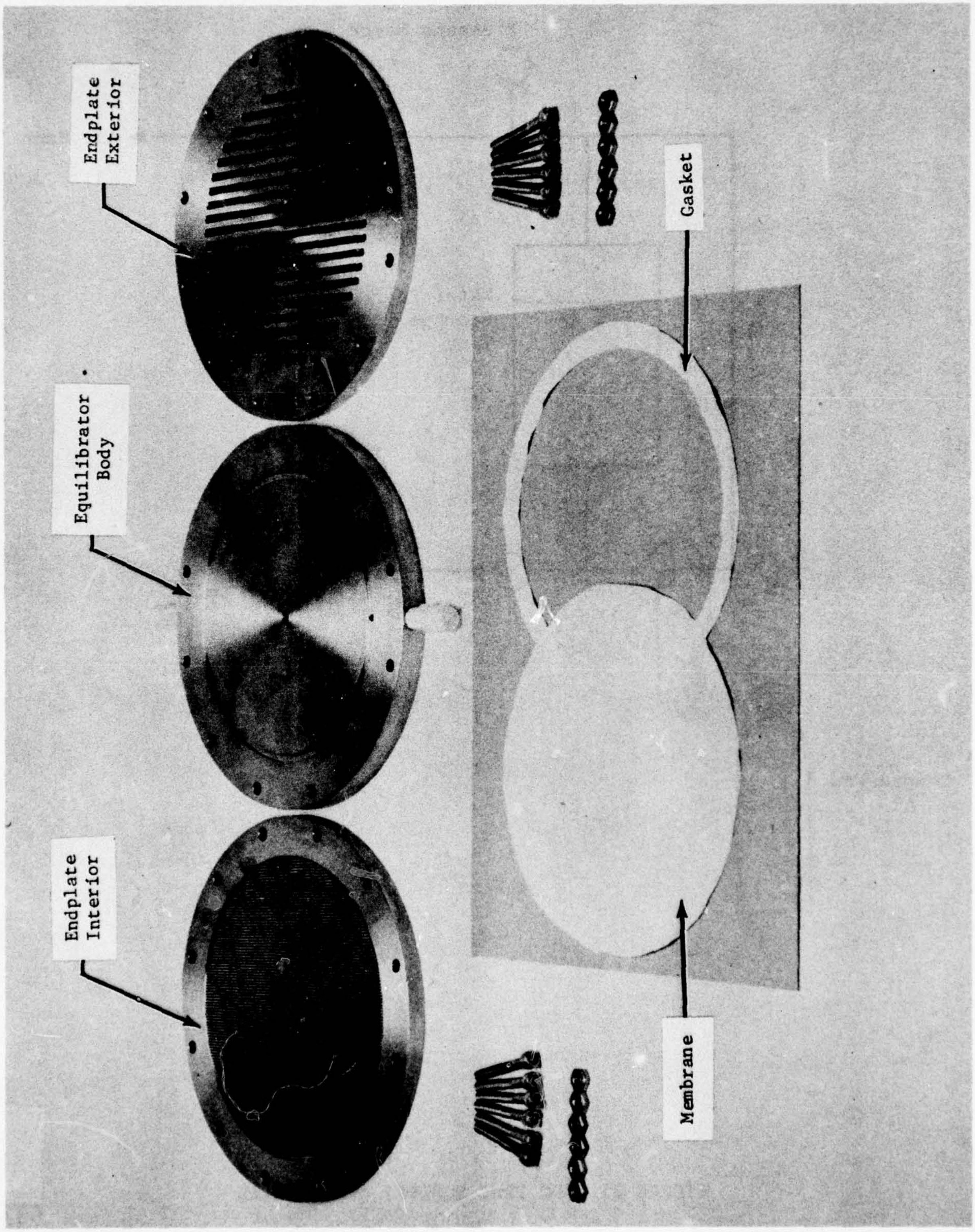

FIGURE 20 MEMBRANE EQUILIBRATOR

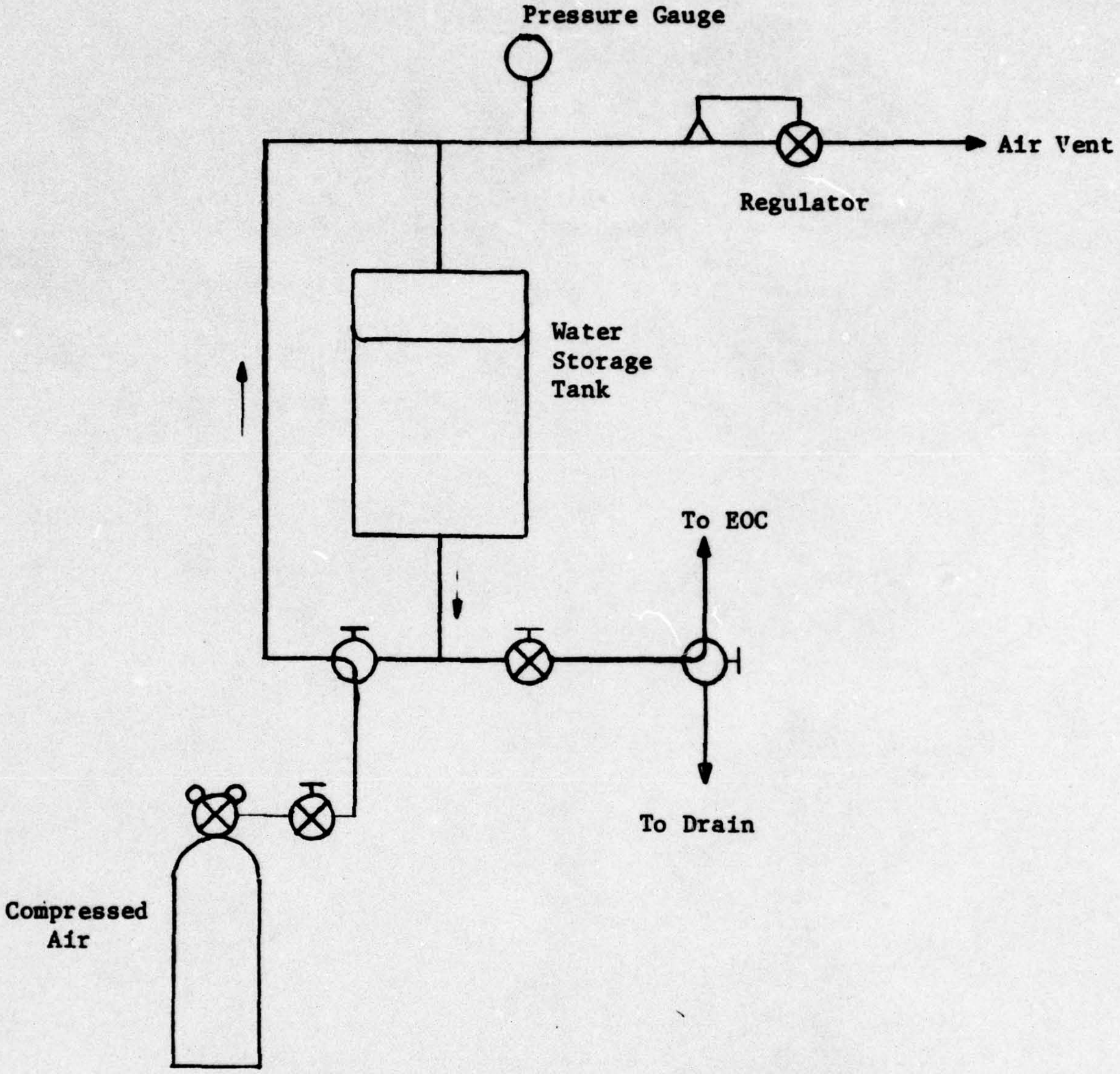

FIGURE 21 EOC TEST SUPPORT ACCESSORIES

During this phase of the test program, checkout and reproducibility tests were performed. The effectiveness of the overkill techniques was quantified during the Parametric Tests. Then, the continuous operation capability of the analyzer was tested during the Design Verification Test (DVT).

Checkout Tests

The Checkout Tests consisted of an Initial Checkout, during which the analyzer was set up, and an Eight-Hour Shakedown.

Initial Checkout. During the checkout all components of the analyzer exposed to the pressurized sample stream were pressure-checked. The components successfully withstood a pressure of 40 psig and no leakage was observed.

Next, the analyzer was assembled and the analyzer and TSA were functionally checked out. Pump flow rates were calibrated and the sample solution was pressurized to 10 psig, the pressure also used in subsequent tests.

Eight-Hour Shakedown. The Eight-Hour Shakedown consisted of eight hours of operation with the purpose of verifying that the analyzer and TSA operated properly. This insured that accurate data could be collected during later tests.

During the shakedown, the sample solution contained urea at a concentration of 5 ppm TOC. Urea was used as the baseline solute during the entire test program because it is one of the major solutes of the ozonated WPE effluent. It is a nonvolatile, nonhygroscopic, crystalline material. It therefore can be weighed accurately, and this makes it possible to prepare solutions of known concentration on a weight basis without other more costly concentration measurements. The 5 ppm TOC concentration was selected for use because it is the maximum level allowable in the WPE for nonconsumptive reuse.

The shakedown demonstrated that the analyzer hardware and TSA performed functionally within their design specifications. This made tests of the analyzer reproducibility and the performance of the overkill components possible.

Reproducibility Test

The goal of this test was to quantify the day-to-day reproducibility of the analyzer so that the normal variability of the analyzer response could be determined. The normal variability must be measured before an interpretation can be made of data in which small changes in the EOC values are measured. During the Reproducibility Test, the response of the EOC Analyzer to a solution containing urea at a concentration of 5 ppm TOC was obtained once a day for six days. Between each data point, the analyzer was shut down. Therefore, the reproducibility data includes any variability that might result from the analyzer shutdown and startup procedures.

The electrochemical parameters used for the electrode preconditioning sequence were adjusted to values previously shown during an IRAD program to result in effective electrode cleaning. The oxidation potential, E_O, was 0.95V versus the reference electrode potential. The time period used for oxidation, T_O, was 30 sec. The reduction potential, E_R, was -0.4V and the reduction period, T_R, was 10 sec. The adsorption potential, E_A, was 0.60V and the period for adsorption, T_A, equalled 80 sec.

The response of the analyzer during six days is shown in Figure 22. The average value is 325, and all data points are within one EOC unit of the average. Therefore, the reproducibility test demonstrates that the EOC Analyzer is capable of measurements with three significant figures.

Parametric Tests

During the Parametric Tests, the performance of the overkill techniques in the Breadboard Analyzer was demonstrated to effectively eliminate or compensate for the effects of chemical and physical parameters over the ranges expected in the WPE effluent.

Dissolved O_2 and O_3 Study. The effectiveness of the membrane equilibrator was tested during the Dissolved O_2 and O_3 Parametric Tests. The experimental conditions used for these tests were identical to those used during the Reproducibility Test, including the concentration of urea in the sample.

These tests were designed to independently investigate the effects of O_2 and O_3 on the analyzer performance. As shown in Table 5, three solutions were prepared and tested. Each solution had either a high or a low concentration of O_2 and O_3. However, it is not possible to have a solution containing a high concentration of O_3 with a low concentration of O_2 if conditions like those to be found in the WPE Pilot Plant are simulated.

The data in Table 5 indicates that dissolved O_2 and O_3 do not affect the response of the analyzer to urea when the membrane equilibrator is used. To three significant figures, the response of the analyzer remained constant at 325, regardless of the concentrations of O_2 and O_3.

Temperature Study. The effectiveness of the temperature controller and heat exchanger was tested by varying the temperature of the sample solution entering the analyzer, while the analyzer's response was monitored. As shown in Figure 23, the EOC values are constant over the temperature range of 18 to 48C. Therefore the temperature control components are effective in maintaining the temperature of the sample/electrolyte mixture and EOC cell constant.

The average response of the EOC Analyzer to the baseline urea test solution is shown as 271 in Figure 23. This value is lower than the values obtained in prior tests because a partial connection was found in one of the leads to the thermistor in the EOC cell before the temperature study. The stray resistance in this lead caused the cell to be thermostated at a temperature above the baseline 25C. This affected the EOC output, but not the significance of the Reproducibility and Dissolved O_2 and O_3 Tests.

Inorganic Salt Study. The maximum concentrations of common inorganic anions anticipated in the WPE effluent are 150 ppm Cl^-, 10 ppm NO_3^-/N, and 32 ppm SO_4^{-2}. The effects on EOC response of the sodium (Na^+) salts of these anions was investigated during the Inorganic Salt Study. This data is listed in

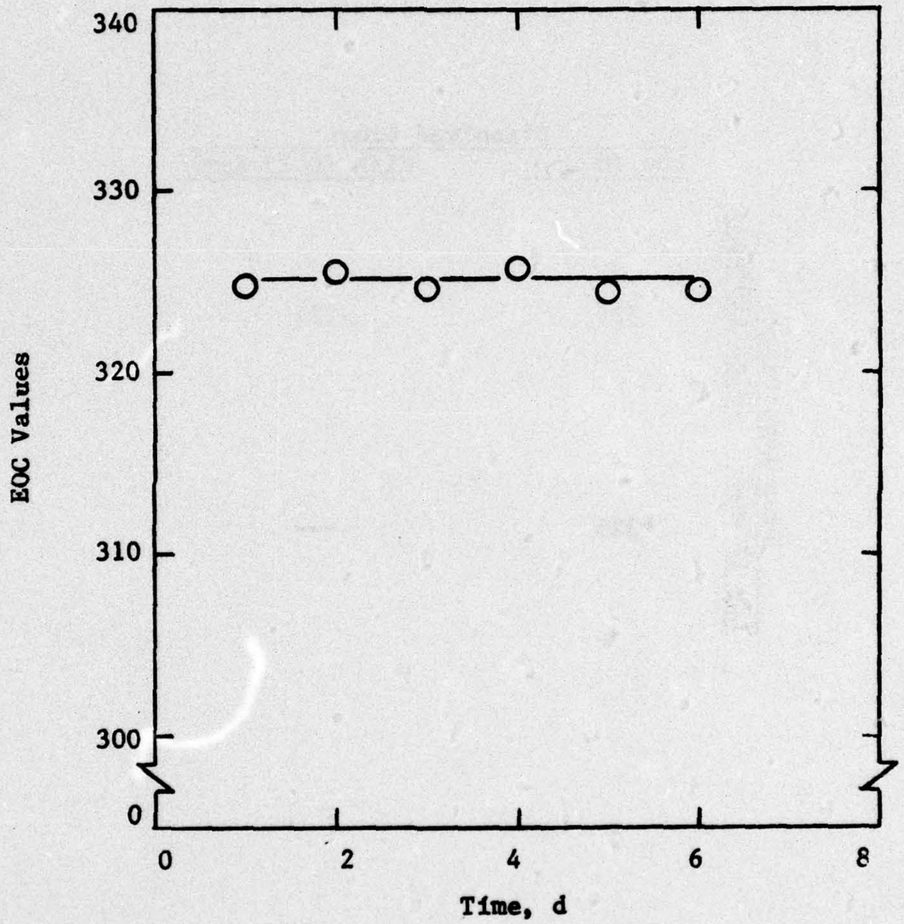

FIGURE 22 EOC REPRODUCIBILITY STUDY

TABLE 5 RESULTS OF DISSOLVED OXYGEN AND OZONE PARAMETRIC TESTS

		Dissolved Ozone	
		Low (0 ppm)	High (0.75 ppm)
Dissolved Oxygen	High (10 ppm)	325	324
	Low (8 ppm)	325	---

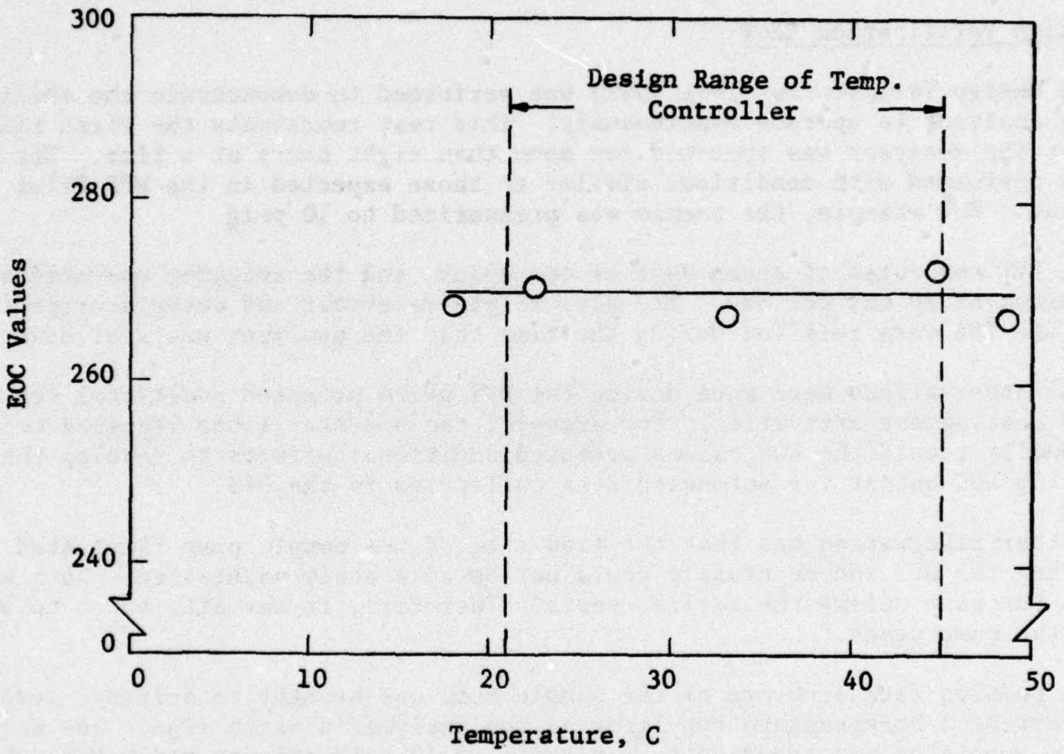

FIGURE 23 RESULTS OF EOC TEMPERATURE STUDY

Table 6. Three solutions were tested. During Test No. 1, the solution contained no inorganic salts. During Test No. 3, the test solution contained the maximum concentrations of all three salts, and Test No. 2 involved a sample having half the maximum concentrations. The experimental conditions were those used during the Reproducibility Test. As indicated in Table 6, the EOC value did not change with the concentration of the anions in the test solutions. The average response was 271 EOC units for the three solutions. From this data, it is concluded that the electrolyte used in the Breadboard Analyzer is effective in eliminating interferences from the common inorganic salts expected in the ozonated WPE effluent.

Design Verification Test

The Design Verification Test (DVT) was performed to demonstrate the ability of the analyzer to operate continuously. This test represents the first time that the analyzer was operated for more than eight hours at a time. The DVT was performed with conditions similar to those expected in the WPE Pilot Plant. For example, the sample was pressurized to 10 psig.

The DVT consisted of seven days of operation, and the analyzer operated a minimum of 20 hrs per day. The electrolyte reservoir and water storage tank on the TSA were refilled during the time that the analyzer was shut down.

Some observations were made during the DVT which prompted additional testing and development activities. For example, the operator labor required to manually record the EOC values prompted additional efforts to develop the analog EOC output for automated data collection in the DAS.

Another observation was that the flow rate of the sample pump fluctuated during the DVT and eventually could not be accurately maintained. This was not the case during the earlier tests. Therefore, it was attributed to wear in the pump seals.

The pumping rate accuracy of the sample pump was brought to original levels by inserting a backpressure regulator on the analyzer's drain line. The backpressure regulator was adjusted to a setting of 10 psig and was monitored with a pressure gauge attached to the regulator.

During the DVT it was observed that the Teflon bodies of the heat exchanger and EOC cell experienced cold-flow. The Teflon-coated O-rings used in those components also eventually acquired a compression set. Compression of the membrane in the membrane equilibrator caused it to slowly degrade. Because of these materials problems, it was concluded that long-term testing of the analyzer in the WPE Pilot Plant would not be feasible, although short-term tests could be performed. This conclusion prompted additional efforts related to increasing the long-term durability of these analyzer components.

A secondary goal of the DVT was to establish a preliminary relationship between EOC response to organic solute mixtures and the TOC concentrations for these samples. The response of the analyzer was projected to be similar to that shown in Figure 24. Any solution having a given total TOC concentration could produce a range of EOC values, depending upon its composition. A

TABLE 6 INORGANIC SALT INTERFERENCE STUDY

Parameter	Test No. 1	Test No. 2	Test No. 3
Urea Concentration, ppm TOC	5.0	5.0	5.0
Cl^- Concentration, ppm	0	75	150
NO_3^- Concentration, ppm NO_3^-/N	0	5	10
SO_4^{-2} Concentration, ppm	0	16	32
EOC Values	271	272	271

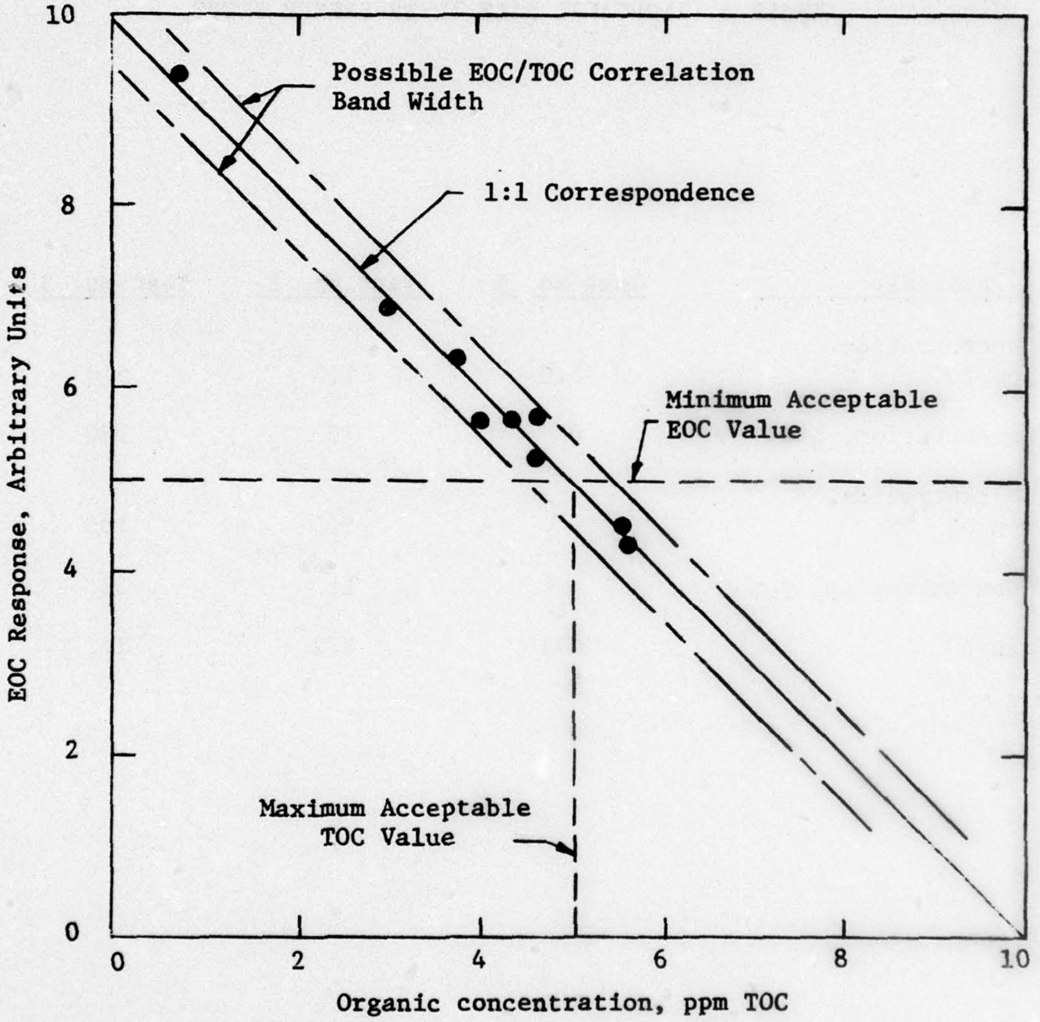

FIGURE 24 ILLUSTRATION OF EOC/TOC CORRELATION

solution having many strongly adsorbed solutes would produce a small EOC value, while a mixture of weakly adsorbing solutes would produce a larger EOC value. It was predicted that if the composition of the water sample did not vary greatly from measurement to measurement, then the range of EOC values for any TOC level would be narrow. The correlation between the EOC response and TOC values would be satisfactory for monitoring the water treatment process producing the samples.

Ozonation tests of simulated composite hospital wastes have shown that, of the many organic solutes present in the wastewater entering the O_3 Contactor, only methanol, acetone and urea are major constituents of the ozonated effluent.(7) Therefore, the composition of the ozonated effluent from the WPE Pilot Plant may not vary greatly. The correlation of EOC and TOC values may then be sufficiently precise for relating the analyzer response to TOC concentrations.

To obtain a preliminary correlation between EOC and TOC values, each day of the DVT was performed with a different sample solution. Table 7 lists the composition of each solution in the order that the solutions were tested. The composition of each sample simulates the actual composition of an ozonated composite hospital waste, with the exception of sample 7. This sample was used to quantify the response of the analyzer to a solution having a low TOC concentration.

The response of the analyzer to the seven solutions is shown in Figure 25. Some data points were repeated, and the analyzer's response to distilled water is indicated. Also, the response of the analyzer to the baseline 5 ppm TOC urea solution is shown.

As expected, the EOC values range on either side of a line representing the best correlation. More data is necessary before an accurate relationship between EOC and TOC values can be made. However, the analyzer has demonstrated a definite response to organic solutes at concentrations around the 5 ppm TOC limit for nonconsumptive reuse.

ADDITIONAL EOC DEVELOPMENT AND TESTING

Certain modifications were made to the Breadboard EOC Analyzer during an addition to this phase of Contract DAMD17-75-C-5070. The development of circuitry for interfacing the analyzer with the DAS was included in this effort. Also, activities related to simplifying the analyzer and increasing its capability for long-term testing in the WPE Pilot Plant were included.

Following these modifications, tests were performed to determine if the performance of the analyzer was significantly different from that before the modifications. Included among these tests was a 30-Day Reproducibility Test, during which the analyzer was successfully operated continuously without any component failures.

DAS Integration

Integration of the Breadboard Analyzer with the DAS was accomplished by developing a circuit capable of converting the 6-digit display signal, originally in the analyzer, to a 0-5V DC analog signal. This signal is linearly

TABLE 7 COMPOSITION OF SIMULATED O_3 CONTACTOR EFFLUENT USED IN DVT

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

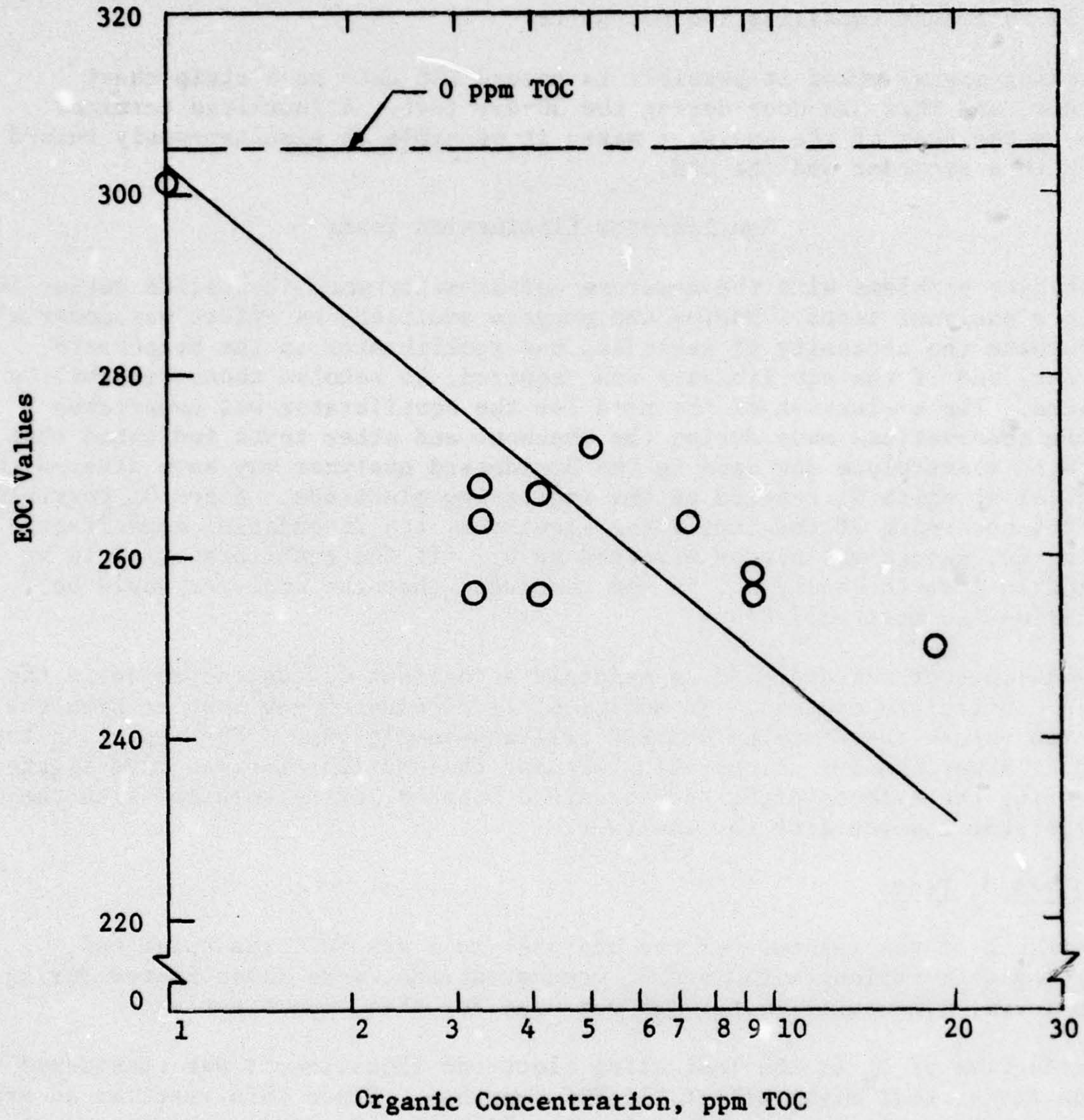

FIGURE 25 RESTULTS OF EOC DVT

proportional to EOC values. It covers a range of 100 to 600 EOC units, with each 1V increment equalling 100 EOC units.

The analog signal makes it possible to record EOC data on a strip chart recorder, and this was done during the 30-day test. A four-lead terminal strip on the rear of the analyzer makes it possible to simultaneously record data with a recorder and the DAS.

Equilibrator Elimination Tests

Reliability problems with the membrane equilibrator were identified during the previous analyzer tests. During the program addition, an effort was undertaken to evaluate the necessity of including the equilibrator in the Breadboard Analyzer, and if the equilibrator was required, to resolve those reliability problems. The evaluation of the need for the equilibrator was undertaken because observations made during the checkout and other tests indicated that the basic electrolyte now used in the Breadboard Analyzer may have altered the potential at which O_2 reacted at the indicating electrode. Since O_2 possibly does not now react at the indicating electrode, the interfacial capacitance and the EOC values may not be affected by O_2. If the equilibrator could be eliminated from the analyzer, it was concluded that the analyzer would be simplified and more reliable.

The equilibrator was designed to maintain a constant O_2 concentration in the sample/electrolyte mixture. In addition, it eliminated any bubbles from the solution before they entered the EOC cell and sample pump. The impact on the analyzer's performance of operating without the equilibrator was investigated by testing the effects of O_2 and entrained bubbles in the solution with the equilibrator removed from the analyzer.

Dissolved O_2 Tests

The effects on the response of the analyzer to 5 ppm TOC urea solutions, resulting from various dissolved O_2 concentrations, were investigated during these tests. The equilibrator was not used for this investigation.

The reduction of O_2 at the indicating electrode (Equation 1) was considered to be the factor that might affect the EOC response. Since this reaction occurs only at certain electrode potentials, the Dissolved O_2 Tests were done with two adsorption potentials and two reduction potentials to determine if certain potentials result in better performance than others.

The data collected during a two-day period is shown in Figures 26 and 27. In Figure 26 data collected with E_A equal to 0.00V is displayed, and Figure 27 shows data obtained with E_A equal to 0.60V. Curves obtained with E_R values of -0.40 and -1.00V are included in both figures.

The EOC value varies little when the dissolved O_2 concentration is around the level expected in the WPE effluent (Figure 26). A small decrease is noted when the sample is deaerated. Good day-to-day reproducibility is obtained when the adsorption potential is 0.00V, and larger EOC values are obtained

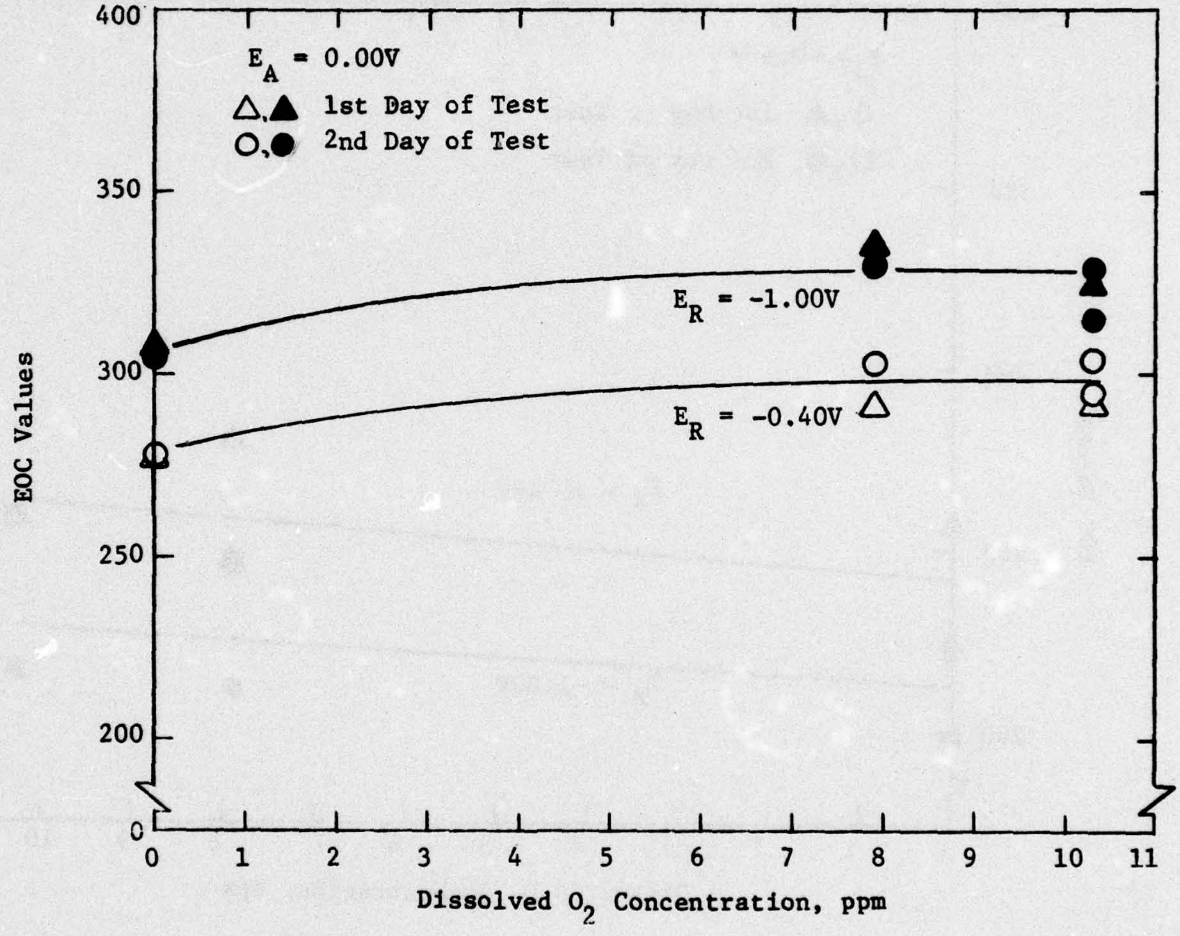

FIGURE 26 DISSOLVED OXYGEN TEST, ADSORPTION AT 0.00V

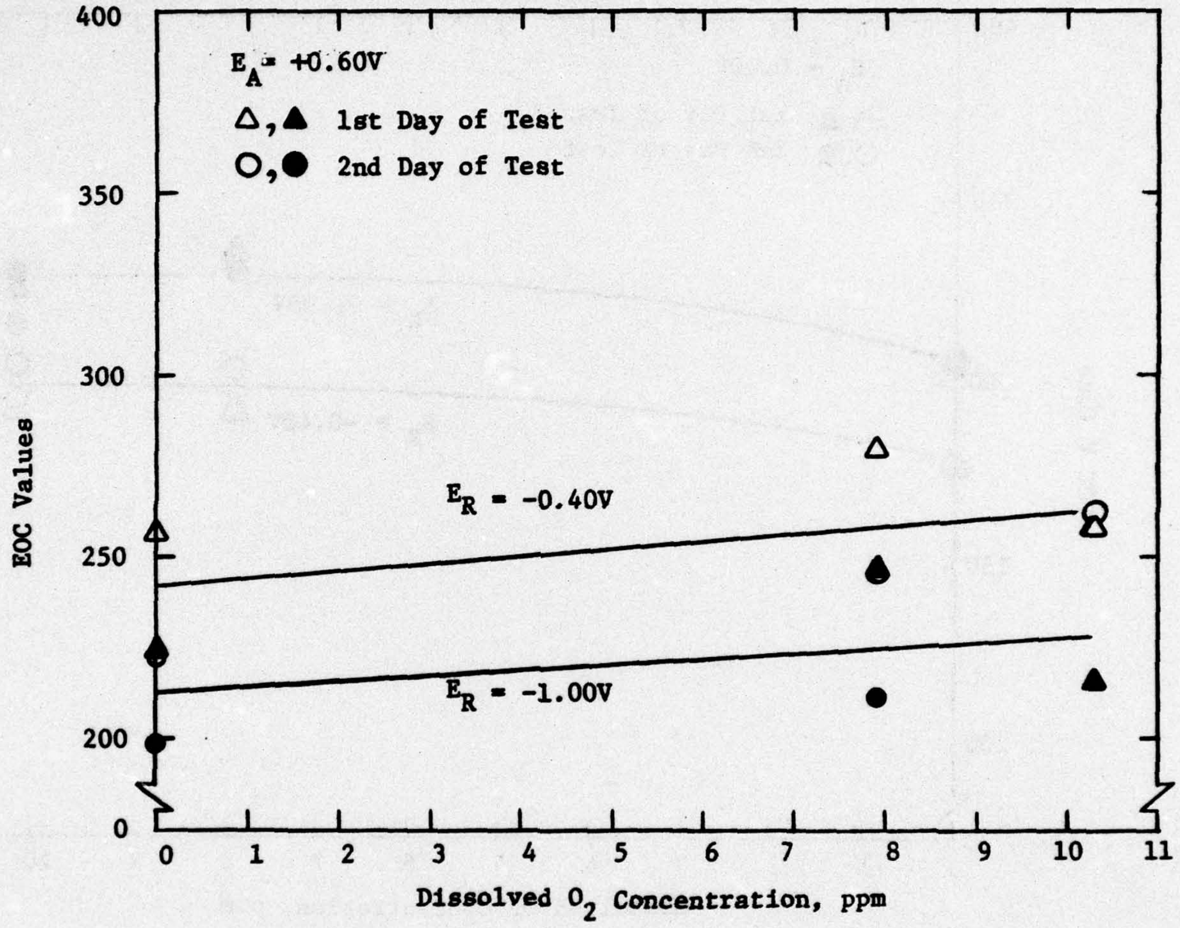

FIGURE 27 DISSOLVED OXYGEN TEST, ADSORPTION AT 0.60V

when E_R equals -1.00V. However, less day-to-day reproducibility is obtained when E_A equals 0.60V.

It is concluded from these tests that the membrane equilibrator is not required in the analyzer to compensate for the effects of dissolved O_2. The adsorption potential of 0.00V has been demonstrated to produce better reproducibility than an E_A value of 0.60V. Larger EOC values are obtained with E_R equal to -1.00V. It is therefore advantageous to use this reduction potential to result in larger analyzer output signals. For these reasons, subsequent tests were performed with adsorption and reduction potentials of 0.00 and -1.00V, respectively.

Entrained Bubble Test

The sample/electrolyte mixture occasionally contains bubbles, usually resulting from the degassing of dissolved air. The equilibrator eliminated these bubbles by forcing them, under pressure, through the porous membrane. During this test, the effect on the analyzer's performance of these bubbles was investigated.

The analyzer was operated for 20 hours with the equilibrator removed. During this period no bubbles were collected in the EOC cell, and the analyzer's response to 5 ppm TOC urea did not change. However, bubbles did accumulate in the sample pump, resulting in a decrease in the sample flow rate. This problem was eliminated by reorienting the pump so that bubbles could rise vertically through the pump head.

The equilibrator is not necessary to prevent interferences due to O_2 or bubbles in the Breadboard Analyzer. Unlike earlier EOC Analyzers which operated with acidic electrolytes, the Breadboard Analyzer is not susceptible to errors from O_2 because of its basic electrolyte. Also, the EOC cell and other components were designed and oriented to avoid the collection of bubbles. Therefore, the equilibrator has been eliminated from the analyzer.

High-Reliability Analyzer Modifications

Long-term tests of the Breadboard EOC Analyzer will be performed after the analyzer is integrated with the WPE Pilot Plant. To perform extended tests, modifications to the EOC cell and heat exchanger were required as shown by some of the results of the DVT. These modifications were designed and implemented during this program addition.

EOC Cell Modifications

The modifications to the EOC cell did not affect the electrodes or their orientation, so that data collected with the cell before these modifications is expected to also represent its performance now. The modifications consisted of the use of larger Teflon-coated O-rings in the cell and stainless steel endplates beneath the bolts that secure the cell parts (Figure 28). These parts tend to minimize the effects of cold-flow in the Teflon cell parts and result in increased ability for the cell to operate for extended periods without leakage.

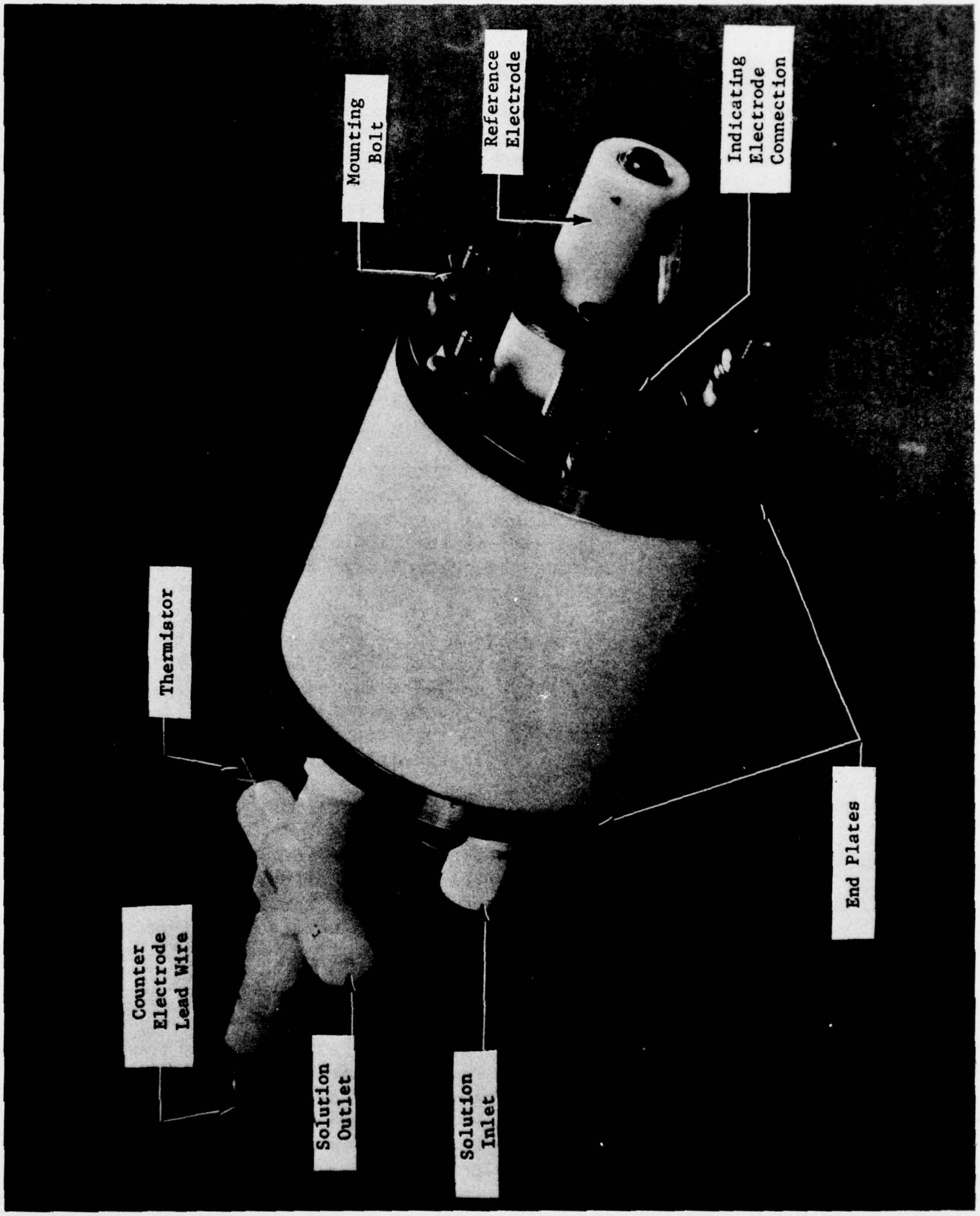

FIGURE 28 BREADBOARD EOC CELL

In addition to these changes, two O-rings are now used to seal the indicating electrode and an O-ring is used to seal the reference electrode. The hole in the rear of the cell, through which the counter electrode lead wire extended, has been eliminated to avoid a possible leakage site. The lead now extends through the solution exit port of the cell and through a cross fitting. The solution exits from one arm of the fitting, and the thermistor extends into the solution from the other arm.

Heat Exchanger Modifications

Fewer modifications were required by the heat exchanger than the EOC cell. A double O-ring seal with larger Teflon-coated O-rings was used for maximum reliability. Also, a thicker stainless steel endplate was used under the mounting screws to more evenly distribute the force on the body of the heat exchanger.

The interior of the Breadboard Analyzer is shown in Figure 29. The modified heat exchanger and EOC cell are shown. Also, the terminal strip for the 0-5V DC analog output, and the backpressure regulator and pressure gauge are shown attached to the rear of the instrument. The equilibrator is not shown as the result of the Dissolved O_2 and Bubble Tests discussed above.

Additional EOC Tests

The final tests performed with the Breadboard Analyzer were a repetition of the DVT data and a 30-Day Reproducibility Test. The DVT data was repeated to quantify the analyzer's response to organic solutes following adoption of new adsorption and reduction potentials and other modifications. The 30-Day Test was performed primarily to establish the response of the modified analyzer to the baseline urea solution, and to identify any small changes in the EOC response that may occur during long-term testing.

Repetition of DVT Data

The data obtained during the DVT was repeated by introducing into the analyzer test solutions having the compositions listed in Table 7. The solutions were tested in the same order as in the DVT, but each solution was sampled for one hour instead of one day.

To begin the test, the indicating and counter electrodes were lightly polished with 0.3μ alumina to remove dirt accumulated during assembly of the cell after the cell modifications were completed.

The data, shown in Figure 30, was obtained with the modified cell and heat exchanger and without the membrane equilibrator. The adsorption and reduction potentials were 0.00 and -1.00V, respectively.

The response of the analyzer to the DVT test solutions remains similar to that obtained before the modifications were made. The absolute values of the EOC response is different because of the new electrode potentials used. Comparison of the DVT data in Figure 25 with Figure 30 shows that the new conditions produce less scatter of the data points around the line of best correlation, but the slope of the response curve is somewhat less.

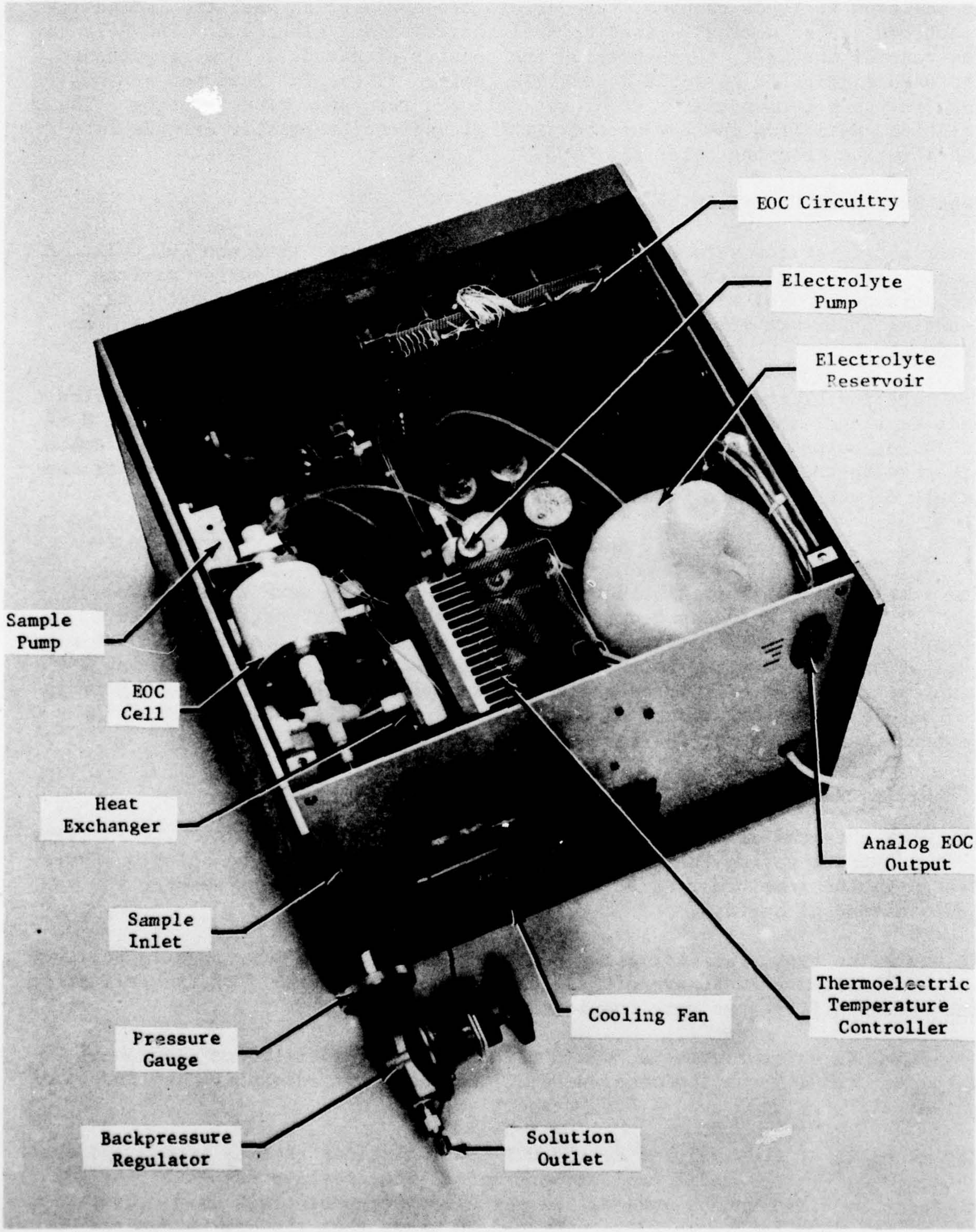

FIGURE 29 INTERIOR OF BREADBOARD EOC ANALYZER

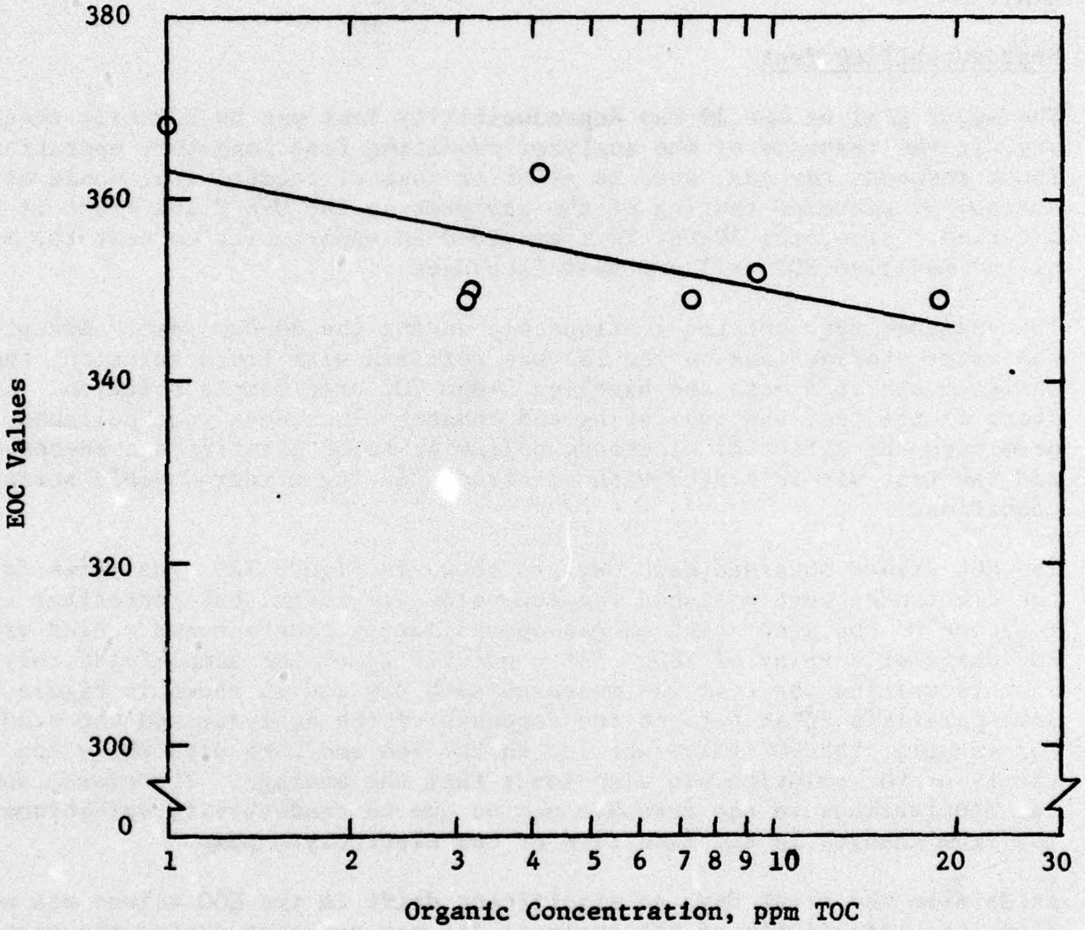

FIGURE 30 SHORT-TERM EOC DVT

Of the three solutes in the sample solutions, the analyzer responds most to urea. When the response of the analyzer to the DVT test solutions is plotted against the concentration of urea, instead of versus the total TOC concentration in the samples, this fact is demonstrated. Figure 31 shows good correlation between the EOC response and the concentration of urea, except for one data point at a concentration of 2.6 ppm TOC. This point was the first obtained after the indicating electrode was polished. Therefore, polishing the electrode apparently results in large EOC values for a short period of time.

Reproducibility Test

The major goal of the 30-Day Reproducibility Test was to identify changes, if any, in the response of the analyzer resulting from long-term operation. These response changes, such as drift or loss of sensitivity, would affect the success of extended testing of the analyzer in the WPE Pilot Plant if they occurred. Also, the 30-Day Test provided an opportunity to test the reliability of the modified EOC cell and heat exchanger.

The analyzer was operated continuously during the 30-Day Test. Except while the water storage tank in the TSA was refilled with fresh solution, the analyzer operated with the baseline 5 ppm TOC urea sample solution. At the start of the test the indicating and counter electrodes were polished. This permitted the effect of electrode polishing to be quantified a second time, and the test was initiated with electrodes having a reproducible surface condition.

The EOC values obtained each day are shown in Figure 32. The first day after the electrodes were polished the EOC value was large, but thereafter the EOC response to the urea solution was approximately constant and varied within 10 EOC units of a value of 280. The conductivity of the sample/electrolyte mixture exiting the cell was measured each day and is shown in Figure 32. Some parallels exist between the response of the analyzer and the conductivity. For example, the EOC value was low on the 7th and 26th days while the conductivity of the solution was also lower than the average. Therefore, some of the fluctuations in the response may be due to conductivity variations resulting from changes in the flow rate of the electrolyte pump.

Aside from the first day, no significant drift in the EOC values was observed. Also, the sensitivity of the analyzer did not decrease during the test. The sensitivity of any analyzer is the change in the analyzer's response resulting from a given change in the concentration of the species being measured. During the 30-Day Test, the sensitivity of the Breadboard Analyzer was quantified each day by introducing standard 0 ppm and 10 ppm TOC urea solutions into the analyzer. This was done while the water storage tank in the TSA was refilled. Therefore, these standard solutions were not pressurized and the conductivity of the sample/electrolyte mixture was about 0.09 mho/cm instead of the normal value of 0.06 mho/cm used when the 5 ppm TOC urea solution in the TSA was analyzed. The conductivity increase is because of the effect of the sample pressure on the electrolyte pump flow rate. The result of the higher conductivity is that the EOC values obtained with the standard solutions are larger than would be expected from the data on the 5 ppm TOC solution.

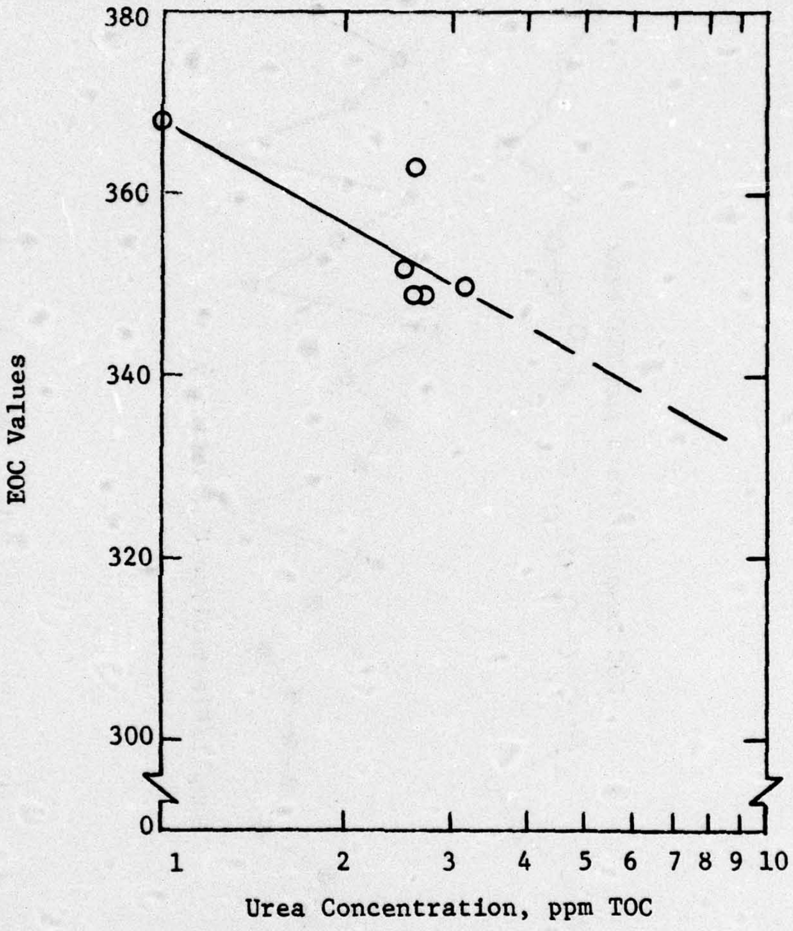

FIGURE 31 EOC RESPONSE TO UREA DURING DVT

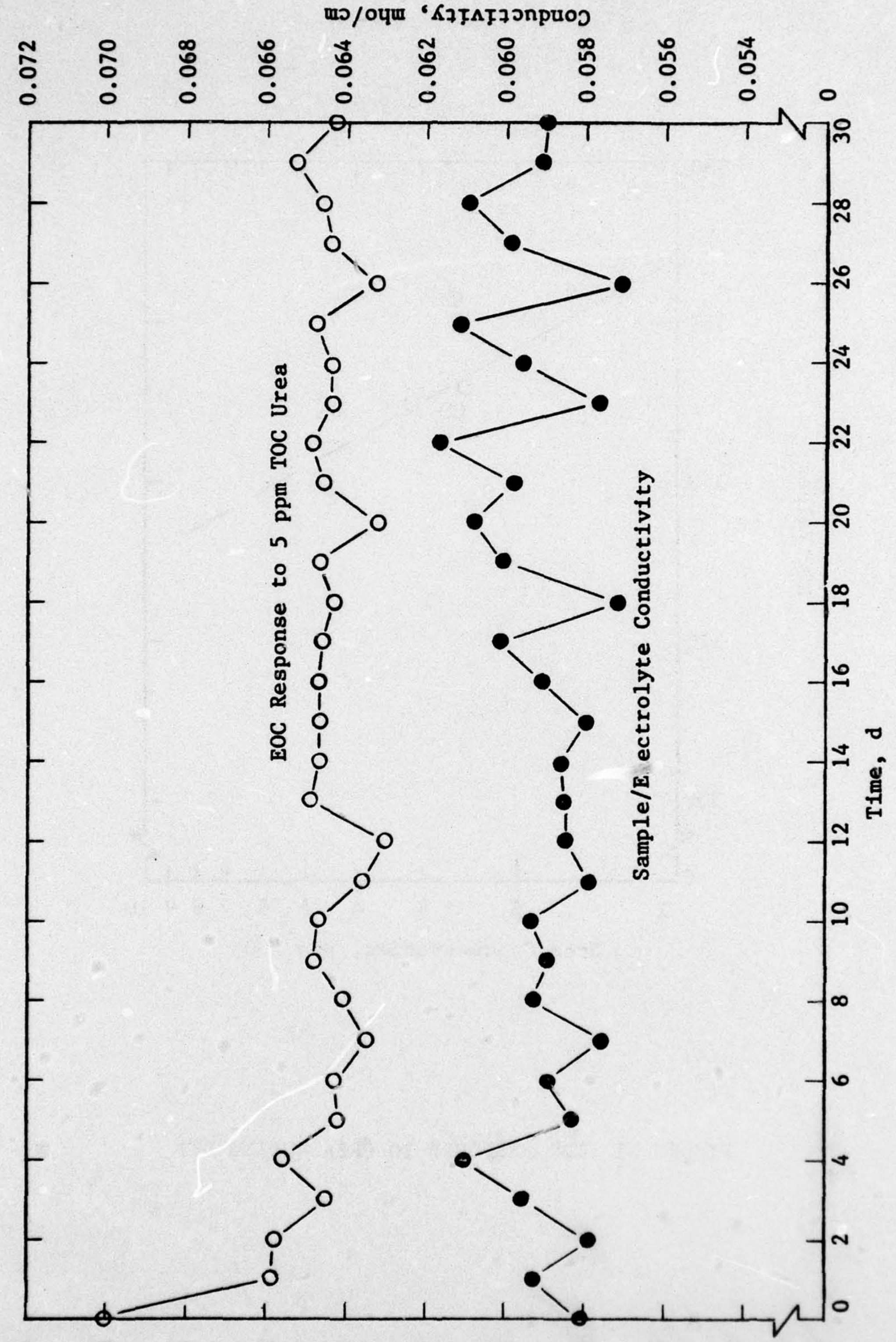

FIGURE 32 RESULTS OF 30-DAY TEST

Nevertheless, this data is useful in demonstrating long-term effects on the analyzer's sensitivity.

In Figure 33, the data collected for the 0 ppm and 10 ppm TOC urea solutions is shown. The sensitivity of the analyzer is indicated by the difference between the EOC values for the two solutions. This difference ranged from 148 EOC units the last day to 82 units the 11th day of the test. Although the EOC values were larger the first day of the test because of the polished electrodes, the sensitivity of the analyzer was an intermediate 132 EOC units.

From this data it is concluded that the sensitivity of the analyzer does not degrade even during extended operation. Although the absolute values of the EOC output are affected by polishing the indicating electrode, the sensitivity is not affected. The daily fluctuations of the EOC values are due, in part, to the variations in the conductivity of the sample/electrolyte mixture. Other causes may be changes in the internal resistance of the EOC cell or its electrodes.

The 30-Day Test demonstrated that the analyzer is capable of long-term, reliable operation. During the test there were no component failures or leaks. The only operator labor required was a daily resupply of the sample and electrolyte solutions, and adjustment of the electrolyte flow rate two or three times per day. Four times during the 30 days the electrolyte pump head filled with bubbles from gases originally dissolved in the electrolyte. The pump did not function effectively in those cases, but the bubbles were readily eliminated by releasing the sample inlet pressure and momentarily increasing the electrolyte flow rate. Also, the data points obtained with the two standard solutions on the 26th day of the test were nonrepresentative because the conductivity of the sample/electrolyte mixture had the unusually high value of 0.17 mho/cm. For that reason the sensitivity data for that day was omitted from Figure 33.

CONCLUSIONS

Development of a Breadboard EOC Analyzer, which is capable of continuous, on-line monitoring of the ozonated effluent from the WPE Pilot Plant, has been successfully achieved. Analysis has indicated that the addition of electrolyte to the sample is an effective means of eliminating measurement errors resulting from changes in the pH and conductivity in the sample. The basic electrolyte used in the Breadboard Analyzer has demonstrated the ability to avoid interferences from O_3, Cl^-, NO_3^-, and SO_4^{-2} when those species are present at the maximum concentrations expected in the ozonated effluent. Because the electrolyte is basic, dissolved O_2 does not affect the EOC measurements, and the membrane equilibrator, originally designed to eliminate interference from O_2, has been eliminated from the analyzer. Also, temperature affects were demonstrated to be eliminated by the analyzer's temperature controller.

The program resulted in the successful development of a flow-through EOC cell that, like the analyzer in general, is capable of on-line measurements. The analyzer and cell are capable of reliable, extended operation as demonstrated in the 30-Day Test.

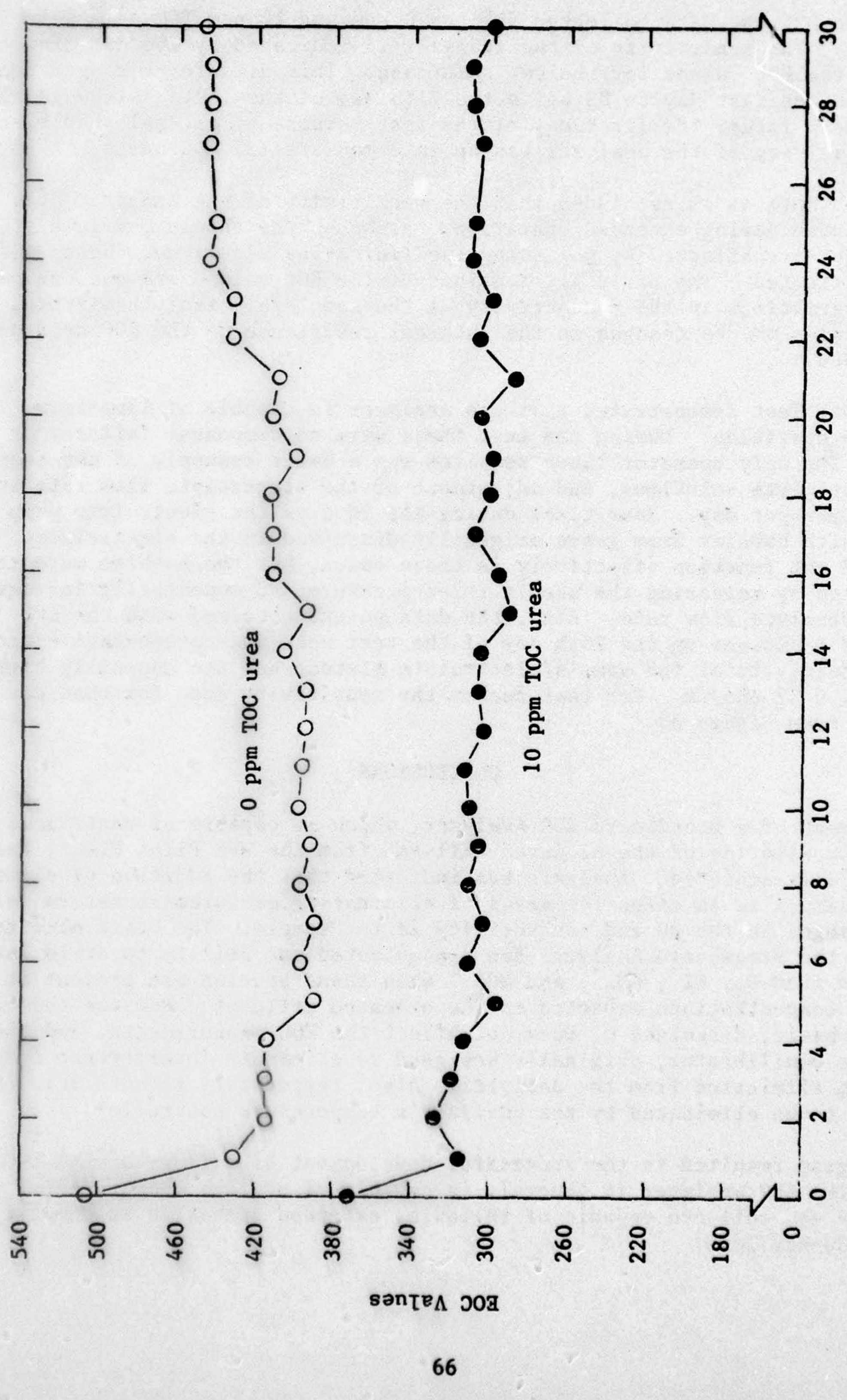

FIGURE 33 EOC RESPONSE TO STANDARD SOLUTIONS

Other new features included in the Breadboard Analyzer are in situ electronic calibration and the provision of analog signals for automated data collection with the DAS or a strip chart recorder. Also, for the operator's convenience, lights are included on the analyzer's front panel to indicate the phase of the preconditioning sequence the indicating electrode is undergoing.

The major operator labor required by the analyzer is preparation of the electrolyte solution. This labor could be minimized by pursuing efforts designed to reduce electrolyte consumption. Other electrolyte solutions or forms of electrolytes could be investigated to result in a more cost-effective way of operating the analyzer.

A second function of the operator is to monitor the conductivity of the sample/electrolyte mixture and adjust the flow rates of the electrolyte and sample solutions as necessary. This effort may be reduced by automatically monitoring the conductivity, and adjusting the electrolyte pump flow rate to maintain the desired conductivity value. Besides reducing the labor required for operating the analyzer, this feature would result in improvement in the reproducibility and precision of the EOC response.

The Breadboard Analyzer responds more to urea than to methanol and acetone, the two volatile organic solutes expected to be normally present in the ozonated WPE effluent. Methanol and acetone are among the smallest, and therefore least strongly adsorbed solutes. Other larger and more strongly adsorbed solutes would be present in the case of a failure in the O_3 Oxidation Unit Process or if ineffective ozonation occurs. Since these solutes would have adsorption characteristics more like urea than methanol or acetone, it is expected that the analyzer would respond significantly to those solutes. Therefore, the analyzer would indicate a system failure and situations in which the effluent was ineffectively ozonated.

The EOC Analyzer may now be an effective go/no-go indicator of the efficiency of the ozonation process. With increased sensitivity in the response of the analyzer to methanol, acetone and other low molecular weight organics, the analyzer may develop into an analytical monitor of the organic concentrations in the effluent. It may then be useful for feedback control of the O_3 Oxidation Unit Process. The Laboratory Breadboard EOC Analyzer demonstrated a high sensitivity to methanol and acetone. A major difference between that analyzer and the Breadboard Analyzer is the electrolyte. The earlier analyzer used 0.1 $\underline{M}$ $HClO_4$, while a basic electrolyte is now used. Therefore, a possible route to increased sensitivity is the investigation of electrolyte effects with the goal of optimized sensitivity to poorly adsorbing solutes. Also, other electrode materials and adsorption potentials may be effective in improving the analyzer's response.

Performance of the analyzer may also be improved through the adoption of a calibration procedure. The 30-Day Test has shown that the analyzer has a relatively constant sensitivity, regardless of the time that it is operated or the condition of the indicating electrode. The absolute value obtained from the analyzer for a given solution does vary somewhat, but this variation can be electronically eliminated by performing a periodic calibration with two standard solutions. In analogous fashion to the calibration of pH meters, the EOC output to one solution could be electronically adjusted to a convenient value. The other solution could then be used to adjust the sensitivity (sometimes called span) of the EOC readout to a standard value. With this system, the day-to-day fluctuations in the response would be greatly minimized, and the accuracy of the organic solute concentration measurement would be increased.

This phase of the EOC program has mainly involved development and tests of the analyzer hardware. However, as indicated by the observations made above relating to means of improving the analyzer's analytical performance, work remains before all the analytical aspects of the EOC Analyzer are optimized.

RECOMMENDATIONS

Several recommendations are made for further development of the EOC Analyzer concept. The Breadboard Analyzer will be useful in performing many of these tasks. Other recommendations are made that relate to development of future, advanced versions of the EOC Analyzer that have advantages in reliability, portability, and hardware and operating costs.

The Breadboard EOC Analyzer will be integrated with the WPE Pilot Plant and extended tests will be performed. Existing Life Systems EOC hardware, including a duplicate Breadboard Analyzer, is available for development studies. It is recommended that a study of electrode materials, electrode potentials and electrolytes be performed with this hardware with the objective of increasing the EOC response to poorly adsorbing organic solutes. Improvements identified during this study may be incorporated into the analyzer integrated in the WPE Pilot Plant for timely upgrading of the data collected there.

The conductivity measurement and automated electrolyte flow rate adjustment may also be developed with existing hardware. Then this feature could be added to the Breadboard Analyzer to minimize operating costs during the extended tests in the WPE.

It is recommended that an automated calibration procedure be developed. Since electronic adjustment of the analyzer's output signals will be part of the calibration technique, it is suggested that the output signals be modified electronically to result in increasing EOC values in linear proportion to increasing organic solute concentration. This human engineering feature would simplify the interpretation of the EOC data.

Other development activities may result in simplified, low-cost, advanced EOC Analyzers. For example, development of alternatives to electrolyte addition, as a means of controlling the effects on EOC response of some chemical parameters, may result in a lower cost, simplified analyzer. The electrolyte requirement may be greatly minimized or eliminated by modifying the EOC circuitry and cell to operate under low conductivity conditions. If the electrolyte solution is eliminated from the analyzer, the electrolyte reservoir and pump can also be eliminated. Many applications, such as the MUST WPE, involve monitoring pressurized effluents. Therefore, the EOC Analyzer will not require a sample pump since the pressure of the effluent can be used to force solution through the EOC cell.

Elimination of the consumption of the electrolyte solution would result in elimination of the reservoir, and sample and electrolyte pumps. The analyzer would consist of the EOC cell, temperature controller and EOC circuitry. The temperature controller may be replaced by a temperature monitor and temperature compensation of the EOC response, in a manner similar to that used in many pH meters.

With elimination of the temperature controller and electrolyte solution, the EOC Analyzer would be simplified greatly beyond what it now is. This effort may result in low-cost hardware for organic solute monitoring in process applications. Because the analyzer would be automated and would contain few components, reliability would be high and it could be operated by unskilled personnel.

For these reasons, it is recommended that efforts be undertaken to result in elimination or simplification of present overkill techniques used in the Breadboard Analyzer. An analyzer that is useful not only in the WPE, but in many other process-control applications, may result from these efforts.

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