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TESTING EVALUATION OF THE ELECTROCHEMICAL ORGANIC CONTENT ANALYZER

FINAL REPORT

by

R. J. Davenport

November, 1979

Prepared Under Contract NAS9-15402

by

Life Systems, Inc.
Cleveland, OH 44122

for

LYNDON B. JOHNSON SPACE CENTER
National Aeronautics and Space Administration

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FOREWORD

This report was prepared by Life Systems, Inc., for the National Aeronautics and Space Administration Lyndon B. Johnson Space Center in accordance with the requirements of Contract NAS9-15402, "Testing Evaluation of the Electrochemical Organic Content Analyzer." The period of performance for the program was September 1, 1977 to November 2, 1979. The objective of the program was to evaluate the Electrochemical Organic Content Analyzer as a technique for monitoring organic solute concentrations in the effluent of water recovery subsystems. The Electrochemical Organic Content Analyzer, if found to be a successful technique, would be part of a Water Quality Monitor Subsystem. Tests were also performed to determine the feasibility of operating the Electrochemical Organic Content Analyzer without the use of expendable reagents.

All measurements and calculations contained in this report are expressed in SI (metric) units; conventional units are given in parenthesis.

The Program Manager was Dr. R. J. Davenport. Technical support for the evaluation was provided by Dr. J. B. Lantz, Mr. L. E. Wolfe and Dr. R. A. Wynveen.

The Contract Technical Monitor was Mr. Gene Winkler, Crew Systems Division, Lyndon B. Johnson Space Center, Houston, TX 77058.

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LIST OF ACRONYMS

EOC	Electrochemical Organic Content
IRAD	Internal Research and Development
RLSE	Regenerative Life Support Experiment
TOC	Total Organic Carbon
UV	Ultraviolet
VCDS	Vapor Compression Distillation Subsystem
WQM	Water Quality Monitor

SUMMARY

Environmental Control/Life Support Systems for habitations in space lasting 30 days or more will incorporate water recovery subsystems for production of water for use by the crew, and for cooling and other purposes. It is expected that long-term missions will involve experimentation and even manufacturing under zero-g conditions. These activities will require large quantities of water that can be obtained only through the use of a water recovery subsystem. To ensure the health and well-being of the crew, as well as to prevent the failure of experiments and manufacturing processes because of substandard water, a water quality monitor will be incorporated in the water recovery subsystem.

The objective of water quality monitors evaluated by the National Aeronautics and Space Administration has been to quantify total solids in the water, including, in some cases, measurement of microbiological activity. The total solids content can be approximated by measurements of conductivity (which indicates the concentration of ionic species that are predominately inorganic) and measurement of the organic solute concentrations, which are predominately nonionic and not quantified in the conductivity measurement. Conductivity is a valid measure of ionic solute concentration only over a narrow pH range between 6 and 9 because of the high conductivities of hydrogen ions and hydroxyl ions existing in significant concentrations outside this pH range. Therefore, pH measurements are made to assure the validity of the conductivity measurement.

In the past, the organic solute concentration measurement was made by measuring the total organic carbon concentration. Total organic carbon analyzers, however, require the use of several components because of the inherent nature of the measurement. Inorganic carbon (dissolved carbon dioxide, carbonates and bicarbonates) must be removed from the sample in the analyzer prior to the measurement. After that, the total organic carbon measurement consists of the oxidation of the organic solutes in the sample by a strong chemical oxidizing agent or by heat, followed by the measurement of carbon dioxide produced in the oxidation. Thermal oxidation of organics requires the use of high temperature ovens and catalysts which become inactivated from the sample. Chemical oxidation of organics is possible using a strong oxidizing agent such as persulfate, catalyzed by ultraviolet radiation. The use of ultraviolet catalysis necessitates use of a quartz reactor and mercury vapor filled lamps. These components result in significant reliability problems in an aerospace environment. The total organic carbon analyzer requires the use of at least two reagents with a peristaltic pump containing rubber tubing, which is another reliability consideration. The oxidizing agent and acidic and basic reagents used in the analyzer impose certain risks. Because of the complexity of the analyzer, flight units may weigh between 9.1 and 3.6 kg (20 and 80 lb).

An alternative to a total organic carbon analyzer in the Water Quality Monitor is the Electrochemical Organic Content Analyzer. This analyzer is a general indicator of organic concentrations and is analogous to conductivity monitors, which are general indicators of the concentration of ionic solutes in water.

The feasibility of the Electrochemical Organic Content Analyzer concept was originally demonstrated in one of Life Systems' Internal Research and Development Programs. The feasibility evaluation was expanded under Army Contract

DAMD17-75-C-5070. That contract culminated in the development of the Breadboard Electrochemical Organic Content Analyzer which was designed for automated, on-line monitoring of ozonated effluents.

The Breadboard Electrochemical Organic Content Analyzer was developed with the goal of demonstrating the Electrochemical Organic Content Analyzer concept with automated hardware, but with limited research and development prior to the analyzer fabrication. As a result, an overkill approach was adopted to eliminate interferences that potentially might cause errors in the organic measurements. This plan called for eventual elimination of the overkill components in future developments if the results of the evaluation justified it. A change in the priorities involving the use of ozonation by the Army prevented the evaluation of the Breadboard Electrochemical Organic Content Analyzer from being completed.

The interferences that were considered during the development of the Breadboard Analyzer consisted of variations in temperature, pH and conductivity, and in chloride and dissolved oxygen concentrations.

The overkill technique used to eliminate temperature variations was a temperature controller and heat exchanger, while a basic electrolyte mixed with the sample eliminated the effects of pH, conductivity and chloride. In situ electrochemical reduction of dissolved oxygen eliminated interferences due to that species.

The objectives of the present effort involved the evaluation of the Breadboard Electrochemical Organic Content Analyzer for aerospace applications. An awareness of the disadvantages of expendables in some systems resulted in an effort to investigate ways of reducing the consumption of the analyzer's electrolyte from the rate of 5.17 kg/30 days (11.4 lb/30 days). This investigation was successful and demonstrated the feasibility of operating the Electrochemical Organic Content Analyzer with consumption of electrolyte as little as 0.02 kg (0.04 lb) per 30 days of continuous operation.

The evaluation has shown that temperature compensation is a practical approach to eliminate the overkill temperature controller and heat exchanger used in the Breadboard Analyzer. Temperature compensation could be automated electronically, resulting in a smaller, lower weight and more reliable analyzer.

In situ electrochemical reduction of dissolved oxygen resulted in relatively little increase in Analyzer complexity and was therefore retained in the Electrochemical Organic Content Analyzer concept.

The feasibility of operating the Electrochemical Organic Content Analyzer without use of any expendables was also evaluated during this contract. This evaluation involved tests of the Mark V cell which utilizes an insoluble electrolyte between electrodes in the cell. Test results showed it is possible to operate the Mark V cell without expendables and detect organic concentrations. However, compensation must be extended from temperature to include conductivity and chloride concentrations. Ultimately it was found that when the cell's response was compensated for the above parameters its sensitivity to organic concentrations was insufficient to meet the needs of the Water Quality Monitor.

It is concluded that the Electrochemical Organic Content Analyzer can result in an organic monitor in the Water Quality Monitor having a range of 0.1 to 100 mg/l total organic carbon for a large number of common organic solutes. In a flight version it is anticipated the analyzer would occupy 2 x 10^{-4} m^3 (0.008 ft^3), weigh 1.4 kg (3 lb) and require 10 W or less of power. With the optimum method of injecting electrolyte into the sample (saturation of the sample with a salt) it would expend only 0.04 kg (0.08 lb) of electrolyte during 30 days of continuous operation.

INTRODUCTION

The development of space as a habitation and work place of man will mean the increasing use of solar cells for energy and decreasing use of fuel cells. Water used aboard spacecraft will be reclaimed from condensation, wash water and urine in order to supplement water produced by the fuel cells. An immediate need is to ensure a source of high quality potable water for the crew. The reclaimed water will also be used as wash water, for cooling, eventually for experiments and possibly even for industrial processes. A Water Quality Monitor (WQM) has been projected for use during long-term missions to ensure that the health requirements of the crew are met and to prevent the fouling of components in the cooling system or other subsystems utilizing reclaimed water. This need will become increasingly apparent as more experiments and industrial processes are performed in space. The investment made in the experiments and other activities must be protected through the use of a WQM.

The objective of the WQM is to quantify the concentration of dissolved solids in the water. Conductivity can be used as an indicator of inorganic species which are generally ionic. Measurements of pH are necessary to avoid errors resulting from the high concentrations of hydrogen ions (H^+) and hydroxyl ions (OH^-) which exist at extreme pH ranges. Organic solutes are generally nonionic and therefore not detected through conductivity measurements. In the past, total organic carbon (TOC) measurements have been used to determine organic solute concentrations. This measurement requires the oxidation of the organic solutes to carbon dioxide (CO_2) followed by a measurement of the CO_2 concentration. The oxidation, as it has been most recently employed, utilizes the oxidation of the organics by a strong chemical oxidizing agent in an acidic solution. A basic reagent is required for the removal of inorganic carbon (in the form of dissolved CO_2, carbonates (CO_3^{-2}) and bicarbonates (HCO_3^-)). Several components are required to perform the TOC measurement.(1) An inorganic carbon stripper is necessary to remove the inorganic carbon, and a quartz reactor and mercury (Hg) vapor lamp is necessary to perform the oxidation of the organic solutes catalyzed by ultraviolet (UV) radiation. The addition of reagents to the sample in a controlled fashion requires the use of a peristaltic pump which involves the metering of reagents and the sample through rubber tubing.

The complexity of this hardware and the inherent reliability problems involved with it motivated an investigation of alternative organic solute monitoring techniques. Specifically, the Electrochemical Organic Content (EOC) Analyzer developed by Life Systems, Inc. (LSI) was evaluated during the present program.

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

The EOC Analyzer concept is consistent with the goals of a low weight, compact organic solute monitor, operating with minimal expendable consumption. The EOC Analyzer has demonstrated a high sensitivity for many organic solutes (detection limit of less than 0.1 mg/l TOC).

The EOC Analyzer is a general indicator of organic solute concentrations based on the direct electrochemical measurement of the organic solutes following adsorption of those solutes on the surface of an indicating electrode. No prior oxidation of organics or removal of inorganic carbon is necessary for the EOC measurement. The EOC Analyzer is therefore inherently simplier and more reliable than a TOC analyzer.

Background

The concept of the EOC Analyzer was conceived in 1975 under Life Systems' Internal Research and Development (IRAD) program. The feasibility of the concept was initially investigated using in-house electroanalytical instrumentation. The circuitry for automated measurement of EOC values was designed during that program. This circuit was subsequently assembled and the EOC Analyzer feasibility evaluation was expanded under Army Contract DAMD17-75-C-5070.(2) The Laboratory Breadboard EOC Analyzer was the first analyzer having the automated EOC circuitry. The response of the analyzer to several organic solutes was quantified with the Laboratory Breadboard using a batch type cell and a rotating disk electrode as the indicating electrode.

The feasibility evaluation resulted in the conclusion that the EOC Analyzer was feasible for on-line, industrial monitoring of organic solute concentrations. The realization that such an analyzer required a flow-through EOC cell containing the indicating electrode resulted in the development, under LSI's IRAD program, of the Prebreadboard EOC Analyzer containing the Mark II EOC cell. This was the first flow-through EOC cell and consisted of the indicating electrode, reference and counter electrodes mounted in a Teflon body.

Contract DAMD17-75-C-5070 culminated in the development of the automated Breadboard EOC Analyzer, designed for on-line monitoring of ozonated effluents.(3,4) A few refinements in the EOC cell were made for improved sealing under pressurized conditions so that the Breadboard EOC Analyzer ultimately contained the Mark IV EOC cell.

The Breadboard EOC Analyzer utilizes a temperature controller and heat exchanger to maintain the temperature of the sample and EOC cell at 298 K (77 F), thereby eliminating variations in EOC response to changes in temperature. The basic electrolyte is added to the sample to mask the potential effects of pH changes and variations in the conductivity and chloride (Cl^-) concentrations in the sample. Dissolved oxygen (O_2) variations which affect the EOC response are eliminated by in situ electrochemical reduction of the O_2 prior to the EOC measurement. The overkill techniques were incorporated to cost effectively result in an automated instrument capable of making EOC measurements under pilot plant conditions. It was realized at the time of the Breadboard EOC Analyzer development that the overkill components, such as the electrolyte reservoirs, pump and temperature controller with heat exchanger, could be simplified or eliminated through a later extended design effort. It was anticipated at the start of the EOC Analyzer development that the eventual result of the development would be a compact, lightweight monitor of organic solute concentrations. The electrochemical technique on which the EOC Analyzer is based is very sensitive to low concentrations of many organic solutes; therefore, the EOC Analyzer was expected to be more sensitive to organic solute concentrations than most other organic solute monitors.

It was these characteristics that led to the evaluation of the EOC Analyzer for aerospace applications. The evaluation of the EOC Analyzer under Contract NAS9-15402 started with an evaluation of the Breadboard EOC Analyzer to identify ways of reducing the quantity of electrolyte consumed in operation. During a second phase of the program the investigation was extended to the Mark V EOC cell which allowed detection of organic solutes without utilizing an expendable electrolyte.

Program Objectives

Of the overkill components used in the Breadboard EOC Analyzer, those required to store the electrolyte and to meter it into the sample stream were the largest and occupied the greatest volume within the analyzer. Therefore, in order to result in the greatest benefit, minimization of the electrolyte consumption and simplification of the electrolyte injection technique were considered first.

An extension of the electrolyte minimization effort was the investigation of the Mark V EOC cell which was developed as a possible method of operating without any expendable electrolyte. Under phase two of this program, LSI's Mark V cell was tested and its response characteristics were evaluated. The cell was found to be affected by variations in temperature, conductivity and Cl^- concentration. During the latter part of this phase the relationships between EOC response and the variations in those parameters were quantified to permit later automation of the response compensation for those parameters. The response of the Mark V cell to several organics was investigated with and without response compensation.

Program Organization

The program was organized into several tasks whose specific objectives were:

1.0 Perform a preliminary evaluation of the response of LSI's Mark V cell to organic solutes that may exist in effluents from the Vapor Compression Distillation Subsystem (VCDS) and other effluents.

Deleted 2.0 Quantify the response of the EOC Analyzer to actual or simulated VCDS samples.

3.0 Investigate means of minimizing sample adjustment techniques (overkill) presently used in the Breadboard EOC Analyzer to eliminate interferences.

4.0 Incorporate the Contractor's data management functions to provide internal procedures to control the collection, preparation, quality, assessment, distribution and maintenance of data.

5.0 Incorporate the management needed to successfully meet the program's Cost, Schedule and technical Performance objectives to result in Customer satisfaction.

6.0 Quantify the effects of potential interferences on the performance of the Mark V cell.

7.0 Develop compensation technology for the Mark V EOC cell.

The objectives of the program were met. The following sections review the EOC Analyzer concept and hardware previously developed, the results of the work completed, the conclusions reached and recommendations made.

Definitions

The organic solute concentration indices referred to in this report are defined below:

1. Electrochemical Organic Content: Two terms are used in referring to the output of the EOC Analyzer: EOC value and EOC response. The EOC value refers to the measured output of an EOC Analyzer, reported in instrument units. The EOC response is the difference between the EOC value for water containing organic solutes and the value obtained for distilled water.

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

BREADBOARD ELECTROCHEMICAL ORGANIC CONTENT ANALYZER

Basis of Operation

The Breadboard EOC Analyzer determines the concentration of organic compounds in water by measuring the decrease in interfacial capacitance produced when these compounds adsorb at an electrode surface.

The process of organic adsorption is illustrated in Figure 1. This adsorption displaces water molecules from the electrode surface, decreasing the dielectric constant at the interface, and therefore the capacitance, in proportion to the fraction of the surface covered by the organic. This measurement is quantitative because the fractional surface coverage increases with the organic concentration. Such a relationship for ethylene glycol is shown in Figure 2.

Prior to each new adsorption/capacitance measurement operation, the electrode surface is thoroughly cleaned electrochemically by first applying an oxidizing potential, then a reducing potential. The entire cleaning/measurement cycle is performed automatically according to the scheme depicted in Figure 3.

The response of an EOC Analyzer for organic solute levels is general and analogous to the response of a conductivity sensor to inorganic solute levels. That is, it responds to the cumulative effects of the individual species in solution, each of which makes a contribution dependent on its concentration and chemical characteristics.

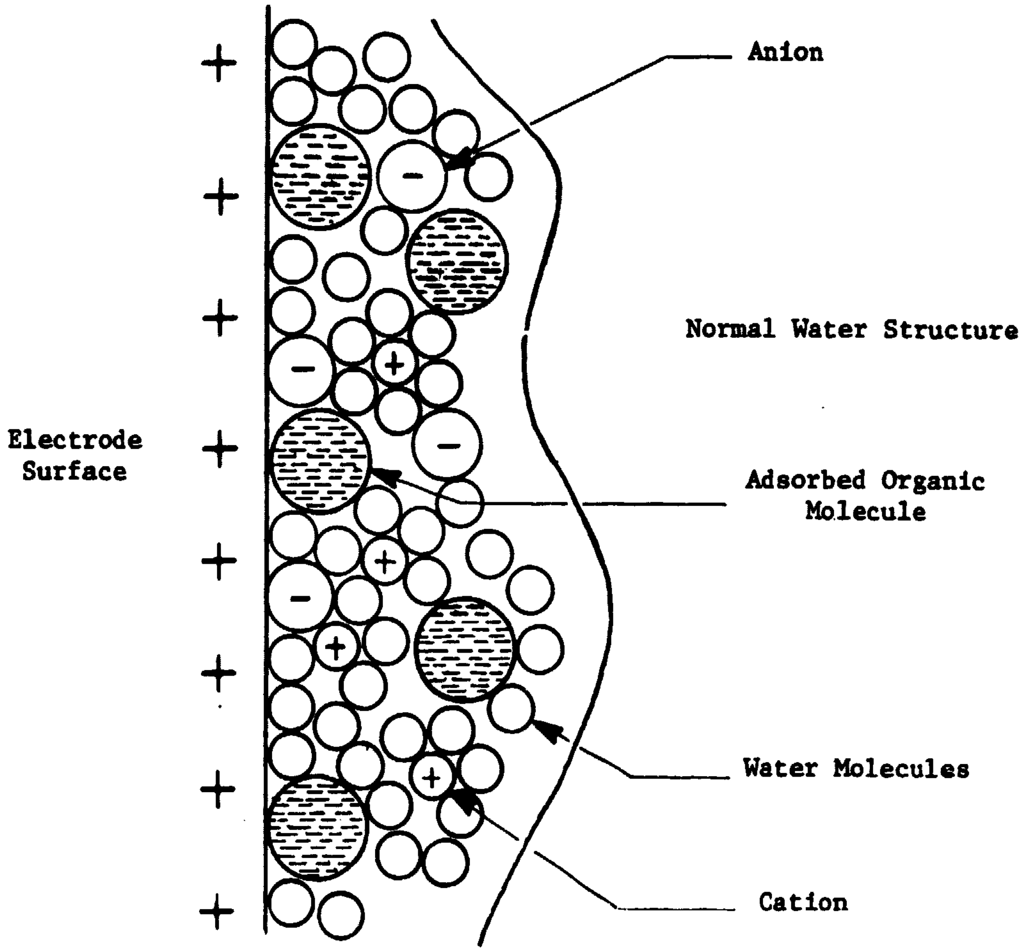

FIGURE 1 ELECTRODE/SOLUTION INTERFACE SHOWING ADSORBED ORGANIC MOLECULES

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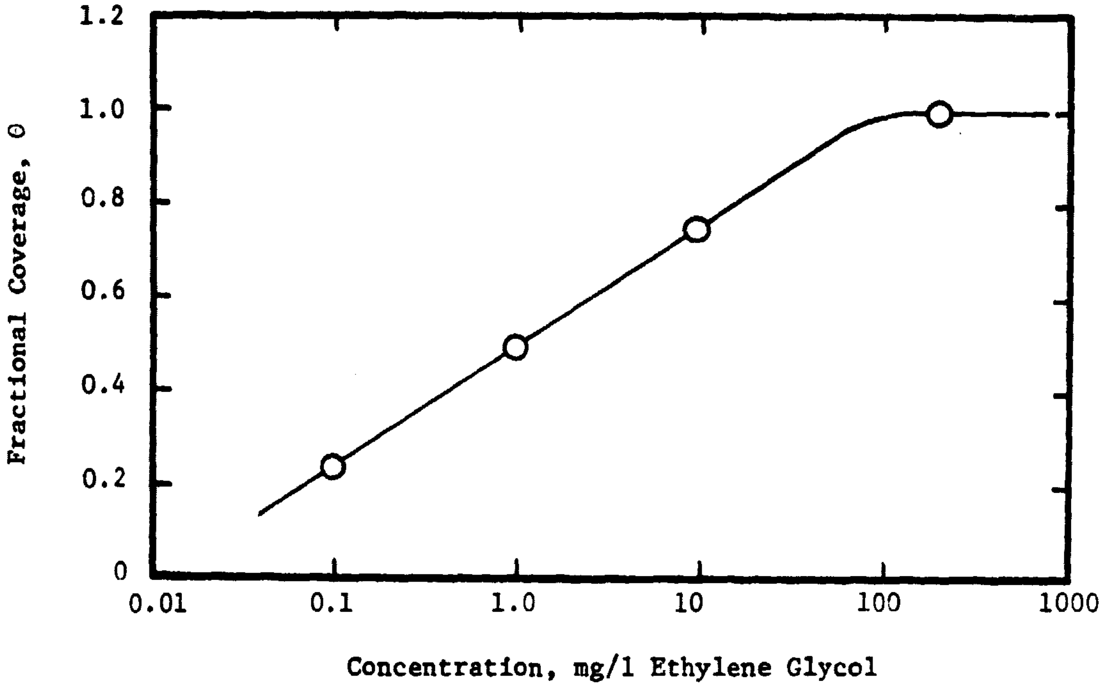

FIGURE 2 ADSORPTION ISOTHERM OF ETHYLENE GLYCOL ON PLATINUM AT 35 C

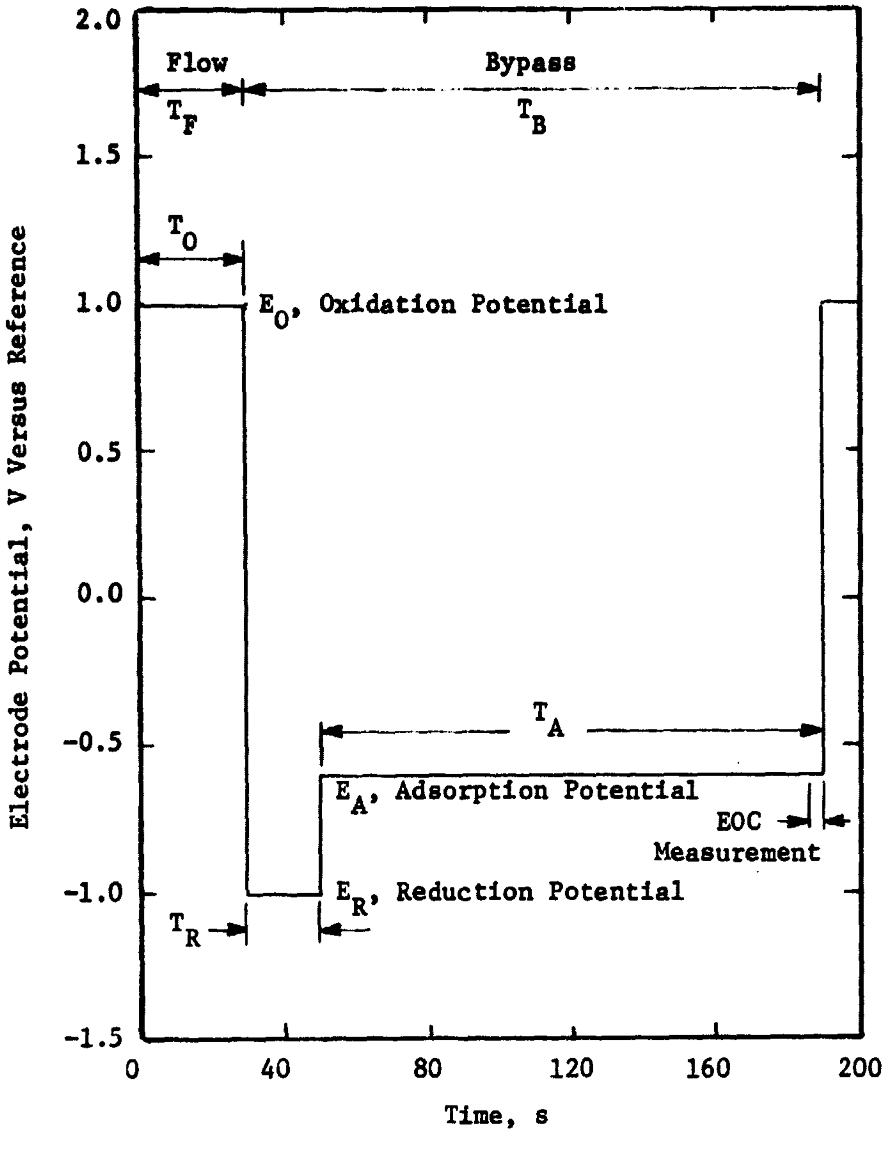

FIGURE 3 ELECTRODE PRECONDITIONING AND MEASUREMENT SEQUENCE FOR BREADBOARD EOC ANALYZER

Description

The Breadboard EOC Analyzer is shown pictorially in Figure 4 and schematically in Figure 5. The EOC response is affected by temperature, conductivity and dissolved O_2 and chloride concentrations of the sample.(2,4) Overkill sample preconditioning was originally included in the Breadboard Analyzer to guarantee proper conditions for the analysis of ozone contactor effluents. The need for the sample conditioning devices is expected to be eliminated or reduced in the ultimate device developed for monitoring the purer, more consistent spacecraft water. For the Breadboard Analyzer, however, electrolyte is injected into the sample stream to optimize cell resistance and to override pH, conductivity and dissolved salts effects on EOC response. A temperature controller using a thermoelectric cooler/heater thermostats the incoming sample to minimize effects of temperature. An intermittent flow accessory (cell bypass loop and associated logic) eliminates interferences due to O_2 via electrochemical reduction (as illustrated by the equation below) after the flow of solution through the EOC cell has been diverted through the bypass loop.

$$O_2 + 2\,H_2O + 4\,e^- = 4\,OH^- \tag{1}$$

Electrochemical oxidation occurs during the reduction and adsorption portions of the cleaning cycle in the stagnant solution in the EOC cell. The EOC cell is depicted in Figure 6.

The response of the Breadboard EOC Analyzer to various organic compounds is illustrated in Figure 7.

Evaluation

The use of a large volume of consumable electrolyte solution in the Breadboard EOC Analyzer results in a weight, volume and power penalty because of the solution, pumps and other dispensing hardware. The primary objective of the Breadboard EOC Analyzer evaluation was therefore to minimize, or eliminate, electrolyte consumption while still providing an indication of organic solute content of spacecraft water precise enough to safeguard the health and well-being of crew members. The methods considered for achieving this goal include cell spacing modifications and the following changes in electrolyte technology.

- Reduction of electrolyte concentration requirements in EOC cell
- Reduction of sample/electrolyte flow rate
- Sample equilibrium with low solubility salt
- Electrochemical injection of electrolyte
- Recycling of electrolyte
- Permanent, insoluble electrolyte within the electrochemical cell

Cell Modifications

A key reason for injection of electrolyte into the sample stream is to maintain a relatively low cell resistance so that current can flow through the EOC cell. A low cell resistance is also required for good sensitivity and, if no compensation for variations in sample conductivity is employed, for good precision. Reduction of the spacing between the electrodes of the EOC cell reduces the cell resistance. Conversely, a lower electrolyte concentration

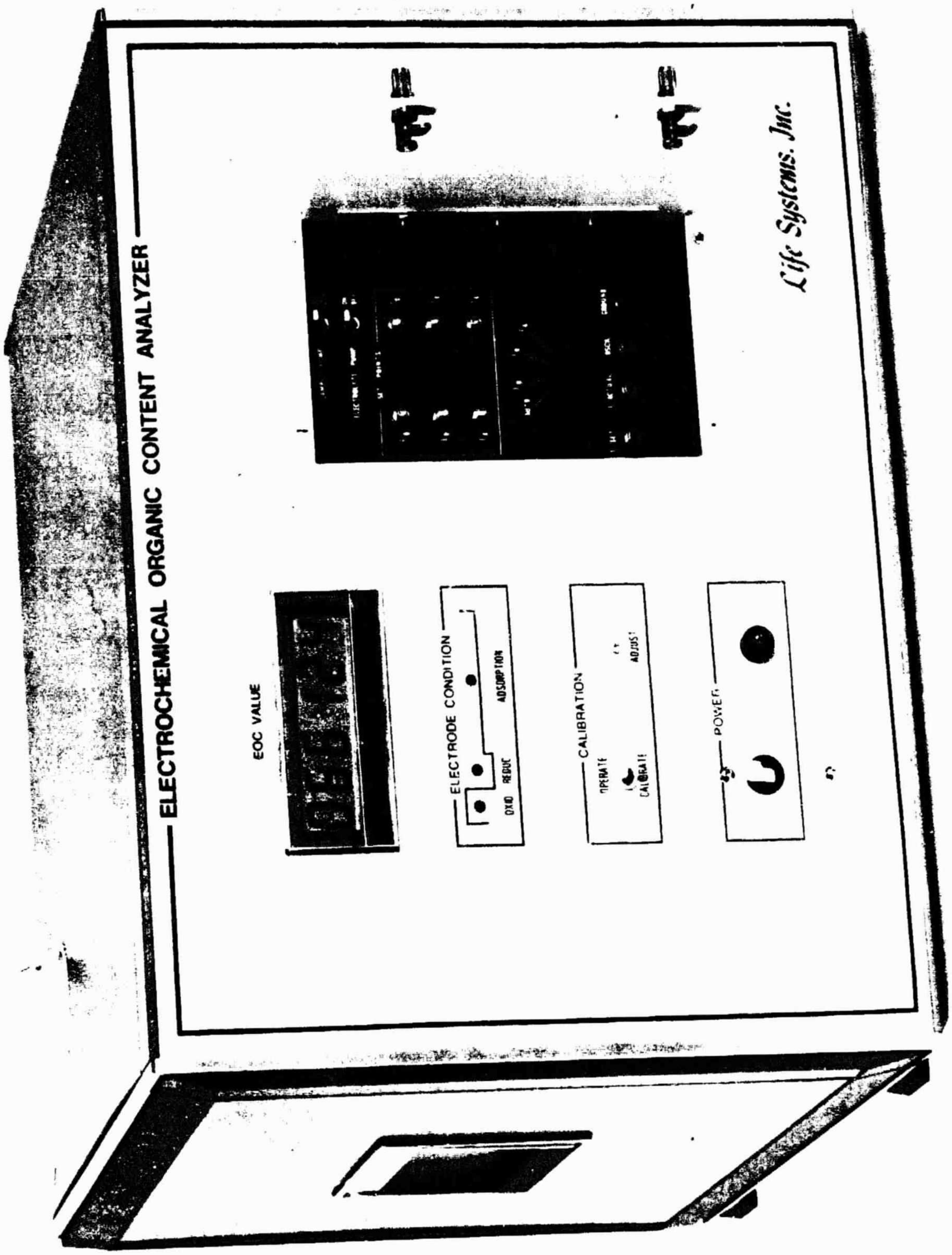

FIGURE 4 BREADBOARD EOC ANALYZER

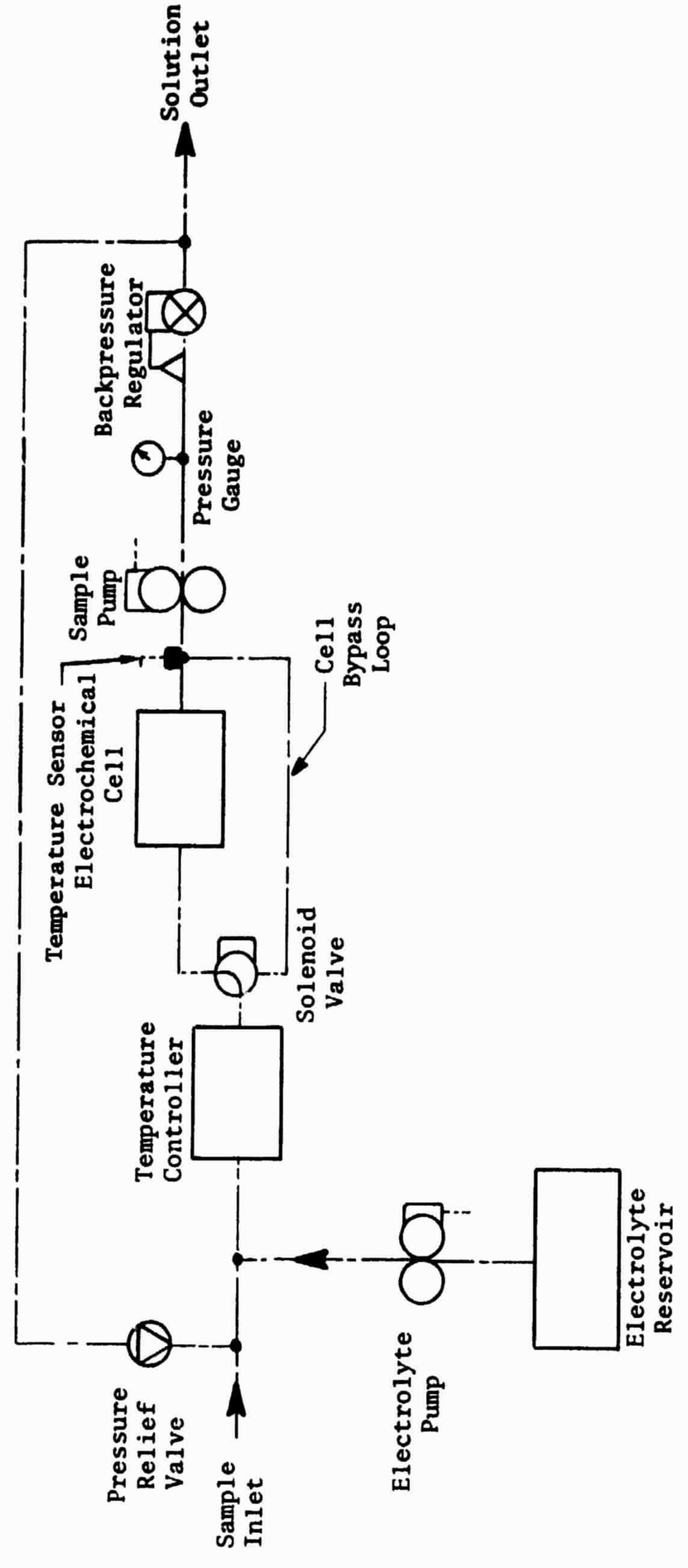

FIGURE 5 MECHANICAL SCHEMATIC OF BREADBOARD EOC ANALYZER

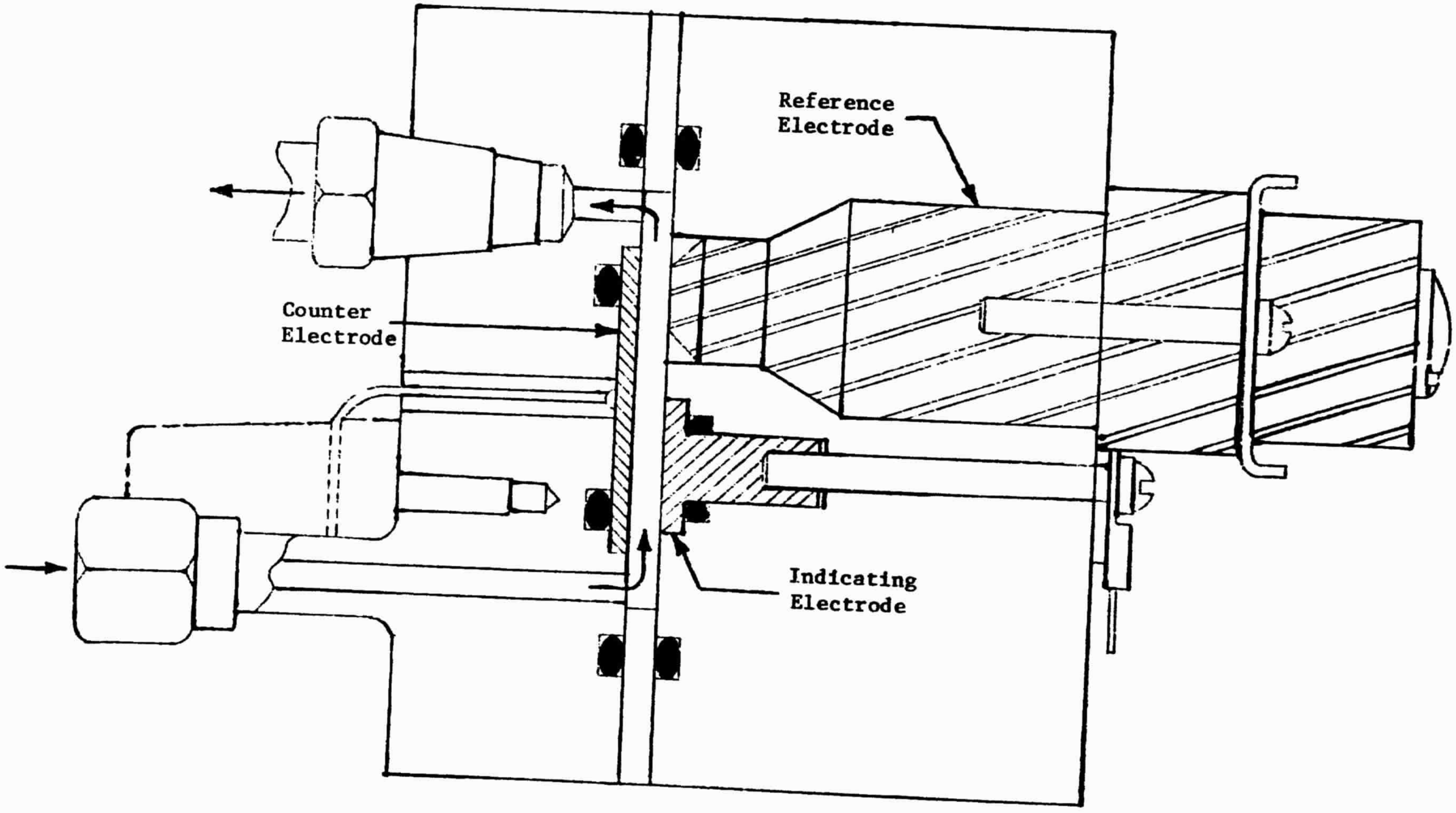

FIGURE 6 BREADBOARD ANALYZER EOC CELL

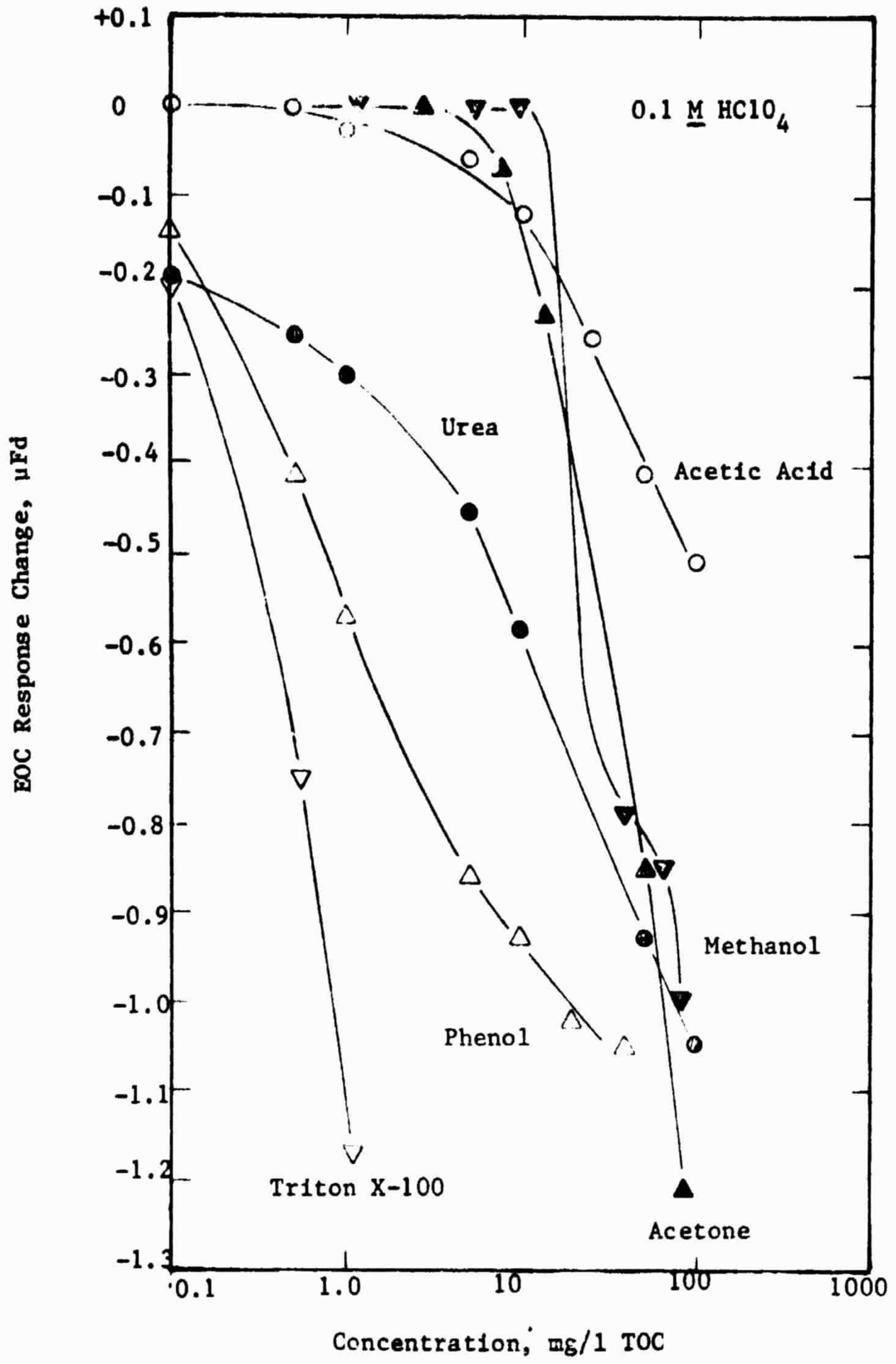

FIGURE 7 RESPONSE CURVES FOR BREADBOARD EOC ANALYZER

can be used (reducing the quantity of electrolyte salts carried in the Analyzer) to maintain a given cell resistance if the electrode spacing is reduced. Therefore, the performance of the Breadboard EOC Analyzer was evaluated for variable electrode spacing.

The spacing between the working electrode and counter electrode in the Breadboard EOC cell was varied, down to a minimum of 0.008 cm (0.003 in), and the instrument response to water and methanol solutions was evaluated. Nonlinear response curves were obtained following this modification, however, which indicated that interactive effects were occurring between the working and counter electrodes. Therefore, the baseline electrode spacing for the Breadboard EOC Analyzer, 0.25 cm (0.1 in), was retained during subsequent evaluations.

Electrolyte Modifications

The method and extent of electrolyte injection into the sample affect the weight, volume, power and service frequency for the electrolyte and associated hardware. Several concepts for minimizing electrolyte usage were developed during Life Systems' IRAD efforts. These concepts were examined during the present program as discussed below.

Circuit Modifications. The measurement circuitry used to determine capacitance in the Breadboard EOC Analyzer was optimized for a given cell resistance. Therefore, as a preliminary step to investigating electrolyte modifications, the measurement circuits were modified to permit operation of the EOC cell with lower conductivity (low inherent electrolyte concentration) samples. The circuits were designed to permit reduction of the sodium hydroxide (NaOH) baseline electrolyte concentration to levels as low as 0.001 M.

Soluble Electrolyte Minimization. The weight and volume of expendables required per unit time by the EOC Analyzer were reduced in proportion to the reduction of electrolyte concentration in the sample/electrolyte mixture. Therefore, experiments were performed to determine how low the electrolyte concentration could be while retaining useful analytical performance.

The baseline electrolyte in the Breadboard EOC Analyzer is 0.3 M NaOH plus 3×10^{-4} M NaCl. Adequate response was obtained using the circuit modification discussed above, with electrolyte concentrations as low as 0.01 M NaOH (Figure 8). This concentration represents a 30-fold reduction in electrolyte usage from the baseline value of 5.2 kg (11.4 lb) to 0.17 kg (0.38 lb) for a 30-day mission.

Sample Flow Reduction

In the spacecraft EOC analyzer the entire instrument, as well as the measurement cell, will be smaller. Reduction of the cell volume and modification of its geometry will permit reduction of the sample flow rate. Electrolyte usage will be reduced proportionately since the electrolyte injection rate is proportional to the sample flow rate.

It is projected that sample flow rates will be reduced from the 10 cm^3/min (3×10^{-3} gal/min) baseline for the Breadboard EOC Analyzer to 1 cm^3/min (3×10^{-4} gal/min) for the end-item EOC Analyzer. By combining this electro-

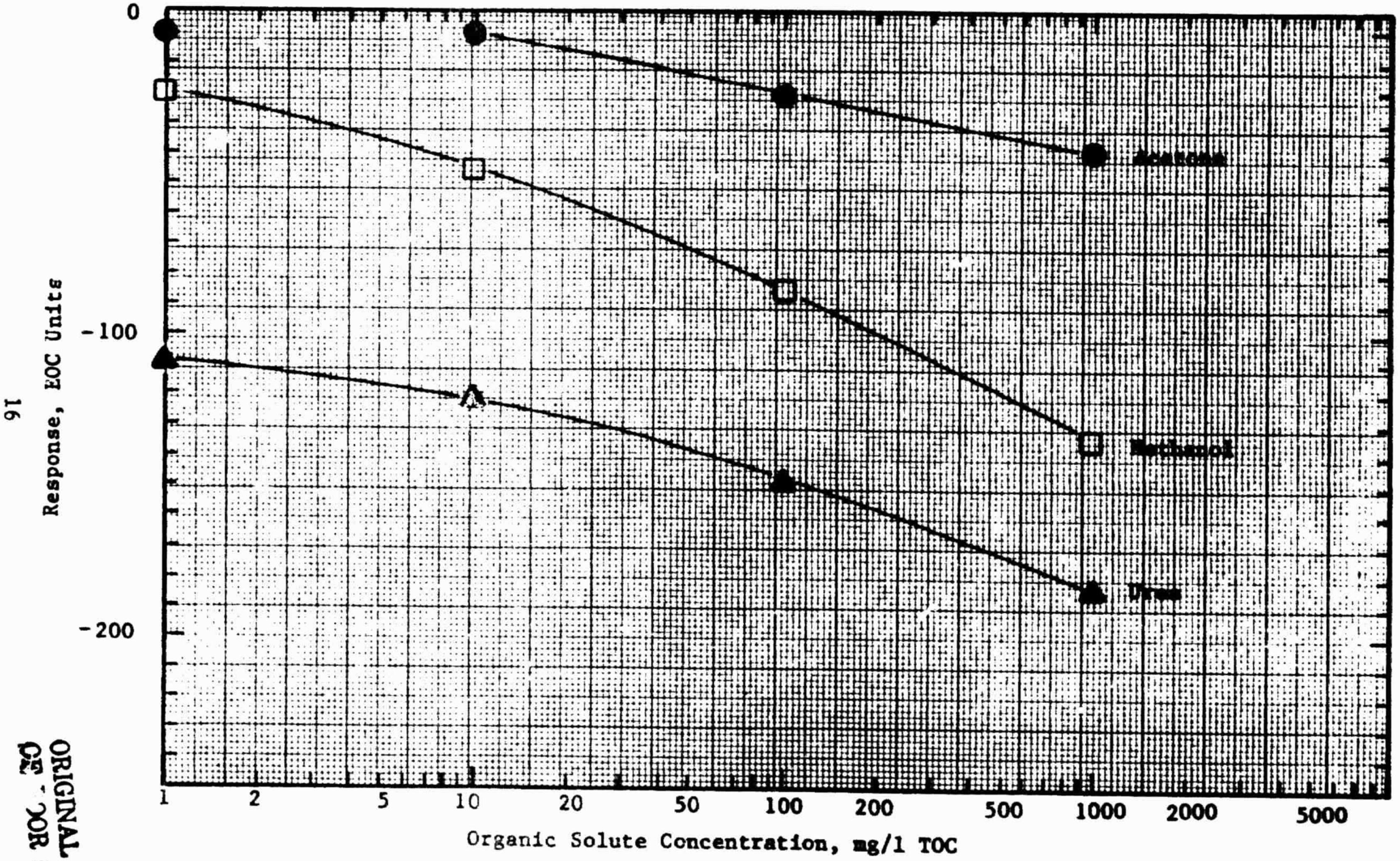

FIGURE 8 BREADBOARD EOC ANALYZER RESPONSE TO ORGANICS IN 0.01 M NaOH

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lyte flow rate with an electrolyte concentration of 0.01 $\underline{M}$, a 300-fold reduction in electrolyte weight to 0.038 kg (0.017 lb) per 30-day mission will be possible.

Solid Salt. The instrument weight and bulk can be further reduced by storage of the electrolyte in the form of a sparingly soluble salt in pure solid form. A constant concentration of this salt can be maintained in the sample stream simply by equilibrium contact. The power requirements, volume and mass of metering pumps, plus the bulk and weight of a stored solution would be eliminated. The instrument would be simpler and more reliable.

Published solubility data were screened to select salts that would be appropriate for this application.(5,6) Solubility versus temperature curves for four candidate salts are plotted in Figure 9. Calcium sulfate ($CaSO_4$) has the advantage of a relatively constant solubility of about 0.02 $\underline{M}$ (2.1 g/l) over a fairly broad temperature range. Only 0.09 kg (0.2 lb) would be required to treat samples analyzed during a 30 day mission. The response of the EOC to samples saturated with $CaSO_4$ is illustrated in Figure 10.

Electrochemical Injection. Alternatively, a basic electrolyte, such as NaOH can be stored as a slurry in equilibrium with only a bare minimum of liquid to form a saturated solution. The NaOH can then be metered into the sample via Life Systems' in situ electrochemical hydroxide generator (Figure 11). Because the electrolyte is stored almost entirely as a solid its weight and volume are much lower and it requires less power than an electrolyte pump. Sodium hydroxide usage would be only 0.017 kg (0.038 lb) per 30-day mission.

Recycle of Electrolyte. A method was devised to recycle the electrolyte via evaporative recovery. However, it became apparent that the complexities of removing dissolved organics from the electrolyte prior to recycling would violate the overall goals for simple instrument hardware. Further consideration of this technology was therefore terminated.

Insoluble Electrolyte. To completely eliminate expendables an insoluble electrolyte material can be used to conduct current across the cell. This material is stationery and permanent and, therefore, no replenishment is needed. This concept was implemented in an experimental cell called the Mark V, as illustrated in Figure 12.

Tests of the Mark V cell, using the capacitance-measuring circuitry in the Breadboard EOC Analyzer, demonstrated that the capacitance changes that occur at the indicating electrode are insignificant compared to the capacitance resulting from the insoluble electrolyte (which is a dielectric) between the indicating and counter electrodes. Measurements of organic solute concentrations using the Mark V cell with a different measurement technique is discussed below.

Conclusions. The best approach to electrolyte injection was deemed to be saturation of the sample with a sparingly soluble salt (such as $CaSO_4$) or in situ generation of hydroxide. In combination with either approach the flow rate of the sample would be 1 cm^3/min (3×10^{-4} gal/min). The savings in expendables consumption resulting from these changes are summarized in Table 1.

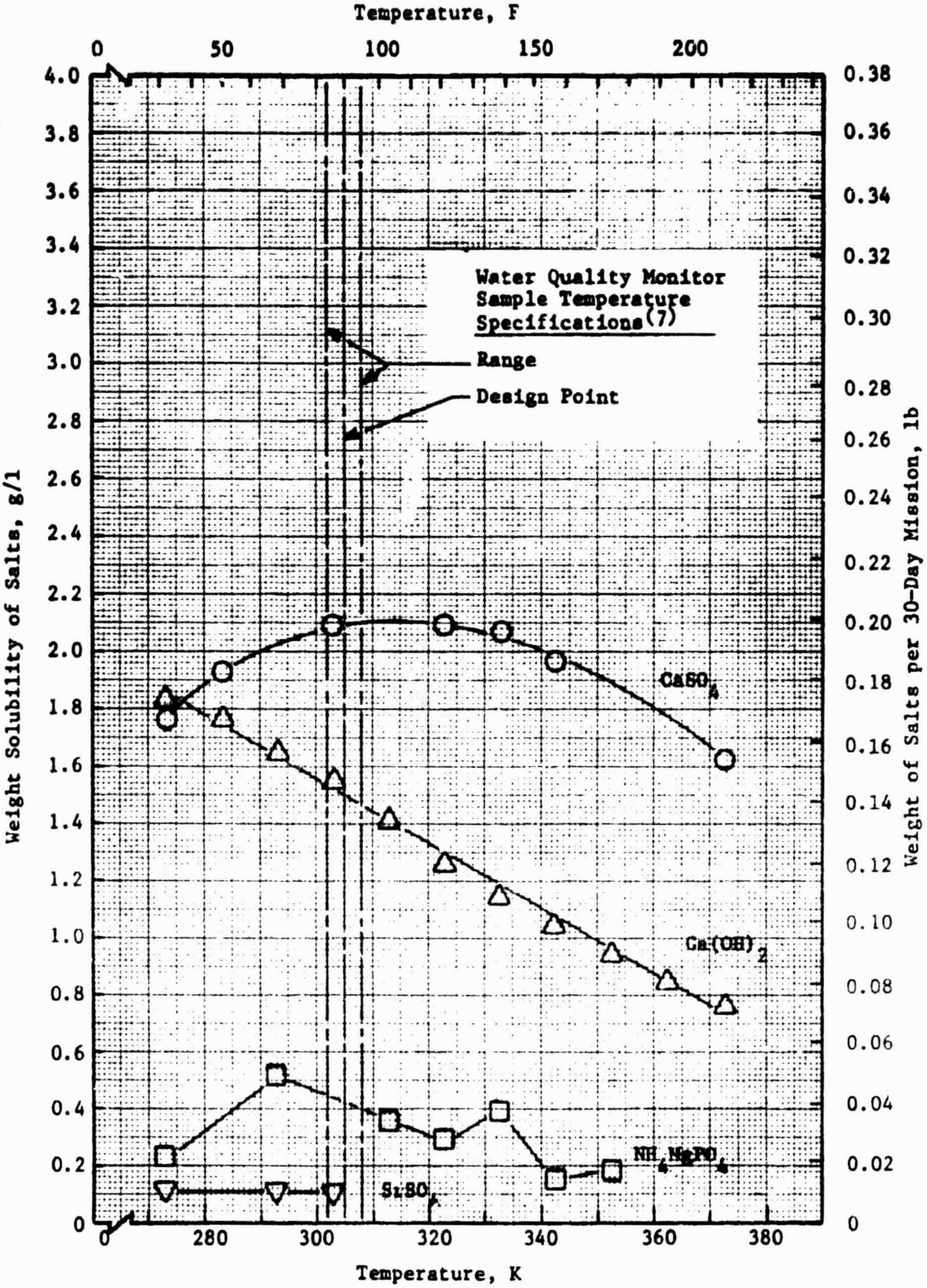


FIGURE 9 SOLUBILITY OF SLIGHTLY SOLUBLE SALTS

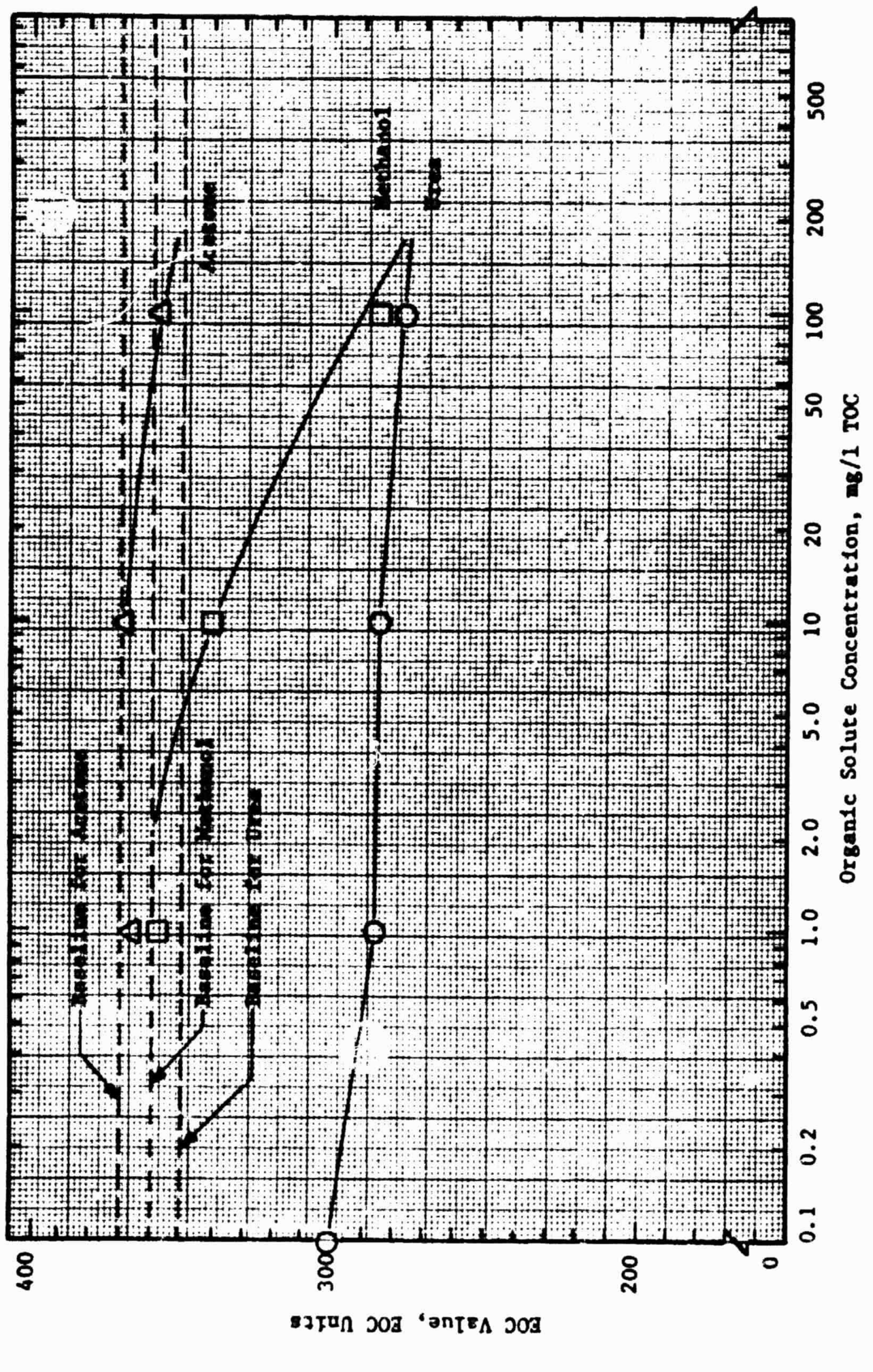
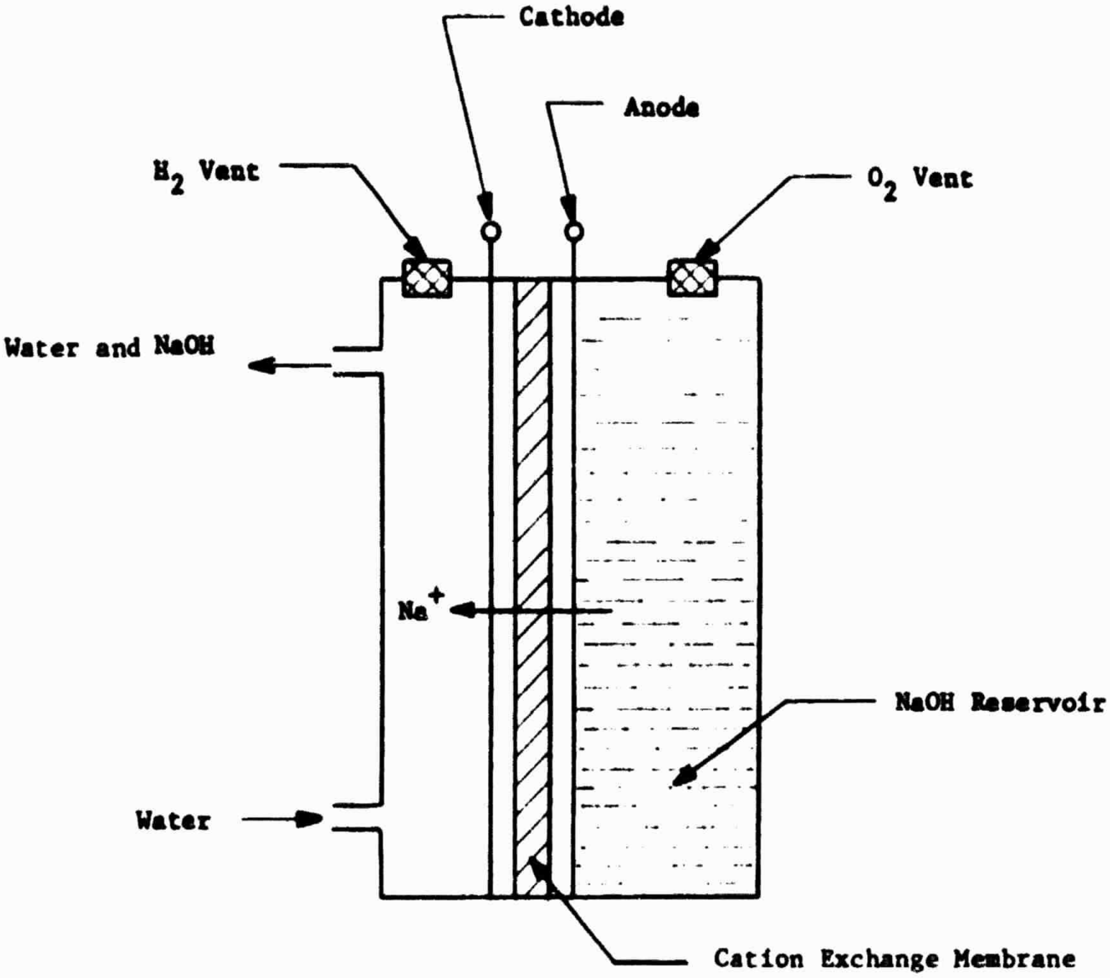


FIGURE 10 BREADBOARD EOC ANALYZER RESPONSE TO ORGANICS IN SATURATED CALCIUM SULFATE



Cathode Reaction: $2H_2O + 2e^- = H_2 + 2OH^-$

Anode Reaction: $4OH^- = 2H_2O + O_2 + 4e^-$

FIGURE 11 HYDROXIDE GENERATOR FUNCTIONAL SCHEMATIC

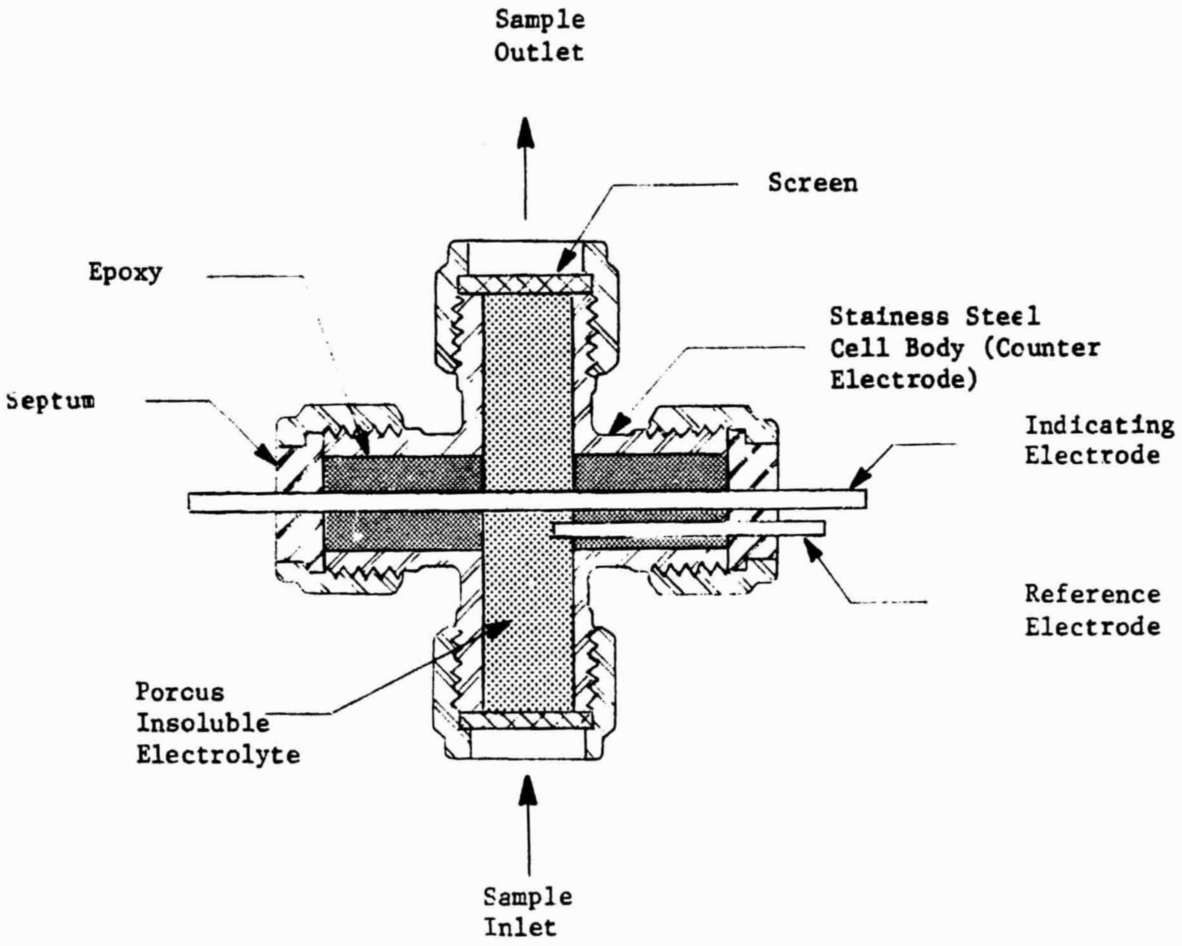


FIGURE 12 MARK V EOC CELL

TABLE 1 BENEFITS OF ELECTROLYTE MINIMIZATION

Approach	Electrolyte Weight for Continuous Operation, kg (lb) 30 Days	180 Days
Breadboard EOC Analyzer (Baseline)	5.2 (11.4)	31 (68.7)
Saturation of Sample with $CaSO_4$ and 1 cm^3/min (3×10^{-4} gal/min) Sample Flow Rate	0.091 (0.20)	0.55 (1.2)
In Situ Electrochemical Generation of 0.01 M NaOH and 1 cm^3/min (3×10^{-4} gal/min) Sample Flow Rate	0.017 (0.038)	0.10 (0.23)

MARK V TECHNOLOGY ANALYZER DEVELOPMENT

The Mark V cell demonstrated a potential for operating without any expendables. A joint decision was made between LSI and NASA JSC to investigate new methods of measuring organic concentrations using the Mark V cell technology. Complete elimination of expendables was projected not only to simplify the EOC Analyzer and minimize its size, but to also eliminate servicing of the instrument between missions.

In one measurement technique the degree to which adsorbed hydrogen (H_2) on the indicating electrode is displaced by organic molecules is measured. In a second technique, the oxidation of adsorbed organics on the electrode surface is measured.

A Laboratory Breadboard Mark V EOC Analyzer, composed of discreet pieces of laboratory test instrumentation, was developed. Portions of the analysis sequence were operated manually because of the nondedicated nature of the instrumentation. This hardware is shown in Figure 13.

Hydrogen Adsorption EOC Technique

Basis of Technique

Organic compounds are adsorbed at the electrode interface at the double layer region of potential, as shown in Figure 14. The potential is then decreased at a constant rate to scan the H_2 reduction region. The amount of charge transferred in that region, as evidenced by the peaks shown in Figure 14 in the H_2 reduction region, decreases in proportion to the concentration of organic solutes present in the sample and adsorbed on the electrode surface.(8)

Response

Response curves were evaluated to determine the capability of the technique to quantify the presence of various types of organic solutes. These experiments indicated that the method is indeed sensitive to some organics, as shown in Figure 15. The response is positive or negative, depending upon the type of organic compound; therefore, it may also be possible to use this technique as a qualitative tool to identify certain classes of organics.

Organic Oxidation EOC Technique

Although the H_2 adsorption method is sensitive, positive and negative responses for different compounds make it impractical for monitoring solute mixtures. Since spacecraft water will contain a mixture of solutes a second technology based on the oxidation properties of organic compounds was evaluated. Subsequent efforts concentrated on the development of this technology.

These investigations, which have included some upgrading of test conditions and hardware as the technology developed, have been relatively extensive and in keeping with the apparent potential of this analysis technique for spacecraft water quality monitoring. The data discussed in the remaining sections of this report highlight these developments.

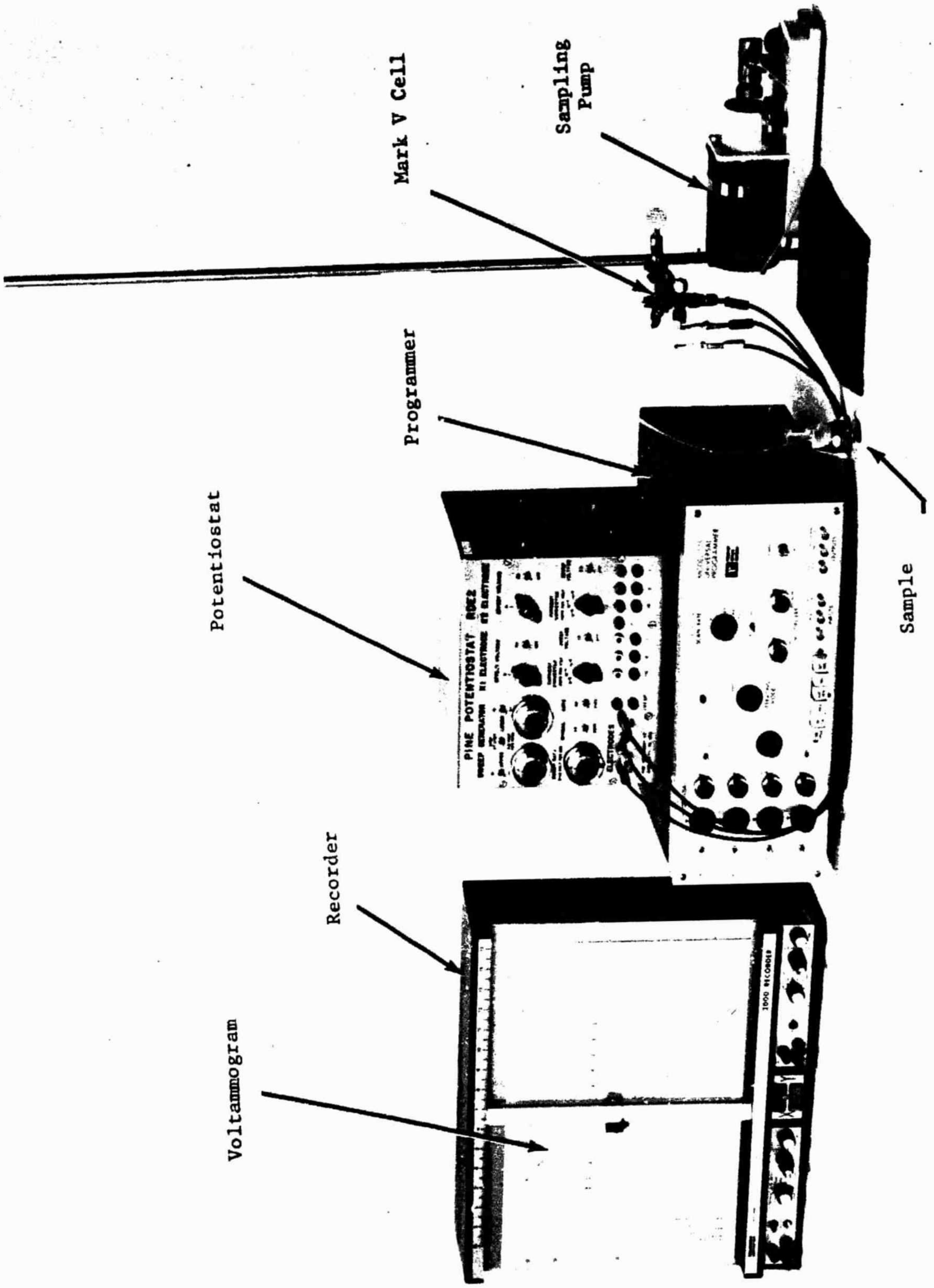


FIGURE 13 MARK V TECHNOLOGY LABORATORY BREADBOARD ANALYZER

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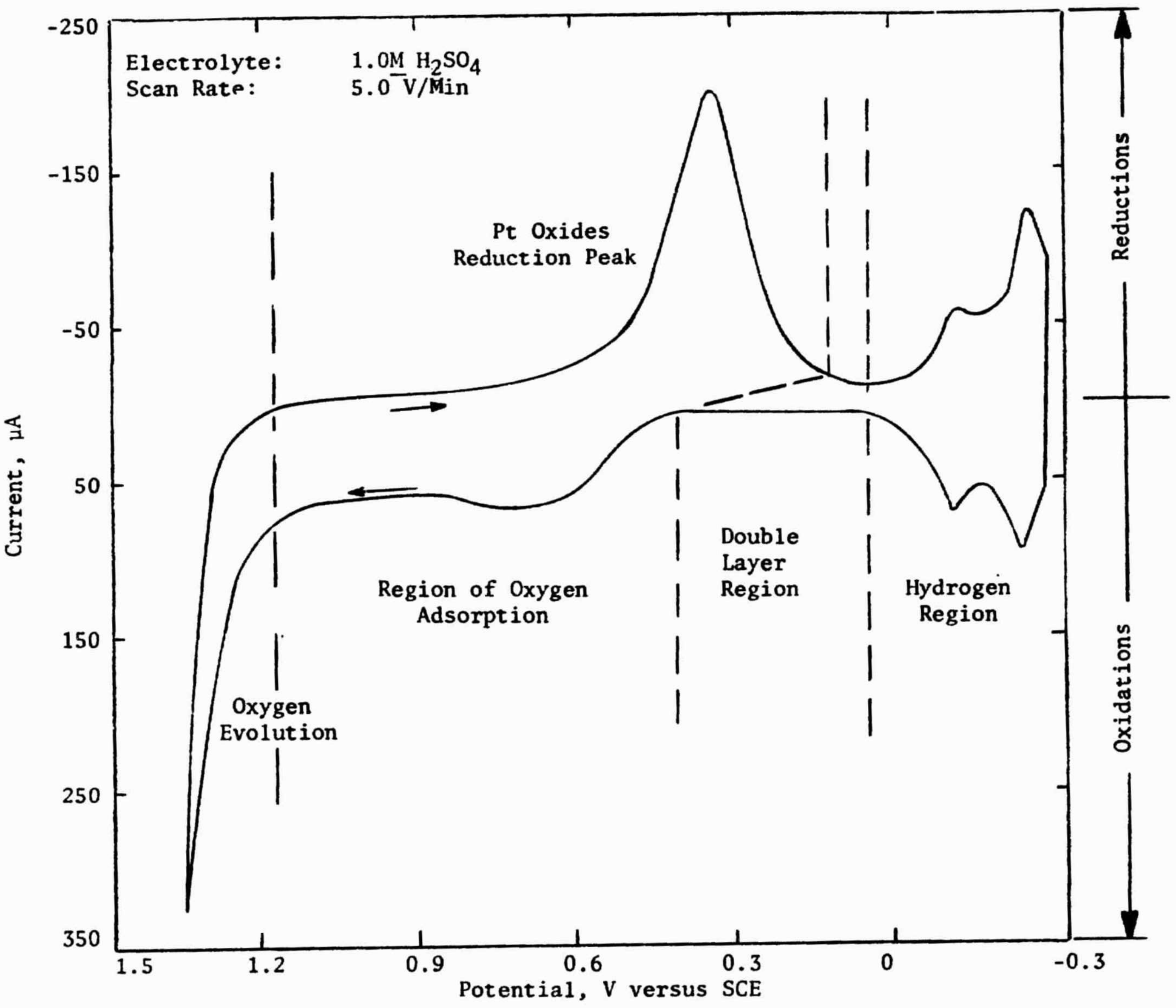

FIGURE 14 TYPICAL VOLTAMMOGRAM OF PLATINUM

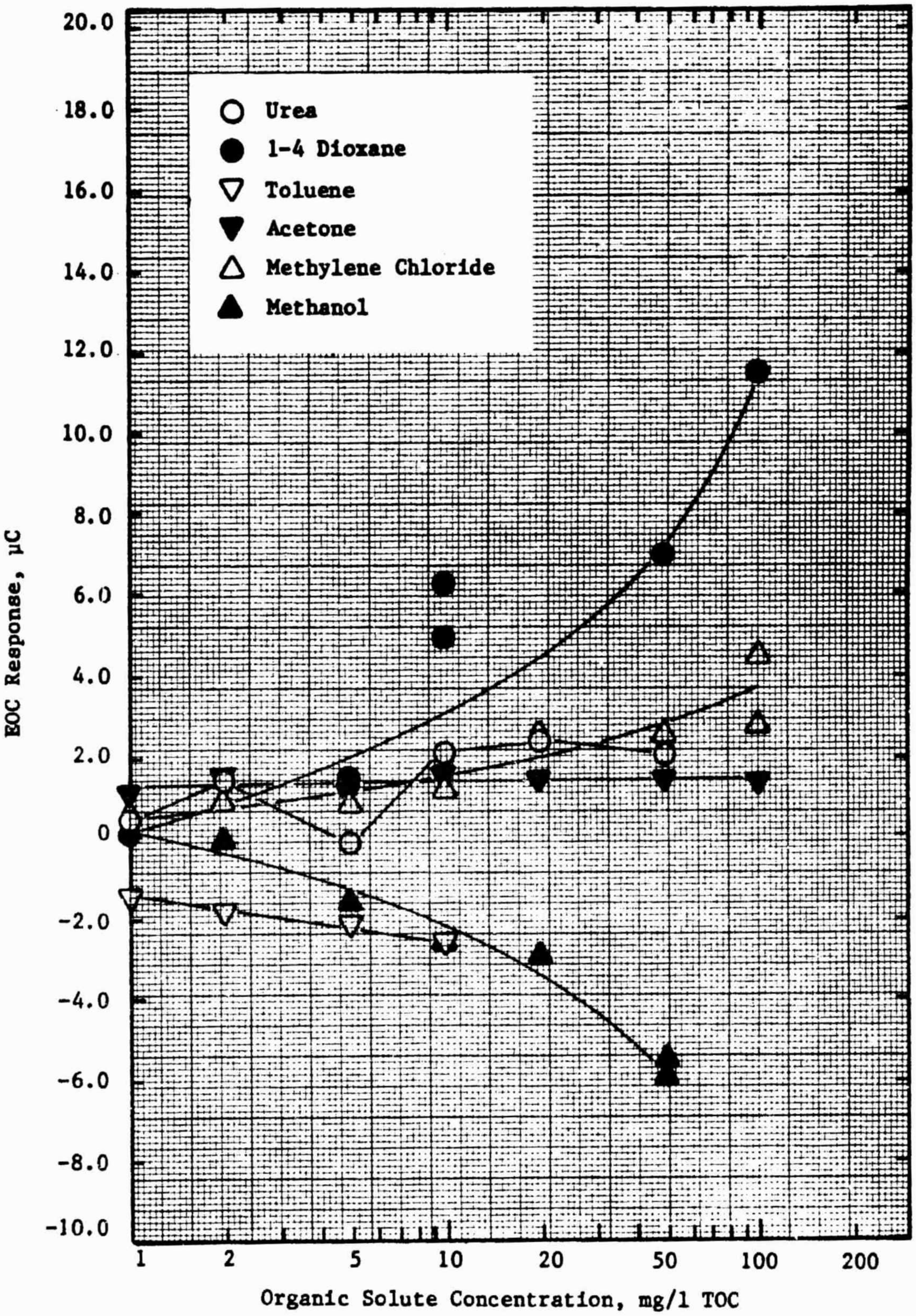

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FIGURE 15 RESPONSE CURVES FOR HYDROGEN ADSORPTION TECHNIQUE

Basis of Technique

As in the H_2 adsorption technique, organic compounds are initially adsorbed on the electrode surface in the double layer potential region (see Figures 1 and 14). The oxidation region of O_2 adsorption is then scanned. Organic compounds in this region are oxidized at the electrode surface, giving rise to an increase in current flow.

$$CH_3OH + H_2O = CO_2 + 6H^+ = 6e^- \qquad (2)$$

This oxidation is manifested as a peak area expansion in the O_2 adsorption region for the platinum electrode, as illustrated in Figure 16. To obtain an EOC value the area under the peak is integrated over the potential scan range. To obtain a net EOC response the peak area obtained from a solution containing no organics is subtracted. The EOC response is illustrated by the cross-hatched area of Figure 16.

The adsorption portion of the analysis cycle is carried out at a potential of -0.1 V. The flow is stopped at the start of adsorption, both to provide adequate time for organic compounds to adsorb on the electrode and also to electrochemically reduce O_2 content in the sample (Equation 1).

Oxygen in EOC water samples was considered to possibly interfere with analysis by the organic oxidation technique by competing with organic molecules for adsorption on the electrode surface and/or by modifying the rate of platinum oxide formation in the oxygen adsorption potential region.

Response

Response curves were obtained to quantify the sensitivity of this technique for organic solute that are representative of compounds likely to be present in the monitored water.

Individual Solutes. The response curves for various individual organic compounds are plotted in Figure 17. The analyzer was responsive to most of the compounds tested, although the response is limited for acetone and methylene chloride. Furthermore, all responses are in the positive direction, indicating that solute mixtures will not create ambiguous indications due to a mixture of positive and negative responses to some individual components as would be the case using the H_2 adsorption technique.

Solute Mixtures. Ultimately the Mark V Analyzer will quantify the overall level of organic solutes in water. These solutes will generally be present as mixtures rather than as single compounds. Therefore the response of this technique to mixtures of organic solutes was investigated.

The response to mixtures of test compounds is plotted in Figure 18. The composition of these mixtures is listed in Table 3. This data illustrates that a response can be obtained proportional to overall organics levels.

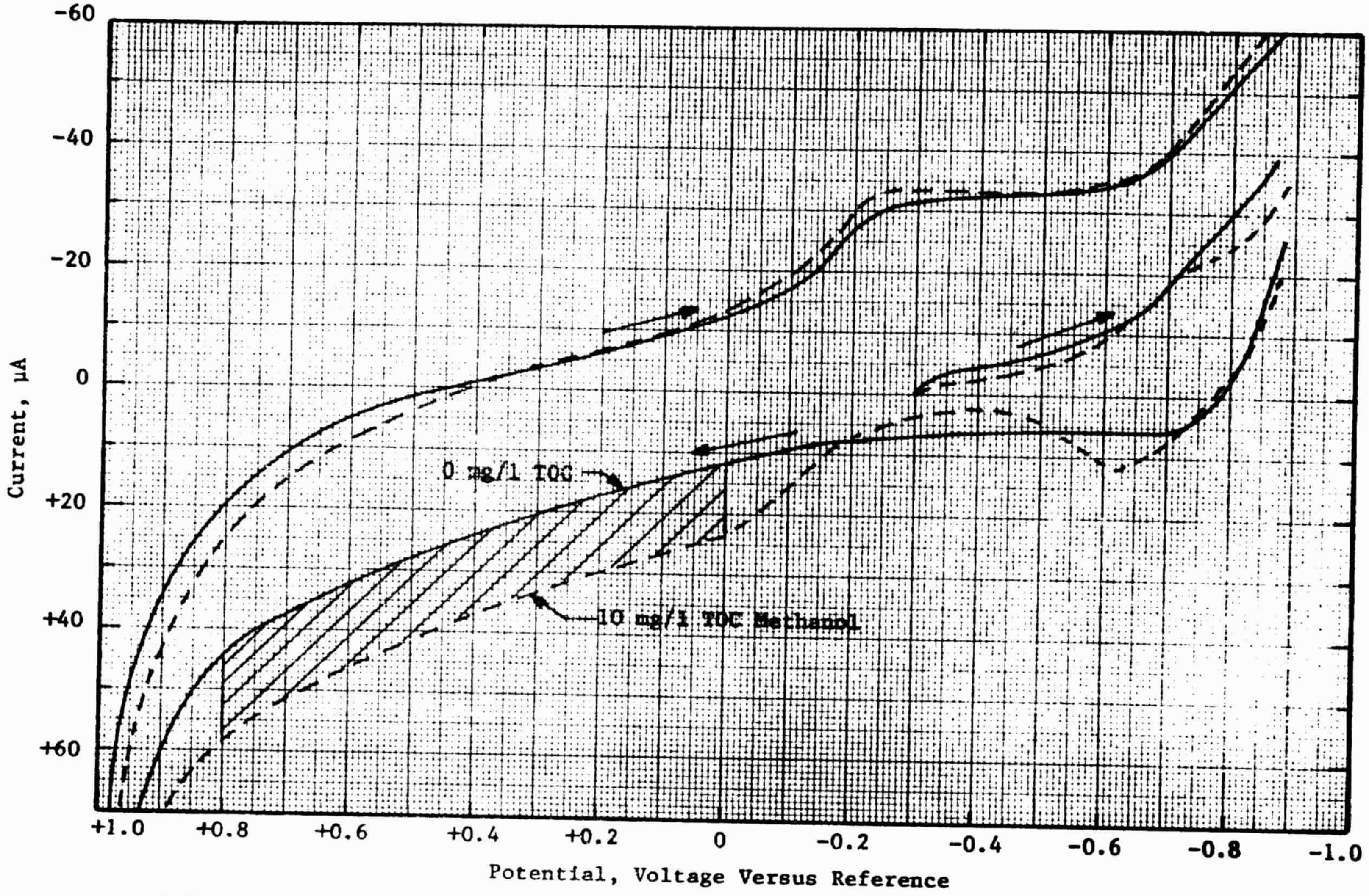

FIGURE 16 ORGANIC OXIDATION PEAK AREA EXPANSION IN THE PRESENCE OF METHANOL

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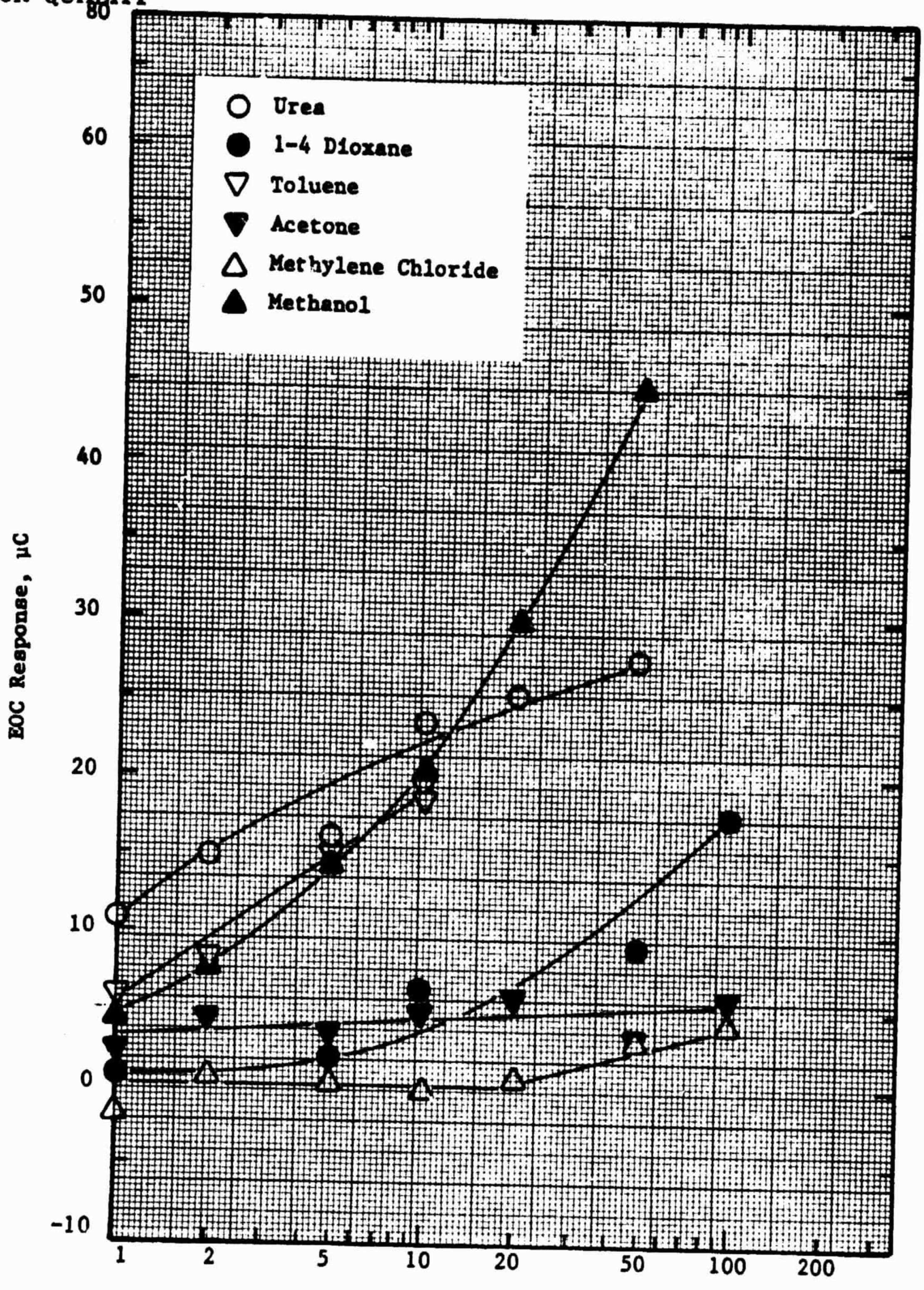

FIGURE 17 RESPONSE CURVES FOR ORGANIC OXIDATION TECHNIQUE

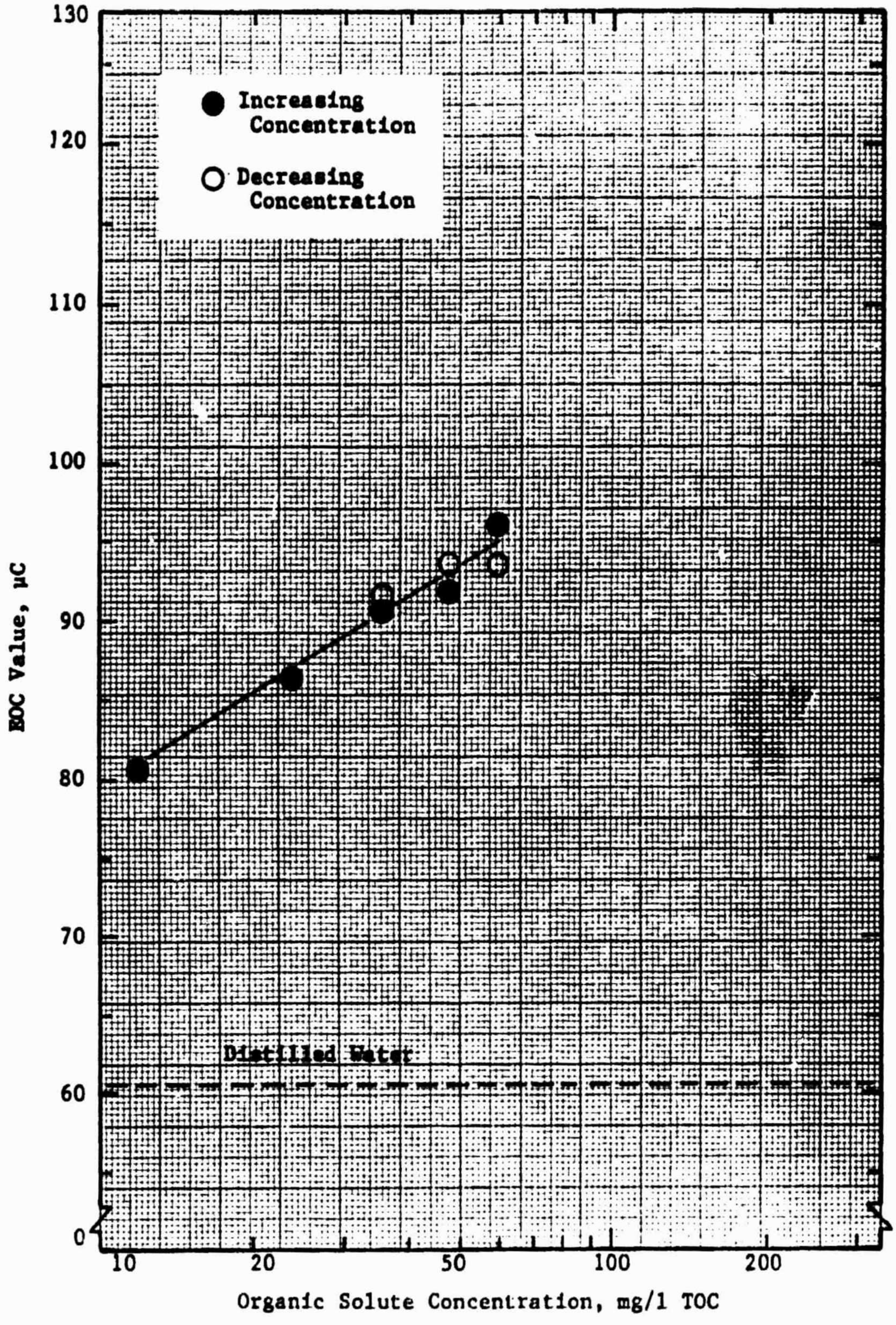

FIGURE 18 RESPONSE OF ORGANIC OXIDATION TECHNIQUE TO SOLUTE MIXTURES

TABLE 2 COMPOSITION OF SOLUTE MIXTURE TEST SAMPLES

	Concentration, ppm TOC				
Sample No.:	1	2	3	4	5
Solutes					
Methanol	2	4	6	8	10
Acetone	2	4	6	8	10
Urea	2	4	6	8	10
Toluene	2	4	6	8	10
1 - 4 Dioxane	2	4	6	8	10
Methylene Chloride	2	4	6	8	10
Total	12	24	36	48	60

Parametric Tests

Although spacecraft water will be more consistent than the effluents of terrestrial waste treatment effluents, variations in sample conditions will occur. Parametric tests were performed to determine the response of the organic oxidation technique to various physical and chemical parameters that could be encountered and to elucidate the technology that must be developed to further eliminate or reduce sample pretreatment requirements.

Dissolved Oxygen. In the capacitive-type Breadboard EOC Analyzer, reduction and adsorption potentials are applied during a stopped flow interval (Figure 3) instead of a single potential of 0.1 V used in the Mark V cell. Implementation of dual reduction and adsorption potentials during the stopped-flow period was not possible for the Laboratory Breadboard Mark V EOC Analyzer due to the limitations of the off-the-shelf instruments and manual sequencing. Automatic sequencing will be relatively straightforward to incorporate into the end-item analyzer. An experiment was performed to characterize the Laboratory Breadboard Analyzer for dissolved O_2. Mark V EOC values were determined for 0 and 10 mg/l TOC methanol solutions in both air-saturated and deaerated water, both with continuous flow and stopped flow measurement cycles. The results are presented in Table 3 as relative EOC response (difference between 0 and 10 mg/l TOC results, referenced to the response curve for methanol). These results imply that the stopped flow portion of the cycle, as currently implemented, has limited benefit and that variations in O_2 content of the laboratory EOC samples cause variations in the response. This factor must therefore be considered in evaluating response data obtained with the Laboratory Breadboard Analyzer.

It is anticipated that using the same electrode potential and stopped-flow sequences that have proven to be effective in the Breadboard EOC Analyzer would eliminate this problem in the Mark V EOC Analyzer.

Temperature. Small temperature fluctuations are projected for samples analyzed by a spacecraft Water Quality Monitor.(7) The effect of temperature on response is plotted in Figure 19. This data indicates that a strong temperature effect exists and that appropriate temperature compensation (or regulation in extreme cases) will be required if the temperature in the measurement environment varies significantly.

Conductivity. The conductivity of spacecraft water will vary depending on the degree of carry-over of salts during water recovery processes. Although a conductive solid electrolyte is used between the Analyzer electrodes, variations in sample conductivity still affect the response characteristics of the analyzer (Figure 20). The response is enhanced at higher conductivities and compensation of the response will be required.

Specific Ions. Certain ionic species present in water samples can also adsorb on or chemically affect electrode surfaces, thus modifying instrument response. Therefore, the effects of suspect ions were investigated.

The effects of sulfate (SO_4^{-2}) and nitrate (NO_3^-), plotted in Figures 21 and 22, are small even at the worst case ion concentrations that would be encountered in water from a VCDS (less than 1 x 10^{-3} M and 1 x 10^{-5} M, respectively).(9) The measurement of these effects was made at constant ionic strength instead

TABLE 3 RESULTS OF DISSOLVED OXYGEN EXPERIMENTS

	Relative Response, as mg/l TOC Methanol	
	Air Saturated Water[(a)]	Deaerated Water[(b)]
Continuous Flow	7.8	4.6
Stopped Flow	8.4	5.0
Difference	0.6	0.4

(a) 9 mg/l dissolved oxygen concentration.
(b) 0.2 mg/l dissolved oxygen concentration.

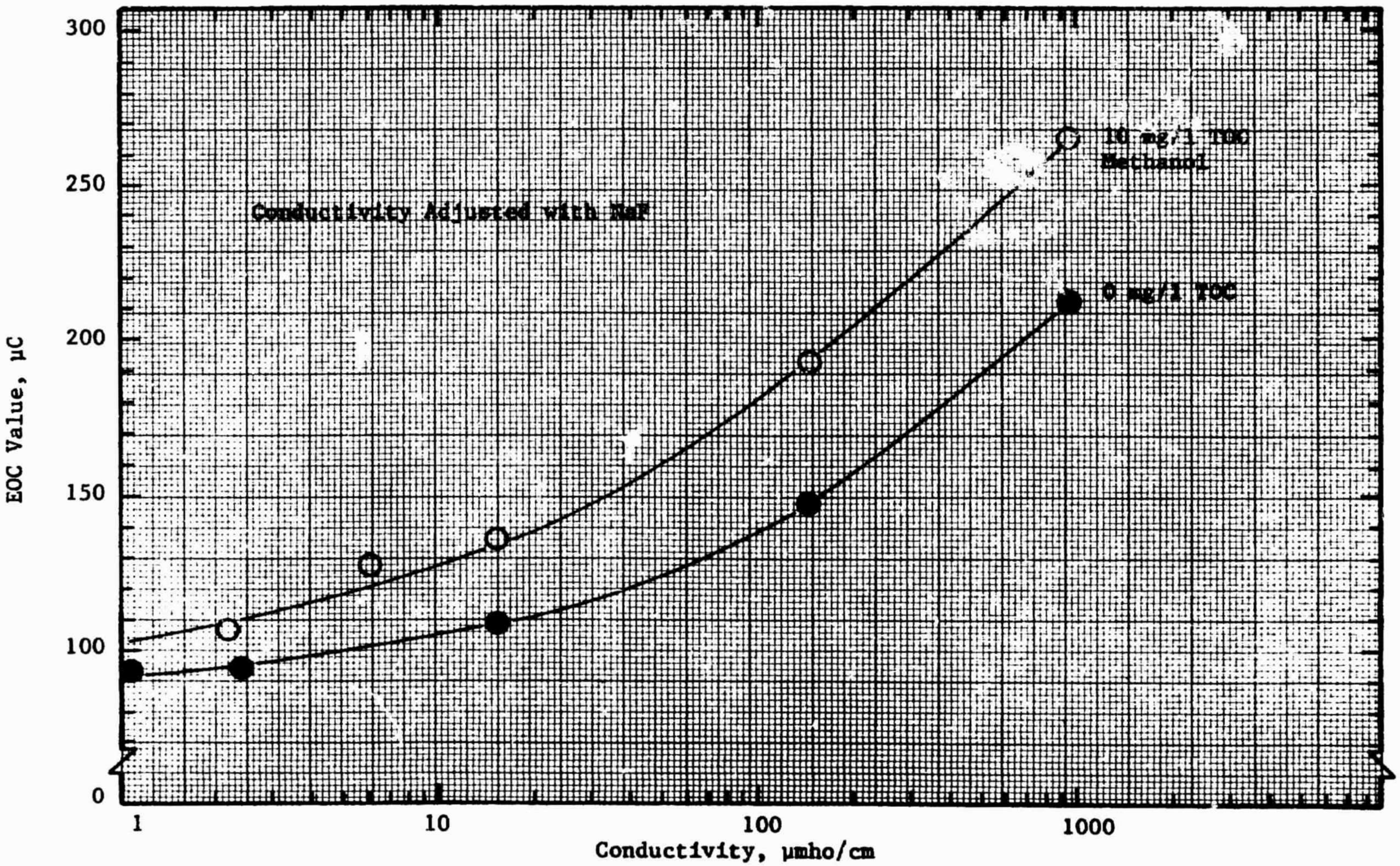

FIGURE 20 EFFECT OF CONDUCTIVITY ON MEASUREMENTS BY ORGANIC OXIDATION TECHNIQUE

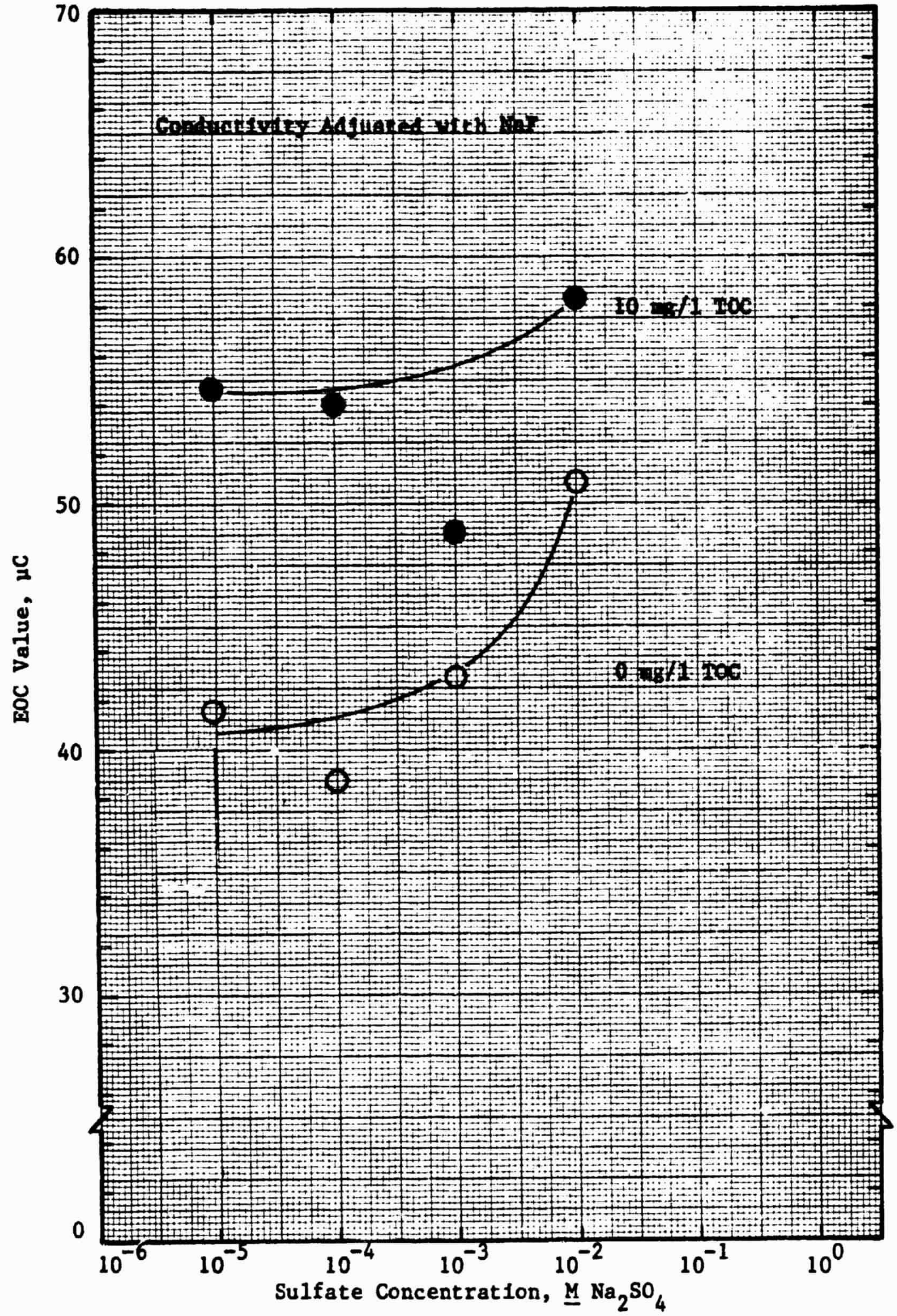

FIGURE 21 EFFECT OF SULFATE ON MEASUREMENTS BY ORGANIC OXIDATION TECHNIQUE

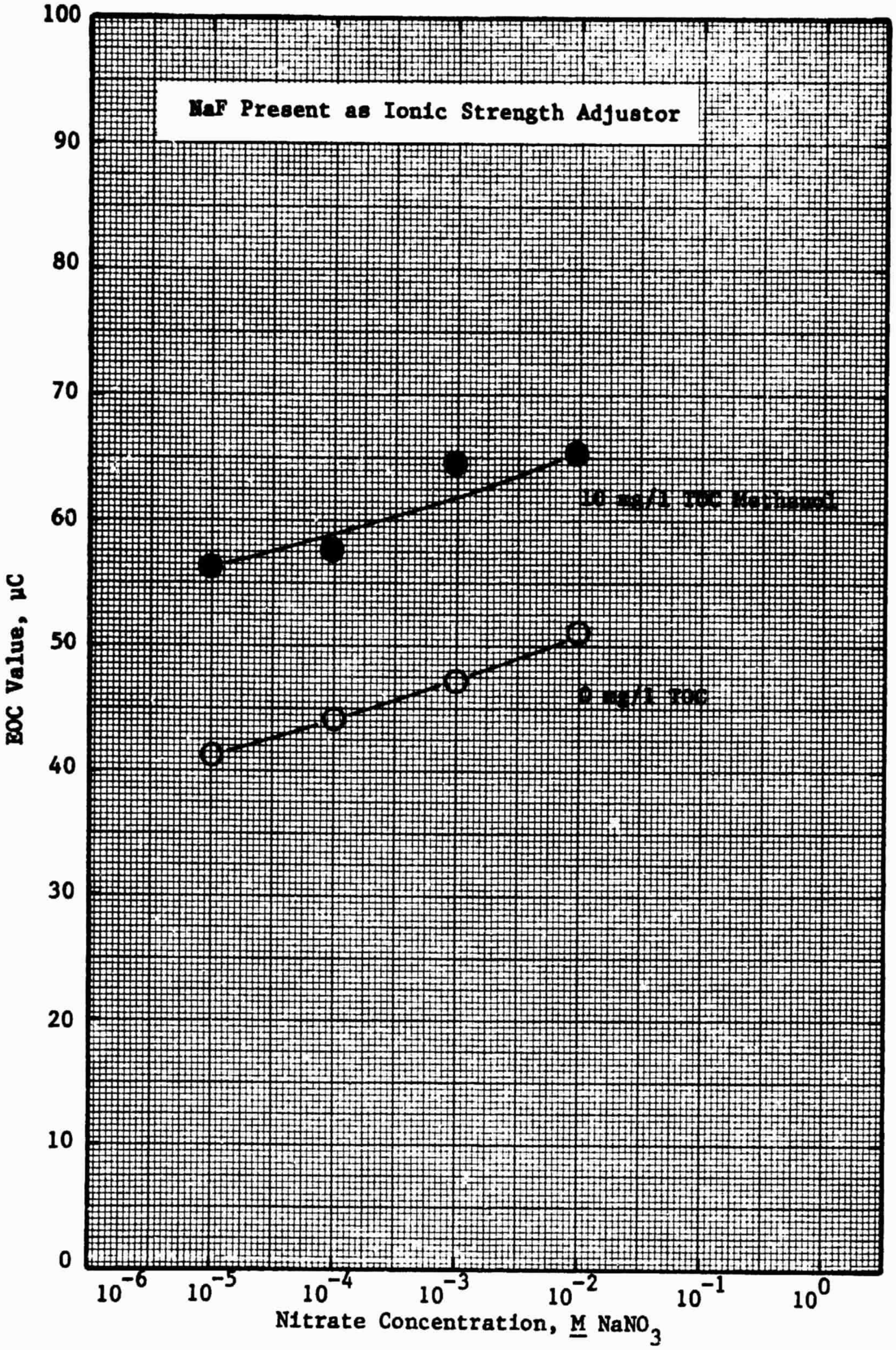

FIGURE 22 EFFECT OF NITRATE ON MEASUREMENTS BY ORGANIC OXIDATION TECHNIQUE

of constant conductivity. Therefore, the effects observed in Figures 21 and 22 are due to conductivity changes rather than to other electrode effects. It is expected that conductivity compensation will eliminate the effects of SO_4^{-2} and NO_3^-.

Figure 23 indicates, however, that the presence of Cl^- represses EOC values even at concentrations of 1×10^{-5} M. Although concentrations of Cl^- in spacecraft water are expected to be typically at or below 1×10^{-5} M,(10) compensation (or sample pretreatment) for Cl^- will be required to prevent errors.

pH. The pH of spacecraft water will vary and the extent of possible pH effects was evaluated. These results are illustrated in Figure 24. There was almost no change in the net response with pH, although a small change was observed in absolute EOC value that indicated that pH compensation for pH values below 6 could be required. It is also possible that a conductivity effect was being observed, although 0.001 M sodium sulfate (Na_2SO_4) was used as a supporting electrolyte to minimize changes in conductivity. If so, conductivity compensation would eliminate the pH effects observed in Figure 24.

Reproducibility Tests

The EOC Analyzer will need to provide reliable indications of organic content over extended periods; therefore, the reproducibility of the instrument is important.

The manual sequencing employed during evaluations of the organic oxidation technique doubtless produces measurement fluctuations that would not occur in a dedicated, automatic device. Preliminary evaluations of the response for 10 mg/l TOC methanol versus time were performed to get an idea of the reproducibility of this technique on an hourly and daily basis. For the long-term reproducibility test, EOC values for distilled water and a sample containing methanol at a concentration of 10 mg/l TOC were obtained each day. The instrument was not operated at night, and in the morning it was powered up and allowed to come to a steady-state condition with distilled water as the sample. Therefore, the flucuations in EOC response shown in the long-term experiment include fluctuations due to daily startup and shutdown effects. The EOC values were compared to a calibration curve obtained for methanol at an earlier date to obtain the relative response data listed in Tables 4 and 5. The relative response, in units of mg/l TOC for methanol, represents the output that would be obtained from the Analyzer if logic circuitry was provided to produce an output signal in concentration units rather than the instrumental EOC units now used.

Table 4 presents the results of the short-term reproducibility tests, while Table 5 lists the results of the long-term test.

The precisions indicated are adequate for providing a general indication of organic solute level. However, none of these EOC response values were corrected for temperature, conductivity or pH variations and Cl^- was not in the solutions. Compensation, if incorporated, would probably have improved the reproducibility.

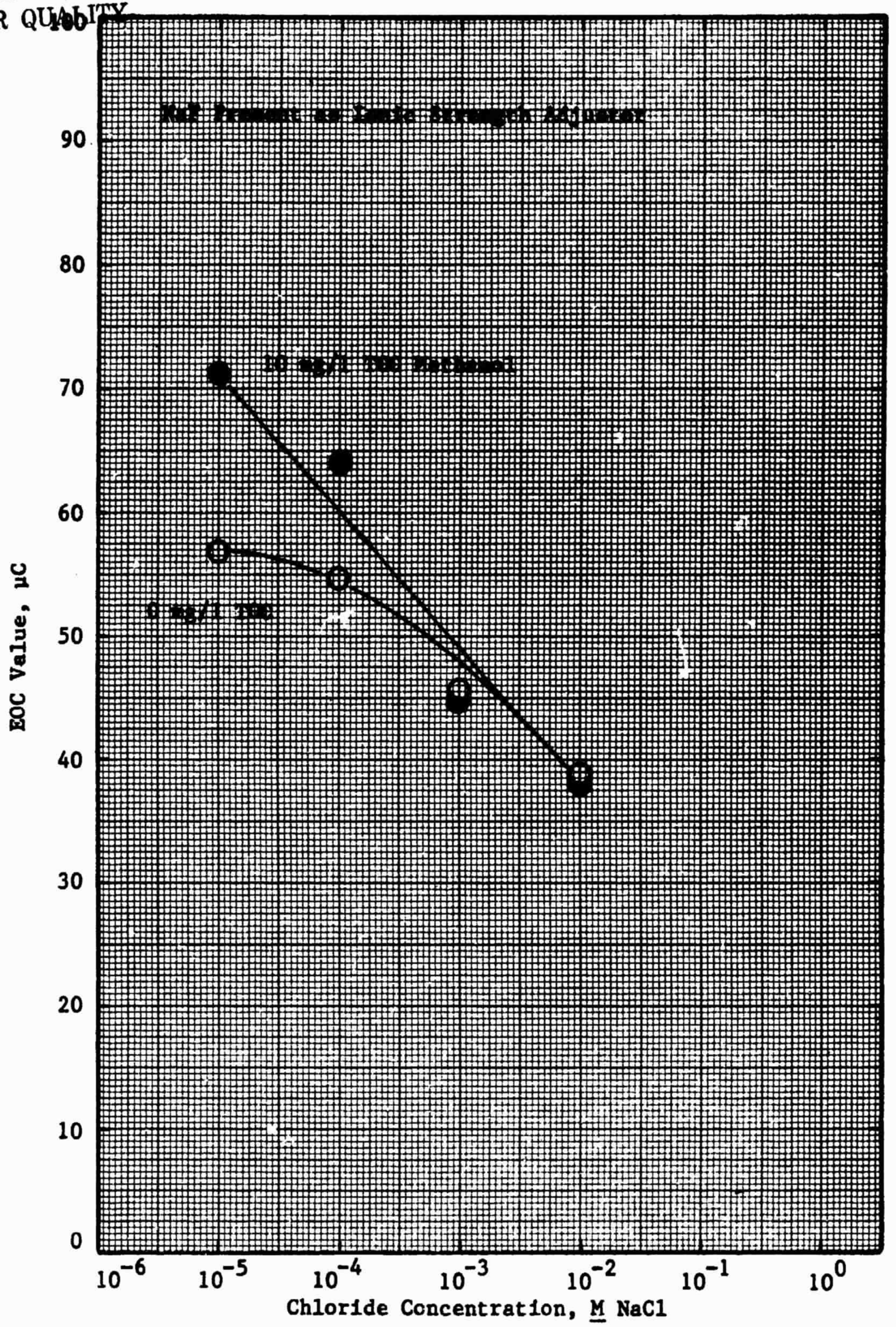

FIGURE 23 EFFECT OF CHLORIDE ON MEASUREMENTS BY ORGANIC OXIDATION TECHNIQUE

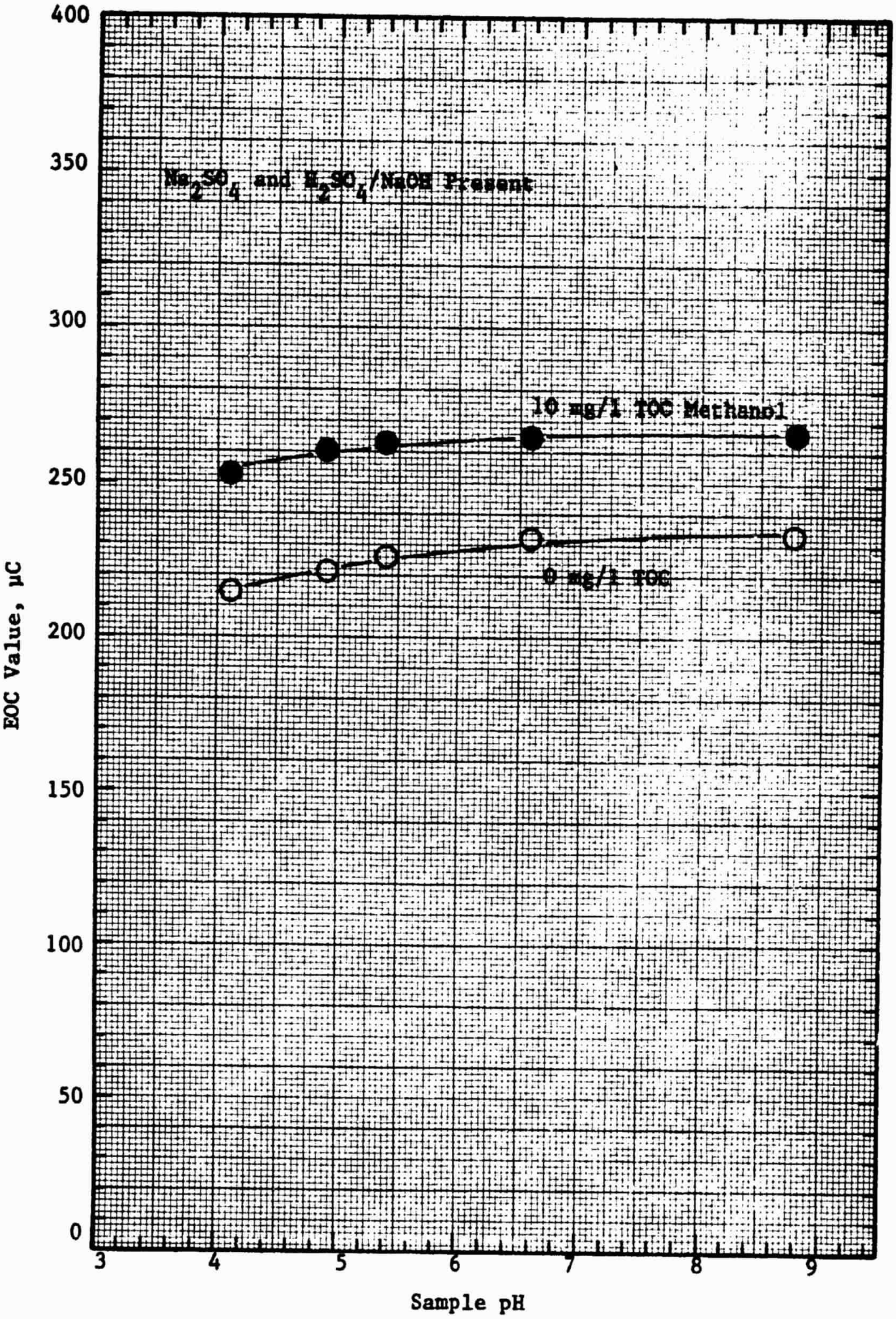

FIGURE 24 EFFECT OF pH ON MEASUREMENTS BY ORGANIC OXIDATION TECHNIQUE

TABLE 4 RESULTS OF SHORT-TERM REPRODUCIBILITY TEST FOR ORGANIC OXIDATION TECHNIQUE

Hour	Response to 10 mg/l TOC Methanol, µC	Relative Response as mg/l TOC Methanol[a]
1	59.0	7.2
2	62.5	10.5
3	63.5	11.5
4	60.3	8.3
5	65.4	13.2
6	61.0	9.0
7	60.4	8.4
8	64.2	12.2
	Average	10.0
	Standard Deviation	2.1

(a) Based on response versus concentration curve for methanol.

TABLE 5 RESULTS OF LONG-TERM REPRODUCIBILITY TEST
FOR ORGANIC OXIDATION TECHNIQUE

Day	Response to 10 mg/l TOC Methanol, μC	Relative Response as mg/l TOC Methanol[a]
1	24.3	13.5
2	14.7	5.5
3	15.8	6.2
4	17.7	7.6
5	22.3	11.5
6	19.7	9.2
	Average	8.9
	Standard Deviation	3.1

(a) Based on response versus concentration curve for methanol.

Conclusions of the Parametric Evaluation

The organic oxidation method was concluded to be the most desirable of the two Mark V measurement techniques based on its positive response characteristics for a variety of organic compounds. However, temperature, conductivity and Cl^- compensation will be required if variations in these parameters are significant. Modifications to the analysis cycle will also be required in the end-item analyzer to eliminate the influence of dissolved O_2.

Development of Compensation Technology for Organic Oxidation EOC Technique

The results of the parametric evaluation indicated that relationships should be developed to demonstrate the feasibility of automatic compensation for temperature, conductivity, Cl^- and possibly pH variations. Such technology could ultimately be implemented using conventional parametric sensors and established electronics technology.

Temperature Compensation

Automatic compensation for variations in temperature will require use of a mathematical relationship in the EOC instrument to perform appropriate modifications to its electrical output. The objective of the temperature compensation study was to develop such a relationship.

The effects of temperature on the response of the Mark V cell after maintenance and reassembly were evaluated. Uncompensated data for 0 and 10 mg/TOC methanol solutions is plotted in Figure 25 (unfilled circles and triangles, respectively). This data was then analyzed with least squares statistics. The exponential factor in the equation below produced good compensation, as shown by the solid circles and triangles in Figure 25.

$$R' = R\, e^{0.050\ (25-T)} \qquad (3)$$

where R' = Temperature Corrected EOC Value, μC
R = Uncorrected EOC Value, μC
T = Solution Temperature, C

Compensation was within ±0.3 mg/l TOC methanol equivalent over the 302 to 308 K (85 to 95 F) temperature range selected for the water quality monitor for the Regenerative Life Support Experiment (RLSE)(7) and within ±2 mg/l TOC methanol equivalent over a 293 to 318 K (68 to 113 F) temperature range. The compensation is effective for both distilled water and water containing methanol, indicating that it likely has general validity for other solutes and concentrations.

Extended Conductivity/pH Effects Evaluations

Unlike temperature, conductivity and pH are chemical parameters. The effect of conductivity and pH variations on organic oxidation-type EOC measurements was projected to possibly vary with both the type of organic solute being analyzed and the composition of the ionic species in the spacecraft water.

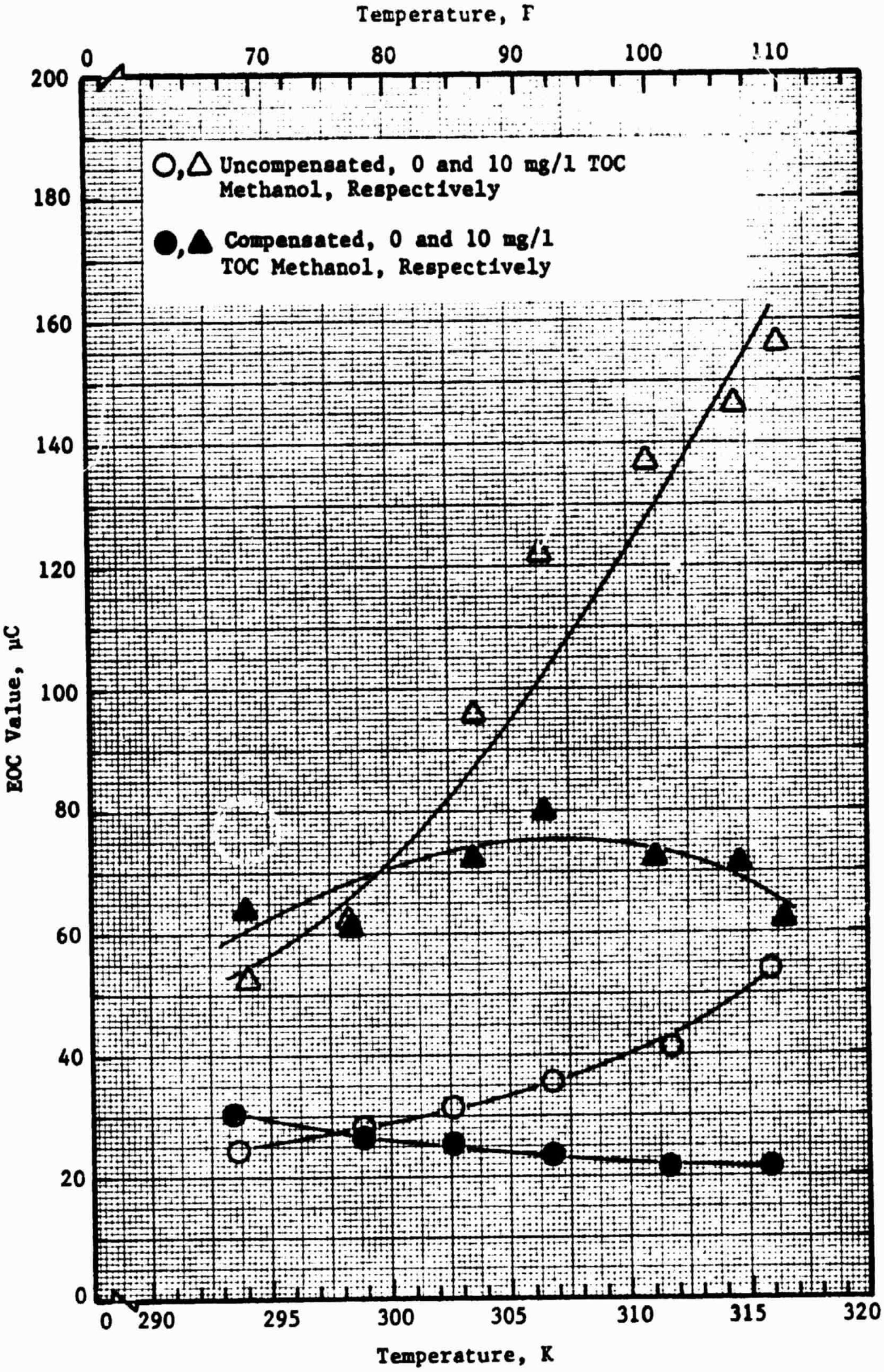

FIGURE 25 RESULTS OF TEMPERATURE COMPENSATION

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The following evaluations were performed to establish a basis for development of a conductivity compensation relationship and also to further investigate whether pH compensation was required.

Multiple Organics. Experiments were performed to determine the effects of conductivity and pH on the EOC response to different organic compounds. The conductivity and pH were varied by varying the concentration and ratio of NaOH and sulfuric acid (H_2SO_4). Both sodium (Na^+) and SO_4^{-2} ions are components of spacecraft water. However, no other ions were added so as to simplify this portion of the evaluation.

A strong conductivity enhancement effect was observed as illustrated in Figure 26. Similar results were observed for 1 mg/l and 5 mg/l TOC methanol solutions. No correlation between response and deliberately random pH variations over the range 5 to 9 was observed, indicating that the pH effects were minimal and that the EOC response would not require pH compensation.

VCDS Water Simulant. The response of the organic oxidation method to a series of solutions containing multiple salts at variable concentrations was evaluated to determine the effects of the ionic composition and conductivity of spacecraft. The formulations of these solutions, listed in Table 6, were based on published best-case and worst-case VCDS effluent compositions.(9) Although the effluent quality for a properly operating VCDS was expected to approximate the best-case composition(10) it was considered necessary to evaluate this range of solutions to assess the practicality of simultaneously compensating the response of the EOC Analyzer over wider conductivity and Cl^- concentration variations. Salt concentrations were based on VCDS effluents because more relevant data were available than for other water recovery systems. The value of these tests extends beyond merely the VCDS application, however.

The EOC value(a) is plotted versus conductivity in Figure 27 for both plain water simulant samples and samples containing 10 mg/l TOC methanol. Similar data is reported in Figure 26. The EOC response is temperature corrected in both cases but the curves show differences. In Figure 27 the two curves converge at high conductivities while in Figure 26 the curve for 10 mg/l TOC methanol diverges from the curve for 0 mg/l TOC. This difference is attributed to the fact that the simulated water samples contain Cl^-, the concentrations of which generally increase with increasing conductivities. The convergence of the two curves in Figure 27 is due to the increasing Cl^- concentration at higher conductivities.

A mathematical analysis of the EOC values for the 0 mg/l TOC curves in both figures indicated that they varied with conductivity in a similar manner. Therefore, it was concluded that Cl^- does not affect the EOC response in the absence of organics.

Conductivity Compensation

As for temperature compensation, automatic compensation for conductivity variations in the water sample was performed in the EOC Analyzer using a

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(a) Raw EOC values, temperatures and conductivities for these samples are tabulated in Appendix 1.

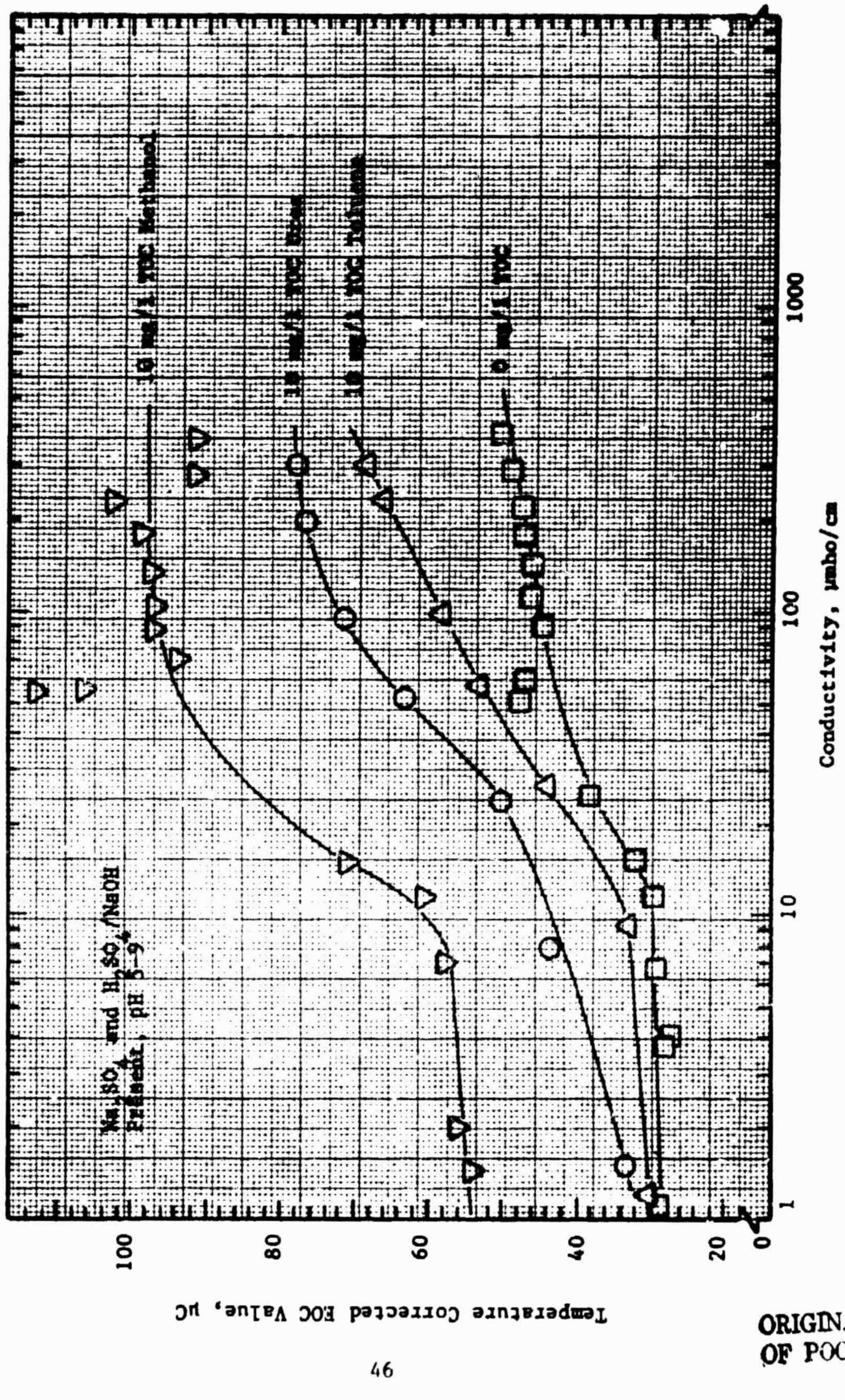

FIGURE 26 · EOC VALUE VERSUS CONDUCTIVITY FOR 10 mg/1 TOC ORGANICS

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TABLE 6 ION CONCENTRATION USED IN VCDS WATER SIMULANT STUDY(a)

	Solution Number							
Ion	1	2	3	4	5	6	7	8
$CO_3^{=}$	0.007	1.6	0.5	2.0	0.3	0.7	0.4	0.007
Na^+	0.08	1.8	0.5	1.8	0.8	5.7	5.1	9.2
K^+	1.3	1.9	1.0	0.2	2.1	1.1	0.5	2.8
NH_4^+	1.1	1.5	0.8	0.0	0.3	0.6	0.7	2.3
$SO_4^{=}$	3.6	2.8	2.0	1.4	2.9	12.3	10.2	23.0
Cl^-	3.1	4.8	2.5	0.2	1.8	2.5	2.1	6.0
PO_4^{-3}	0.06	0.04	0.01	0.01	0.12	0.09	0.10	0.11
B(b)	0.06	0.02	0.02	0.01	0.07	0.08	0.03	0.11
Fe^{+3}	0.04	0.01	0.02	0.0	0.002	0.04	0.01	0.08
Cu^{+2}	0.003	0.002	0.001	0.0	0.001	0.003	0.001	0.003
Al^{+3}	0.3	0.2	0.2	0.05	0.3	0.2	0.03	0.6
	9	10	11	12	13	14	15	16
$CO_3^{=}$	0.6	0.1	0.6	1.8	6.0	10.0	2.9	1.9
Na^+	12.0	11.0	20.0	17.0	27.0	13.0	36.0	23.0
K^+	3.5	1.9	6.2	1.8	2.1	7.8	5.5	17.0
NH_4^+	4.5	1.9	5.4	3.7	3.6	9.6	13.0	7.4
$SO_4^{=}$	28.8	26.9	47.7	38.0	56.0	28.0	68.0	51.5
Cl^-	12.0	3.8	15.4	8.2	14.0	25.8	31.0	29.0
PO_4^{-3}	0.07	0.07	0.14	0.4	0.2	0.4	0.5	1.1
B(b)	0.17	0.06	0.02	0.23	0.07	0.26	0.17	0.41
Fe^+	0.06	0.001	0.1	0.1	0.2	0.02	0.03	0.1
Cu^{+2}	0.003	0.002	0.001	0.003	0.001	0.001	0.05	0.03
Al^{+3}	0.7	0.8	0.9	0.7	0.2	1.5	11.0	1.0

(a) Ion Concentrations in mg/l.

(b) As $B_4O_7^{-2}$

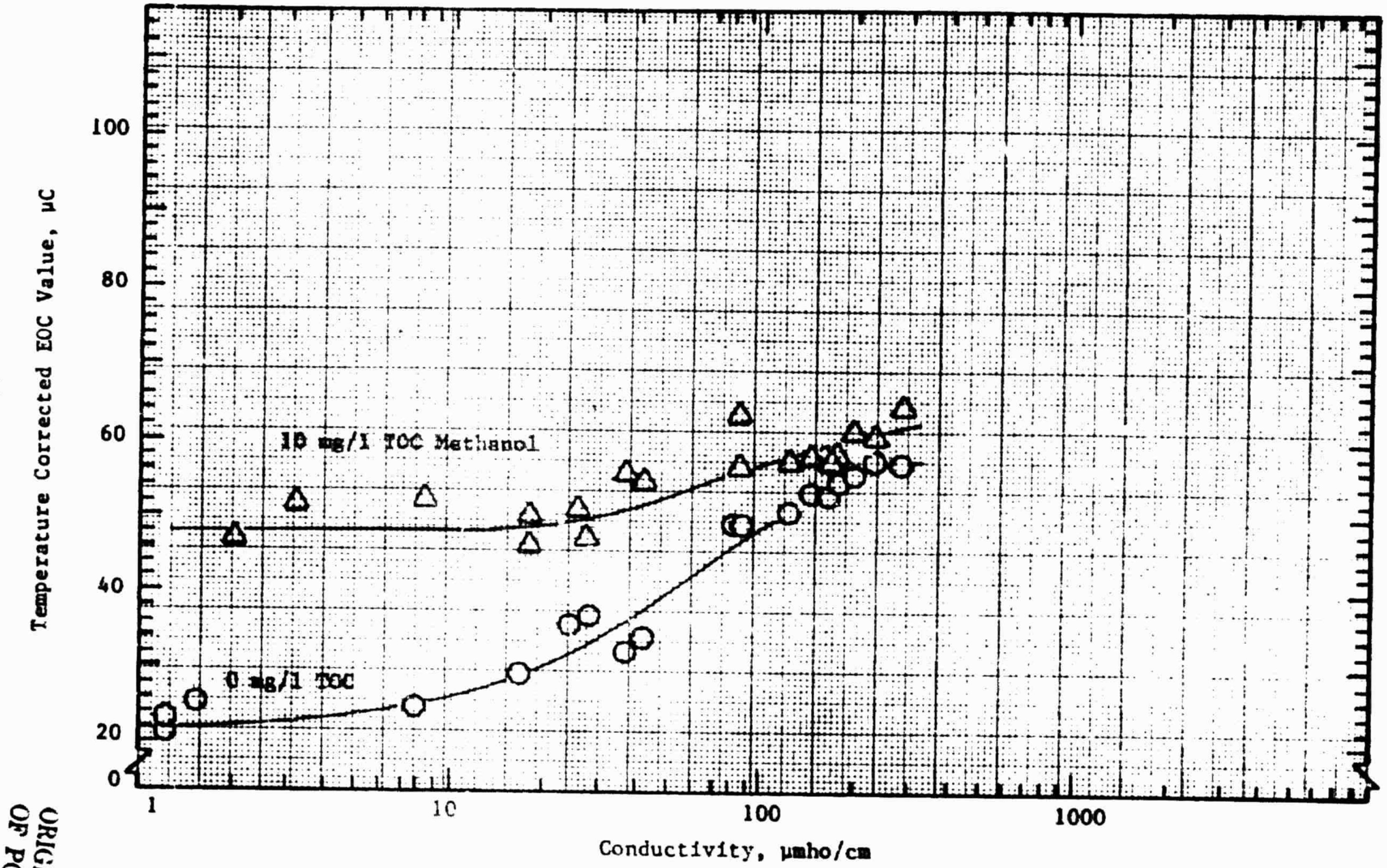

FIGURE 27 EFFECT OF CONDUCTIVITY AND IONIC COMPOSITION ON EOC VALUES FOR VCDS WATER SIMULANTS

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computational function. The results of the extended conductivity evaluations enabled the development of such a relationship.

Data from the extended water composition test were used to develop a compensation equation for correction of the EOC response to conductivity changes. This relationship, shown in Equation 4, corrects temperature compensated EOC values to 1 μmho/cm conductivity.

$$R'' = R' \, k^{-0.19} \qquad (4)$$

where R" = EOC Value Compensated for Temperature and Conductivity, μC
k = Solution Conductivity, μmho/cm

The data in Figure 28 results when Equation 4 is used to compensate the response of the EOC values for VCDS water simulant conductivity variations. The low EOC value at higher conductivities was again correlated with suppression of the response by the presence of Cl^-, as discussed above. As expected, when the EOC value for solutions containing no Cl^- (Figure 26) is corrected using Equation 4, relatively consistent response sensitivity over a range of conductivities is obtained, as illustrated in Figure 29. The points falling above the 10 mg/l TOC methanol curve reflect scatter in the uncompensated data (compare Figures 29 and 26) and the limitations of the compensation relationships.

These results indicate that compensation of the Mark V EOC values for conductivity variations is feasible. The need to compensate the EOC response for variations in Cl^- content is also reconfirmed.

Chloride Compensation

The development of a relationship for automatic compensation of analyses for the effects of Cl^- in water samples was also believed to be possible. Therefore, additional mathematical analyses of the VCDS water simulant data was performed.

Prior to developing a Cl^- compensation relationship, a logarithmic correlation between EOC response and Cl^- concentration was determined, as shown in Figure 30. The response of the analyzer decreased to approximately 30 mg/l Cl^-. At this concentration there was little difference between the response of the EOC Analyzer to methanol and to solutions containing no methanol. The response of the analyzer to 0 mg/l TOC solutions remained relatively unchanged as Cl^- concentrations increased.

It was possible to establish a compensation relationship for EOC response as a function of Cl^- concentration to approximately 30 mg/l. This relationship is shown in Equation 5 below. It corrects EOC response to correspond to 0.1 mg/l Cl^- and takes into consideration essentially no effect of Cl^- on the baseline (no organic solute).

$$R_o''' = R_o''/(0.64 - 0.39 \log (Cl^-)) \qquad (5)$$

where R_o''' = EOC Response Compensated for Temperature, Conductivity and Cl^-, μC

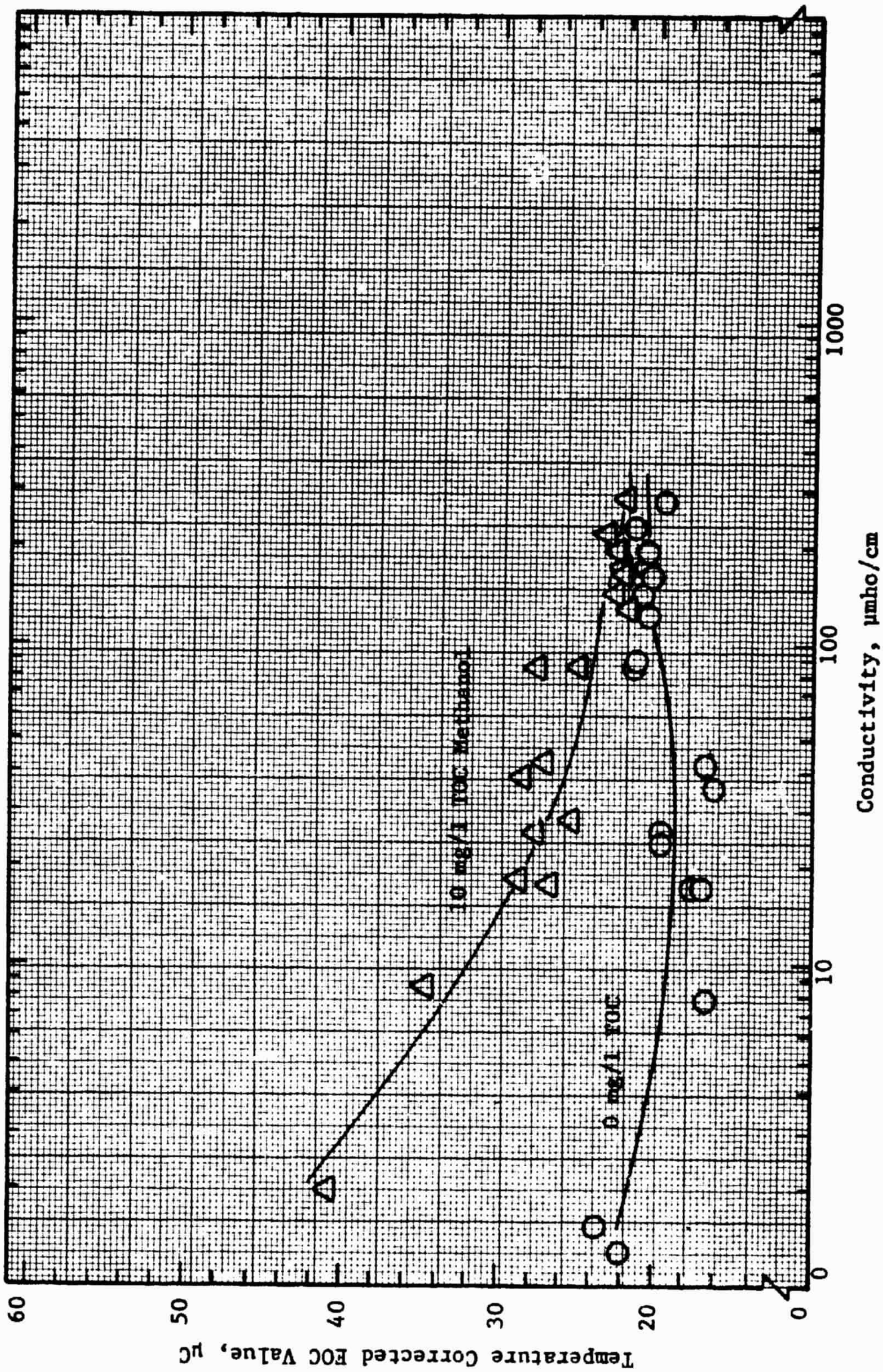

FIGURE 28. RESULTS OF CONDUCTIVITY COMPENSATION OF EOC VALUES FOR VCDS WATER SIMULANTS

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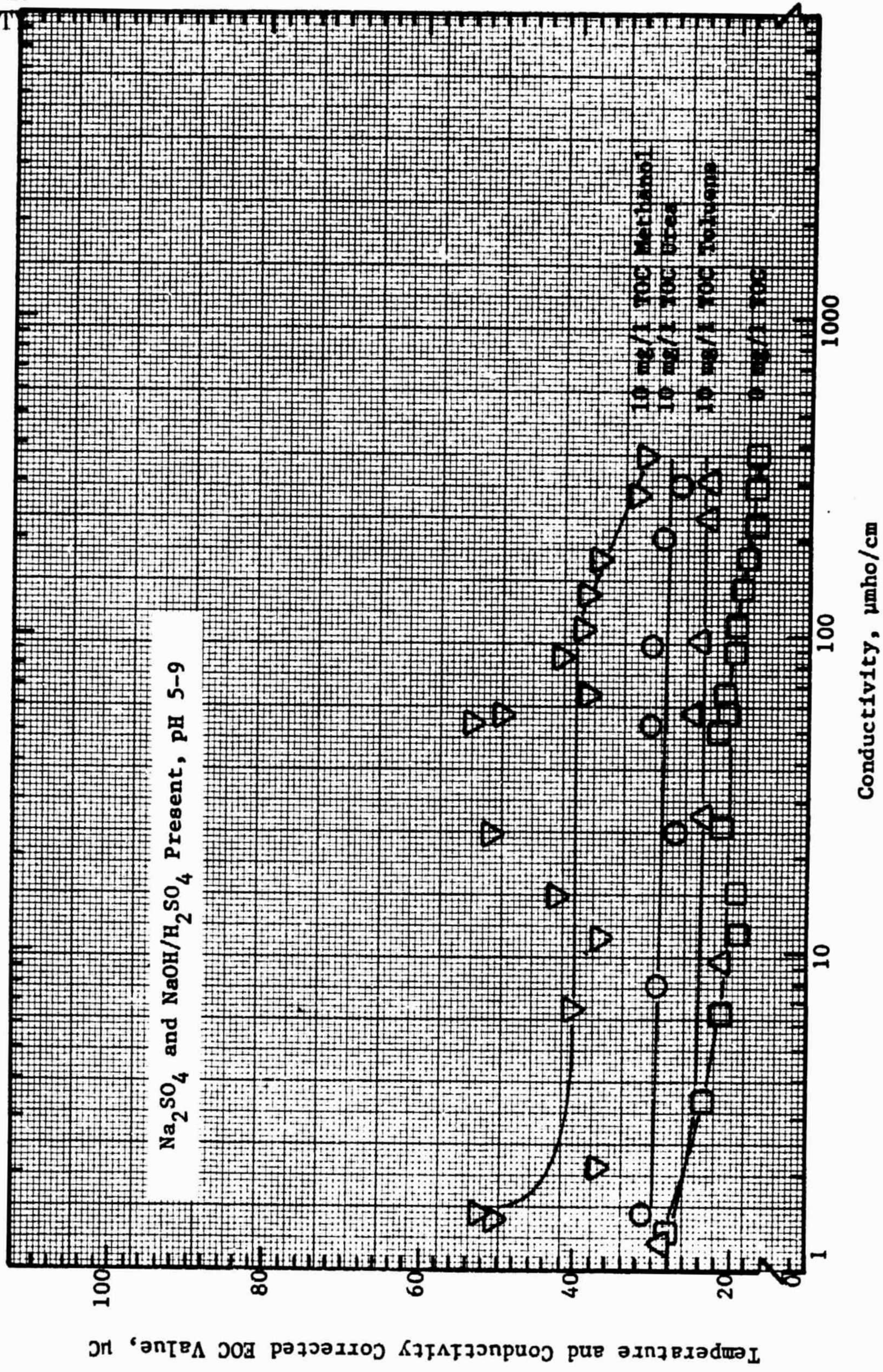

FIGURE 29 RESULTS OF CONDUCTIVITY COMPENSATION OF EOC VALUES FOR 10 mg/1 TOC ORGANICS

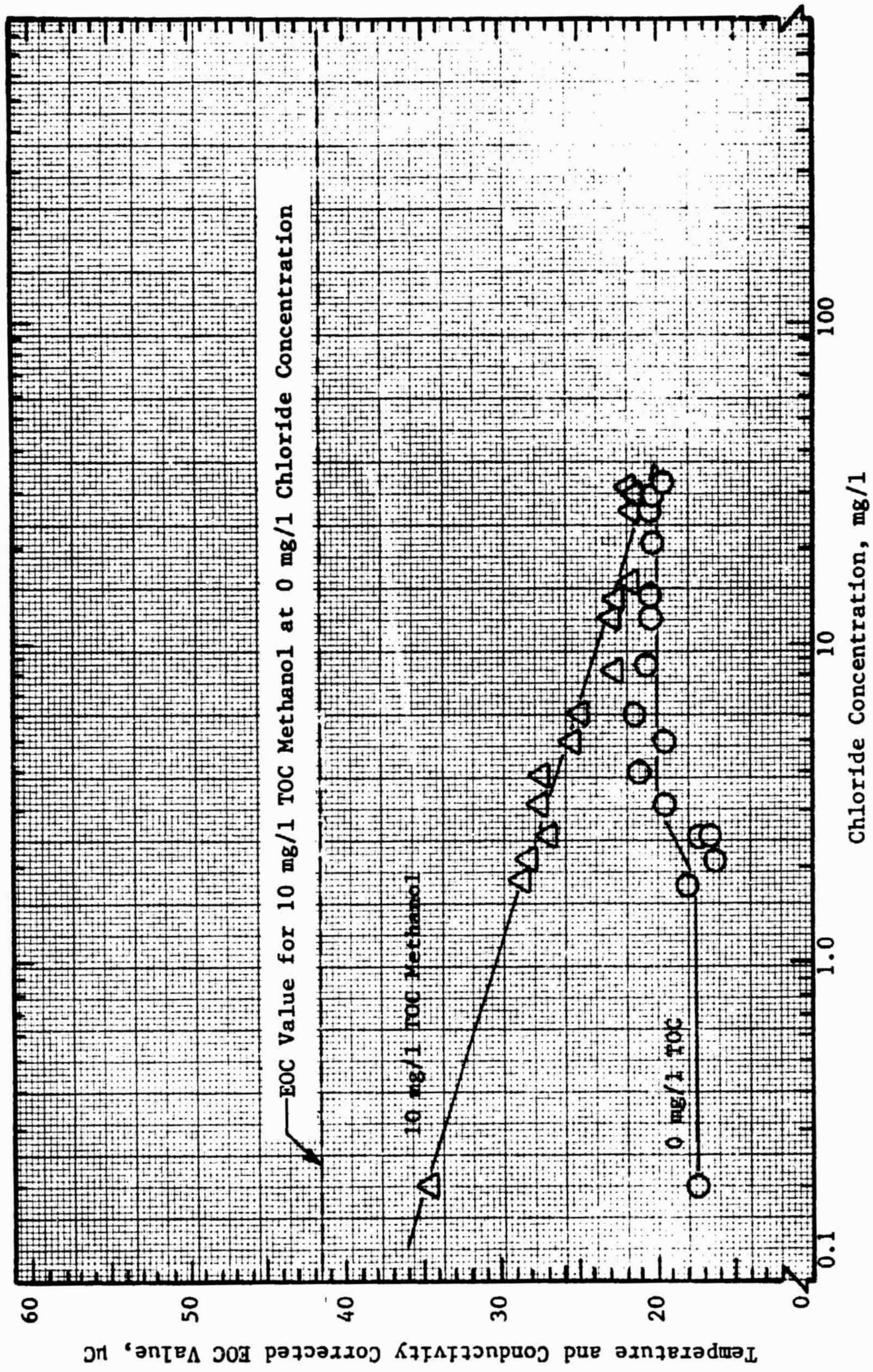

FIGURE 30 EFFECT OF CHLORIDE ON EOC RESPONSE (VCDS WATER SIMULANTS)

R_o'' = EOC Response Compensated for Temperature and Conductivity, μC
(Cl^-) = Chloride Concentration, mg/l

When applied to the data in Figure 28, Equation 5 produced the temperature, conductivity and Cl^--compensated responses and relative responses plotted in Figure 31 and 32, respectively. The combined compensated responses are relatively flat between about 0.1 and 10 mg/l Cl^-. This range corresponds to conductivity variations between 8 and 120 μmho/cm and small ambient temperature changes. This data indicates the feasibility of a combined Cl^- and conductivity compensation at least in those cases where the Cl^- concentrations are less than 10 mg/l and relatively constant.

However, there is still a significant level of scatter in the data mainly at the larger Cl^- concentrations. This occurs because the large compensation factor applied at these concentrations amplifies any response errors. The amplification is particularly notable for random deviations from the standard baseline, even if no organic solute is present. Therefore compensation of Mark V EOC responses for Cl^- interference appears to be practical only if the Cl^- concentration is small.

Overall Compensation

The feasibility and limitations of compensation of the EOC Analyzer for temperature, conductivity and Cl^- concentrations have been demonstrated. It is possible to compensate simultaneously for these three parameters with a single relationship. It is projected that the end-item EOC Analyzer will periodically be zeroed with a solution containing 0 mg/l TOC (commonly referred to as the blank). In most cases the temperature and conductivity of the blank will be different than those of the sample. Equation 6 corrects for the effects of temperature and conductivity in those cases when the temperature and conductivity of the blank and sample are not the same:

$$R_o''' = \frac{R\,k^{-0.19}e^{0.050(25-T)} - R_b\,k_b^{-0.19}e^{0.050(25-T_b)}}{0.64 - 0.39\log(Cl^-)} \qquad (6)$$

where:
R_b = Uncompensated EOC Value for 0 mg/l TOC Blank, μC
k_b = Conductivity of the 0 mg/l TOC Blank μmho/C
T_b = Temperature of 0 mg/l TOC Blank, C

In special cases, the temperature and conductivity of the blank may equal that of the sample. If this is the case the simplified equation below applies:

$$R_o''' = (R-R_b)\,\frac{k^{-0.19}\,e^{0.050(25-T)}}{0.64 - 0.39\log(Cl^-)} \qquad (7)$$

where: R_b = Uncompensated EOC Value for 0 mg/l TOC the Blank, μC

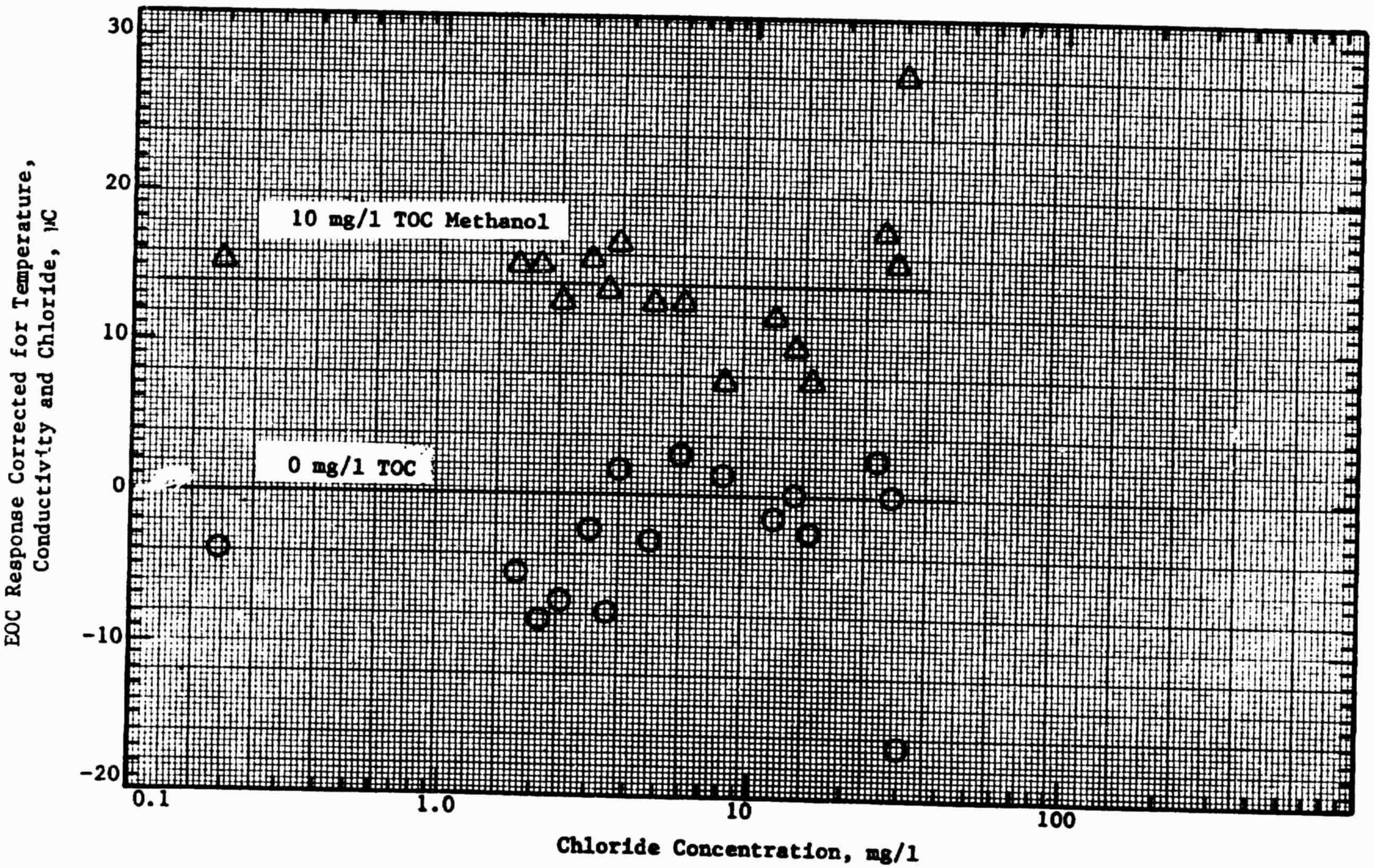

FIGURE 31 FULL COMPENSATION OF EOC RESPONSE (VCDS WATER SIMULANTS)

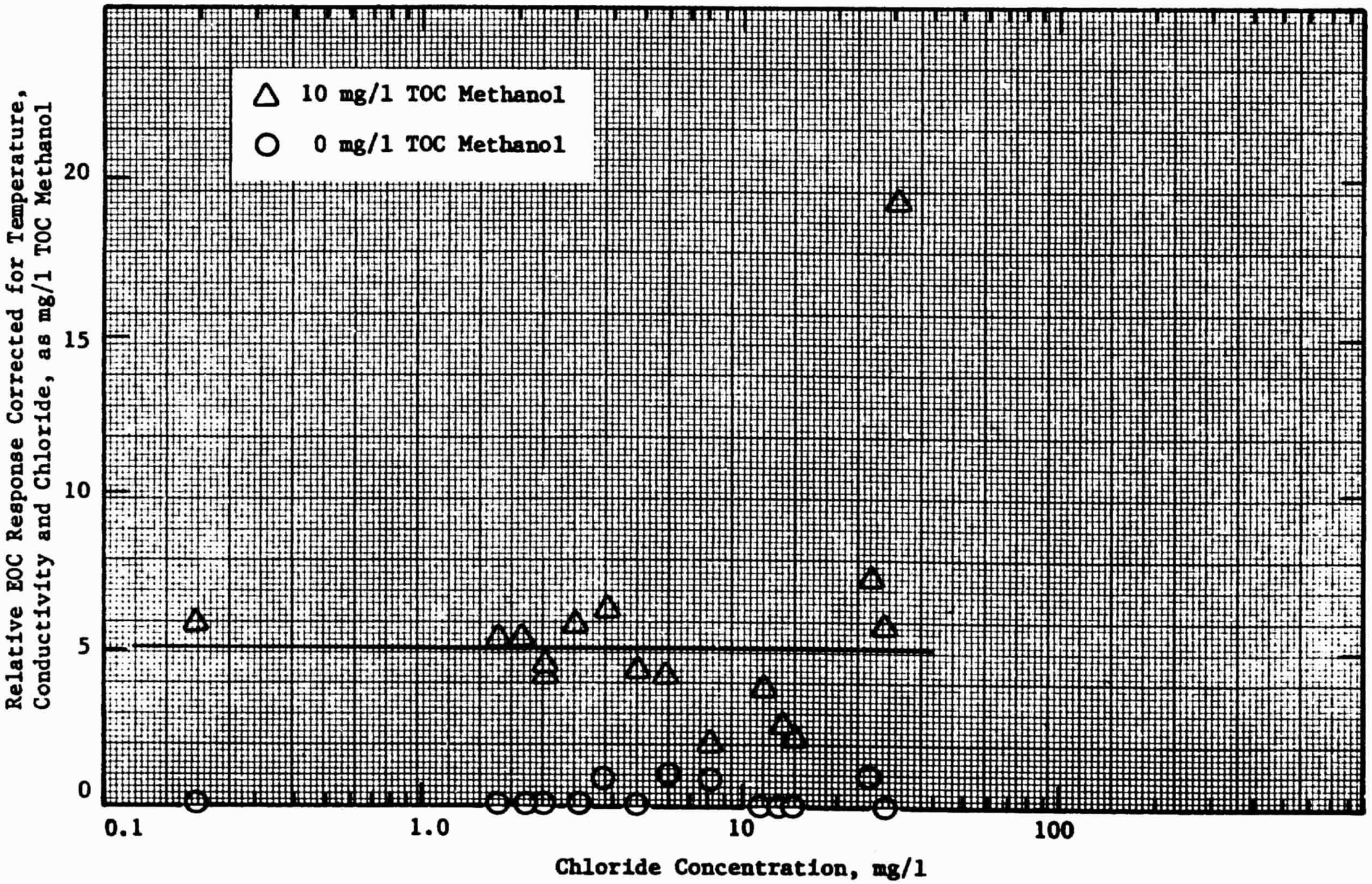

FIGURE 32 FULL COMPENSATION OF RELATIVE EOC RESPONSE (VCDS WATER SIMULANTS)

Response Experiments

The effect of the compensation equations on the response of the Mark V cell was quantified for a wide variety of organic solutes at 10 mg/l TOC concentrations. The results of the survey are listed in Table 7. This survey expands the data base for the organic oxidation technique and demonstrates its applicability to compounds other than those tested thus far.

Compensated response curves were obtained for methanol, 1.4 dioxane, acetone, methylene Cl^-, toluene and urea (Figure 33). The curves were corrected for temperature and conductivity variations using Equations 3 and 4.

Both groups of response tests indicate that the organic oxidation technique, as presently implemented, is particularly sensitive to certain compounds (alcohols such as methanol and ethylene glycol) and relatively unresponsive to others (ketones for example). However, the conductivity compensation relationship appears to distort the natural sensitivity of the organic oxidation technique to many compounds by normalizing all responses to 1 µmho/cm conductivity. The implicit conductivity of all of the solutions was higher in some cases by as much as two orders of magnitude. It is recommended that an improved conductivity compensation relationship be sought that normalizes data to a higher conductivity than 1 µmho/cm.

CONCLUSIONS

The objectives of the EOC evaluation have been successfully achieved. The EOC Analyzer concept has been shown to be compatible with the needs of organic solute monitoring in the WQM. The investigation of the Mark V EOC cell has shown that operation without expendables is possible. It has shown that automated electronic compensation of the EOC response for the effects of temperature, conductivity and Cl^- is feasible. However, the apparent sensitivity of the Mark V cell to organics is greatly reduced for many organics once compensation is applied to the cell's response.

The Mark V cell evaluation has shown that the response of the cell to certain organics which adsorb strongly on the indicating electrode is significantly less than the response observed with the Breadboard EOC Analyzer. It is concluded that these response differences are due to the limited oxidizability of many organics on the indicating electrode. The Mark V EOC cell responds to organics that adsorb strongly on the indicating electrode and then are readily oxidized electrochemically. The Breadboard EOC Analyzer responds to organics that adsorb on the electrode, and oxidizability is not a requirement for the measurement. The significance of this difference can be illustrated in the differences in the response to urea of the Breadboard EOC Analyzer (Figure 7) and the Mark V cell (Figure 33).

Whereas the Mark V EOC cell has limited potential for use in the WQM because of its lack of sensitivity, the Breadboard EOC Analyzer has demonstrated great sensitivity to many organic solutes. This program has demonstrated how to eliminate or simplify the overkill techniques used in the Breadboard EOC Analyzer. Temperature compensation was demonstrated in the Mark V study. Two techniques for simplifying electrolyte injection have been demonstrated.

TABLE 7 RESULTS OF ORGANIC COMPOUND SURVEY

Organic Compound[a]	Compound Class	Uncompensated Relative Response mg/l TOC Methanol	Compensated Relative Response mg/l TOC Methanol[b]
Methanol	Alcohol	19.0	10.0
Ethanol	Alcohol	43.0	2.6
2-Propanol	Alcohol	2.5	<1.0
Ethylene Glycol	Alcohol	45.5	24.2
Glycerol	Alcohol	33.0	22.7
Phenol	Alcohol	1.8	<1.0
2,3 Dimethyl Phenol	Alcohol	1.8	<1.0
Formic Acid	Acid	53.5	1.5
Acetic Acid	Acid	9.8	NR[c]
Oxalic Acid	Acid	87.0	2.1
Ascorbic Acid	Acid	13.0	<1.0
EDTA	Acid	14.8	1.3
Potassium Acid Phthalate	Ester	6.5	NR
Sodium Lauryl Sulfate	Ester	8.6	0.9
Chloroform	Chlorinated Hydrocarbon	5.2	3.1
Methylene Chloride	Chlorinated Hydrocarbon	2.0	NR
Urea	Urea	4.0	<1.0
Thiourea	Urea	4.4	2.0
Acetone	Ketone	1.5	NR
1 - 4 Dioxane	Ketone	2.0	NR
Triton X-100	Wetting Agent	4.6	2.7
Toluene	Aromatic Hydrocarbon	2.0	NR
Glycine	Amino Acid	2.0	<1
Dimethylphenylenediamine Oxalate	Amine Salt	3.5	NR

(a) Organic concentration = 10 mg/l TOC.
(b) Temperature and conductivity corrected.
(c) No response or slightly negative response.

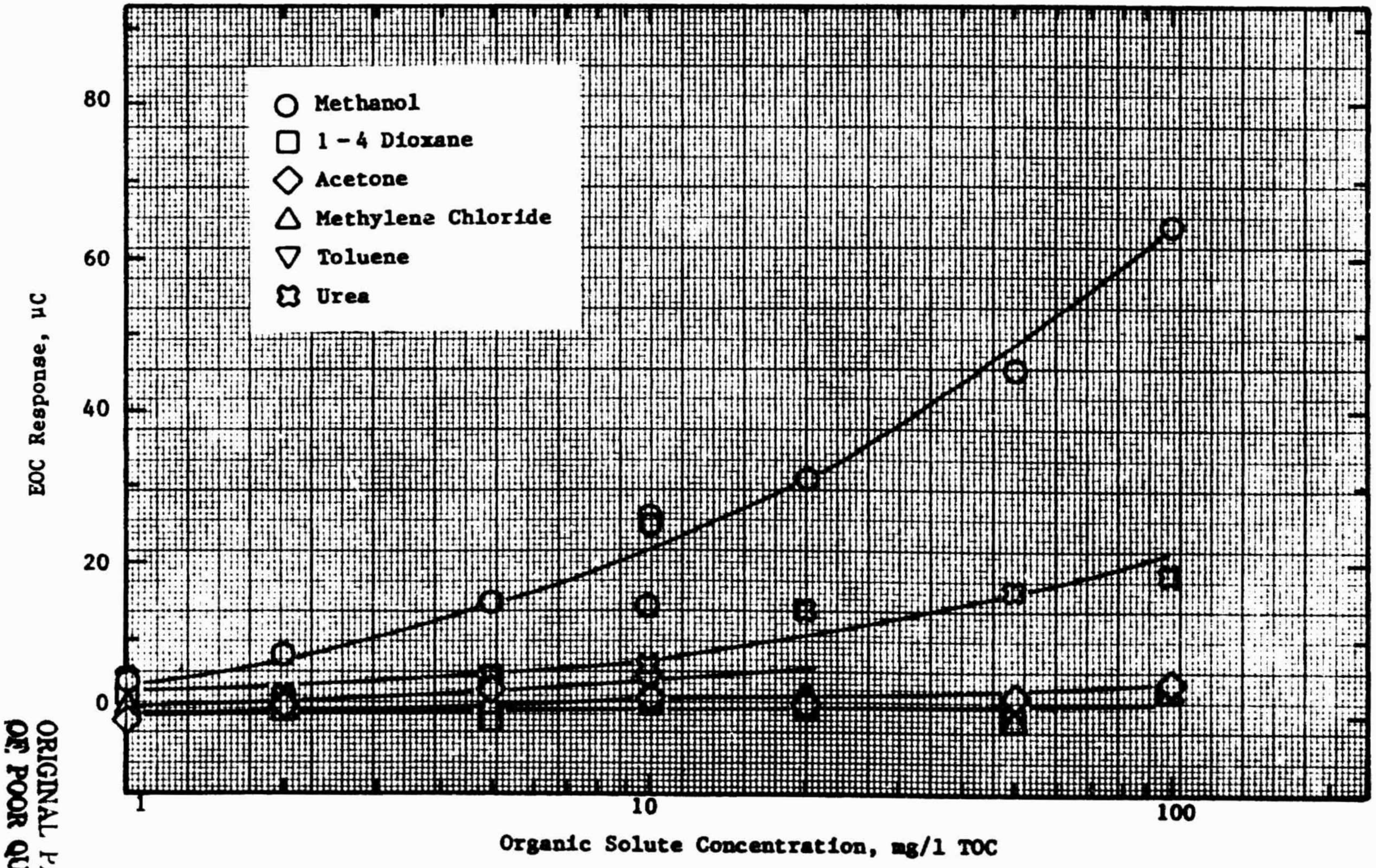

FIGURE 33 RESPONSE CURVES FOR VARIOUS ORGANIC SOLUTES

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Electrochemical in situ generation of electrolyte has been shown to be feasible, and analytical response to organic solutes in 0.01 M NaOH has shown that the analyzer's response characteristics satisfies the needs of the WQM. Injection of electrolyte by saturating the sample with a slightly soluble salt has also been evaluated using $CaSO_4$.

Comparison of the two techniques shows that the response of the EOC Analyzer with 0.01 M NaOH is more sensitive than when the sample is saturated with $CaSO_4$. However, electrochemical injection of NaOH would generate H_2 and O_2 which must be vented. Therefore, two additional interfaces would be added to the analyzer. A zero-g gas/liquid separator would also be required to avoid errors due to the presence of bubbles in the EOC cell. Electrochemical in situ generation of the electrolyte would also be more flow rate dependent than the saturation technique since the NaOH generation current would have to be adjusted in proportion to the sample flow rate in order to maintain a constant electrolyte concentration.

The saturated salt technique, however, requires the bed be sized to ensure saturation of the sample over the normally expected range of flow rates. No gases are produced so no interfaces other than the sample inlet and outlet are required in the analyzer. Conductivity and/or temperature compensation would be required to overcome the effects of temperature changes on the solubility of the salt in the sample. This would be implemented in the same way as in the Mark V technique.

In either case, the in situ electrochemical reduction of dissolved O_2 would be required and implemented using the stop flow technique incorporated in the Breadboard EOC Analyzer. This technique is extremely simple, requiring only a solenoid valve and circuitry to operate it.

The analytical response of some salts may be better than that obtained with $CaSO_4$. Past EOC tests have shown that high concentrations of electrolyte and either strongly basic or strongly acidic solutions produce the best EOC response. A slightly soluble base such as calcium hydroxide ($Ca(OH)_2$) may produce better response than $CaSO_4$ since it is strongly basic and more soluble.

In summary, the tests that have been performed during this contract have shown that the development of a small organic solute monitor based on the EOC concept is feasible and practical. It is projected that an analyzer at the flight level could occupy as little as 2×10^{-4} m^3 (0.008 ft^3) and weigh 1.4 kg (3 lb), including expendables. Only 0.04 kg (0.08 lb) of expendables would be required for 30 days of continuous operation. Power consumption by the analyzer is projected at 10 W or less.

RECOMMENDATIONS

The technology required for the development of an advanced version of the EOC Analyzer as described above has been accumulated through this and other programs. The questions that remain to be answered are those involving the integration of an electrolyte injection system in the EOC cell and the integration of automated instrumentation (including automated compensation for conductivity and/or temperature) with the EOC cell. An instrument such as this at the advanced breadboard level would provide data in a cost-effective manner and would allow the final decision to be made regarding the applicability of the EOC Analyzer in the WQM. Until such time as the Advanced Breadboard EOC Analyzer is tested it must be concluded that the EOC Analyzer provides the analytical response and physical attributes required for the next generation WQM. The results obtained so far in the evaluation of the EOC concept have utilized the Breadboard EOC Analyzer or laboratory breadboard level equipment with standard electroanalytical instrumentation. Although the Breadboard EOC Analyzer contains many of the basic features required in the EOC Analyzer design for aerospace applications, many differences exist due to the fact it was designed for a specific terrestrial application. Precise comparative data between the EOC Analyzer and other organic solute monitors that may be evaluated for use in the WQM can only be obtained using integrated instrumentation at the advanced breadboard level. It is recommended that an Advanced Breadboard EOC Analyzer be developed, tested and evaluated to define its complete potentialities for the WQM.

It is also recommended that the Advanced Breadboard EOC Analyzer be designed to consist of two parts; the sensor assembly and the instrumentation assembly. The sensor assembly would contain the EOC sensor and sensors for temperature and conductivity to be used in compensating the EOC response. In the sensor assembly a salt canister with a solenoid valve would be contained to provide the electrolyte injection and in situ electrochemical dissolved O_2 reduction functions, respectively.

The instrumentation assembly would contain signal conditioning circuitry for the sensors, plus signal processing circuitry to convert the logrithmic EOC response to a response that is linear and increases with increasing organic concentration. The signal processing circuitry would include adjustments for calibrating the EOC output.

The test program for the Advanced Breadboard Analyzer would include checkout and shakedown tests following its assembly. Parametric tests would be incorporated to verify the effectiveness of compensation for sample temperature changes. The parametric tests would also include tests of the effectiveness of the salt bed in maintaining a constant electrolyte concentration under the conditions of varying sample conductivities, pH values and Cl^- concentrations. The Design Verification Test would be performed to test the performance of the analyzer during continuous operation over a 30-day period. After disassembly and inspection of the analyzer, it would be reassembled prior to performance of an acceptance test and shipment to NASA Johnson Space Center for extended tests.

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APPENDIX 1 SAMPLE CONDITIONS AND UNCOMPENSATED EOC VALUES FOR VCDS WATER SIMULANTS

	Solution Number															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Conductivity, µmho/cm	24.5	27.6	17.4	7.92	17.4	43.0	36.7	82.6	122.0	86.9	165	146	194	175	280	231
Temperature, C C	22.4	22.6	23.2	23.1	23.3	23.3	23.5	22.0	22.4	22.6	23.0	22.9	23.2	23.1	23.2	23.2
EOC Value,[a]																
0 mg/l TOC	31.4	32.4	26.7	22.6	27.7	31.4	29.9	42.5	44.2	43.7	48.0	48.3	51.0	50.2	52.3	52.7
10 mg/l TOC	45.1	42.8	42.5	47.4	46.0	51.1	52.2	50.6	50.6	57.0	52.3	52.5	56.1	53.4	58.8	56.1

(a) For distilled water sample (0 mg/l TOC) and methanol solution (10 mg/l TOC).