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DEVELOPMENT AND TESTING OF BREADBOARD ELECTROCHEMICAL
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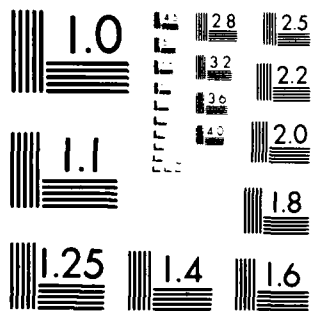
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DEVELOPMENT AND TESTING OF BREADBOARD
ELECTROCHEMICAL ORGANIC CONTENT ANALYZER

FINAL REPORT

By
R. J. DAVENPORT

September 1982

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Manual laboratory instruments have been developed to determine specific organic solute concentrations and general indices of organic contamination. However, development of sophisticated instrumentation for monitoring and control applications has lagged behind the development of laboratory instruments. This is probably due to (1) the added sophistication and development time required to reliably automate the analytical functions, (2) the time required to develop special operator interfaces to simplify control of the instrument, eliminating (Cont.)		

20. (continued)

the need for skilled chemists or technicians, (3) the time required for the development of special electrical interfaces, required in certain applications to permit receiving commands and transmitting status indicators from the instruments to remote operator control panels or to centralize control/monitoring instrumentation, and (4) the time required to develop special features to decrease the frequency of operator maintenance, making it practical to use the instrument in remote locations and in places where skilled maintenance personnel are not available.

The Advanced Breadboard TOC/COD Analyzer was designed with the goal of providing the special features listed above. The Advanced Breadboard incorporates a microcomputer to automate the Analyzer's startup, calibration and shutdown procedures. This simplifies operation and reduces the skill required by the operator. Electrical interfaces are provided to output the Analyzer's status and to receive remote commands. In-situ hydroxide and persulfate generation, and the use of an electrolyte recycle loop were designed to extend to 30 days the period between the resupply of reagents. Therefore, the Advanced Breadboard was designed to achieve a level performance that previously has not been achieved in monitoring and control instrumentation for organic solute monitoring.

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INTRODUCTION

This document summarizes the work performed on the Advanced Breadboard Electrochemical Total Organic Carbon (TOC)/Chemical Oxygen Demand (COD) Analyzer. Since completion of the prior Annual Report. (1)

Manual laboratory instruments have been developed to determine specific organic solute concentrations and general indices of organic contamination. However, development of sophisticated instrumentation for monitoring and control applications has lagged behind the development of laboratory instruments. This is probably due to (1) the added sophistication and development time required to reliably automate the analytical functions, (2) the time required to develop special operator interfaces to simplify control of the instrument, eliminating the need for skilled chemists or technicians, (3) the time required for the development of special electrical interfaces, required in certain applications to permit receiving commands and transmitting status indicators from the instrument to remote operator control panels or to centralize control/monitoring instrumentation, and (4) the time required to develop special features to decrease the frequency of operator maintenance, making it practical to use the instrument in remote locations and in places where skilled maintenance personnel are not available.

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Program Objectives

The objectives of the overall Advanced Breadboard TOC/COD Analyzer development program were as follows:

- 1.0 To design, fabricate and assemble the Advanced Breadboard TOC/COD Analyzer.
- 2.0 To assemble and checkout required Test Support Accessories (TSA).
- 3.0 To establish, implement and maintain a Mini-Product Assurance Program.
- 4.0 To test and evaluate the design and performance of the Analyzer.

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

- 5.0 To perform supporting studies necessary to define design parameters of the Analyzer.
- 6.0 To incorporate the Contractor's data management functions to provide internal procedures for control of the collection, preparation, quality, assessment, distribution and maintenance of data.
- 7.0 To incorporate the management needed to successfully meet the program's Cost, Schedule and technical Performance requirements, to coordinate with the Contracting Officer's Technical Representative (COTR) through telephone discussions and to result in Customer satisfaction.
- 8.0 To design, fabricate, assemble and checkout the Advanced Breadboard Analyzer persulfate generation cell.
- 9.0 To evaluate advanced COD sensor concepts for ultimate incorporation in the Analyzer.

These objectives were accomplished, as reported in the Annual Report.⁽¹⁾ However, the following observations were made during the testing and performance evaluation of the Advanced Breadboard since that report was submitted:

1. The TOC sensor, as originally designed and integrated in the Advanced Breadboard, produced a response having significant short-term variability and a longer-term drift. The short-term variability was traced to formation of bubbles in the internal filling solution within the sensor, which caused resistance changes between the reference and pH electrodes. The voltage output of the sensor varied, depending upon the number and location of these bubbles.

The bubbles were caused by the abrupt movement of the internal filling solution through the sensor body by its fast response accessory.⁽²⁾ These changes in velocity of the internal filling solution (which contains sodium bicarbonate (NaHCO_3)) through the constrictions in the sensor produced pressure changes in the solution that formed carbon dioxide (CO_2) bubbles.

The longer-term drift in response was attributed to contamination of the surface of the pH electrode in the sensor. The design of the sensor, does not lend itself to convenient cleaning or replacement of the pH electrode when needed, since the electrode is sealed in the sensor body.

2. A relatively minor problem relating to electrical noise in the output of the TOC Sensor was detected. The high impedance pH electrode was connected to the signal conditioning logic in the Advanced Breadboard instrumentation package by shielded a cable and connectors, having a total length of approximately three feet. The shielding of the cable was inadequate to prevent the pickup of noise from other electrical components within the Analyzer and Test Stand.

The solution to this problem was quickly recognized to be the incorporation of a preamplifier located close to the pH electrode.

The specific objectives of the efforts performed since the submittal of the last Annual Report were concerned with the resolution of the above problems, and they are listed below:

1. To modify the TOC sensor to eliminate the formation of bubbles within the internal filling solution, and to permit cleaning or replacement of the pH electrode when necessary. This modification was also to incorporate a preamplifier to reduce electrical noise.
2. To continue the testing and evaluation of the Analyzer with the goal of evaluating its TOC measurement capabilities.
3. To evaluate the Analyzer's COD measurement capability, upon completion of evaluation of its TOC measurement performance.
4. To evaluate and select candidate techniques for the elimination of errors in the TOC and COD measurements resulting from the presence of chloride (Cl^-) within the samples. This evaluation was to focus specifically on technique that would be applicable to measuring TOC and COD simultaneously, while using the electrolyte recycle loop in the Advanced Breadboard to minimize consumption of the Analyzer's electrolyte.

The funding available to the Medical Research and Development Command (MRDC) to complete these efforts was decreased during the reporting period, as a result in changes in the MRDC's mission. Therefore, the planned evaluations of the TOC and COD measurement performance and part of the Cl^- removal techniques evaluation could not be completed.

Analyzer Description

The Advanced Breadboard Analyzer was described in detail and its Final Design Report⁽²⁾ and the last Annual Report.⁽¹⁾ Briefly, the Analyzer incorporates six processes' listed below, that are essential for the measurement of TOC and COD with the minimal use of consumables.

1. Electrochemical generation of the persulfate from an acidic electrolyte.
2. Continuous sampling and mixing of the sample with the electrolyte and persulfate.
3. Removal of inorganic carbon (bicarbonate (HCO_3^-), carbonate and dissolved CO_2) from the sample.
4. Oxidation of the organics.
5. Measurement of the CO_2 produced and persulfate consumed in the oxidation.
6. Elimination of the water introduced during sampling from the analyzer.

These processes make it possible to operate the Analyzer without the use of compressed gases and with minimal consumption of reagents. This was considered, during the design of the Analyzer, to be an important consideration since future versions of the Analyzer were intended for use in remote locations.

Other functions were added to the Analyzer for operator convenience, to achieve enhanced Analyzer performance, to demonstrate the capabilities of the functions, or to evaluate their effectiveness. Among these additional features are:

1. A capability for filtering the sample through a 0.45 mm filter to determine dissolved organic carbon.
2. The capability of measuring total carbon (TC).
3. Automated calibration.
4. A fast response accessory within the TOC sensor to achieve faster response dynamics.
5. Electronic aids for simplified operation and maintenance, and more effective integration of the Analyzer in automated water and wastewater treatment processes.

RESULTS

This section summarizes the results of the testing and evaluation that were achieved since the last Annual Report.

Modified TOC Sensor

The membrane electrode concept was originally selected for use in the TOC sensor because it is responsive to CO₂ over the concentration range to be encountered by the Advanced Breadboard.² The membrane electrode is simpler and potentially more reliable than other readily available types of CO₂ detectors.

The TOC sensor determines the concentration of CO₂ contained in the sample/electrolyte mixture. By detecting the pH change caused by the diffusion of CO₂ from the sample/electrolyte mixture into an internal filling solution that contains HCO₃⁻. Sample and internal filling solutions are separated by a gas-permeable membrane. The potential difference between the pH and reference electrodes located in the internal filling solution, is logarithmically proportional to the CO₂ concentration in the sample solution. Automated electronic compensation for temperature changes is accomplished using a thermistor located in the sensor close to the pH electrode.

Steady-state sensor response is obtained when the partial pressures of CO₂ on both sides of the gas-permeable membrane are equal. Like all membrane electrodes, the TOC sensor requires more time for steady-state response to be achieved after the CO₂ concentration in the sample has decreased than when it has increased. This is because diffusion of CO₂ from the stagnant internal filling solution, through the membrane, into the flowing sample stream is slower than the reverse process. This is partly due to the difference in the rate of mass transport of CO₂ to the membrane from a stagnant solution (internal filling solution) and a flowing solution (sample/electrolyte mixture). Additionally, the relatively slow kinetics for the evolution of CO₂ from carbonic acid (H₂CO₃) slows the rate of CO₂ discharge from the internal filling solution. The relative kinetics for the reactions involved in the discharge of CO₂ from the internal filling solution are indicated in Equations 1 and 2:



Relying upon evolution of CO_2 from H_2CO_3 , and then diffusion of CO_2 from the internal filling solution to achieve steady-state sensor response can require more than 50 minutes when the TOC concentration of the sample decreases from 100 to 1 ppm TOC. In order to reduce this time, a fast response TOC sensor accessory was developed and incorporated into the Advanced Breadboard. This accessory consisted of a solenoid pump, internal filling solution reservoir and required circuitry. It was based on the principle that the internal filling solution within the sensor would be mechanically replaced with fresh solution from the reservoir every three minutes. Each TOC measurement was made immediately before the filling solution in the sensor was replaced. Therefore, after each TOC measurement, the pH electrode within the sensor was exposed to fresh internal filling solution that never has a higher CO_2 concentration than that in the sample/electrolyte mixture. Carbon dioxide always diffused from the sample/electrolyte mixture into the internal filling solution.

Once the internal filling solution was removed from the sensor, equilibration with air removed the excess CO_2 in the internal filling solution reservoir, and the filling solution attained its original composition.

The original TOC sensor proved the effectiveness of the fast response accessory. The response of the sensor to decreasing TOC concentrations was virtually the same as for increasing concentrations. The only problem with it was the formation of the CO_2 bubbles, as discussed above.

The design of the TOC sensor was modified to utilize a standard, laboratory-style, flat-surface combination pH and reference electrode. The solenoid pump, used in the fast-response accessory for the original TOC sensor, was eliminated to prevent the formation of CO_2 bubbles in the internal filling solution. The modified sensor also incorporated a preamplifier located at the pH electrode to eliminate objectionable electrical noise.

Figure 1 is a schematic of the modified TOC sensor. The sensor is designed for the sample solution to flow through it, with an upward angle to permit bubbles in the sample/electrolyte mixture to pass through the sensor without being trapped within it. The internal filling solution is separated by the gas permeable membrane from the sample/electrolyte mixture in the same manner as the original sensor. The pH electrode is positioned close to the membrane and is separated from the membrane by a thin film of the internal filling solution. The major difference in the design of the sensor from its predecessor is that the internal filling solution does not flow past the pH electrode; rather, the electrode moves up and down in the sensor, after each measurement causing the internal filling solution in the space between the membrane and the electrode to be replaced by fresh solution.

The electrode is raised by means of a solenoid and then is immediately lowered to its original position by means of a spring. The up and down plunging action of the electrode mechanically replaces the liquid between it and the membrane, and has exactly the same effect as that originally achieved by using a solenoid pump to force liquid past the surface of the electrode.

Since the thin film of internal filling solution that contains the high concentration of CO_2 is a small volume compared to the volume of the internal filling

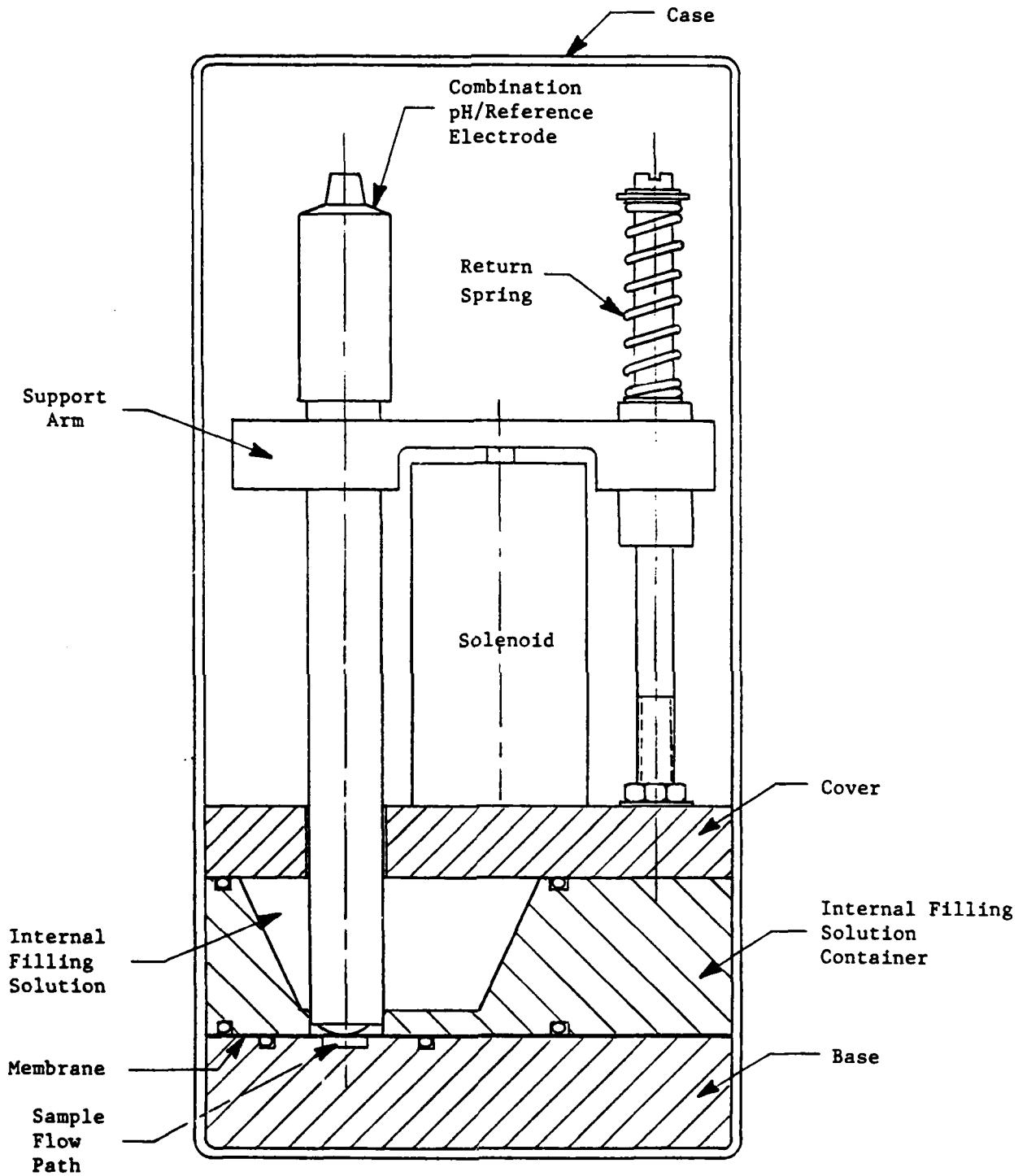


FIGURE 1 MODIFIED TOC SENSOR

solution, a significant dilution takes place. The surface of the internal filling solution is in contact with ambient air, and a CO₂ absorber is located over the solution to remove CO₂ discharged from the internal filling solution. Throughout the testing program no accumulation of CO₂ in the internal filling solution was observed (as indicated by the lack of drift in sensor response), even after several hours of operation.

The pH/reference combination electrode is commercially available and therefore could be replaced when necessary. Furthermore, it could be quickly removed from the sensor and easily cleaned, should that be required.

The preamplifier is mounted inside a grounded metal cover, and located adjacent to the TOC sensor. This eliminates the pick up of noise from the other electrical components in the Analyzer and Test Stand.

Tests of the Analyzer's response to solutions containing CO₂ demonstrated that the sensor provided the same sensitivity and linearity of response demonstrated by the other breadboard versions of the TOC sensor tested earlier. (1)

Organic Oxidation Efficiency

With the modified TOC sensor integrated in the Analyzer, and providing precise, reliable measurements of the CO₂ produced in the Analyzer from the oxidation of organic solutes, it was possible to accurately evaluate the performance of the Analyzer in oxidizing organic solutes in the sample solutions. Because the prior TOC sensor had not performed adequately, certain data obtained with it was reproduced using the modified sensor.

Figure 2 shows the response of the Analyzer with the modified TOC sensor to solutions containing concentrations between 0 and 300 ppm TOC of potassium hydrogen phthalate (KHP), methanol and urea.

Although the Analyzer had undergone the automated calibration sequence prior to the measurements, it is apparent from Figure 2 and the fact that all three curves are above the theoretical line that the calibration was not accurate. Also, if the organics had all been oxidized with 100% efficiency, all data points would fall along that theoretical line. Instead, three curves were obtained, indicating that methanol was oxidized more efficiently than urea, and urea was oxidized with somewhat greater efficiency than was KHP.

Since previous breadboard versions of the Analyzer had achieved quantitative oxidation of all of these organics, it was concluded that the non-quantitative oxidation demonstrated in Figure 2 was the result of the Advanced Breadboard Analyzer operating at non-optimum conditions.

Figure 3 contains data obtained from an investigation of the effect of the acidity of the electrolyte on KHP oxidation efficiency. Since the TOC sensor response, in mV, increases with increasing CO₂ concentrations, it can be seen from Figure 3 that the efficiency of the oxidation increases with decreasing acid strength. An optimum oxidation efficiency with respect to acidity is projected to be between 0.1 and 0.5 M acid.

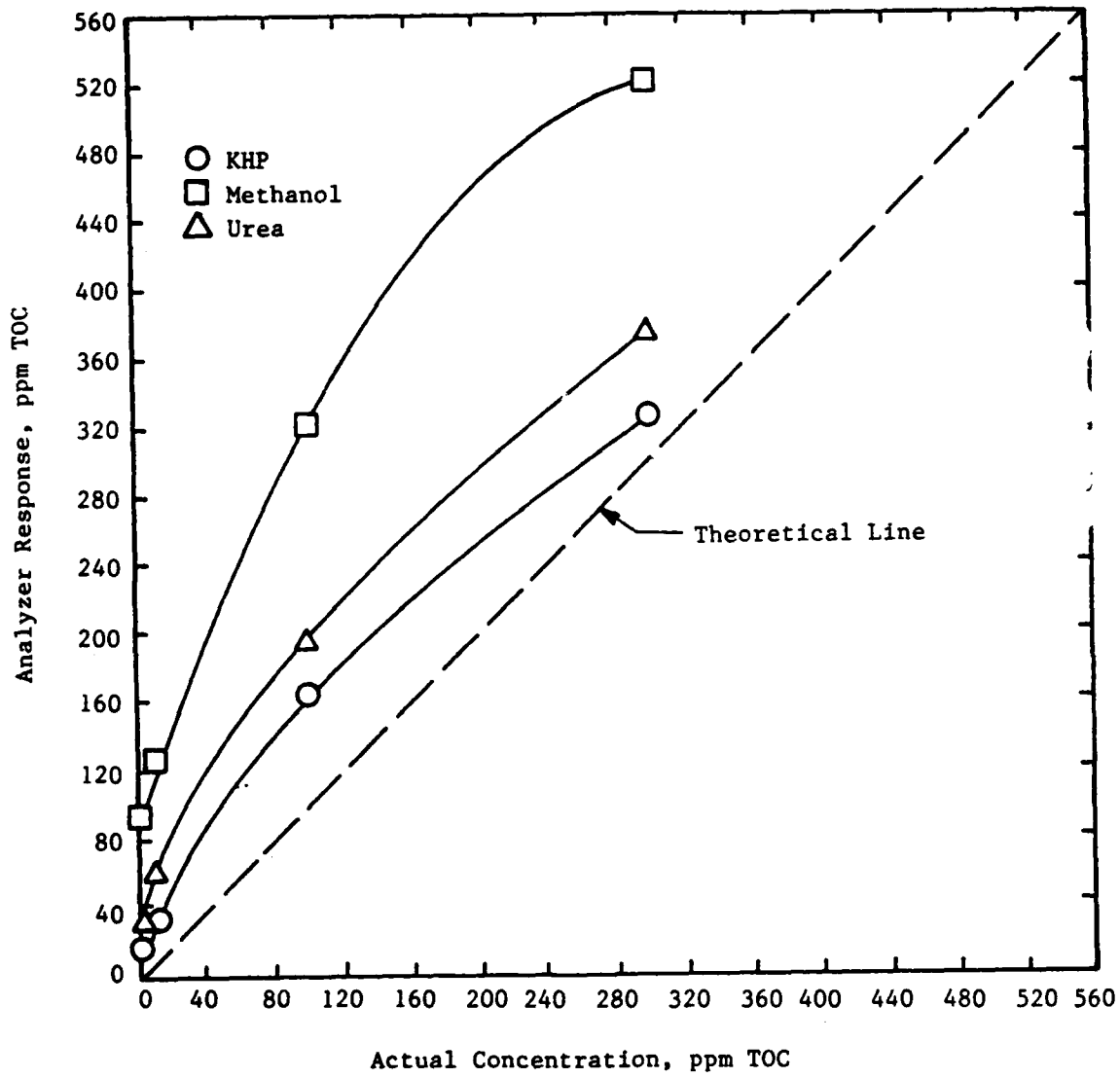


FIGURE 2 ORGANIC RESPONSE TEST

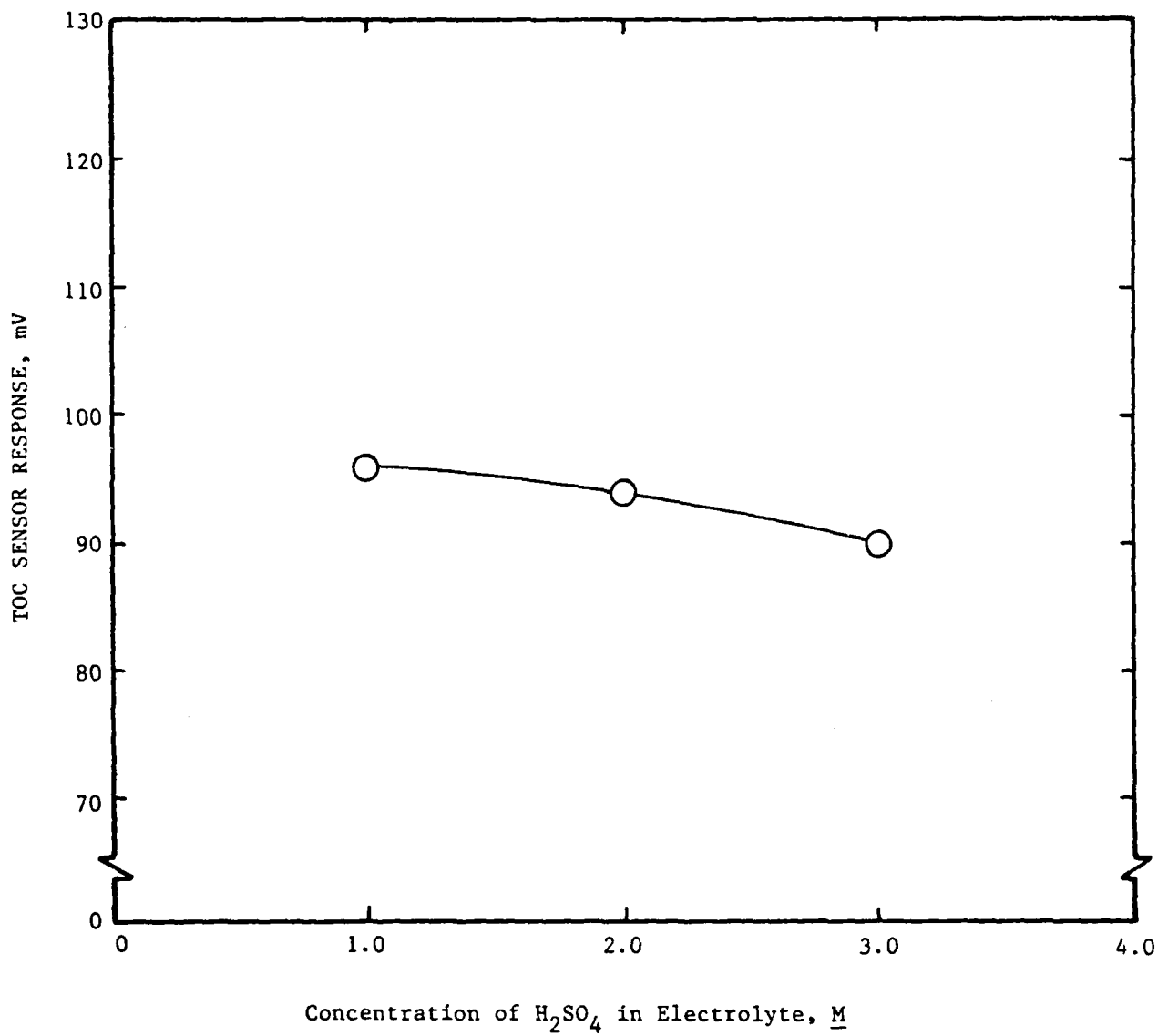


FIGURE 3 OXIDATION OF KHP AS A FUNCTION OF ELECTROLYTE ACIDITY

The design point for acidity in the electrolyte was selected at 2 M for the Advanced Breadboard since the efficiency of electrochemical generation of persulfate is the maximum at that concentration. Therefore, the energy requirements and dimensions of the persulfate generator are minimized for that electrolyte concentration. The data in Figure 3 suggests that the size and power requirements of the ultraviolet (UV) reactor could be minimized if lower acidities were used in the electrolyte. Therefore, a trade-off analysis should be performed to determine the optimum electrolyte acidity for the Analyzer as a whole.

Analyzer Response Time

The inaccuracy of the automated calibration process, as illustrated in Figure 2, was investigated. The time required for the Analyzer to achieve steady-state response to the standard solutions used for calibration was found to be substantially longer than the time period allocated for it in the automated calibration sequence. The Analyzer required 210 minutes to achieve a steady-state response, in going from a sample containing a high concentration (100 ppm TOC) to a lower concentration (10 ppm). Therefore, when the Analyzer was exposed to a sample containing a high concentration, and then entered the calibration sequence in which the first standard, containing 10 ppm TOC, was introduced into the Analyzer, instead of the 20 minutes allocated by the automated calibration sequence, a period almost 10 times longer was required for steady-state response to the standard solution to be achieved.

It was not possible to isolate the cause of this larger than expected response time. The expected response time was, however, calculated assuming plug-flow conditions for the solution going through the Analyzer. Due obvious possibility is that the flow of the sample/electrolyte mixture through the Analyzer components markedly differs from a plug-flow condition. The interface between a sample solution containing a high TOC concentration, and a sample solution introduced into the Analyzer later having a very low TOC concentration, may simply mix as it passes through the Analyzer to such an extent that there is a concentration gradient in the solution as it flows through the UV reactor and TOC sensor.

A second possibility is the absorption (or partitioning) of the organic solutes in the sample/electrolyte mixture onto (or into) the materials wetted by the solution. If this occurs, it may be that when the sample/electrolyte mixture contains a much lower concentration than the original solution, the organic solutes are released from the wetted materials into the sample/electrolyte mixture, causing a slow and gradual concentration change.

The sample/electrolyte mixture comes into contact with the peristaltic pump tubing (rubber) and polysulfone used for the fabrication of the bodies of several of the components. The solution also contacts Teflon tubing between the sample inlet and sample filter, and between all Analyzer components. Teflon is noted for its resistance to attack by corrosive chemicals. Because of this, it is seldom considered a material that would adsorb significant amounts of organic material. It nevertheless may be partially responsible for the observed result, especially if it is somewhat porous and the results that have been reserved are caused by partitioning of organic solutes between (1) the solution trapped in microscopic pores in the tubing and (2) the bulk of the solution passing through the tubing.

Chloride Removal Techniques

Chloride interferes with both TOC and COD measurements when they are made using the UV-catalyzed oxidation of organics by persulfate. The TOC measurement is subject to high errors caused by the oxidation of Cl^- to chlorine (Cl_2), and the subsequent diffusion of Cl_2 through the gas permeable membrane into the internal filling solution. There, the Cl_2 is hydrolyzed to form hydrochloric acid (HCl) which causes the same pH change as does high CO_2 (i.e., high TOC) concentrations. The COD measurement is also subject to high errors caused by the consumption of persulfate, as it oxidizes Cl^- to Cl_2 .

During the period summarized in this report, several techniques for eliminating Cl^- from the sample were evaluated for use in the Analyzer. Each technique was evaluated on the basis of its compatibility with use in the Advanced Breadboard Analyzer, measuring both TOC and COD, and the use of the electrolyte recycle loop to minimize consumption of the Analyzer's electrolyte.

Table 1 lists the priorities used in the evaluation, and Table 2 lists the results of the evaluation of each technique with respect to those important characteristics.

CONCLUSIONS AND RECOMMENDATIONS

The modified TOC sensor has successfully achieved the performance goals established for it. It has demonstrated the precision and response stability necessary for use in the Advanced Breadboard. Because of this improvement in the performance of the TOC sensor, characteristics of the Analyzer as a whole have been detected that were previously not noticeable. The data so far obtained with the modified TOC sensor, integrated in the Advanced Breadboard, indicate that all organics may not be totally oxidized at the operating conditions selected for use in the Advanced Breadboard. Although this has not been verified, the apparent oxidation of the three organics tested is consistent with the expected reactivity of those chemicals in an oxidizing environment.

The response of the Advanced Breadboard has also been shown to be slower than anticipated when it encounters abrupt changes in the concentration of the sample. The exact cause or causes of this have not been unequivocally determined. However, it is likely to be a combination of (1) non-plug flow conditions, caused by the extremely low linear flow rate of fluids through the Analyzer and the tortuous fluid passages in components such as the inorganic carbon stripper, and (2) adsorption (or partitioning) of organics on (or in) the wetted materials in the Analyzer.

If the adsorption (or partitioning) phenomenon occurs, it is highly likely that the material most susceptible to it is the rubber peristaltic pump tubing. One of the activities that is suggested by this conclusion is an evaluation of rearrangements of Analyzer components that would locate the pump downstream of the TOC sensor. In this arrangement the organics would not come in contact with the pump tubing because they would first pass through the UV reactor where they would be oxidized.

TABLE 1 CHLORIDE REMOVAL TECHNIQUES EVALUATION CRITERIA

<u>Priority</u>	<u>Criteria</u>
1	Effective in eliminating Cl^- error in TOC measurements.
2	Effective in eliminating Cl^- error in COD measurements.
3	Removes Cl^- from sample stream, with residual Cl^- concentration of less than 1 ppm.
4	Does not significantly change the TOC and COD concentrations in the sample.
5	Does not discharge substances that are potentially hazardous to the environment.
6	Does not remove particulates (which may have adsorbed or accluded organic material) from the sample stream.
7	Does not significantly increase the complexity or development time of the Analyzer.
8	Removes Cl^- from the sample/electrolyte mixture, rather than allowing the concentration of Cl^- in the electrolyte to increase as the electrolyte is recycled.
9	Does not significantly increase the Analyzer's response time with respect to changes in TOC and COD concentrations.
10	Does not significantly increase the volume of the sample required for analysis.

TABLE 2 EVALUATION OF CANDIDATE CHLORIDE REMOVAL TECHNIQUES

Criteria	Evaluation (a)					
	Cl ⁻ Precipitation	Cl ⁻ Complexation	Reverse Osmosis	Anion Exchange	Electro- deposi- tion	Electro- dialysis
1. Effective for TOC	B	A	A	A	A	A
2. Effective for COD	B	A	A	A	A	A
3. Efficiently removes Cl to less than 1 ppm.	A	A	B	A	A	A
4. TOC and COD concentrations unchanged.	D	A	C	D	D	C
5. No hazardous discharges.	E	E	A	A	A	A
6. Particulates not removed.	E	A	A	E	B	A
7. Complexity and development time not significantly increased.	E	B	E	D	D	D
8. Cl ⁻ does not build up in electrolyte recycle loop.	A	E	A	A	A	A
9. Response time not significantly longer.	C	A	D	D	D	D
10. Sample volume not significantly larger.	C	A	C	C	C	C

(a) Key: A = Satisfies criteria.
 B = Likely to satisfy criteria.
 C = May or may not satisfy criteria -- needs to be demonstrated.
 D = Unlikely to satisfy criteria.
 E = Does not satisfy criteria.

Another way of decreasing the response time is to increase the flow rate of sample and electrolyte through the Analyzer. This approach bears investigation, but any investigation must include an evaluation of the effect that increasing the flow rate would have on the dimensions and power consumption of the inorganic carbon stripper, the UV reactor, the persulfate generator and the water removal unit.

Another effort suggested by the data is an evaluation of the impact on the Analyzer of decreasing the electrolyte acidity to increase its oxidation efficiency. It has previously been shown that this action would decrease the efficiency of persulfate generation, thereby resulting in an increased power consumption. However, the overall effect on the Analyzer may be a benefit.

The evaluation of techniques for elimination of the Cl^- interference has not been completed. At this point electrodialysis appears to be one of the few techniques that are compatible with both TOC and COD measurements and with the use of the electrolyte recycle loop.

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