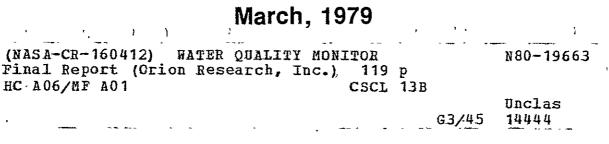
8.0-10.0.57 CR-160412

WATER QUALITY MONITOR

FINAL REPORT

by

Steven West, John Crisos, Wilfred Baxter



Prepared Under Contract NAS9-14229

by

Orion Research, Inc 380 Putnam Avenue Cambridge, Massachusetts 02139

for

LYNDON B. JOHNSON SPACE CENTER National Aeronautics and Space Administration NASA Contract NAS 9-14229 WATER QUALITY MONITOR

> Final Report March, 1979

Authors: Steven West, John Chrisos, Wilfred Baxter

Orion Research, Inc. 380 Putnam Avenue Cambridge, Massachusetts 02139

TABLE OF CONTENTS

			PAGE
SUMMARY			1
PROGRAM ACCON	MPLISHM	ENTS	ii
СН. 1	INT	RODUCTION	1.1
		Program Objectives	1.2
		Water Quality Monitor Concept	1.3
CH. 2	WAT	ER QUALITY MONITOR DESIGN SPECIFICATIONS	2.1
сн. з	WAT	ER QUALITY MONITOR SYSTEM DESCRIPTION	3.1
		Fluidic System	3.1
		Electronics	3.8
	•	Photo Section	P-1 to P-17
	•	WQM Operation Specifications and Physical Data	3.16
CH. 4	WAT	ER QUALITY MONITOR HARDWARE DEVELOPMENT	4.1
		(Breadboard to Preprototype Modifications)	
CH. 5	EVA	LUATION AND TESTING	5.1
CH. 6	CON	CLUSION AND RECOMMENDATIONS	6.1
Appendices:	I	Statement of Work Requirements	I.1
	II	Failure Modes and Effects Analyses	II.1
	III	Instruction Manual	III.]
	IV	Background Literature	

LIST OF FIGURES

Figure		Page
1.1	WQM Plumbing Diagram	1.4
3.1	Flow Sensor	3.11
3.2	Flow Sensor Circuitry	3.12
4.1	Flow-Thru Capillary pH Sensor	4.6
4.2	Flow-By Capillary pH Sensor	4.6
4.3	Flow Sensor Response	4.8
5.1	Pressure Regulator Test Set Up	5.5

LIST OF TABLES

Table		Page
5.1	Materials Tested for Intended Use on NASA WQM	5.2, 5.3
5.2	Master Test Plan Solution Results	5.6, 5.7

LIST OF PHOTOS

рното		
1	Electronics Packages	P-1
2	Fluid Package	P-1
3	Top-View, Fluids Package	P-2
4	Reagents Section	P-2
5	Valve Manifold	P-3
6	Peristaltic Pump	P-3
7	Close-Up of Input Tubing Manifold	P-4
8	Flow Sensor Block	P-4
9	Sensor Manifold, Top View	P-5
10	Sensor Manifold, Bottom View	P-5
11	Sensor Manifold, Side View	P-6
12	Sensor Manifold, Side View	P-6
13	Input Pressure Regulator	P-7
14	Filter	P-7
15	Conductivity Cell	P-8
16	PH Electrode	P-8
17	PH Capillary	P-9
18	Mixer Block	P-9
19	CO ₂ Stripper, Acidic Half	P-10
20	CO ₂ Stripper, Basic Half	P-10
21	UV Lamp	P-11
22	Quartz Coil	P-11
23	UV Chamber	P-12
24	CO ₂ or NH ₃ Sensor	P-12
25	Flow Sensor Assembly	P-13
26	Conductivity Circuit Board	P-13

PAGE

LIST OF PHOTOS (Continued)

PAGE

<u>PHOTO</u>		
27	NH ₃ Auto-Cal Board	P-14
28	Flow Sensor Board	P-14
29	NH ₃ or TOC Anti-log Circuit Board	P - 15
30	"Time-Out" Board	P-15
31	Relay Logic Circuit Board	P-16
32	Mode Control Circuit Board	P-16
33	Electronic Controller, Rear View	P-17
34	Waste Tubing Manifold	P-17

LIST OF ACRONYMS

~

WQM	Water Quality Monitor
RLSE	Regenerative Life Support Evaluation
тос	Total Organic Carbon
NH ₃	Ammonia
ASME	American Society of Mechanical Engineers
со ₂	Carbon Dioxide
РРН	Pounds Per Hour
LED	Light Emitting Diode
UV	Ultraviolet
FS	Flow Sensor
hso ₅	Peroxymonopersulfate
SS	Stainless Steel
STD	Standard
AC	Alternating Current
PTFE	Polytetrafluoroethylene
VDC	Volts, Direct Current
DST	Design Support Testing

SUMMARY

The preprototype Water Quality Monitor (WQM) subsystem was developed as part of the Regenerative Life Support Evaluation (RLSE) Program. This unit was designed based on the technology and use of components resulting from a breadboard monitor for pH, specific conductance, and total organic carbon (TOC). The breadboard equipment demonstrated the feasibility of continuous on-line analysis of potable water for a spacecraft. The preprototype WQM subsystem, designed by Orion Research, Inc., incorporated these breadboard features and, in addition, measures ammonia and includes a failure detection system.

The WQM samples water continuously using a peristaltic pump to meter the sample, reagent, and standard solutions to the analytical system. These fluids are delivered to the sensing manifold where chemical operations and measurements are performed using flow through sensors for conductance, pH, TOC, and NH₃. Fault monitoring flow detection is also accomplished in this manifold assembly. In the interest of rapid response, all components, assemblies and interfaces `handling the fluids were designed to have minimum hold-up volumes.

The WQM is designed to operate automatically using a hardwired electronic controller. This controller provides the necessary electronics to control and readout pH, TOC, specific conductance, and NH₃. In addition, automatic shutdown is incorporated which is keyed to four flow sensors strategically located within the fluid system. Automatic calibration is accomplished every six hours and lasts 15 minutes.

i

PROGRAM ACCOMPLISHMENTS

- Successfully integrated breadboard system and proven sensor components into a modularized structure representative of flight hardware.
- o Minimized reagent consumption, thus reducing system weight due to expendable requirements.
- o Incorporated reliability by minimizing the number of connections and tubes by using a manifold base plate assembly.
- o Incorporated a failure detection system utilizing ultrasensitive flow sensors located at strategic points in the fluid system.
- Identified an elastomeric peristaltic pump tubing material which resists chemical attack from the reagent solutions, resulting in demonstrated pump tubing life over 75 days.
- Demonstrated a total of 30 days of successful in-house operation design verification and baseline testing.

CHAPTER 1. INTRODUCTION

This report describes the development of a Preliminary Prototype Water Quality Monitor by Orion Research, Inc. under NASA Contract NAS 9-14229. Initial work on this contract resulted in production of a breadboard monitor for pH, specific conductance, and total organic carbon (TOC). This unit demonstrated the feasibility of continuous on-line analysis of potable water within the restrictive specifications of spacecraft use. Upon completion of the breadboard work, the contract was modified to include the development of a "Preliminary Prototype" instrument, one in which the design considerations for the fluid-handling and sensing systems were those of space hardware. The preprototype system also measures ammonia, and includes a failure detection system.

Included in Appendix I are pertinent paragraphs from the original Statement of Work, as well as from the contract modifications and the preprototype Design Review. These provide background information pertaining to the scope and purpose of our work. A detailed account of the breadboard development is contained in the "Interim Report on the Breadboard Water Quality Monitor" which is available from Orion, and additional information is contained in copies of two ASME publications in the Appendix. This report concentrates specifically on work connected with the "preprototype phase" of development and completes the documentation of this contract.

PROGRAM OBJECTIVES

The primary program objective was to develop an improved Water Quality Monitor Subsystem for assessing water purity on advanced spacecraft where water stores are recycled. The preprototype Water Quality Monitor was to be designed with the same basic operating principles that were successfully incorporated into the breadboard system, but with the following improvements:

- Integration of the system components into a modularized flight representative package.
- 2. Minimization of reagent consumption.
- 3. Improvement in reliability.
- 4. Minimization of fluid connections and tubing.
- 5. Improvement in sensor design.
- 6. Incorporation of a failure detection system.

12

WATER QUALITY MONITOR CONCEPT

The water quality monitor concept is depicted in block diagram form in Figure 1.1. The water sample enters the system through a pressure regulator and a particulate filter. The sample is then split into two streams before entering the pump. One sample stream goes to a conductivity cell where the specific conductance is measured. Then the acidified monopersulfate solution is added, lowering the pH and providing an oxidizing agent. The other sample stream goes to the pH sensor where the pH is determined. The sodium hydroxide is then added and the stream is agitated in a mixer. This results in a basic sample stream, which is necessary for the determination of ammonia in the ammonia sensor. The two streams, one basic and one acidic, then enter the stripper on opposite sides of a gas permeable membrane. The inorganic carbon in the acidic stream diffuses as carbon dioxide across the membrane where it is fixed as carbonate. In this way, inorganic carbon species in the sample is removed prior to determination of organic carbon. The acidified sample then goes to the UV digester where the action of the UV light and the oxidizing agent serve to oxidize all of the organics in the sample to carbon dioxide. The $\rm CO_2$ concentration is measured by a gas-sensing CO, electrode. This measurement is proportional to the organic carbon concentration of the original sample. Periodically, standards A and B are introduced into the system in place of the water sample to permit automatic system calibration. Four flow sensors are located at strategic places on the fluid lines to detect failures resulting from a fluid leak, an occluded channel, or a failed pump tubing.

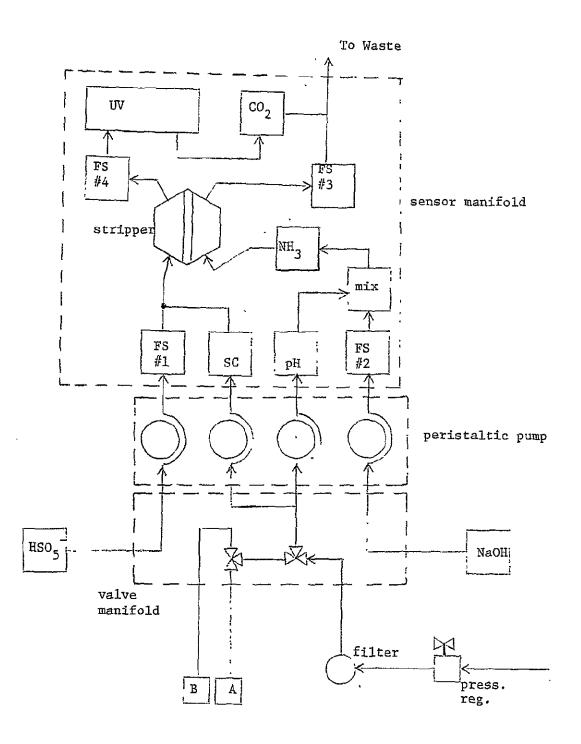


Figure 1.1 WQM Plumbing Diagram



2.1 Design Considerations

2.1.1 Water Quality Monitor Specifications Goals -

As a goal, the water quality monitor shall meet the following specifications when tested at the water conditions defined in section 2.1.2.

2.1.1.1 Range and Precision

pH	4 to 10 <u>+</u> .1
Conductivity	.l to 1000 µmho/cm <u>+</u> 5% or
	$\dot{\pm}$ 1 µmho (whichever is greater)
Ammonia Content	.1 to 50 ppm <u>+</u> 2% or <u>+</u> .5 ppm
	(whichever is greater)
TOC Content	1 to 100 ppm <u>+</u> 10% or <u>+</u> 1 ppm
	(whichever is greater)

2.1.1.2 <u>Response Time</u>

pH	2 minutes
Conductivity	2 minutes
Ammonia Content	2 minutes
TOC Content	5 minutes

2.1.1.3 System Operation

<u>Capacity</u> : 30 o	lays continuous automatic water quality
moni	itoring.
Calibration:	Automatic calibration of all four measurement
	parameters at set time intervals. Manual
	initiation of calibration when desired.
Fail Safe:	Automatic safe shutdown in event of system
	failure.

3

2.1.1.3 System Operation (Continued)

Read-Out: Direct-reading digital display, 0-5 volt d.c. signal output.

2.1.1.4 <u>System Design</u> Minimum weight, power, and volume. Minimum consumption of expendables and water.

2.1.2 <u>Water Quality and Supply Characteristics</u>

2.1.2.1 Sources

Urine Water Recovery Subsystem CO₂ Reduction Subsystem

- 2.1.2.2 Flow Rate, CC/MIN (PPH) Nominal 15 cc/min (1.98 PPH) Maximum 23 cc/min (3.04 PPH) Minimum 0
- 2.1.2.3 <u>Water Supply Pressure</u> Maximum 15 psig Minimum 10 psig

2.1.2.4 Temperature

- Nominal 32.2 (90°F)
- Maximum 35.0 (95[°]F)

Minimum 29.4 (85[°]F)

2.1.2.5 Fail Safe

Automatic safe shutdown in event of system failure.

2.1.2.6 Read-Out

Direct-reading digital display, 0-5 volt d.c. signal output.

2.1.2.7 Instrumentation and Data Display

	Data	Range	Display
1.	рH	4 to 10 <u>+</u> .1	Digital, LED
2.	NH 3	.1 to 50 ppm <u>+</u> 2% or	Digital, LED
	~	<u>+</u> .5 ppm (whichever is	
		greater)	
3.	TOC	1 to 100 ppm <u>+</u> 10% or	Digital LED
		<u>+</u> lppm (whichever is	
		greater)	
4.	Conductivity	.1 to 1000 mho/cm <u>+</u> 5%	Digital, LED
		or <u>+1</u> mho (whichever	
		is greater)	
5.	Fluid	Reagent - 3.5 ml/hr	Edgewise Meter
	Flow	<u>+</u> .5 ml/hr	High-Low Indicator
	Rates	Sample & Reagent	
		18.5 m1/hr <u>+</u> 5 m1/hr	

2.3 7

CHAPTER 3. WATER QUALITY MONITOR SYSTEM DESCRIPTION

Fluidic System

The preprototype WQM consists of three packages. Two of these contain the operation and read-out electronics and the third is the fluid-handling package.

The fluid system is the heart of the WQM and represents the bulk of the contractual effort. The design of the fluidic system represents a dramatic departure from that of current commercial instrumentation. The high degree of reliability demanded for spacecraft hardware necessitated the elimination of plastic tubing, threaded fittings, etc., so the WQM fluidic system is designed around a manifolding concept. The fluid system is best described as four principal assemblies.

The first is the <u>fluid input assembly</u>. It acts as the interface between the WQM and the potable water supply. It consists of a pressure regulator for the sample and a valve manifold which interfaces 2 reagents, 2 standardizing solutions and the sample to the pump.

The peristaltic pump is used to meter the sample, reagent and standard solutions to the analytical system.

The <u>sensing manifold</u> is where the chemical operations and measurements occur. Flow-thru sensors for conductance, pH, TOC, and NH₃, as well as for flow rate monitoring are located here. The components are designed in the form of individual blocks which are bolted and oring sealed to a master block which contains the appropriate geometry of conduits.

The <u>UV chamber</u> is a separate fluid component, not integral with the sensing manifold because of its thermal characteristics.

In general, all of the components, assemblies and interfaces which handle the fluids are designed to have a minimum hold-up volume in order to promote rapid responses to changes in sample composition at low flow

3.1

rates. Fluid conduits are in the order of 0.75 mm I.D. wherever possible, and in some instances such as in the CO_2 stripper and sensor orifices are as small as 0.2 mm in width.

Fluid Input Assembly

The fluid handling system is depicted in Figure 1.1. The WQM transports five fluids in its various modes of operation -sample, 2 reagents, and two standardizing solutions. The sample enters the monitor at a specified pressure range of 10-15 psia. and passes first through a pressure regulator (Go, Inc., Photo 13.) where the sample pressure is reduced to 2 psia. The sample is drawn from the regulator and through a small in-line filter (Angar Scientific) by a peristaltic pump (Photo 6) and through a tubing manifold (Photos 5,7) where the 4 other fluid lines are connected. These four lines are from the reagent and standard containers located below the base plate (Photo 4). All five tubing lines are 0.75 mm I.D. 316L SS and are welded to the tubing manifold plate which is also 316L.

The fluid lines pass straight through the tubing manifold into the polysulfone block of the valve manifold (Photo 5). These blocks are bolted together and the fluid interfaces are sealed with Viton o-rings. The two reagent lines pass directly through the valve manifold into two channels of the four channel peristaltic pump.

The sample enters the "normally open" port of a three-way miniature solenoid valve. In the normal "on-line" condition, the sample flows out the "common" port of the valve to a "tee" which is integral with the block and where it is split and drawn through the remaining two channels of the pump. The first standardizing solution "STD A" is plumbed to the "normally open" port of a second valve, the "common" port of which is connected to the "normally closed" port of the first valve. The second standard solution "STD B" runs to the "normally closed" port of the second valve. Thus when the valves are not energized, sample solution is pumped. When only the first valve is energized, STD A is pumped, and when both valves are energized STD B is pumped.

The solenoid valves were constructed integrally with the polysulfone blocks by Angar Scientific, Inc. The valve manifold is bolted to

3,2

the pump frame and the four exiting fluid lines are interfaced with Viton o-ring seals.

Peristaltic Pump

The peristaltic pump (Photo 6) was designed with extra caution for this application. Only in this component does the transport of fluids through elastomeric tubing occur, and therefore it is the area of highest. risk in terms of leakage. Extensive testing of pump tubing was required in order to ensure reliability over thirty days of continuous pumping and these test results are contained in Chapter 5. We selected 1.5 mm I.D. silicone rubber for the sample channels and 0.75 mm I.D. Elkay (peroxide cured Viton) for the reagent channels. These tubes provide flow rates of 12 and 4 m1/hr respectively.

The pump housing and frame are 316L SS and the rollers and pressure plates are Teflon coated SS. The four pump tubes are clamped to SS barbed fittings which are welded to the frame on both the input (valve manifold) and output sides of the pump. The tubes lie across spring loaded pressure plates, and the roller carriage-motor assembly is bolted down, pressing the tubes against the pressure plates to a specified spring loading which provides sufficient pumping pressure without excessive tubing wear. The AC synchronous motor rotates the carriage and drives a planetary gear system which rotates each of the twelve rollers so as to eliminate abrasion of the tubing. The tubing, tefloncoated rollers and pressure plates are lubricated with silicone oil to further reduce friction. When the pump is not running, the pressure plate assembly can be disengaged with a knurled bolt located on the bottom of the pump, so that the tubing will not remain compressed.

. The entire pumping assembly is housed in a stainless steel shell which is sealed with Viton o-rings. In the event of a pump tube rupture, no fluid will escape the pump and become a hazard to crew safety.

Sensor Manifold

All of the chemical operations of the WQM except the UV digestion occur in the sensing manifold, which is machined from polysulfone

3.8

(Photos 9, 10, 11, 12). The individual components are bolted to the main block and all fluid interfaces are Viton o-ring sealed. The sensing manifold contains the following components: specific conductance sensor, CO₂ stripper assembly, TOC sensor, pH sensor, NH₃ sensor, two thermal flow sensors, magnetic mixer and waste block.

The general plumbing scheme (Figure 3.1) of the monitor is largely determined by the TOC measurement requirements because this analysis requires the greatest number of operations to be performed on the sample solution. In the TOC determination the inorganic carbon $-H_2CO_3$, CO_2 , HCO_3^{-} and CO_3^{-} - must be removed from the sample so that it will not be measured as TOC. This requires the use of an acid reagent to free the inorganic carbon from the sample, and an alkaline reagent to absorb it. After removal of inorganic carbon, the oxidation of organic carbon is carried out, and then the TOC (CO_2) measurement is taken. The measurement of specific conductance, pH, and NH₃ is accomplished by the proper location of these sensors within the flow pattern dictated by the TOC measurement.

The sensing manifold interfaces with the pump via a SS block which contains two thermal flow sensors (Photo 8). The stainless steel block contains straight conduits (0.75 mm I.D.) for the four fluid lines exiting the pump, and each is Viton o-ring sealed to the pump at the input ends and to the sensing manifold at the output ends. Thermal flow sensors are potted into this block on the two reagent lines.

Once split in the valve manifold, the two sample lines do not meet again until they enter the waste block. Thus, the analytical system of the WQM can be considered as two nearly independent and parallel systems, which we refer to as the "acid" and "base" sides.

The TOC and specific conductance measurements are made on the acid side. This sample portion is pumped into the manifold and flows first to the conductivity block (Photo 15). This sensor consists of two 6 mm lengths of thinwalled platinum tubing (0.75 mm I.D.) which are cast by a "lost-epoxy" technique into an acrylic block. The fluid flows in series through the platinum tubes which act as electrodes, and the acrylic block is bolted to the manifold. The sample describes a "U- like" path through the sensor and re-enters the manifold where it meets the acid-oxidant in a "tee". The combined streams then flow through the block to the CO₂ stripper.

The CO_2 stripper (Photos 19 and 20) consists of two 316L SS plates with mirror-image channels milled in their opposing surfaces. A CO_2 permeable membrane is sandwiched between the plates resulting in two parallel fluid paths which are separated only by the membrane. The CO_2 diffuses readily out of the acidified solution, crosses the membrane and is trapped by the other sample stream which has been basified and flows through the opposing channel. Volatile organics do not transfer because their activities are equal on each side of the membrane. Volatile organic acids such as formic and acetic do not transfer to a measurable extent because their vapor pressures are too low for significant diffusion to occur in the 30 sec. residence time in the stripper.

The acidified sample stream exits the stripper and flows through a thermal flow sensor which is housed in a SS block and is bolted to the outside of the stripper (Photos 9 and 12). The sample re-enters the polysulfone manifold and then exits to the UV chamber. The sample re-enters the manifold after irradiation and flows through the CO_2 (TOC) sensor (Photo 24). The CO_2 sensor consists of a capillary pH electrode (Photo 17) which is in contact with an aqueous NaHCO₃ electrolyte. The electrolyte and capillary are separated from the irradiated TOC sample by a silicone rubber membrane. Equilibration of the sample CO_2 with the NaHCO₃ reservoir across the membrane results in an electrode output proportional to the log of the CO_2 concentration. The sensor is housed in an acrylic block and is bolted to the manifold. The sample follows a "U-like" path through the sensor and flows back into the manifold. It passes then to a SS waste block where it is combined with the other sample portion. The mixed effluent then flows to a waste accumulator.

The pH and NH₃ measurements are made on the "base" side of the unit. This sample stream enters the polysulfone block and immediately exits to the pH electrode (Photo 16). This sensor also utilizes a capillary pH electrode and is geometrically identical to the CO₂ sensor, however, in this case the electrode contacts the sample directly there is no intervening membrane. The sample negotiates a "U-like" path through this component also and is combined with the alkaline reagent upon re-entry to the manifold. The sample-reagent mixture next enters a mixing assembly (Photo 18). The fluid is agitated by two miniature teflon-coated magnets which sit in the fluid conduit and vibrate in an alternating field. The mixer is necessary to insure complete conversion of NH_4^+ to free dissolved NH_3 prior to measurement. The mixed basic sample flows out of the mixer and straight through the manifold to the NH_3 sensor. The NH_3 sensor is mechanically identical to the CO_2 sensor but uses an NH_4 Cl electrolyte and a microporous PTFE membrane. The chemistry of the measurement is exactly analogous to the CO_2 .

The final utilization of the alkaline solution is as the CO_2 stripping reagent. The solution exits the NH₃ electrode and passes through the stripper. It then flows through a thermal flow sensor before meeting the acid sample at the waste block.

UV Chamber

The UV irradiation chamber (Photos 21, 22 and 23) could not be designed integrally with the sensing manifold because of thermal and materials compatibility problem associated with it. The ultraviolet light source is a low-pressure mercury vapor arc in a quartz envelope which is sealed into an epoxy tube at the electrode end. (Ultra-violet Products, Inc. Model SC-1 Pen-Ray Lamp, Photo 21).

The UV chamber consists of the lamp, a quartz coil for the sample mixture (Photo 22) and an aluminum reflector and is housed in a 316L SS block and potted in place with epoxy. The coil is fashioned from 1 mm I.D. 2 mm O.D. quartz tubing. It fits snugly around the lamp (6.25 mm dia., 5 cm long) in 22 closest packed turns. The coil-lamp assembly is wrapped with aluminum foil and the foil is sealed with epoxy. The assembly is placed in the SS block where the ends of the quartz coil are captured in compression o-ring seals. This entire assembly is then potted in place with silicone rubber. The sample fluid contacts steel, Viton, epoxy and quartz during irradiation. The aluminum foil not only reflects stray UV light back into the sample, but protects the epoxy and silicone rubber from the radiation also. Should the lamp somehow break, the mercury (< 0.5 mg total) cannot escape the chamber.

3.6

The lamp output is 4 watts, only 0.5 watts of which is 2537 angstrom UV. A small portion of the heat which is generated is carried from the chamber by the sample fluid which reaches a temperature of nearly 60°C and flows through the chamber at 0.25 ml/min. The remaining heat is absorbed by the SS block which is sunk to the WQM frame.

Electronics

The WQM electronics is housed in two packages (Photo 1). The main electronics package, which was built for the breadboard monitor, contains the basic operational mode controls and indicators and houses the pH, TOC and specific conductance meters. An auxiliary electronics unit was constructed in the preprototype development phase and contains the controls and displays for the NH₃ measurement, the flow sensors and the automatic shut-down sequence. The only circuits which are not located in one of these packages are the flow sensor amplifier boards and the electrode pre-amp boards. These are located in the fluid-handling package so that lead-length can be minimized as a guard against electrical interference.

Breadboard Electronics

The complete breadboard electronics package is described in the "Interim Report on the Breadboard Water Quality Monitor." The operational logic of the main electronics unit has not been altered. Here we describe only the modifications to this package which occurred in the preprototype phase of development.

Since the preprototype has a number of modifications in the area of UV oxidation requirements, certain electrical changes were possible. The elimination of the cold UV chamber resulted in the need for only one UV transformer. In order to simplify the inclusion of the UV failure detection circuitry, the remaining transformer was transferred to the auxiliary electronics package. The electronics associated with temperature control of the sensors was also removed from the system.

Most of the work required to adapt the old electronics to the monitor was in interfacing the two packages. In the present system, 115

VRMS comes into the original electronics box only. The \pm 24VDC and \pm 15VDC power supplies are all located in this package as well. The AC and DC power are connected to the auxiliary package via separate shielded cables. All DC grounds are connected together only in the main package in order to prevent ground loops or noise problems.

Auxiliary Electronics

The incorporation of the NH_3 measurement, the flow rate monitoring and the auto shut down into the preprototype WQM necessitated the construction of an auxiliary electronics package. The front panel contains a digital display for the NH_3 measurement, four "edgewise" meters for the display of flow rates, an edgewise meter for display of the NH_3 autocal potential and the necessary controls and indicator lights (Photo 1).

NH₃ Electronics

The NH₃ meter circuitry consists of an electrode pair, a high impedance differential pre-amplifier (with a gain of 1) and a digital mv meter. In addition an anti-log (\log^{-1}) circuit is employed so as to provide direct NH₃ concentration readout. The high impedance differential pre-amplifier is located in the fluid section to keep the lead lengths short. The meter is a standard Orion 601 digital ionalyzer, specially modified for this application. All external connections excluding 115VRMS power are made through the rear connector (P10) and the required rewiring for this is done.

Modificiations have also been made at the mode switch. When set at "mv", the differential voltage of the electrodes is directly read as in the unmodified meter. When set at NH₂ (in unmodified meter "pH") the electrode signal goes through a \log^{-1} circuit (Photo 29) which provides the meter with a reading of NH₂ in mg/1.

The log⁻¹ circuit has five parts, an offset adjust, a volts/ decade adjust, a log⁻¹ section, a divide-by-ten attenuator, and a recorder interface. The offset adjust provides a weighted sum of input electrode voltage, calibration potentiometer voltage and autocal potentiometer

voltage. The volts/decade adjust section includes the slope potentiometer and provides a variable gain amplifier for the input to the \log^{-1} section. The \log^{-1} section is an Analog Devices \log^{-1} circuit, AD755N. The resistor which determines the calibration value is in this section. The attenuator is a simple voltage divider which provides an output for the digital mv meter of 1/10 of the output of the \log^{-1} section. The recorder interface is an amplifier with a gain of 10 which provides a recorder output of 5.0 VDC for a meter reading of 50.00 ppm. When the mode switch is in the "mv" position, this amplifier provides a recorder output equal to 10 times the absolute mv reading.

The original offset voltage control pot ("CALIB" on unmodified meter) is located on the rear panel. The calibrate potentiometer from the log⁻¹ circuit is substituted for the original calibrate potentiometer. The slope potentiometer is located where the original TEMP/SLOPE potentiometer (which also has been removed) used to be, and the ISO ADJUST potentiometer has been removed.

The automatic calibration loop for NH₃ (Photo 27) is exactly like those for the other measurements. It includes five units: the auto-cal board, a motor, a pot, the actual meter, and a restandardization meter. The autocal board compares the output of the meter with a set calibration voltage. If the two are not equal, when triggered, the autocal board drives the motor causing it to turn the pot which changes the output of the meter. This happens until the meter output is equal to the calibration voltage. The restandardization meter reads the voltage of the wiper of the potentiometer, and displays the position of the wiper.

The autocal board itself has five parts: a calibration voltage source, a comparator, a power amplifier, a switch, and a timer. The calibration voltage is taken from a voltage divider. The comparator compares the meter output with the calibration voltage, and drives the power amplifier with its output. When the timer is triggered, it closes the switch for 15 seconds. When the switch is closed, the output of the power amp goes to the motor.

Flow Sensor Circuitry

Referring to Figure 3.2, the flow cell operates in the following manner. TI measures the temperature of the fluid in the flow cell. The heater supplies heat to the flow cell around the region of T2. T2 is now used to maintain the power to the heater so that the flow cell around T2 is about 1° higher than that at T1.

In operation, the fluid will flow by Tl and then by T2. As the fluid flows by T2 some of the heat is drawn away by the fluid. T2, sensing the temperature change, applies more power to the heater to maintain the constant ΔT at about 1°C. The increase in power is now measured as an indication of fluid flow.

The flow cell and electronics interface in the following manner to provide measurement of flow. The reference voltage (\circ + .1V) is applied to both the ramp generator and the temperature amplifier to give them an equal offset (see Figure 3.3). The temperature amplifier now senses and amplifies the reference voltage and Tl with a gain of -1. This output is inversely proportional to temperature and is used (as described later) to temperature compensate the flow cell. The output of the temperature amplifier and T2 are now summed and inverted in the ΔT amplifier. This signal is now applied to the non-inverting input of the comparator. It can be seen at this point that if T1 and T2 were equal, then the output of the ΔT amplifier would be equal to the reference voltage. The ramp generator produces a triangle wave signal symmetrical around the reference voltage. This signal is applied to the inverting input of the comparator.

The comparator at this point has the triangle wave on the inverting input and a voltage equal to the reference voltage on the non-inverting input. This produces a square wave with a 50% duty cycle on the output of the comparator and into the driver. The heater now turns on at half power and heats the area around T2. As T2 heats up, the ΔT amplifier will reduce the power to the heater to some value less than 50%.

To calibrate the system for zero flow, the gain of the ΔT amplifier is adjusted so that when there is zero flow the output of the comparator

3~10

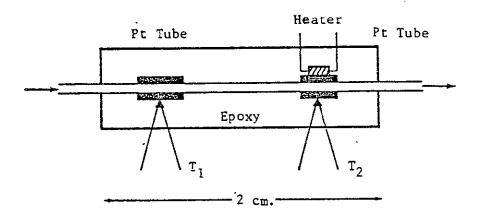


Figure 3.2 Flow Sensor

3.21 18

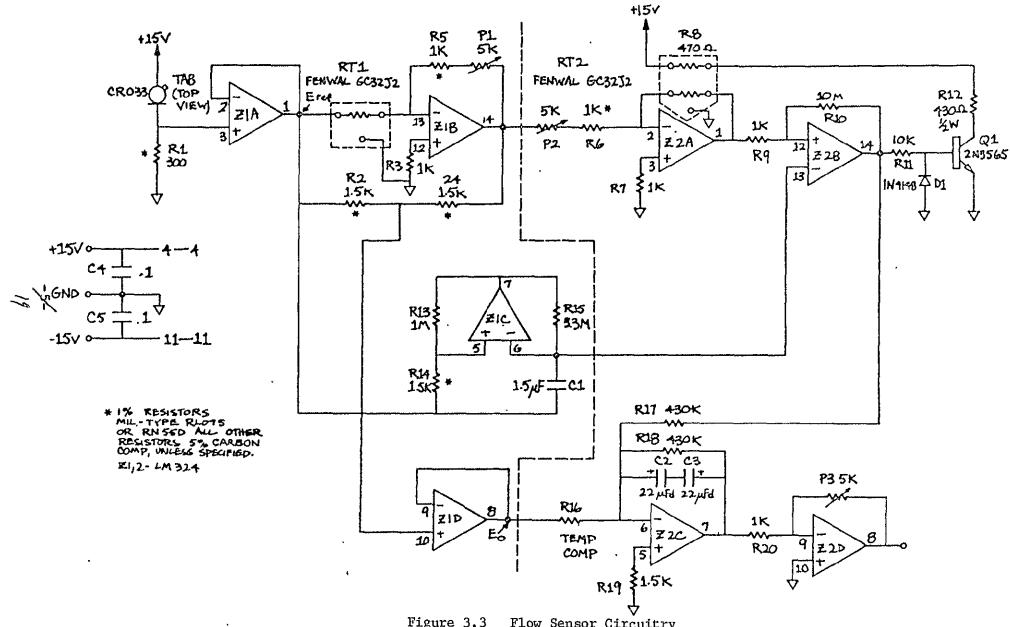


Figure 3.3 Flow Sensor Circuitry

٠

has a 50% duty cycle. Because this signal also goes into the integrator and the output amplifier it is easier to adjust the gain of the ΔT amplifier so that the output of the output amplifier is zero. (This is a result of the integration of the 50% duty cycle). Because of the physical configuration of the flow cell and the heater this 50% power makes T2 about 1°C higher than T1.

When the flow is brought up to some finite value, heat is drawn away from the T2 area. This will cause more power to be applied to the heater to bring the difference between T1 and T2 back to 1°C. The power is increased by increasing the duty cycle greater than 50%. This is seen by the integrator and the output amplifier, and the output is increased in proportion to the power.

The gain of the output amplifier is now adjusted to give the output needed for the maximum input flow. Note that, because the output was set to zero with flow, the full scale adjustment does not affect the zero adjustment. If the flow meter is to be used with a constant temperature fluid and/or environment it will work as described up to this point. But if fluid temperature and/or environment temperature change, the following procedure must be appended to the above.

The output of the uncompensated flow meter will rise as the fluid temperature and/or environment rises. One will recall that the output of the temperature amplifier was inversely proportional to the temperature of the fluid. As fluid and/or environment temperature rises the temperature amplifier output will go down. If the proper resistor is selected for the temperature compensation network, the effect will be cancelled out in the integrator and the flow meter will be temperature compensated.

Front Panel Operation and Fault Detection

Most of the controls and indicators on the auxiliary electronics package are part of the fault detection system. The NH₃ meter has only three controls - mode switch, calibrate and slope knobs, and these are described in the previous section.

3,13

Each of the four flow meters gives the flow rate at a specified point within the system. Two nonvisible setpoints are associated with each meter for high and low flow alarms. When the flow rate exceeds these setpoints, a non-latching alarm light on either side of the respective flow meter will come on. These lights will remain on as long as the flow rate is beyond the set limits, as determined by the "time out" board (Photo 30).

Below the four flow meters is a U.V. fail indicator. If the UV lamp fails this light will come on. The system has a built in fault indicator that will recognize a problem with either the UV lamp or any of the four flow channels. If a fault is detected the fault/reset lamp will illuminate and one of the nine error indicators will remain on while the others will be forced off. This will indicate which fault caused the fault/reset condition to latch. After the error condition has been repaired the fault/reset can be reset by either pressing the fault/reset button or it will be reset automatically upon power-up of the system. The conditions for a fault indication are as follows: a UV failure at any time, will cause the UV failure lamp to light even if a fault indication has been recognized and latched in previously; and if a flow rate is outside the set points for more than a two minute variable, the fault circuit will be triggered. If two flow rates exceed their limits simultaneously within six and one fourth percent of the two minute interval, there is a possibility that two or more of the error indicators will stay on when the fault indicator latches.

When a fault indicated, one may wish to shut down the pump and mixer in the fluids section. This is the function of the auto shut-down button. When the auto shut-down is activated, the light in the pushbutton will come on to indicate the active state. If the fault/reset now comes on while the auto shut-down is in the active state, the pump, UV and mixer in the fluids section will automatically shut off.

There are two non-labelled functions associated with the front panel switches. The normal function of UV failure indicators is to indicate to the operator the status of the UV lamp in the fluids section. The indicator is also a momentary action switch and when de-

pressed illuminates all of the panel lamps to check for burned out bulbs.

An additional function is also associated with the four high indicators for the flow meters. These indicators are alternate action switches which when depressed disable the setpoint indicators and alarm functions for each respective channel. A disabled channel is indicated by simultaneous activation of high and low error indicators. `A second depression of the high error indicator will return the respective channel to the normal mode of operation.

General

Familiarization with the electronics section and operations manual of the "Interim Report", in combination with this material and the instructions contained in Appendix IV should be adequate for an operational understanding of the WQM electronics. All of the circuit boards are labeled adequately with test points such that an electronic engineer should be capable of troubleshooting the system with the aid of the circuit board photographs and the schematics contained in the WQM documentation package.

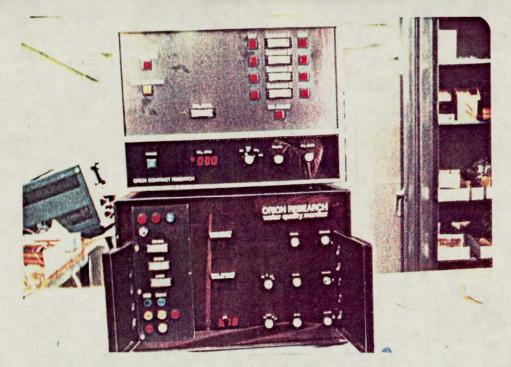


Photo 1. <u>Electronics Packages</u>. The lower unit is the original breadboard electronics. The upper unit is the auxiliary package which contains the NH₃ readout and the fault detection circuit.

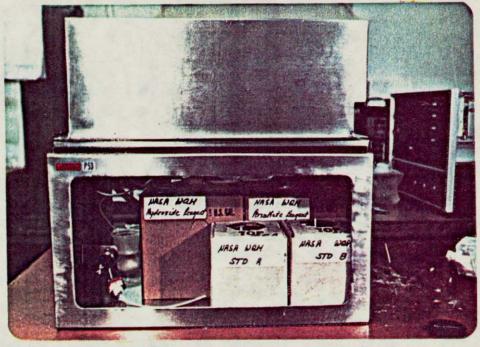


Photo 2. <u>Fluid Package</u>. The top half contains the pump, valves, sensors, etc., the lower half contains the reagent and standard containers, the filter and the pressure regulator.

REPRODUCIBILITY OF THE ORIGINAL PAGE IS POOR

PA

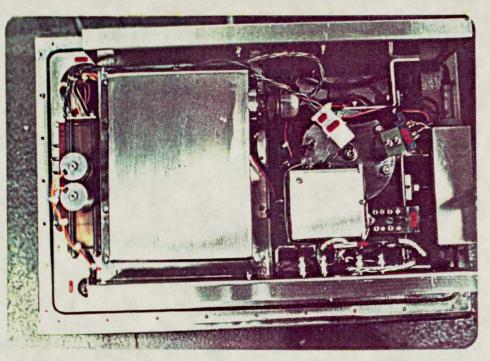


Photo 3. <u>Top-view FluidsPackage</u>. From left to right are the valve manifold, peristaltic pump, sensor manifold and UV chamber.

NON the				
A.			NACA LUC	2H
	CONTRACTOR OF THE OWNER OWNER OF THE OWNER OWNE	WRM TD A	Hydroxis A NASA	lengent 105

Photo 4. <u>Reagents Section</u>. This view shows power connections, input and waste manifolds as well as reagents and standards.

REPRODUCIBILITY OF THE ORIGINAL PAGE IS POOR

P2 34

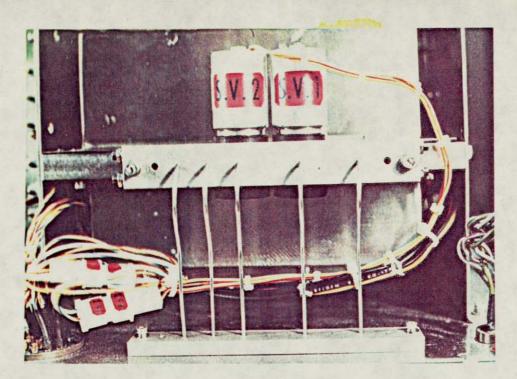


Photo 5. <u>Valve Manifold</u>. A stainless steel tubing manifold interfaces the sample, reagents and standards with the valve manifold (Angar Scientific). The valve manifold has two 3-way solenoid valves and a "tee" for splitting the sample. Reagents pass straight through to the pump.

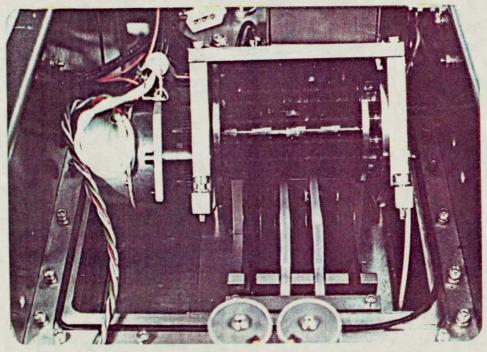


Photo 6. <u>Peristaltic Pump</u>. This view shows the pump with the rollers lifted to show the tubing.

REPRODUCIBILITY OF THE ORIGINAL PAGE IS POOR

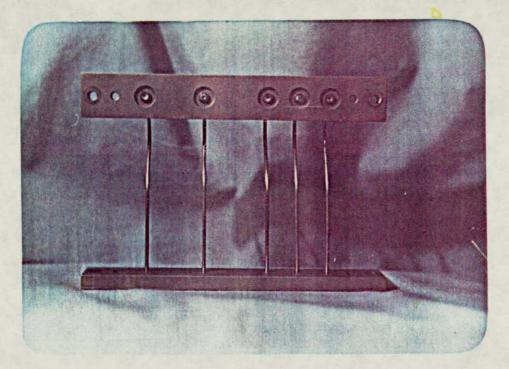


Photo 7. <u>Close-up of Input Tubing Manifold</u>. This view shows the o-ring grooves which are used for sealing interfaces throughout the system.

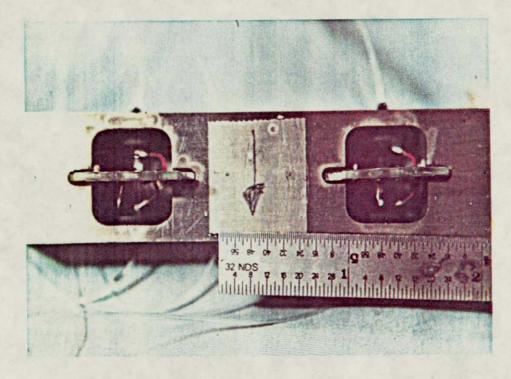


Photo 8. <u>Flow Sensor Block</u>. This block connects the four pump channels to the sensor
manifold. This shot shows the reagent flow sensors in the assembly stages before potting. In the final version the block is teflon coated.

26

REPRODUCIBLITY OF THE ORIGINAL PAGE IS POOR

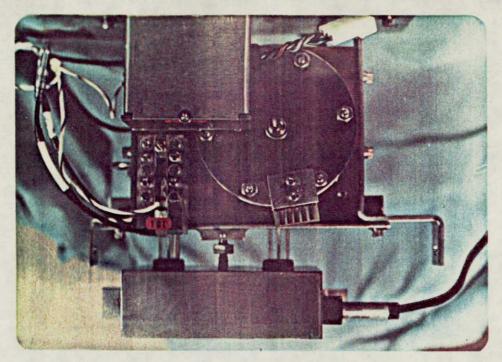


Photo 9. Sensor Manifold. In this top view the fluid would enter at the top of the photo. In the upper left is the mixer, center left - CO_2 (TOC) sensor, right - stripper with flow sensor mounted at lower edge, and bottom - the UV chamber.

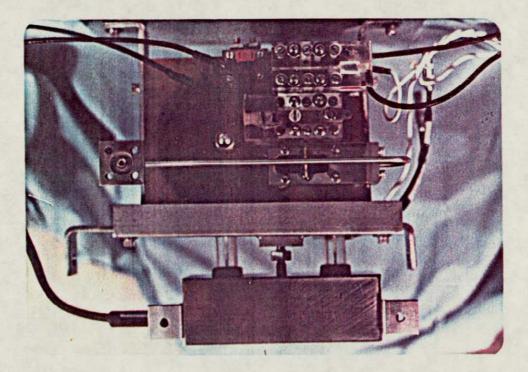


Photo 10. <u>Sensor Manifold</u>. The bottom view shows the conductivity cell (with red label), the pH sensor to its right, the NH₃ sensor below the pH, and the waste block - flow sensor assembly below that.

27

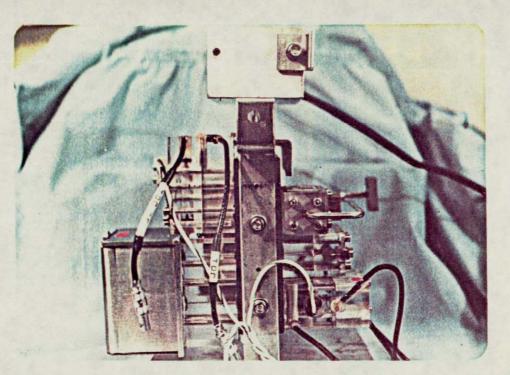


Photo 11. <u>Sensor Manifold</u>. Here the manifold is shown such that the "top" (Photo 9) is on the left. Fluid flow is from bottom to top in this shot. The steel case on the left houses the mixer, the acrylic assembly on the lower right is the pH sensor.

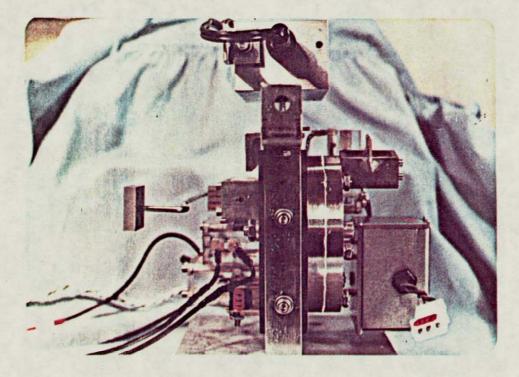


Photo 12. <u>Sensor Manifold</u>. The opposite side-view shows the UV lamp as it mounts in the chamber at the top. The stripper is seen on the right bolted directly to the polysulfone manifold.

28

REPRODUCIBILITY OF THE ORIGINAL PAGE IS POOR There 13. <u>Input Pressure Regulator</u>. Sample will be received from the water reclamation system at 10-15 psig. This valve (Go, Inc) reduces the pressure to less than 2 psig at which pressure it is aspirated by the peristaltic pump.





Photo 14. Filter. This miniature in-line filter is a safeguard against aspiration of - particulate matter into WQM (Angar Scientific).

REPRODUCIBILITY OF THE ORIGINAL PAGE IS POOR

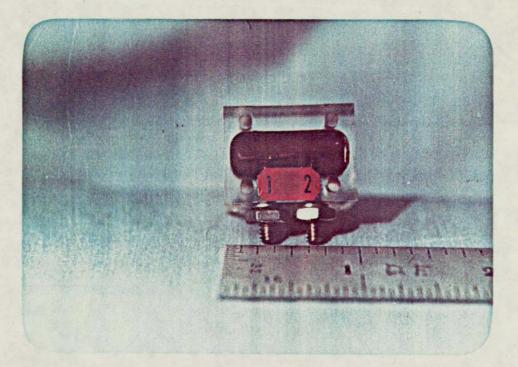


Photo 15. <u>Conductivity Cell</u>. The untreated sample flows through two 6 mm. lengths of 1 mm. I.D. platinum tubing which serve as electrodes. The fluid path and electrodes are potted in epoxy.

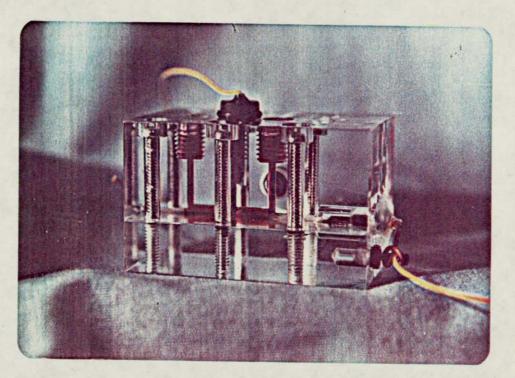


Photo 16. <u>pH Electrode</u>. Red dye fills the sample channel while blue dye fills the reference electrolyte reservoir of this prototype WQM pH sensor.

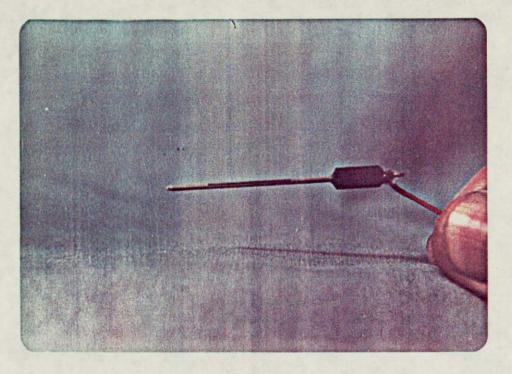


Photo 17. <u>pH</u> <u>Capillary</u>. This miniature glass electrode acts as sensing element in the pH, CO_2 , and NH_3 electrodes.

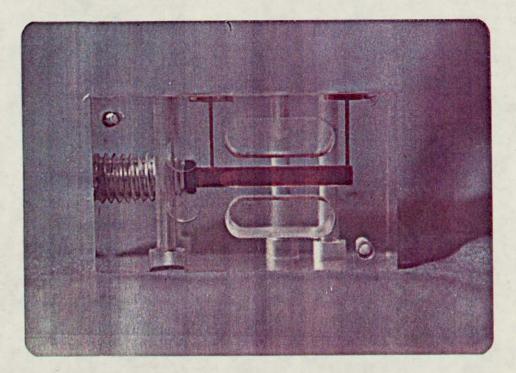
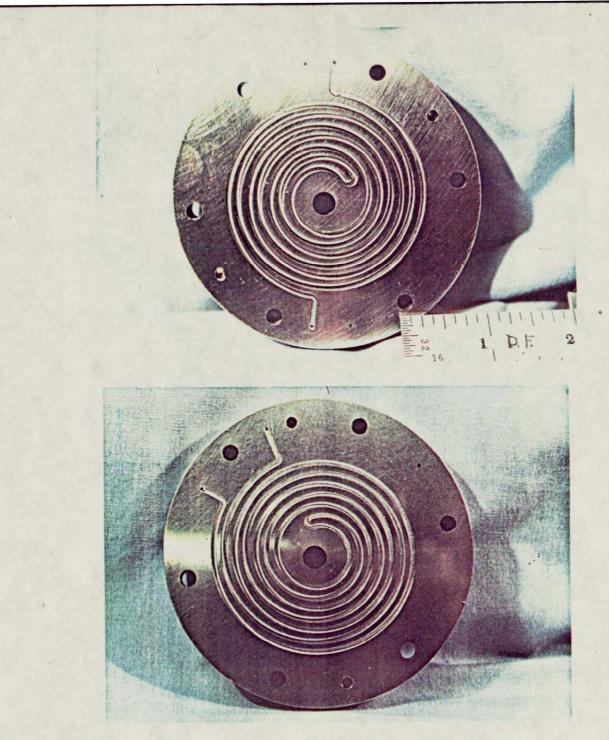


Photo 18. <u>Mixer Block</u>. Two teflon-coated magnets can be discerned through the red dye. In operation, an AC field causes these bars to vibrate and mix the NaOH reagent with the sample prior to the NH₃ measurement.

P-9 31



Photos 19 and 20. <u>CO₂ Stripper</u>. In operation the two stripper plates clamp a piece of microporous teflon between them. The solution passing through the top side must pass through the lower block in transit to and from the manifold.

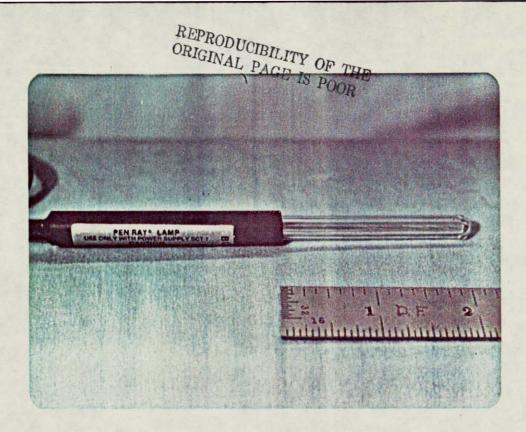
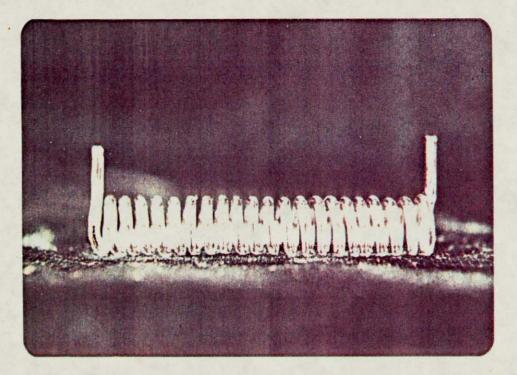


Photo 21. UV Lamp. Ultraviolet Products Model SC-1 Pen-Ray lamp.



- Photo 22. <u>Quartz Coil</u>. The lamp shown above fits into this coil. The sample flows through the coil which is covered with reflective foil.

33

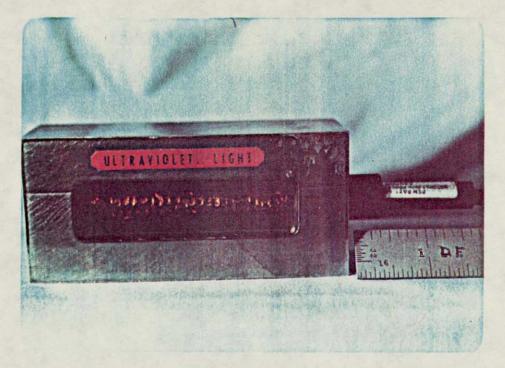


Photo 23. <u>UV Chamber</u>. The quartz coil is potted into this chamber and the Pen-Ray lamp is inserted from the right. The foil-wrapped coil can be perceived through the potting compound.

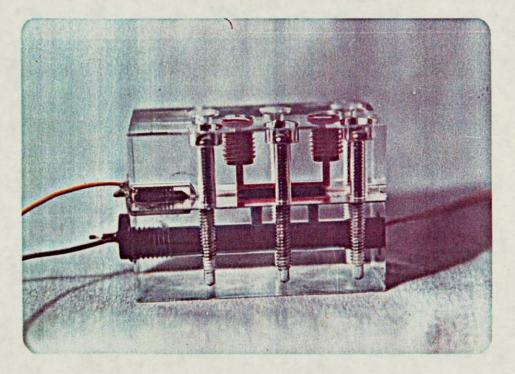


Photo 24. CO₂ or NH₃ Sensor. The CO₂ and NH₃ sensors are identical except for the type of membrane and reference solution. Red dye fills the sample channel and blue dye the reference chamber. The membrane and capillary are clamped between the acrylic blocks.

31

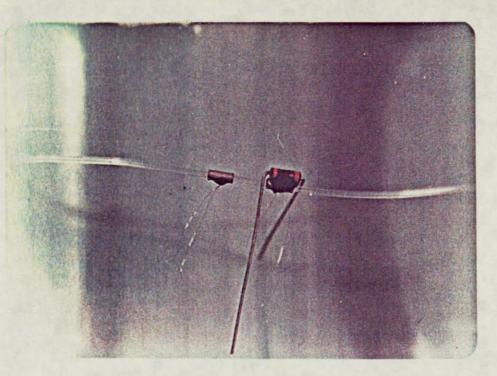


Photo 25. Here the platinum tubes, thermistors and resistors of a flow sensor are shown mounted and ready for potting into a block.

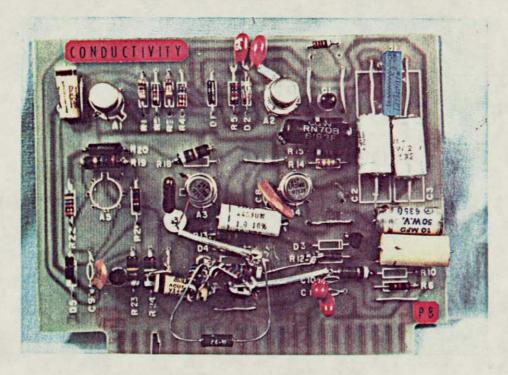


Photo 26. This shot shows the conductivity circuit board.

REPRODUCIBILITY OF THE ORIGINAL PAGE IS POOR

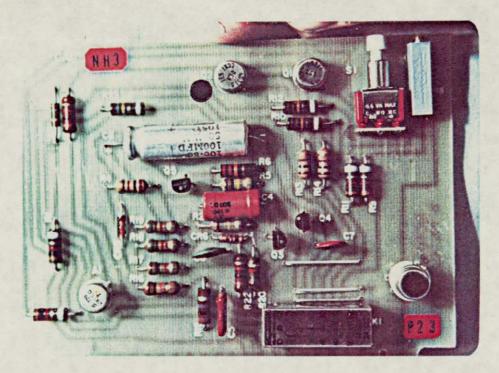


Photo 27. <u>NH₃ Auto-Cal Board</u>. The other 3 auto-cal boards are the same. The white button on the top right can be used to manually activate the servos. This board is located in the breadboard electronics.

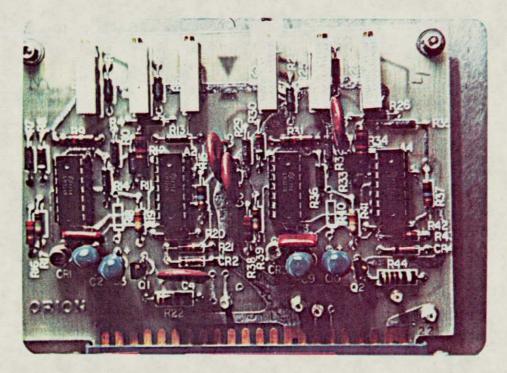


Photo 28. Flow Sensor Board. Each of the 2 flow sensor boards control 2 sensors. R5 or R27, R6 or R28, are the pots for adjusting zero and span respectively for the corresponding sensors.

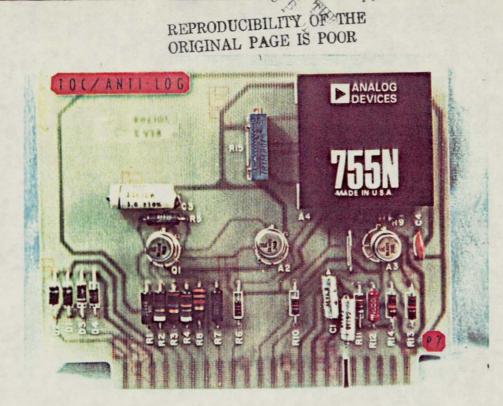


Photo 29. The NH3 measurement utilizes an anti-log board identical to the above.

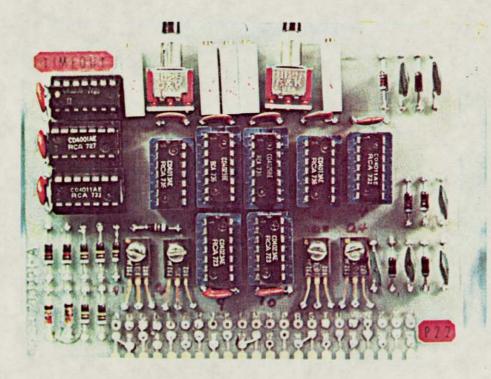
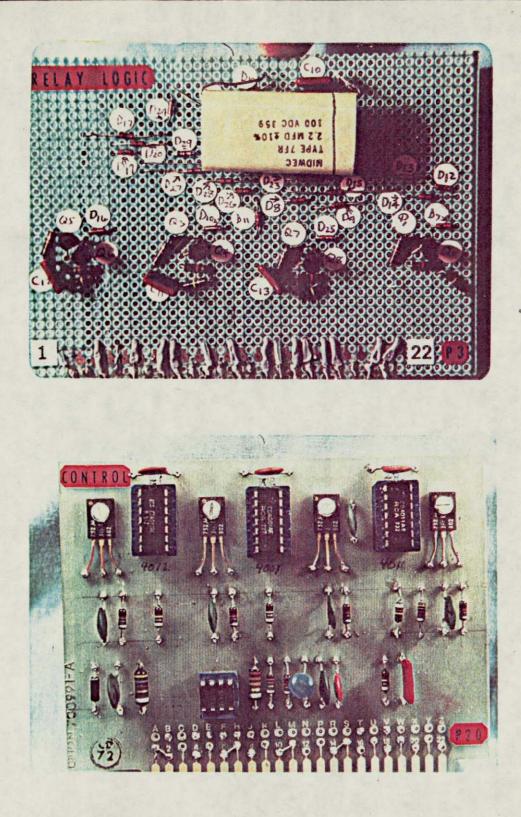


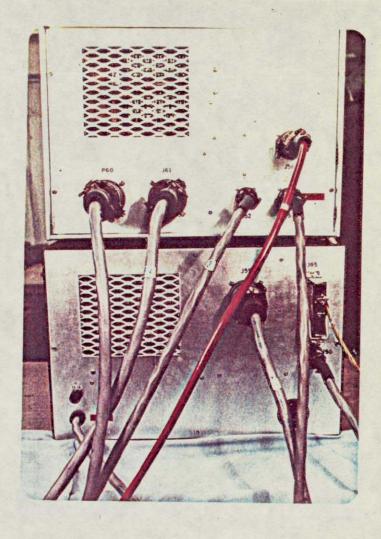
Photo 30. "Time-out" Board. This board senses deviations of the flow sensor output. If a sensor signal is outside the set-points for 2 minutes FAULT/RESET will be triggered.

> P-15 37



Photos 30 and 31. These boards control the operational logic and mode controls on the WQM.

P-16 38 Photo 33. Rear view of electronics showing cable connections.



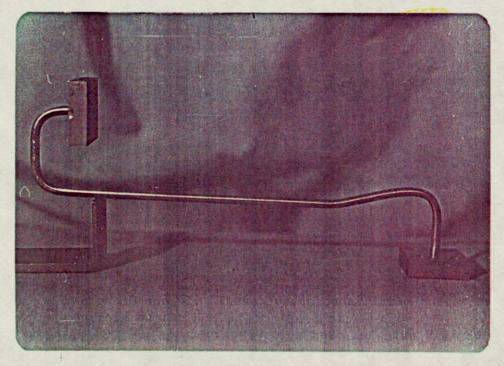


Photo 34. Waste tubing manifold.

II. Fluid Consumables

,

a) Sample 24 ml/hr x 22.5 hr/day x 30 day =	16,200 ml =	16.2 1
b) Standard A 24 ml/hr x .75 hr/day x 30 day =	1	540 ml
c) Standard B		
1. 24 m1/hr x .75 hr/day x 30 da	y =	540 ml
2. For Washout Mode		
24 ml/hr x .25 hr/day x 30 da	y =	180 ml
d) Reagent A		
4 ml/hr x 24 hr/day x 30 day	=	2.8 1
e) Reagent B		
$4 \text{ ml/hr} \times 24 \text{ hr/day} \times 30 \text{ day}$	=	2.8 1
III. Overall W.Q.M. Package Size		
The overall physical dimensions are 20	<u>.35"</u> x <u>17.25</u> "	x <u>12.75</u>
IV. Power Consumption		
The W.Q.M. will use a maximum of 5 amp	s at 110 volt	s A.C.
MAINTENANCE SCHEDULE		
1. Pump Tubing - The pump tubing should be	replaced on	a 30 day basis.
2. Reagents and Standards - The reagent an should be refilled on a 30 day basis.	d standard fl	uid supplies

3. Sensors - Each individual sensor (pH, Cond, TOC and NH_3) should be replaced on a 6 month basis. Used sensors should be shipped back to Orion for reconditioning. New sensor blocks can be stored, dry, for an

3,21

indefinite period of time. When a new sensor block is needed the internal filling solution will be added to the sensor and the entire sensor block will be exchanged with the old sensor block.

4. U.V. Lamp - The U.V. lamp in the U.V. Chamber should be replaced every 3 months to insure proper U.V. intensity.

5. Pump Motor - The A.C. Synchronous motor should be replaced every 12 months. This will guarantee desired motor characteristics.

6. Stripper - The stripper membrane should be replaced every 3 months.

CHAPTER 4. WATER QUALITY MONITOR HARDWARE DEVELOPMENT (Breadboard to Preprototype Modifications)

The "preprototype" WQM for the most part is an advanced version of the "breadboard" WQM, however, several design changes were implemented. Some of them arose directly as a result of breadboard experience and testing and others arose as specific ideas regarding the scope of the development work evolved or were modified.

Alternative UV Source

Low-pressure mercury vapor lamps are the least expensive and most widely available sources of "middle" wavelength ultraviolet radiation. Mercury is clearly specified (NASA Design and Procedural Standard No. 116) as being an unacceptable material in spacecraft instrumentation, however, in developing the oxidation technique for the TOC determination, mercury lamps were used because of their convenience. The use of mercury lamps in the breadboard WQM was approved by NASA with the understanding that alternate UV sources would be evaluated in the preprototype work.

UV light reacts both with the TOC reagent and with many of the organic constituents of the sample in effecting their oxidations. The "peroxy" linkage in the monopersulfate ion, which is contained in the reagent, is cleaved by UV light to produce atomic oxygen radicals which are the principal oxidizing species. Some of the organic compounds react directly with the UV to form radicals and thus become more easily oxidized by the reagent. The overall rate of oxidation is dependent on both the intensity and wavelength of the light. For example, the reaction of photons of 2537 angstroms with peroxydisulfate ion has a quantum efficiency of 60%. The quantum efficiency at 3200 angstroms is nearly zero and at 2000 angstroms nearly 100%.

The problem of finding an alternate UV source for the WQM is that of finding one which emits a wavelength where the quantum efficiency of the reaction with the oxidant is high at an intensity sufficient to catalyze the oxidation in a short time. Another important consideration

> 41 43

is the efficiency of the source. Power is at a premium aboard spacecraft and an inefficient lamp also presents heat disposal problems in the WQM.

UV lamps are available as either "line" or "continuum" sources. Continuum sources are unsuitable for the WQM because of low output efficiency compared to line sources. Other than mercury, only a handful of line sources are available in the proper spectral region. These are either rare gas - xenon and neon for example, or metal based such as zinc or cadmium. Although estimations based on the output spectra of non-mercury sources indicated that there were no presently available lamps which met the TOC requirements, we nonetheless evaluated several in the laboratory (zenon, neon, argon, and krypton and zinc) and obtained virtually no oxidation of organic carbon with any of them.

Mercury lamps were concluded to be better for this application than any other type presently on the market based on cost, power consumption, TOC efficiency and overall size. The preprototype WQM utilizes a lowpressure mercury vapor lamp (Photo 21) which is manufactured by Ultraviolet Products, Inc. (Model SC-1 Pen-Ray Lamp). Total lamp length is 10 cm., 5 cm. of which is the exposed quartz tube 6 mm. in diameter. The other half is contained in an epoxy body which houses the electrodes and seals the power connections. The lamp is designed to be submersible and its small size makes it ideal for this application. It contains less than 0.5 mg total mercury. The UV chamber is designed to contain the mercury should the lamp be broken.

Pump Tubing Evaluation

Like the preprototype WQM, the breadboard utilized four channels of a peristaltic pump to meter the sample and reagents. All four pump tubes were of silicone rubber. In altering the nature of our work from the breadboard to preprototype stage, it was necessary to perform extensive tests on pump tubes. Silicone rubber is not entirely resistant to the oxidant and tends to cold flow in its presence. The fact that the pump tubing is the only elastomeric material which carries fluid in the WQM created the need for extensive evaluation of this "high-risk" leakage area.

The WQM is geared to a 30-day continuous operating cycle. The goal of the pump tube testing was to select tubing materials which could maintain the desired flow rates for periods in excess of the 30-day minimum. Silicone rubber is the most widely used peristaltic pump tube material. The only other materials available for a low-volume application are types of Viton. Silicone rubber and various Viton materials were compared while pumping concentrated reagents at accelerated pump rates. One type of Viton tube (Elkay Acid-Flex) was singled out in early testing as the best non-silicone rubber tube. It is peroxide cured to increase oxidation resistance and showed good flexibility for peristaltic pumping. In the final life-test, nine 0.75 mm I.D. Elkay tubes were compared to nine 1.0 mm I.D. silicone rubber tubes while pumping the oxidant at both nominal and accelerated rates. After 75 days continuous pumping during which frequent flow data were gathered, only one of the 18 tubes, a silicone rubber piece, failed completely due to rupture. All 9 Viton and the eight remaining silicone tubes survived the testing. The silicone tubes, however, all showed gradually increasing flow rates, as if the effective I.D.'s of the tubes were increasing with use. These testing results are discussed further in Chapter 5.

We concluded that the 0.75 mm I.D. Elkay tubes are suitable for use in the reagent channels, and that 1.5 mm. silicone rubber tubes are acceptable in the sample lines.

Reagent Evaluation

In the Breadboard monitor, the TOC reagent was ammonium peroxydisulfate. In testing the breadboard unit we observed a decrease in oxidation efficiency with acetic acid as the test compound when a batch of reagent was a few days to a week old. Acetic acid is one of the most difficult organic compounds to oxidize and is the only compound with which we have observed incomplete oxidation in the "old" reagent. The cause of the problem is believed to be the gradual decomposition of peroxydisulfate $(S_2O_8^{-})$ to peroxymonopersulfate (HSO_5^{-}) . The monopersulfate is also a very powerful oxidant and is activated by UV through the same mechanism as the peroxydisulfate.

The monopersulfate is a very stable species and therefore we are

using it as the preprototype oxidant. Its inefficiency in oxidizing acetic acid is a drawback, however its effectiveness for other compounds is good. We investigated another compound - potassium peroxydiphosphate $(K_2P_2O_8)$. We found that it was capable of oxidizing acetic acid but that it was not stable enough to utilize.

Elimination of "Cold" UV Chamber

In our early studies of the UV oxidation concept it became apparent that certain volatile organics could not be oxidized completely if the solution were allowed to be heated by the UV lamp. Oxygen is a byproduct of the reaction and the bubbles which form provide spaces for compounds such as methane or ethane to be driven from solution where they fail to react. We found that by building a UV irradiation chamber which was air-cooled, compounds such as methane and ethane could be completely oxidized.

The decision was made to forego inclusion of a "cold" chamber in the preprototype WQM. The presence of volatiles such as methane in the potable water supply is not considered to be a problem by NASA. The simplification of the overall system and the reduction in space and power requirements as a result of elimination of the cold chamber was felt to outweigh its advantages.

Chloride Interference

Chloride ion is oxidized to chlorine by the oxidizing agent and chlorine is an interference to the CO_2 electrode. We investigated the addition of reducing reagents to the sample after irradiation but prior to the CO_2 measurement. Ferrous ion or hypophosphite ion formula were found to be satisfactory in preventing the chloride interference.

During this work, additional process information became available to the effect that the WQM sample would probably not contain greater than 12 mg/1 of chloride ion. We tested solutions containing this amount of chloride and saw no TOC interference. Addition of a third reagent to the monitor then became unnecessary.

> 4.4 46

pH Sensor Mofidication

The Breadboard pH sensor consisted of a thin-walled pH glass capillary 1.0 mm in diameter and 1.5 cm long. The capillary was wound in silver wire which was bonded to the glass with molten silver chloride. This resulted in a solid-state device which was connected at each end with silicone rubber tubes bonded in place. The sample simply flowed through the capillary and then a sealed reference electrode. (See Figure 4.1). This sensor did not give sensible pH readings in distilled or de-ionized water. The solid-state glass-silver-silver chloride junction was of excessive electrical resistance and other problems could have contributed to the noise and drift that was encountered.

In the preprototype work, rather than attempt to diagnose and correct all of the problems associated with the solid-state design, a more conventional "flow-by" device was developed(see figure 4.2). This is constructed from the same capillary material as the old "flow-thru" type (Photo 17) but in this instance an aqueous solution and silver chloride reference element are sealed into the capillary. The outside surface is first glazed so as to render all but a narrow strip insensitive to pH. The sensor is lain in a sample conduit in such a way as to expose the narrow sensor area to the sample. The reference junction is located directly across the conduit from the glass electrode resulting in a low-resistance geometry (Photo 16). This same capillary design is utilized for the internal sensing elements of the CO₂ and NH₃ sensors. Tests have shown very good response in both buffered solutions as well as distilled water. Prolonged use has indicated some reference junction problems with this design (see Chapter 5 for details).

NH, Measurement

NASA indicated that NH_3 may be one of the contaminants in reclaimed water. It was decided to incorporate an NH_3 measurement in the preprototype WQM because little additional work would be required to do so. The measurement of NH_3 by gas-sensing electrode requires only that the sample be made sufficiently alkaline to convert any ammonium ion to dissolved ammonia. The necessary reagent was already present in the breadboard and thus it appeared necessary only to design the NH_3

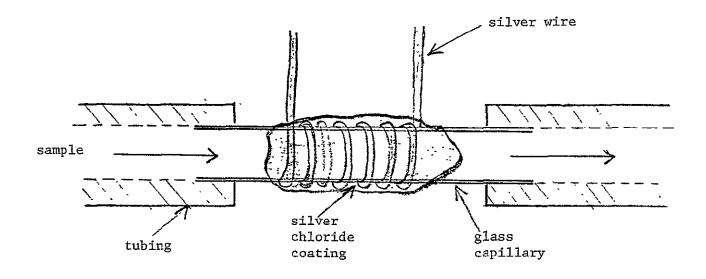


Figure 4.1 Flow-Thru Capillary pH Sensor

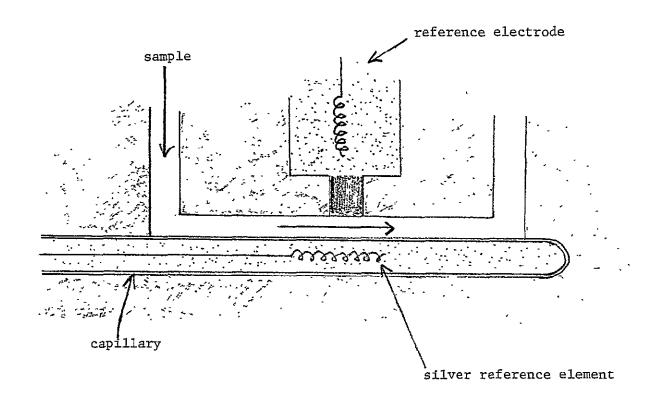


Figure 4.2 Flow-By Capillary pH Sensor

REPRODUCIBILITY OF THE ORIGINAL PAGE IS POOR

48

sensor into the flow scheme. Initial tests of the NH_3 sensor on a bench-top mock-up of the WQM revealed that a considerable mixing time was required between the NaOH reagent addition and actual measurement. We therefore incorporated a magnetic mixing device at this point in the flow system. The NH_3 sensor (Photo 24) is mechanically identical to the CO_2 sensor.

Failure Detection System

The preprototype WQM design incorporates several checks on proper system operation which were not utilized in the breadboard monitor thermal flow sensors and a UV lamp monitor. These failure detectors are capable of triggering an automatic shut-down in order to prevent the creation of a hazardous situation in the event of fluid leakage or lamp breakage. Thermal flow sensors were developed expressly for the WQM. The vast majority of potential failure modes can be indicated and diagnosed by monitoring flow rates at strategic locations within the fluid schemes.

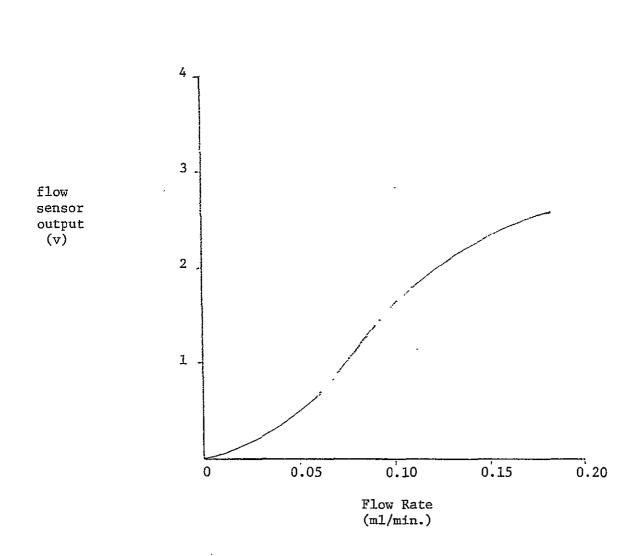
The flow sensors operate by measuring the rate at which heat is transferred from a warm body to the flowing liquid. The sensor consists of two thin-walled platinum tubes (0.75 mm I.D., 6 mm. long) which are cast by the "lost epoxy" technique into a stainless steel block (Photos 8, 25). The fluid flows through the epoxy path and through each platinum tube in series. The first platinum tube has a thermistor in contact with it and is used to indicate fluid temperature. The second tube has both a thermistor and a small resistor in contact with it (Figure 3.2).

The flow-related parameter is the quantity of power required by the resistor to maintain a constant ΔT (ΔR) between the two thermistors. In the absence of flow a quantity of power required equal to the amount of heat lost by conduction through the epoxy to the outside, is required to maintain ΔT . As flow begins and increases, a greater quantity of power is necessary to maintain ΔT .

The curve in Figure 4.3 demonstrates the variation of flow sensor output with flow. The curve starts out concave upward, goes through an

Figure 4.3 Flow Sensor Response

.





inflection at 0.2 ml/min and then tapers off as flow increases. (The curve has the same form as a "wind-chill factor" curve.) The cell calls for more power slowly at low flows, because the platinum tube is insulated by a "diffusion layer" in the liquid which limits heat flow. The diffusion layer becomes thinner as flow increases, and thus the loss of heat becomes more rapid. At the point of inflection, the diffusion layer has essentially disappeared and heat loss becomes limited by conduction through the platinum. The point of inflection is the point of maximum sensitivity of the sensor. This point can be optimized to monitor flow in various ranges by varying AT or the diameter of the flow path. Variation in output due to changes in ambient fluid temperature are compensated electronically.

Four thermal flow sensors are used in the WQM. Both reagent lines are monitored as they exit the peristaltic pump. Two other flow sensors monitor the two sample lines downstream of the stripper after they have been combined with reagent. These measurements are taken near the waste outlet of the monitor so as to detect any leaks or clogs upstream where most of the fluid components are located. In this manner the sensors are able to detect fluidic malfunctions in the greatest number of areas and many problems will be detected by two sensors simultaneously, providing a self-checking mechanism.

In addition to monitoring the fluid flow rates, the input to the UV lamp is also monitored in the WQM. The current to the lamp is continuously measured and deviations from the proper rating trigger the auto shut-down.

Elimination of Temperature Control

The individual sensor modules in the breadboard fluids package were thermostated to insure maximum precision. The sample water supply specifications were altered from a 10-50°C range to a 29-35°C range during the interim and therefore a thermal control system for the sensors was not considered necessary in the preprototype system.

CHAPTER 5. EVALUATION AND TESTING

In this chapter, data are presented from experiments performed during the preliminary design stages as well as from final testing of the completed WQM. While designing the preprototype unit, critical materials and components such as pump tubing and o-rings were subjected to extensive life tests under "worst-case" conditions. These tests are described below. In the section which follows, the results of testing the assembled unit and in carrying out the Master Test Plan are presented.

Initial Component Evaluation

Both reagents used in the WQM are very caustic - one contains 5% sulfuric acid and oxidant, the other is 6% sodium hydroxide. The materials which contact these fluids in the WQM were tested by exposure to these solutions before their use in the instrument could be accepted. Table 5.1 lists materials which were considered for the WQM and briefly describes the nature and results of the tests. Figure 5.1 is an example of data we obtained while testing pump tubes (see also Chapter 2). The increasing rates shown in the silicone rubber tubes are typical of the test results.



TABLE 5.1

Materials Tested for Intended Use on NASA WQM

Material	Proposed Function in WQM	Testing Conditions	Results of Testing
Silicone Rubber	Sample Pumping Channels-material of choice	35-day continuous pumping of Std A using an ORION 375-A peristaltic pump	-flow rates unchanged throughout test -no visible tubing wear or degradation
	Reagent Pumping Channels-ruled out	35-day continuous pumping of acidified monopersulfate using an ORION 375-A peristaltic pump	 -after 21 days flow rates steadily increase -tubing cold flows, fusing together when pinched -tubing ruptures in some cases after extended use
.Viton	Reagent Pumping Channels-material of choice is Elkay "Acid Flex"	35-day continuous pumping of acidified monopersulfate using an ORION 375-A peristaltic pump	-flow rates unchanged throughout the test -no visible tubing wear or degredation
Viton	Preprototype UV Chamber o-rings ruled out	40-day continuous pumping or irradiated persulfate through mock-up chambers designed specifically for this experiment after 40-days the chamber was pressurized to 30 psi for half an hour	50% of the o-rings tested leaked after pressurizing .
Kalrez	Preprototype UV Chamber o-rings material of choice*	same as that for Viton o-rings	all o-ring seals remained
316L Stainless Steel	Stripper, Sample Intake Manifold, Waste Lines	in separate experiments, hydroxide and irradiated persulfate reagents were pumped through 6" lengths of 1/4" tubing	no visible degradation after 30-days of continuous pumping of reagents

20

TABLE 5.1.

|--|

Material	Proposed Function in WQM	Testing Conditions	Results of Testing
Goretex- porous	Stripper and NH ₃ sensor membranes material of choice	continuous bench-top operation in both of these components for over six weeks	-maintainence of inorganic CO ₂ removal efficiency in stripper -no change in ability of calibrated sensor to detect known levels of NH ₃
Celguard poly- propylene	Stripper and NH ₃ sensor membranes ruled out	continuous bench-top operation in stripper for over six weeks	-shows tendency to be wetted by base and some organics -tears easily; readily damaged by sudden changes in line pressure
Titanium	Preprototype UV Chamber (outer shell containing fluid path) - material of choice*	continuous bench-top operation for over six weeks	-shows no interference with TOC measurement -surface forms protective oxide coating that prevents further oxidative degradation by reagent or UV light

*successful in "preprototype" components; ultimately not used because of design changes.

Pressure Regulator

Testing was performed on the inlet pressure regulating valve, Go Inc., prototype Model #4878, to verify its ability to drop an incoming pressure of 10-15 psig down to 1-2 psig.

Initially the valve was tested separately and on the bench top. The valve was subjected to a variety of incoming pressures, and was able to drop them down to the desired 1-2 psig range. This test was done very quickly and was only to indicate improper regulation. It was felt that in-depth testing should be done, when the valve was mounted into the WQM unit.

Once the WQM and all fluidic components functioned as designed, the Pressure Regulating Valve was installed. Using city water as a source, a garden hose was run from a faucet to the WQM. Before entering the system a reducer was made and installed on the hose end dropping the opening to accomodate Lee Tubing Fitting (1/4 - 28 UNF) with .031 inch I.D. teflon tubing (See Fig.5.1).

A mercury monometer was installed into the system downstream of the pressure regulator. A 0-20 psig pressure gauge was placed prior to the regulator. City water was turned on and a pressure of 15 psig was read on the gauge. The pressure regulator was in the off position. The monometer was relieved of any vacuum problem and stabilized at the 0 inch position. The valve was then opened one revolution at a time and the change in mercury height was closely watched. At exactly six revolutions conterclockwise, the mercury height changed by 4.5 inches. This shows a pressure output of 2.2 psi. The test was run for one hour, whereby the output pressure remained constant.

Master Test Plan Solutions

Twenty solutions were selected for testing the Water Quality Monitor. They were designed to cover the specified operating ranges of the four parameters. Expected TOC and NH₃ contents were calculated and pH and conductivity values were estimated. Results are listed in Table 5.2.

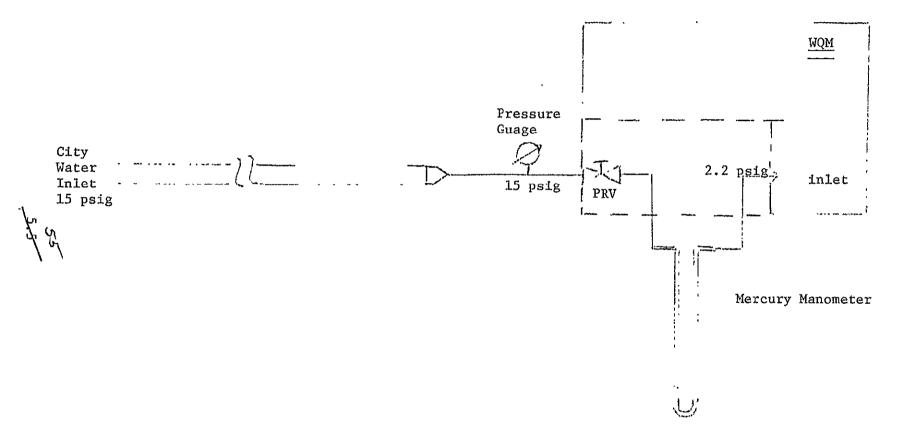


Figure 5.1

Pressure Regulator Test Set Up

Solution		рН		Cond (~ mho/cm)				C (ppm		Ammonia (ppm)			
Number	Solution Composition	exp^{1}	obs ²	JSC ³	exp^1	obs ²	JSC ³	lexpl	obs ²	JSC ³	exp^{1}	obs ²	JSC ³
#1	10^{-3} <u>M</u> Acetic acid 10^{-3} M Sodium acetate	4.76	3.42 3.42	6.8	89	91 91	155	48	25 30	33	0	0.3	0
#2	2 X 10 ⁻³ <u>M</u> phenol 10 ⁻³ M Sodium hydroxide	9.99	8.71 9.19	8.0	83	92 89	164	144	66 77	151	0	0.3 0.3	0 ·
#3	10 ⁻³ <u>M</u> benzoic acid 10 ⁻³ <u>M</u> sodium benzoate	4.21	2.91 3.02	4.4	83	101 98	168	168	160 172	181	0	0.3	0
#4	10^{-3}_{-3} formic acid 10^{-3} sodium formate	3.75	2.97 3.10	4.5	106	133 128	199	24	24 29	21	0	0.3	0
<i>#</i> 5	2 X ₁₀ ⁻³ M p-cresol 10 ⁻³ M sodium hydroxide	10.26	8.52 9.19	8.0	~ 83'	98 103	167	168	90 76	83	0	0.3	0
#6	5 X 10 ⁻⁴ M ethyl alcohol 10 ⁻³ M ammonium sulfate	5.5	5.24 5.16	6.6	307	256 258	426	12	12 15	6	34	36 39	37.2
∦ 7	10^{-4} M acetone 5 X 10^{-4} M Ammonium sulfate	5.5	6.12 `5.80	6.7	154	146 146	241	4	4 6	2	17	15 16	19.8
#8	$2 \times 10^{-3} \underline{M}$ dioxane 1.5 x $10^{-3} \underline{M}$ ammonium sulfate	5.5	4.12 4.32	6.3	461	435 444	556	96	82 86	113	51	46 49	59.1
<i>#</i> 9	$5 \times 10^{-4} \underline{M}$ menthol $10^{-3} \underline{M}$ potassium nitrate	6.0	4.83 5.06	6.9	142	133 135	241	54	9 10	58	0	0.3	0
#10	10^{-4} benzene 2 X 10^{-3} M potassium nitrate	6.0	6.84 5.89	6.7	283	268 258	421	7	5 6	0	0	0.3 0.3	0
#11	10^{-4} M dichloro methane 5 x 10^{-3} M potassium nitrate	6.0	6.86 5.62	6.5	692	640 640	841	1	3 3	0	0	0.3 0.3	0

Table 5.2 Master Test Plan Solution Results

56

Solution	a an a chuinn an bhainn aidein ann an an ann a' machainn ann an an an an ann an ann an Ann Ann	рН		cond (2 mho/cm)				гос (р	om)	Ammonia (ppm)			
Number	Solution Composition ·	exp^1	obs ²	JSC ³	exp^{1}	obs ²	JSC ³	exp^1	obs ²	JSC ³	exp^{1}	2 obs	JSC ³
#12	10 ⁻³ <u>M</u> propanol 10 ⁻² <u>M</u> potassium nitrate	6.0	5.30 5.20	6.6	1328	1357 1294	137 1	36	36 32	36	0	0.3	0
#13	10^{-2} <u>M</u> sodium bicarbonate 2.5 x 10 ⁻³ sulfuric acid	6.4	8.15 8.30	8.7	1081	1008 968,	1201	0	3 3	1	0	0.3	0
#14	5×10^{-3} <u>M</u> sodium bicarbonate 5 X 10 ⁻³ M sodium carbonate	10.3	10.19 10.20			over range	2314	0	3	0	0	0.3	0
#15	2 X 10 ⁻⁴ M dimethyl disulfide	6.0	7.15 6.24	7.7	0	4.6 5.9	31	5	5 4	3	0	0.3 0.3	0
#16	10 ⁻³ <u>M</u> formaldehyde 5 X 10 ⁻⁶ ammonium sulfate	6.0	4.43 4.60		2	11.5 10.8	- Ara	12	14 14		0.2	0.4 0.4	
<i>∦</i> 1.7	5 X 10^{-4} M urea 5 X 10^{-5} M ammonium sulfate	6.0	5.92 5.91	7.2	16	133 133	149	6	10 8	5	1.7	23.5 22.0	10.4
#18	10^{-4} <u>M</u> OMCTS ⁴ 5 x 10^{-4} <u>M</u> ammonium sulfate	5.5	4.05 4.62	6.7	154	131 136	218	10	3 4	1	17	18.2 18.0	19.9
#19	10^{-4} <u>M</u> methyl alcohol 10^{-3} <u>M</u> ammonium sulfate	5.5	4.68 5.24	6.9	307	271 262	440	1	4	1	34	33.1 33.0	38,9
<i>#</i> 20	4 X 10 ⁻³ M' acetic acid 4 X 10 ⁻³ M sodium acetate	4.76	3.85 3.78	5.0	352	325 325	505	192	127 138	200	0	0.3 0.3	0
										4			

Table 5.2 (continued) Master Test Plan Solution Results

1. Calculated or estimated from solution composition

2. Observed results at Orion Research

3. Analyses by standard methods at NASA/JSC

4. Octamethylcyclotetrasiloxane

Unfortunately, these solutions were formulated several months before they were run and as a result some of them may have degraded. The corroborative analyses by NASA on the same solutions were run at a later date. This may account for differences in pH and conductivity.

The solutions were run over a period of approximately one month. Both automatic and manual calibrations were carried out at convenient intervals.

Comments on Test Plan Solution Results

1. The incomplete conversion of acetic acid is characteristic of the monopersulfate oxidant. The low pH value seems characteristic of the low conductivity samples and is discussed further below.

2. Low conversion of phenol was first observed in these tests and appears to be characteristic of the monopersulfate also.

5. p-Cresol, also a phenol, shows low conversion.

9. Low conversion of menthol may be an artifact. The solution was old and possibly decomposed. This should be checked in additional testing.

13. Loss of CO, probably accounts for the high pH.

18. OMCTS is not soluble to 10 ppm.

General

The data indicate two specific areas where the WQM is deficient in performance. The first is the low pH values in low conductivity solutions. We believe that this is a reference electrode problem, namely a liquid "junction potential" which varies with the ionic strength of the sample solution. A close inspection of the data seems to reveal a trend in which the pH artifact is greatest in the least conductive solutions. This problem could be eliminated in several ways, but each would involve the use of an additional component or expendable. As an example, the

> 58 5-8

reference chamber could be pressurized such that a constant outward flow of electrolyte into the sample could be maintained at the liquid junction. Or, an electrolyte solution could be introduced into the sample upstream of the pH cell. It may be possible to design one of the above systems to have very little impact in terms of additional reagent consumption since the liquid junction could be designed to require extremely low flows.

The other deficiency indicated in the test results is the incomplete conversion of some of the organics in the TOC measurement. We believe some of the low numbers (e.g. OMCTS) to be correct and the corroborative analysis at NASA confirms this, however, the low conversion of phenol, p-cresol and acetic acid are best considered limitations of the system. We do not presently know whether an alternate reagent system or improved irradiation configuration would produce better conversion. We know that peroxydisulfate converts phenol and acetic acid but that in aqueous solution it tends to revert to the monopersulfate form in a period of days or a week or two. Perhaps mixed oxidants or some type of stabilized peroxydisulfate could be developed in time.

In addition to these two major areas for improvement, there are modifications in the design of the WQM which we would implement if we were redesigning the unit. One unanticipated problem we found in the early testing stages was the back flow of reagents into the pH and conductivity sensors. We solved the problem by installing stainless steel holding loops between the sensors and the fluid junction points. In hindsight, it is apparent that location of these two sensors upstream of the peristaltic pump, on the valve manifold assembly, would have prevented the problem.

There are aspects of the pH, NH₃ and CO₂ sensors mechanical design which have room for improvement. The design of these sensors arose out of previous work in biomedical instrumentation. This design is very expensive and requires a great deal of assembly technique. We believe that sensor performances could be improved with another iteration of their designs. Specifically, it may be possible to improve the response times of the pH and CO_2 electrodes. There is an area of the fluid conduit in the pH sensor which allows fluid to collect. The CO_2 electrode uses silicone rubber potting compound and since CO_2 is very soluble in silicone rubber, there is an effective " CO_2 sink"" in the electrode, resulting in a slow response.

60 5.10

CHAPTER 6. CONCLUSION AND RECOMMENDATIONS

Our work on the WQM dealt specifically with the fluid transport and chemical sensing aspects of monitoring. The manifolding concept and the exclusive use of o-ring seals produced a miniature analytical system which we feel to be reliable enough for unattended spacecraft use. However, there are other problems in space-hardening a system such as this which we did not address. The principal area to be explored in future efforts is that of reagent handling. The use of bulky containers of caustic fluids in the zero-G situation presents potential hazards to personnel. The use of pressurized containers and subsequent elimination of a metering pump is an approach that has certain attractions. Entirely different concepts such as passive reagent addition by diffusion or insitu generation of reagents by electrolysis are perhaps the waves of the future in this form of analysis. Optimization of such techniques is probably several years down the road, and even so they are not necessarily applicable to all analytical problems.

The electronics of the WQM was not engineered for space. Although the technology exists for drastic miniaturization of the electronics used in the WQM, the design of such a package is an expensive and time consuming process.

In conclusion, we feel that we have advanced the technology for inspace water quality monitoring but that there are areas which still require concerted effort before an instrument of this type will be suitable for its long-range intended use.

61

APPENDIX I

Selected Paragraphs from Statement of Work from Original Contract

Exhibit "A"

1.0 Purpose

1.1 Objective

The objective of this Statement of Work (SOW) is to describe the effort required to design, fabricate, and test a miniaturized breadboard and preliminary prototype water quality monitor unit for continuous, inprocess monitoring of total organic carbon, pH, specific conductivity, and ammonia in advanced spacecraft water reclamation systems.

1.2 End Products

The end products of this contractual effort will be a breadboard water quality monitor (WQM) system, an interim report, a preliminary prototype WQM system, and a final report. The WQM is defined to be an integrated unit composed of a total organic carbon analyzer (TOCA), pH sensor, specific conductivity (SC) sensor, and supported by ancillary equipment. The unit shall feature low power, volume, and weight. The interim report shall describe the results of the breadboard system and include the preliminary design of a preliminary prototype water quality monitoring unit. The contractor shall provide recommendations for additional areas of investigation based on results with the breadboard system. The final report shall describe the results of the preliminary prototype system.

1.3 Background

Long duration manned space flight, involving water reclamation systems, requires reliable, fast on-line water quality monitoring to insure the health of crew and passengers. General assessment of potable



water quality can be realized by monitoring organic carbon content, specific conductivity, and pH. Measurements of chemical purity have been demonstrated in near real time by laboratory instruments under NASA Contract NAS 1-10382. Further development of these concepts is now required to improve water monitoring capabilities and to achieve an integrated design of reduced power, volume and weight. It is the intent of this SOW to continue this effort and develop an integrated breadboard and preliminary prototype Water Quality Monitor (WQM) Units incorporating miniaturized pH and specific conductivity (SC) sensors and a miniaturized total organic carbon analyzer (TOCA).

3.2 Task Description

3.2.1 Concept Study and Ultraviolet (UV) Method Design Support Testing (DST)

This study shall investigate recent, state-of-the-art, miniaturized pH sensors, specific conductivity sensors, ultraviolet radiation methods for conversion of organic contaminants in water to CO_2 , and methods to quantitatively measure the resulting CO_2 in amounts equivalent to a water content of 1 to 200 ppm total organic carbon.

In any concept, the use of expendables such as carrier gas, sorbents, reagents, etc., shall be greatly minimized. Results of the study shall present the sensors and TOCA concepts considered, recommendations of a specific off-the-shelf concept and sensor for each application along with basis for selection, an outline of what must be done to miniaturize and/or modify such including associated electronics, and present a preliminary design concept defining the breadboard system to be delivered. Sensor characteristics such as lifetime, method and ease of calibration, response time to changes in the parameter being measured, drift, accuracy, and precision shall also be considered and discussed. Electrodes employing mercury or mercury salts shall not be considered. Any sensor or concept proposed shall not employ materials which would impart impurities into the water which may be injurious to the crew's health. In addition, potential problem areas shall also be

63 1~2

addressed. A report describing results of this task including DST shall be delivered to JSC for NASA approval. The contractor shall attend a review at JSC for approval of recommendations before proceeding with development of the WQM.

Design Support Testing (DST) shall be conducted on the recommended candidate being considered for the TOCA using methane saturated water and water containing 300 ppm acetone, 500 ppm chloroacetone, 200 ppm diethyl sulfide, and a combination of the four. Inorganic carbon content of the water shall not interfere with analysis results. DST shall obtain sufficient information for sizing and preliminary design of a TOCA/CO₂ sensor which shall be capable of quantifying 1 to 200 ppm organic carbon in water at the flow, pressure and water quality conditions specified in Section: Water Quality and Supply Characteristics. Low power and volume shall be important design factors, in that order, for any TOCA concept. The study shall also address and recommend a simple, in-flight, automated WQM calibration scheme. Early study and selection of the specific conductivity sensor may be required to progress smoothly into Task 3.2.2.

3.2.2 Specific Conductivity Sensor Modification and Test

Drawing modifications to the specific conductivity sensor selected from Task 3.2.1 shall be conducted, followed by modification and testing. Modifications shall be conducted, focus on miniaturization and integration into the common water quality sensing unit with the objectives of volume, weight and power reduction. The modified sensor shall have a minimum water hold-up volume, fast response to concentration changes, features compatible with a zero-g environment, no electrical interference characteristics, and perform reliably with minimum crew maintenance. Testing shall include a minimum of three different specific conductivity values over the range of temperature, flow and pressure conditions specified in Section 3.3.4.

3.2.3 <u>Combustion Tube/CO, Sensor Development</u>

This task involves two parallel efforts to provide as the end product a miniaturized total organic carbon analyzer. These efforts are

64 IS

for a UV approach to convert organic carbon to $\rm CO_2$ and for the $\rm CO_2$ sensor. This analyzer shall consist of a UV concept to convert, as a minimum, organic carbon contaminants in water to $\rm CO_2$ along with a sensor to quantitatively measure the $\rm CO_2$ in a range directly relatable to a water organic carbon content from 1 to 200 ppm. Design modification to drawings of the selected off-the-shelf $\rm CO_2$ sensor shall be conducted followed by modification of the purchased sensor. In parallel with this effort, based on DST results from Task 3.2.1 with the addition of the range limits of pH, flow and pressure indicated in Section 3.3.4.

3.2.4 Modification and Test of pH Sensors

Drawing modifications shall be made to the selected pH sensors, followed by modification and test of the unit. Modifications shall focus on miniaturization and integration into the common water quality sensing unit with the objectives of volume, weight and power reduction. The modified unit shall have a minimum water holdup volume, fast response to concentration changes, features compatible with a zero-g environment, no electrical interference characteristics, and perform reliably with minimum crew maintenance. Testing shall include a minimum of three pH points over the range of temperature, flow and pressure conditions specified in Section 3.3.4.

3.2.5 Breadboard System Integration, Test and Preprototype Development

3.2.5.1 Breadboard System Integration

This task consists of integration of the units from Tasks 3.2.2, 3.2.3 and 3.2.4. The sensors shall be capable of analyzing water at one common point herein defined as the WQM unit. The combination of the three sensors integrated to form this unit shall exhibit no electrical interferences, minimum holdup volume and fast response to changes in organic carbon content, pH and specific conductivity. The electronics shall be housed into a single rack mounted type unit. The WQM unit shall be designed as a plug-in type device with one water inlet port and one water outlet port and be compatible with the flow, temperature, pressure and water quality ranges specified in Section 3.3.4. Commercial off-the-shelf equipment may be incorporated into the breadboard



system to simulate pressure and flow ranges and any required valve switching operations to make the system automatic in sampling and analysis features.

3.2.5.2 Breadboard System Test and Definition of Electronics Modifications

The breadboard shall be tested over the pressure, flow, temperature and water quality ranges specified in Section 3.3.4. Qualities of the water which shall be emphasized are pH, organic contaminant content and ionic salt content. Specific realistic modifications to the electronics shall also be defined (but not fabricated) under this task. The modifications shall focus on an electronics package of no electrical interference and reductions in volume, power and weight.

3.2.5.4 Preprototype Design

In addition to the electronics modifications defined during task 3.2.5.2, other design changes shall also be defined. These design changes shall result in detailed fabrication and packaging drawings and specifications of a preprototype system. The design changes shall result in tangible volume, power and weight reductions over the breadboard system.

The design changes shall include but not necessarily be limited to further miniaturization of the sensors, further miniaturization of the system, reducing the size of the reagent and fluids package, minimizing reagents consumption, improving system response time, and incorporation of in-situ maintenance of life limited items. In addition, the system design will incorporate a safe, automatic shutdown mode, a reagent line purge, and a mode for system isolation upon failure. Appropriate modifications to the breadboard electronics will be made to enable integration of the breadboard electronics package with the preprototype system.

3.2.5.5 Preprototype Design Review Meetings

Upon completion of both the preliminary design layout drawings and the detailed design drawings a design review meeting shall be conducted with NASA. The drawings shall be subject to approval for release to



fabrication by NASA to the extent that all objectives in Section 3.2.5.4 have been met.

3.2.5.6 Preprototype Acceptance Testing

Subsequent to fabrication, the system shall undergo testing at the contractor's facility to verify acceptability to NASA. Design verification testing shall be conducted on the completed preprototype water quality monitor to verify subsystem functionality and that design performance levels are met. Subsystem power requirements, ranges of detection for the four measuring parameters, stripper capacity, effect of I_2 and chloride in the water sample, and overall system operation characteristics shall be experimentally determined. The subsystem performance will be evaluated in all modes of operation. Automatic shutdown will be simulated. The testing shall include minimum, nominal, and maximum limits of pH, conductivity, ammonia, and total organic carbon as defined in section 3.3.

Accuracy of the pH conductivity ammonia content, and total organic carbon shall be within \pm 0.1 pH units, \pm 5 percent of actual conductivity of \pm 1 µmho (whichever is greater) \pm 2 percent of actual ammonia value or \pm .5 ppm NH₃ (whichever is greater) and \pm 10 percent of actual TOC value or \pm 1 ppm (whichever is greater).

Samples of the test solutions will be furnished to NASA/JSC for corroborative analysis. The subsystem testing shall be performed according to a plan to be approved by NASA. As a minimum, the cumulative time during testing at normal subsystem operation conditions during this task shall be ten 8-hour days.

67 1-6

APPENDIX II

OR10N	RESEARCH, INC	•	Failure Mode, Effects & Criticality Analysis			Page 1 of 20 page 1/17/79
TITLE	ATER QUALITY M	ONTTOR (V.	<u>л.м.)</u>		🗍 Subayste 🗍 Loop	
^p art No.	Reliability Logic No.	Nan	ne	Function		
		FILTER S	LTER SCREEN Remove particulate			ontaminates
Pailure Mode and Cause: No sample flow into W.Q.M Excessive build up of particulate matter in filter material.						
	<i></i>					
	e Effect on Co			sembiy:		•
-	le will no lon	ger go thi	ru filter.			
Failm	re Elfect on Sy tem determinati	stem/Subsy	ystem	will not be	e functional.	
Failur Syst	re Effect on Sy	stem/Subsy on of all thod:	ystem parameters		e functional.	

REPRODUCIBILITY OF THE ORIGINAL PAGE IS POOR

68 J.T.1

ORION RESEARCH, THC.				& Criticality Analysis			0f 20		
TITLE W	ATER QUALITY M	NITOR (:1.	<u>n.m.)</u>		🛛 Subsys				
	Reliability Logic No.	Nan				unction			
ł		VALVE ASSEMBLY INPUT SIGNAL VALVE #1		Mode Control of W.Q.M. Sample or standard to system					
lailur	e Mode and Cau	se :					Citicality		
1.	Electrical conr	nection fa	ilure-power	off.					
2.	Electrical conr	nection fa	ilure-power	locked "on"	**				
							{ !		
ailur	e Effect on for	monent / Fr	inctional As	sombly					
	e Effect on Con	-		•			1v		
1.	Lack of electr:	-		•	e in its r	ormal	l.1y		
1.	Lack of electr: open position.	ical power	will cause	e valve to b			ļ		
1. 2.	Lack of electr:	ical power s locked "	will cause	a valve to b may get cau	ght in its	s actu	ated		
1. 2.	Lack of electr: open position. If the power is position (Stand To Effect on Sy	tcal power s locked " lard I or stem/Subsy	on", valve II)	walve to b	ght in its	s actu	ated		
1. 2. Cailar 1.	Lack of electri open position. If the power is position (Stand Te Effect on Sy Electrical con	ical power s locked " lard I or stem/Subsy nection fa	vill cause 'on", valve II) ystem ailure will	e valve to b may get cau limit the W	ght in it: 	s actu	ated		
1. 2. Pailur 1.	Lack of electric open position. If the power is position (Stand Te Effect on Sy Electrical com and therefore With power loc	ical power s locked " lard I or stem/Subsy nection fa will preva-	on", valve II) ystem ailure will ent instrume Valve 1 is	e valve to b may get cau limit the W ent calibrat actuated.	ght in its .Q.M. to stion. The system	s actu sample n can	nated mode only, now		
1. 2. Pailur 1. 2.	Lack of electri open position. If the power is position (Stand To Effect on Sy Electrical cont and therefore With power loc only calibrate	ical power s locked " dard I or stem/Subsy nection fa will preve ked "on", the instr	on", valve II) ystem ailure will ent instrume Valve 1 is rument using	e valve to b may get cau limit the W ent calibrat actuated.	ght in its .Q.M. to stion. The system	s actu sample n can	nated mode only, now		
1. 2. Vailur 1. 2.	Lack of electric open position. If the power is position (Stand Te Effect on Sy Electrical com and therefore With power loc	ical power s locked " dard I or stem/Subsy nection fa will preve ked "on", the instr	on", valve II) ystem ailure will ent instrume Valve 1 is rument using	e valve to b may get cau limit the W ent calibrat actuated.	ght in its .Q.M. to stion. The system	s actu sample n can	nated mode only, now		
1. 2. Pailur 1. 2.	Lack of electri open position. If the power is position (Stand To Effect on Sy Electrical cont and therefore With power loc only calibrate	ical power s locked " dard I or stem/Subsy nection fa will preve ked "on", the instr	on", valve II) ystem ailure will ent instrume Valve 1 is rument using	e valve to b may get cau limit the W ent calibrat actuated.	ght in its .Q.M. to stion. The system	s actu sample n can	nated mode only, now		
1. 2. 2. 1. 2.	Lack of electri open position. If the power is position (Stand To Effect on Sy Electrical cont and therefore With power loc only calibrate	ical power s locked " lard I or stem/Subsy nection fa will preve ked "on", the instr ake place.	on", valve II) ystem ailure will ent instrume Valve 1 is rument using	e valve to b may get cau limit the W ent calibrat actuated.	ght in its .Q.M. to stion. The system	s actu sample n can	nated mode only, now		
1. 2. Vailur 1. 2. Vailur	Lack of electri open position. If the power is position (Stand e Effect on Sy Electrical com and therefore With power loc only calibrate modes cannot t	tcal power s locked " lard I or stem/Subsy nection fa will preve ked "on", the instr ake place.	will cause 'on", valve II) ystem ailure will ent instrume Valve 1 is rument using	e valve to b may get cau limit the W ent calibrat actuated. g Standard 1	ght in its .Q.M. to s ion. The system . Sample	s actu sample a can and S	nated mode only, now		
1. 2. ⁷ .1 j lur 1. 2.	Lack of electri open position. If the power is position (Stand e Effect on Sy Electrical cont and therefore With power loc only calibrate modes cannot t	tcal power s locked " lard I or stem/Subsy nection fa will preve ked "on", the instr ake place.	will cause 'on", valve II) ystem ailure will ent instrume Valve 1 is rument using	e valve to b may get cau limit the W ent calibrat actuated. g Standard 1	ght in its .Q.M. to s ion. The system . Sample	s actu sample a can and S	nated mode only, now		
1. 2. Pailur 1. 2. Sailur	Lack of electri open position. If the power is position (Stand e Effect on Sy Electrical com and therefore With power loc only calibrate modes cannot t	tcal power s locked " lard I or stem/Subsy nection fa will preve ked "on", the instr ake place.	will cause 'on", valve II) ystem ailure will ent instrume Valve 1 is rument using	e valve to b may get cau limit the W ent calibrat actuated. g Standard 1	ght in its .Q.M. to s ion. The system . Sample	s actu sample a can and S	nated mode only, now		
1. 2. 2. 1.11 Jur 1. 2. 2.	Lack of electricopen position. If the power is position (Stander of Effect on Sy Electrical contrained therefore of With power loc only calibrate modes cannot the fore the form of the fo	ical power s locked " lard I or stem/Subsy nection fa will preve ked "on", the instr ake place. thod:	will cause 'on", valve II) ystem ailure will ent instrume Valve 1 is rument using	e valve to b may get cau limit the W ent calibrat actuated. g Standard 1	ght in its .Q.M. to stion. The system . Sample	s actu sample a can and S	now Standard 2		
 2. Pailur 2. Pailur 2. Pailur Pailu	Lack of electricopen position. If the power is position (Stand e Effect on Sy Electrical contant and therefore with power loc only calibrate modes cannot t The 6 hour cal	ical power s locked " lard I or stem/Subsy nection fa will preve ked "on", the instr ake place. thod:	will cause 'on", valve II) ystem ailure will ent instrume Valve 1 is rument using cycle will g	e valve to b may get cau limit the W ent calibrat actuated. g Standard 1	ght in its .Q.M. to stion. The system . Sample	s actu sample a can and S	nated mode only, now		
1. 2. Crew / Repl	Lack of electricopen position. If the power is position (Stander of Effect on Sy Electrical contrained therefore of With power loc only calibrate modes cannot the fore the form of the fo	ical power s locked " lard I or stem/Subsy nection fa will preve ked "on", the instr ake place. thod: ibration of ix electr:	will cause 'on", valve II) ystem ailure will ent instrume Valve 1 is rument using cycle will g	e valve to b may get cau limit the W ent calibrat actuated. g Standard 1	ght in its .Q.M. to stion. The system . Sample	s actu sample a can and S	now Standard 2		

ORION RESEARCH, INC.			Failure Mode, Effects & Griticality Analysis			Рате 3 01 20 1 1/17/79	
	E /ATER QUALITY M	DNITOR (.1.	<u>つ.м.)</u>		D Loop	em Component	
Part No.	Reliability Logic No.	Nam	e Punction			lon	
1		VALVE AS INPUT S VALVE #2		l		W.Q.M. tandard 2 to	
l'ailu 1.	Criticality						
2. Electrical connection failure-power locked on.							
Failure Effect on Component/Functional Assembly: 1. Lack of electrical power will cause valve to be in its normally open position.							
2.	If the power is actuated positi		on", the val	lve may get	caught in i	its	
rai lu	re Effect on Sy	stem/Subsy	/stem	*** * *** -***** *	······································		
	Electrical conm mode only, duri		-	off will 1	imit W.Q.M.	to Standard 1	
2.	Electrical con mode only, dur		-	"on" will	limit W.Q.M.	. to Standard 2	
l'ai lu	re Detection Me	thod:	, 				
1.	The six hour ca	alibration	a cycle will	give off-s	cale reading	gs.	
	Action Required		.cal failure	•	Fine Reg1	()	

•

TITLE	RESEARCH, INC.	Failure Mode, Effects & Criticality Analysis			- <u></u>	DATE 1/17/79		
W.	ATER QUALITY M	NITOR (:1.	0.M.)				- ===	
Part No.	Reliability Logic No.	Nam	e		Punction			
Na	Na		VALVE ASSEMBLY - FLUID BLOCKAGE Mode Control of W.Q.M. (. Operat	ion	
Pailure Mode and Cause: 1. Fluid blockage caused by particulates.								
*	lo fluid flow t							
i i			tandard flow	w, no measu	rements			
Flow Sensors #3 and #4 will indicate low flow, system will shut down. Six hour calibration will yield off scale readings.								
Loca	ction Required te blocked value assembly.		lace or rep	lace entire	fime Rea'c		Tíme Avail.	

. REPRODUCIBILITY OF THE ORIGINAL PAGE IS POOR

71 11.4

ORION RESEARCH, INC. & Crit			[Mode, Effects cality Analysis D Subsystem					
i W	ATER QUALITY M	ONITOR (.I.	0.M.)		🗆 Loop	🗇 Component			
Part No.	Reliability Logic No.	Nam	e		Functi	lon			
	,	PUMP			ple, reagent . sensors.	and standards			
1	re Mode and Cau					Criticality			
Driv	III								
	e. bearing freeze f. shaft breaks								
	f. shaft breaks ailure Effect on Component/Functional Assembly: Pump ceases function								
l. Parlu	re Effect on Sy	stem/Subsy	/stem			· · ····· · ··· · ··· -			
	a of fluid flow active monitori			Subsystem	will no lor	ıger have			
¦ ¦l'ailu	re Detection Mc	thod:	**************************************						
Flow sensors will detect loss of sample and reagent flow.									
Syst repa	Action Required cem will shut d air electrical venient time.	own automa	-	-	fime Reate	4			

}				ode, Effect: ity Analys	is O Subsyst	en	7/7 <u>9</u>
<u> </u>	ATER QUALITY M	ON LTOR (J.	<u>л.м.)</u>				
Part. No.	Reliability Logic No.	Naun	e		Punct	*	
		PUMP		Pump sampl to W.Q.M.		s and standa	ırds •
lailur	e Mode and Cau	se:				C-itical	lītv
Failur Pump Lailur Loss	trical power le c Effect on Co ceases function ceases function ceases function ceases function ceases function ceases function	mponent/Fu on. stem/Subsy to measur	enctional Ass vstcm ing system.	sembly:	will no lo	nger have	
Pailure Detection Method: Flow sensors will detect loss of sample and reagent flow.							
Syst repa	Action Required and will shut d air electrical venient time.	iown automa	-	-	l'inc Rea'		me ail.

				fode, Effects ulity Analysis				
Part		Nam				runcti	ion	
·		PUMP	PUMP Pump sample, reager to W.Q.M. sensors				and st	andards
					ic-11	Icality		
	Pump tube failure, rupture. a. due to upstream or downstream blockage. b. jammed down pressure plate, abrasive failure. c. pressure regulator failure over pressure. d. premature wear failure. e. crystallization in lines due to improper shutdown.							
Leak This woul	Failure Effect on Component/Functional Assembly: Leakage of sample water or aggressive reagents into sealed pump housing. This could cause electrical short of motor assembly. Leakage of reagents would cause corrosive attack on materials on pump or lubricant of bearings - and gears.							
The	e Elfect on Sy W.Q.M. will au be contained	tomaticall	y shutdown.	Any leaka	ige ci	aused in	. the pu	IMP
	e Detection Me							
•	Flow sensors w automatically			and after a	a 2 m:	inute in	terval,	•
В.	Accumulation o	f fluids i	n the pump	housing.				
i	action Required ace pump tubin		e pump at a	convenient		fime Rea ^t d		Time Avail.

REPRODUCIBILITY OF THE ORIGINAL PAGE IS POOR

-

74 17.7

ORION RESEARCH, INC.			Failure Mode, Effects & Criticality Analysis			97 c ⁸ 20 DATE 1/17/79
	R QUALITY M	ONITOR (M.	<u>0.M.)</u>		•	🛛 Component
	Nano		с 	Punct lon		
*		CO2 SENSOR		Continuous rea (For TOC deter drinking water	mination)	
C. Erra D. No m Failure E. Unit will Failure E	ffect on Co ffect on Sy	t - bad el roken capi mponent/Fu r provide	ectrical co llary glass mctional As correct mv			2 level.
Manual		C level or	n standard o be necessar	r at <u>six hour au</u> y.	ito-calibra	ation
	on Required					

75 J.H.8

•

 	ORION RESEARCH, INC. & Critic				Mode, Effects eality Analysis D Subsystem			
 	ATER QUALITY M	ONITOR (J.	<u>().M.)</u>		D Loop	0 0	omponent	
Part No.	Reliability Logic No.	Nam	e	Punction				
		NH3 SEN	SOR	Continuous readout of NH ₃ level i drinking water.				
lailur	e Mode and Cau	se:	**************************************		•		ticality	
B. C. D. Failur Failur	C. Erratic readout - broken electrical connection or electrical interference.							
l' l'ailur	re Detection Mc	thod:						
Manu exce	Manual check of NH3 level on standard or at 6 hour auto-calibration where excessive biasing will be required.							
Crew	Action Required		······································		fime Real	4	Time Avail.	
	egard NH ₃ measu enient time.	irement, r	eplace senso	or at			,,v(l) I •	

17.9

ORION RESEARCH, INC.				ode, Effects Lity Analysis		10 20 10 1/17/79
TITLE W.	ATER QUALITY M	NITOR (1).	<u>ว.м.)</u>		•	Component
Part No.	N N		c		Venction	
		pH SE	NSOR	Continuous read water.	iout of pH	in drinking
Failur	No readout - br re Effect on Cor will no longer	nponent / Fu	nctional As		nal to pH i	level.
Fai lur	e Effect on Sy	stem/Subsy	stem			
Syst Lailur	em determination - Detection Me	on of pH w	rill not be		······	
Syst Lailur Manu	em determination - Detection Me	on of pH w thod: on standa	rill not be	functional. hour auto-calibr	ation wher	e excessive

ORION RESEARCH, DRC.			Failure Mode, Effects & Criticality Analysis					
i • W	ATER QUALITY M	ONLTOR (1.9	.M.)		🗆 Loop	Component		
Part No.	Reliability Logic No.	Nane		Punct Ion				
		CONDUCTIV	CONDUCTIVITY SENSOR Continuous readout of drinking water.			conductivity		
Pailure Mode and Cause:						Calicality		
 A. No output-Broken electrical connection B. High reading -epoxy degradation cuasing electrical short circuit or chemical contamination due to backflow of persulfate. 								
	e Effect on Co Unit will no	-		-	ding.	· · · · · · · · · · · · · · · · · · ·		
1	e Effect on Sy	-		ll not be f	unctional.			
Pailur	e Detection Me	thod:		**** *****				
Visu	Visual check of readout, 6 hr. calibration cycle							
1	Action Required		time.		fime Regio			

78 11.11

ORION	ORION RESEARCH, 19C.			ode, Elfect Lity Analys	12 01 20 1/17/79				
T TTTLE	ATER OUALITY M	ONITOR (.I.	0.M.)						
Part No.	Reliability Logic No.	Nam	ie	Tunction					
		FLOW SEN	SOR	Monitor condition of fluid flow					
A. (B. ,(C. 1	B. Output - Too Low - Electronic Malfunction								
Flow	sensor output	not usabl	e						
	e Eifect on Sy of control dat			effect.					
· ·									
Pattur	e Detection Me	thod:							
Elim	inate other po	ssibilitie "	S						
Insp read	ection Required ectiunit, disr ing. Replace sense Replace_flui	egard out or control	board		Line Rea'e	Time Avail.			

ORION RESEARCH, INC. TITLE WATER QUALITY MONITOR (J.					Page13 0f 20 DATE 1/17/79 Cm X Component			
Part No.		Nam			Fonct	ton		
	-	STRIPP	ER	Chemical	transport a	cross membrane		
l'ailur	e Mode and Cau	se:		!		C"iticality		
Erra	tic TOC reading	g – leak a	cross membr	ane				
İ	e Effect on Co ical contamina	-		sembly:				
l'ailur i	e Effect on Sy	stem/Subsy	stem	• • •• ••	******			
Syst	System determination of TOC will not be functional.							
Pailure Detection Method: 1. Six hour calibration cycle 2. Flow sensors								
None	Action Required e. Disregard T venient time.		ement replac	e stripper	at Regt	,		

ORION RESEARCH, INC.		Failure Mode, Elfect.: & Criticality Analysis		Subsystem	20 14 10 рать 1/17/79			
WATER QUALITY MONITOR (.1."			().M.)			🗖 Component		
Part No.		Nam			Punction			
		U.V. ASS (Light O		Modify sample	for TOC me	asurement		
l'ailur	e Mode and Cau	se:			······································	Criticality		
	of light outpa ection	ut - Bulb	failure or 1	broken electric	al			
	Photo chemical reaction would no longer occur.							
Pailur	e Effect on Sy	stem/Subsy	zst em					
TOC	reading would	be low.						
Pailure Detection Method: 1. Lamp sensor would indicate lamp failure. 2. Manual check of TOC level on standard at 6 hour auto-calibration where excessive biasing would be required.								
) None	Action Required 2. Disregard T Action at conv	OC measure		.ce/repair bulb	Time Reald	Tíme Avail.		

REPRODUCIBILITY OF THE ORIGINAL PAGE IS POOR

81 14.14

ORION RESEARCH, INC. TITLE WATER QUALITY MONITOR (.1.			Failure Mode, Effects & Criticality Analysis			l'are 15 0f 20 DATE 1/17/79	
			Q.M.)		🛛 Subsyste		
Part No.	Reliability Logic No.	Nain	e		Functi	lon	
		U.V. ASSI (Quartz d		Modify sa	mple for TOC	Measurement .	
l'ailur	e Mode and Cau	se:				Criticality	
Photo Fluid	e Effect on Co o chemical rea l leakage would e Effect on Sy	ction would d occur.	i no longer	·			
No Ti	DC reading.						
∵ailur Visu	DC reading. The Detection Mc al signs of fl DC reading wou	uid leakag	e.	-			

ORION RESEARCH, INC.			Failure Mode, Effects & Criticality Analysis			Pare 16 0[20	
TITLE V	ATER QUALITY M	DNLTOR (.1.	<u>0.N.)</u>		🗆 Subsyste 🗆 Loop	i 1/13 em XI Compor	
Part No.	Reliability Logic No.	Nzim	e • •		Puncti	ion	
		PRESSURE	REGULATOR	Constant S	Sample Pres	sure	
rai lur	e Mode and Cau	se:				Caltral	 i 1
F	No pressure reg particulate mat ism in operatic	ter in reg				an-	
в. І	Low or no respo or sticking reg	onse and fl				or	
	e Effect on Co Constant press	-		-	llable.		-
A,B. - !ailur A. V	Constant press e Effect on Sy Varying input, causing excession	stem/Subsy pressure c ve variati	stem causes prope	o longer avai prtion of rea J.Q.M., TOC,	agent to sa NH3 sensor	s.	-
A,B.	Constant press to Effect on Sy Varying input,	sure on out stem/Subsy pressure o ve variati will cause	stem causes prope ton in the W W.Q.M. to	o longer avai prtion of rea J.Q.M., TOC,	agent to sa NH3 sensor	s.	
A,B. !ailur A. V B. I	Constant press e Effect on Sy Varying input, causing excession Low or no flow	sure on out stem/Subsy pressure o ve variati will cause cause auto	stem causes prope ton in the W W.Q.M. to	o longer avai prtion of rea J.Q.M., TOC,	agent to sa NH3 sensor	s.	
A,B.	Constant press to Effect on Sy Varying input, causing excession Low or no flow parameters and	stem/Subsy pressure of ve variati will cause cause auto thod:	stum causes propo ion in the W W.Q.M. to b-shutdown.	o longer avai	agent to sa NH3 sensor ale reading	rs. s on all	
A,B. laitur A. V B. I Failur A. C	Constant press e Effect on Sy Varying input, causing excession Low or no flow parameters and the Detection Me	stem/Subsy pressure of ve variati will cause cause auto thod: cyclical f	Stem causes propo ton in the W W.Q.M. to b-shutdown.	o longer avai	agent to sa NH3 sensor ale reading	rs. s on all	
A,B. a lur A. V B. I Failur A. C B. S	Constant press to Effect on Sy Jarying input, causing excession low or no flow parameters and to Detection Mo Observation of	sure on out stem/Subsy pressure of ve variati will cause cause auto thod: cyclical f nsors will	Stem causes propo ton in the W W.Q.M. to b-shutdown.	o longer avai	agent to sa NH3 sensor ale reading	ressure.	

ORION RESEARCH, INC.			Failure Mode, Effects & Criticality Analysis				1/17/7
TITLE	· _ * * · * * ·		*** = =		D Subsy] Couponent
WA'	TER QUALITY M	ONLTOR (.I.	.0.M.)			L 	
Part No.	Reliability Logic No.	Nan	ne] 	۴(1)	netion	
		"INTERNA FAILURE			NA	A	
l'aiture	Mode and Cau	se:					Collicality
				······································			
ailure	e Effect on Co	mponent/Fi	unctional A	ssembly:			
ailure	e Effect on Co	mponent/Fi	unctional A	ssembly:			
lailure	e Effect on Co	mponent/Fi	unctional A	ssembly:			
	e Effect on Co e Effect on Sy			ssembly:			
lailure Any c		stem/Subs ould cause	ystem e improper a	sensing, imp	proper in nemical e	strumen xposure	
Any c Any c calib	e Detection Me	stem/Subs ould caus sical com	ystom e improper : ponent dama;	sensing, imp ge due to ch	nemical e	xposure	·•
Any c calib	o Effect on Sy of the above c bration or phy	stem/Subs ould cause sical com thod: thod:	ystem e improper a ponent dama; H.P. inside	sensing, imp ge due to ch after obta	nemical e	xposure	
Any c calib	e Effect on Sy of the above c bration or phy e Detection Me Visual inspect readings.	stem/Subs ould caus sical com thod: ion of F.	ystem e improper a ponent dama; H.P. inside	sensing, imp ge due to ch after obta	ining err shut syst	atic wa	ter qualit
Any c calib 'ailure 1. V 2. 1 Crew Ac Power	e Detection Me Visual inspect Flow sensors w	stem/Subs ould caus sical com thod: ion of F. vill indic	ystom e improper a ponent dama; H.P. inside ate abnorma	sensing, imp ge due to ch after obta 1 flow and	ining err shut syst	atic wa	ter qualit

REPROPUCT I STY OF THE ORIGINAL PAGE IS POOR

84 11.17

ORION RESEARCH, INC.			Failure Mode, Elfects & Criticality Analysis			Payel8 01 20 1/17/79
TITLE W	ATER QUALITY M	ONITOR (J.	0.M.)	•	oep	Cemponent
Part No.	Reliability Logic No.	Nram	e	· · · · · · · · · · · · · · · · · · ·	Panet in	211
NA	NA	FLUID HAN PACKAGE		Continuous pot	able wat	er analysis
Exte		rom F.H.P. re inside 1		r and failure of internal leak fa		C-Tricality
	-					
Α.		or board w rs will ca	ill cause e use erratic	lectronic malfur readings. Tota id.		
1.	re Detection Mo Visual observa Flow sensor si	tion of le		. System will a	automatic	cally shut down.
			le input, r	eagent and waste	fime Reald	Time Avail.

-

-

85 14.18

ORION RESEARCH, INC.					is DSubayat	1 1	DATE
WATER QUALITY MONITOR (9.M.)				aponent
Part No.	Reliability Logic No.	Nam	ie }		rmet	Lon	·
•		Reagent Containe	and Standard ers		in reagent of W.Q.M. s		
Cont The 1.	e Mode and Cau ainers have not following are j Line blockage - Container rupt	t been ide g <u>eneral</u> mo - particul		design.	C-it	calify	
] 1.	e Effect on Co Fluids leaving Container rupt	container			culates.		
1.	The Effect on Sy As a result of the system. T for sensing me ment calibrati No flow throug decrease system	line bloc he lack of asurements on. h the pump	kage the flu reagents wi and the lac	ll not com k of stand	nplete chemi lards will n	cal react ot allow	tions jnstru-
Pailure Detection Mathod: Flow sensors will show low flow conditions for reagents. Six hour calibration cycle will show no standard flow from both flow sensors and lack of instrument calibration. 							
		replace b	blocked lines		fime Rea'	1	Time Avail.

11.19

ORION RESEARCH, INC.			Failure Mode, Effects & Criticality Analysis			Uage20 of 20 □ 1/17/79 □ Component	
Part No.	ATER QUALITY M Reliability Logic No.	NITOR (1). Nam			lon		
		REAGENT STANDARI CONTAINE)				
Pailur	Failure Mode and Cause:					C"iticality	
	e Effect on Co e Effect on Sy			sembly:			
2.	Container rupt cavity. Effec						
Pailure Detection Method:							
Crew A	Crew Action Required				fime Rea'		

REPRODUCIBILITY OF THE ORIGINAL, PAGE IS POOR

87 II-20

•

APPENDIX III. INSTRUCTION MANUAL

Initial Start-Up Procedures

The first task in setting up the WQM is to make the appropriate electrical connections.

Before turning on the power, it should be ascertained that there is sample available and that the reagent and standard lines are properly connected to the appropriate containers, and that provision for collection of the monitor's effluent has been made.

Switch the power on (main elec. box) and put the unit in the MAN and WATER modes. If the auto shut-down light on the auxiliary electronics is on, press it to deactivate the shut-down system. The pump motor, magnetic mixer and UV light should be on.

In order to begin pumping the fluids, the pressure plates in the peristaltic pump must first be engaged. They are controlled by a knob located beneath the pump housing. Turn the knob until the pressure plates reach a maximum height, pressing the tubing against the roller carriage.

If the unit is completely dry, it may take as much as 15 minutes for the sample and reagents to fill the system. The four thermal flow sensors are calibrated at Orion to read center scale at the proper flow rates, and left scale when the flow rate is zero. Within fifteen minutes of start-up, the flow meters should settle on the center scale readings. Failure to do so is of course indicative of either a fluid malfunction or bad flow sensor. The flow sensors monitor each of the two individual reagent flows as they pass from the pump to the sensing mainfold, and each of the two "reagent plus sample" streams as they exit the CO_2 stripper. Reagent flow rates are 4 ml/hr. and the sample flow rate is 12 ml/hr. in each channel and thus the flow in each of the combined streams is 16 ml/hr.

The information yielded by the flow sensors can be used to diagnose



most fluidic failures. If in initial start-up of the WQM, all four flow sensors do not achieve center scale readings, the troubleshooting procedures are simple and logical. For example, if one of the reagent flow sensors does not register any flow, the flow sensor which monitors the combined stream for that channel should read low - only 12 ml/hr. instead of sixteen. This would confirm not only that reagent is indeed not flowing but also that both flow sensors are functioning properly since they agree with each other.

A knowledge of the flow schematic and proper interpretation of the flow data allow an operator to easily track down fluidic malfunctions lack of sample, reagent or standard, failure to pump, leaks or blockages of fluid conduits, etc. The flow data determine a troubleshooting path such that individual components and interfaces can be checked for leakage or blockage, replaced or cleaned as required.

There are three lighted pushbuttons on the main electronic panel which are labeled WATER, STD A and STD B. They control the solenoid valves which select the fluid to be pumped. Put the instrument in each of these modes for at least 5 min. and observe the flow meters to check that valve operation is correct, to prime the standard and sample lines and to insure that there are no plumbing problems in these legs of the system.

Once it has been determined that all of the fluid-handling functions are in proper working order, it is possible to calibrate the instrument.

Calibration

Manual calibration procedures are directed from the main electronics front panel with the exception of those adjustments which pertain solely to the NH_3 calibration. Put the WQM in the MAN and STD A condition. Allow 10 minutes for the sensors to stabilize on STD A. Using the COND SLOPE knob and the TOC CAL, pH CAL and NH_3 CAL knobs, adjust the meters to read about 1088 µmho/cm, 72 ppm, and 6.86 and 25.0 ppm respectively. Let the instrument run in the STD A mode for several minutes to check the stability of the readings. Readjust if necessary.



When the values seem stable, press the SERVO button. This activates the servo motors for 15 seconds. During this period it is possible to center the restandardization meters on the left panel. Using the COND SLOPE knob and the TOC, pH and NH₃ CAL knobs, adjust and watch which way the pointers on the RESTD meters move. Pressing the SERVO again if necessary to keep the motor active, turn the knobs until the pointers are centered on the three meters.

The conductivity sensor requires no further adjustment. Its value on STD B is over range. 144 ppm, 1.92 and 50.0 ppm are the values of TOC, pH and NH₃ on STD B. Press the STD B button and allow time for these to stabilize. Then using the SLOPE knobs, adjust them to the correct values. Now press the WATER button. The calibration procedure is complete. If the instrument has been shut down for a period of time, it may be necessary to repeat the calibration procedure until all of the sensors have completely stabilized.

The AUTO Mode

The WQM is designed for continuous monitoring. When monitoring a "real" sample the instrument should be in AUTO so that the automatic calibration will occur.

A timer at the rear of the electronics unit controls the AUTOCAL cycle. In AUTO the AUTOCAL cycle is invoked every 6 hours and lasts 15 minutes (though these intervals can be varied). At all other times the sample is in WATER and the ON LINE indicator at the top left control panel is lit. The timer begins the 15 minute cycle by switching the ON LINE and WATER lights off and the STD A light on. STD A is aspirated for 15 minutes and the timer switches the instrument back to its original condition, and at the same time triggers the SERVO mechanism for 15 seconds.

The AUTO mode can be left at any time by pressing ST/BY, MAN, STD A, or STD B. If an AUTOCAL cycle is in progress it will be aborted. To return to AUTO from MAN, the WATER light must be lit. In MAN, if the timer is in the 15 minute AUTOCAL condition, the AUTO button is deactivated to prevent erroneous calibration. The timer can be advanced by hand if necessary to return to AUTO.

Ģΰ 111.3

The MAN Mode

The MAN mode is most useful when the instrument is used in the laboratory as opposed to ON LINE monitoring. WATER, STD A and STD B positions can be interchanged at will and the running of samples will not be interrupted by the AUTOCAL cycle. The timer continues to operate but its switches are deactivated. This is so the time of AUTOCAL will not be effected by mode switching.

The MAN-WATER Mode

The MAN-WATER mode is for laboratory use. Samples can be introduced into the sample aspiration tube at will.

The MAN-STD A Mode

The MAN-STD A mode is for manual or semi-automatic calibration. This mode is evoked from either the AUTO or MAN mode by pressing STD A. When the sensors have stabilized on STD A, the conductivity SLOPE control can be used to set the 1088 μ mho/cm value on the conductivity meter, and the TOC, pH and NH₃ CAL controls can be used to set the 72 ppm, 6.86 and 25.0 ppm values on the TOC, pH and NH₃ meters. This can also be accomplished by pressing the SERVO button which can be activated only in the MAN-STD A mode. By pressing the SERVO button and then adjusting the COND SLOPE, TOC CAL, and pH CAL and NH₃ CAL knobs, the pointers on the RESTD meters can be centered.

The MAN-STD B Mode

The MAN-STD B mode is for checking/adjusting the slopes of the pH, NH_3 and TOC sensors. These adjustments can only be made after the sensors have been calibrated on STD A. 6.86, 25.0 and 72, the set points for STD A, are the "ISO" points of these meters. The ISO point is the only point whose value is not changed when the SLOPE control is adjusted. Therefore, after these points have been set on STD A with the SERVO button or CAL knobs, the values 144 ppm, 25.0 ppm and 1.92 can be set on STD B with the TOC, NH_3 and pH SLOPE controls.

JHI.4

It should be noted that STD A and STD B share a conduit in the valve manifold - the one connecting the two solenoid valves. Therefore, if the STD A mode is activated from the WATER mode, when the previous STD was STD B, a segment of STD B solution will pass through the sensors before STD A reaches them. The operator should be aware of this to prevent confusion. The reverse case should not be encountered, since STD B is to be run only after having run STD A.

The STD/BY Mode

The ST/BY mode is used when the instrument is to be shut down for brief periods. The timing cycle of the AUTOCAL is not effected, but the pump and UV light are turned off. When the pump is off for more than 1 or 2 minutes, the pressure plates should be released using the knurled knob beneath the pump.

Fluid Package Assembly Procedure

The fluid package consists of three main assemblies; the valve manifold assembly, peristaltic pump, and sensor package assembly. Each is pre-assembled on the bench top, and then installed into the system. The peristaltic pump is placed into position first, followed by the valve manifold and sensor manifold assemblies. A brief assembly procedure of each section is described followed by individual installation procedures.

Peristaltic Pump Assembly Procedure

Assembly should begin from the bottom of the pump. The pressure plate guide and all associated components should be mounted to the frame. The pressure relief shaft is next added, securing the saddle tube release plate and springs into position. The pressure relief shaft should be threaded into the frame to its maximum. This will guarantee proper pressure plate release. The bottom cover should now be added. Tubing is next placed into position and secured with the tubing clamps. The pressure plates should be drawn down allowing easy roller cage mounting. Once secured, the pressure plates are released and the pump is ready for installation.



Place the pump into position and secure by the frame mount screws. Add knob to the pressure relief shaft under the fluids package mounting plate.

Valve Manifold Assembly and Instalation

The valve manifold has been previously assembled by Angar Scientific Corp. It can be directly mounted into position using dowel pins for proper fluidic alignment. Special care should be taken to insure correct "o" ring seating. Once secured the tubing manifold is added.

At this point the pump should be started and checked for proper tubing length and alignment. Channel flow rates should be examined to insure the pump is performing as designed. Valve manifold misalignment may cause low flow, therefore, care should be taken to properly align all fluid paths.

Dowel pins are now added to the effluent side of the pump. Slide the flow sensor manifold into position until it properly butts against the pump frame.

Sensor Manifold Assembly

All components mounted to the sensor manifold are pre-assembled. During assembly, components should be mounted to the manifold on the bench top and hydro tested for proper sensor alignment, insuring desired fluid flow rates. An assembly sequence should be followed to allow for individual component alignment. After installation, each sensor should be tested with the test syringes supplied. By following both the flow diagram and the sensor package layout drawing one can trace the fluid path in question. Injecting water into this path will allow the assembler to identify any misalignment, through excessive back pressure. Sensors that can be pinned into place through fluid holes should be done using the .030" dowel pins supplied.

The following is a list of the assembly procedure starting with the Sensor Manifold Top.

1. Sensor Manifold - Top

A. Mount flow sensor #4 onto the top of the stripper. Utilizing the pinning technique one can adequately align the fluid paths.

B. Cut to size the polypropylene backed teflon membrane for the stripper. When installing, consult the stripper detail drawing to locate the two fluid through holes. Once located, punch the holes, clean, and mount the membrane to the lower half of the stripper. Now add the top section of the stripper, thoroughly bolting the unit together. Hydrostatically test, using syringes, to insure proper membrane alignment. It should be noted that the stripper has the most fluid resistance in the system. This should be considered when hydrostatically testing. Now mount stripper assembly to the sensor manifold.

C. Mount the TOC sensor to the sensor manifold. To test for proper sensor alignment, inject water through the U.V. chamber fluid path openings. Fluid should flow with ease. If a resistance is present, loosen TOC sensor block mounting bolts and jog sensor into position.

D. Secure mixer into position. Mixer misalignment will be checked when mounting sensor manifold bottom components

2. <u>Sensor Manifold - Bottom</u>

A. Mount pH and CONDUCTIVITY loop blocks as well as pH and CONDUCTIVITY sensors to the manifold. Inject water into the sample inlet openings of the manifold. Individually check each sensor for alignment. If resistance is present loosen mounting bolts and jog sensors into position. While hydrostatically checking each sensor, it is important that each corresponding reagent inlet opening be blocked off sufficiently to prevent water from exiting.

B. Now mount the NH₃ sensor. Again through water injection into the sample inlet opening at the pH sensor side, and blocking off the reagent opening on the same side water should



flow through the pH sensor, mixer and then into NH₃ sensor. If resistance is present, jog the NH₃ sensor. Since the water next enters the stripper, more resistance will be present in the line. Therefore, it is up to the judgement of the assembler.

C. Mount the waste block, with waste manifold to the sensor block. Water injected through the system will confirm proper alignment.

The sensor assembly is now ready for installation. Lower electrical connections must be made before placing the manifold into position. Correct conductivity sensor leads and flow sensor #3 leads. Now place the sensor manifold into position. Secure both sensor and flow sensor manifolds with two side plates and two end screws. The elongated allen head wrench (supplied) is used to drive the two end screws into position. Upper electrical connections must now be made including all sensors, flow sensors and mixer connections. Lastly, secure waste manifold to fluids package base plate.

Add the U.V. chamber assembly using the opposite threaded center screw. Secure the chamber through the side mounting screws and connect the U.V. lamp electrically.

The unit is now ready for operation. Fluid should be pumped through the system and examined for fluid leakage. Now add the printed circuit boards to fluids package side channels to complete assembly.

Flow Sensor Calibration

Flow sensors should be calibrated after the system has warmed up and run long enough to fill all tubing lines with fluid. To set zero flow, put the WQM in Stand-by. This will stop the pump but the flow sensor circuitry will still be operating.

Use the center potentiometers on the flow sensor amplifier boards to set zero left on the meters. For sensors 1 and 3 these pots are numbered R5. For 2 and 4 use R27. These pots control the input to the sensors and in actuality adjust " ΔT ". Thus there will be a time delay



in the order of 30 sec. to 2 min. before the readings stabilize.

Once the "zeros" have settled on left scale, put the WQM into "AUTO" or "MAN" and allow several minutes for flows to stabilize. Set center scale with pots R6 for sensors 1 and 3 and pot R28 for 2 and 4. These pots adjust output signal and there is no time delay.





The Society shall not be responsible for statements or opinions advanced in papers or in discussion at meetings of the Society or of its Divisions or Sections, or printed in its publications *Discussion is printed* only if the paper is published in an ASME journal or Proceedings Released for general publication upon presentation. Full credit should be given to ASME, the Technical Division, and the author(s)

\$3.00 PER COPY \$1.50 TO ASME MEMBERS

Development of a Water Quality Monitor for Spacecraft Application

S. J. WEST

M. S. FRANT

J. W. ROSS, JR.

Mem ASME

Orion Research, Inc., Cambridge, Mass

A Breadboard Water Quality Monitoring System has been developed for the NASA Johnson Space Center. Upon continued development, the system will find eventual use in spacecraft water reclamation systems to monitor the potability of reclaimed water. The system has been developed to measure-conductivity, pH, and total organic carbon (TOC) content, and is capable of operation under zero gravity conditions. Conductivity is measured by an a-c bridge method, pH by an all solid-state pH capillary, and TOC by photochemical oxidation of organic material to CO₂, and measurement of the resulting CO₂ with a capillary CO₂ electrode. Inorganic CO₂ is removed via a semi-permeable membrane prior to the oxidation step. Test results indicate good reproducibility for the three measurements in a wide range of test solutions.

Contributed by the Aerospace Division of The American Society of Mechanical Engineers for presentation at the Intersociety Conference on Environmental Systems, San Diego, Calif., July 12–15, 1976. Manuscript received at ASME Headquarters April 2, 1976.

Copies will be available until April 1, 1977.

THE AMERICAN SOCIETY OF MECHANICAL ENGINEERS

UNITED ENGINEERING CENTER, 345 EAST 47th STREET, NEW YORK, N.Y. 10017

Development of a Water Quality Monitor for Spacecraft Application

S. J. WEST M. S. FRANT J. W. ROSS, JR.

INTRODUCTION

In the closed environmental system of a spacecraft, it is essential to maintain satisfactory purity of the recycled water supply. This, in turn, requires that criteria be established for potable water quality, and that those parameters which are considered to be critical indications of purity be closely monitored. After a preliminary study $(\underline{1})^1$ in which a large number of possible monitoring parameters were screened, NASA selected pH, conductivity, and total organic carbon (TOC) as the most representative, since any form of non-biological contamination which might be present in a water supply would be indicated by one or more of these measurements.

This paper describes the development of a continuous automatic monitor for these parameters which meets the specialized requirements of the spacecraft environment. Minimum size and power consumption, as well as the capability of operation under zero-G conditions, were important design criteria.

The measurement of pH and conductivity are well-established analytical techniques, so the specific design features of the components used for these measurements were selected with a view toward integration with the TOC measuring system. The methodology for the continuous measurement of TOC had not been established at the outset of the work, and thus the development of a suitable method comprised the principal effort.

Possible oxidation techniques were examined during preliminary discussions with NASA. As first choice, a literature search indicated that oxidation of organics by ultraviolet (UV) light with or without added oxidizing agents (2-6), was a promising approach, although relatively long UV contact times seemed necessary. The - attractive features of this approach were the ease of designing for continuous operation, the amenability of the method to miniaturization, and

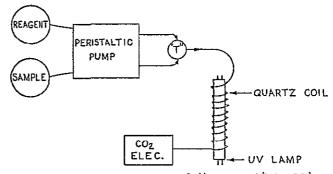
¹ Underlined numbers in parentheses designate References at end of paper. our established capability to measure the resulting CO_2 with a miniature CO_2 electrode. Combustion and wet-digestion methods $(\underline{7}, \underline{8})$ appeared to be more complex and more difficult to adapt to this application, although they are used in some commercial equipment.

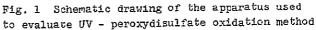
DEVELOPMENT OF MEASUREMENT TECHNIQUES

Oxidation of Organic Carbon

In the initial experiments, several oxidizing agents, such as hydrogen peroxide, sodium dichromate, and ammonium peroxydisulfate, were evaluated. The peroxydisulfate was found to be most effective, and was used in all further work.

The experimental procedure for evaluation of the UV peroxydisulfate technique was simple, and a schematic representation of the apparatus is shown in Fig. 1. Sample solutions of various organic compounds were pumped through one channel of a peristaltic pump (Sage Instruments Div., Orion Research Inc., Model 375A), and were combined with a reagent (1 M H_2SO_{μ} and 1 M (NH_{μ}) $_2S_2O_8$) pumped through a second channel. The mixture was then passed through a quartz coil, which surrounded a 4-w low-pressure mercury vapor lamp (American Ultraviolet, Model G4T5). The





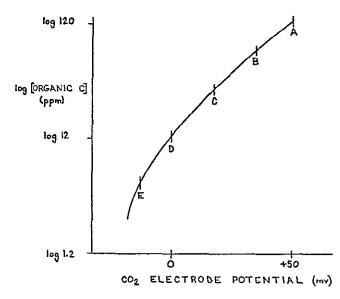


Fig. 2 Typical TOC calibration curve: (a) methanol, 120 ppm C, 100 percent conversion; (b) phenol, 72 ppm C, 100 percent conversion; (c) acetic acid, 24 ppm C, 100 percent conversion; (d) sucrose, 12 ppm C, 100 percent conversion; (e) methane, 15 ppm C, 67 percent conversion

coil and lamp were, in turn, wrapped with aluminum foil for greater UV efficiency. Residence time of the solution in the quartz coil was one min. Downstream from the irradiated coil was a standardsized flow-through CO2 electrode with a flowthrough cap (Orion Research, Inc., Model 95-02 Prototype CO, Electrode, with Model 95-00-25 Flow-thru Cap).

Completeness of oxidation of the organic test compounds was determined by preparation of a calibration curve using known carbonate solutions, and comparison with the measurements obtained on the test compounds. Fig. 2 is a typical calibration curve showing interpolated data for several test compounds, and should be referred to Table 1, which contains the data used to prepare the curve. The curvature at the low end of the calibration curve represents an asymptotic approach to the background level of organic carbon in the distilled water used to make the solutions. A quantitative conversion of organic carbon to CO, is indicated for all of the test solutions except for a saturated methane solution.

The partial conversion of methane suggested that under the proper conditions, complete conversion could be accomplished. Proceeding under the hypothesis that the heat generated by the UV lamp was driving some of the methane out of aqueous solutions, CO_2 is present as a nonvolatile ionic

Table 1 Data for Calibration Curve in Fig. 2

Test	Carbon.	Electrode	
Solution	_mg/1_	Potential, mv.	Conversion
•			
10 ⁻³ н со ₃	12	0	- 2
10 ⁻² x co3	120	+50	-
10 ⁻² н сн ₃ он	120	+50	100
·10 ⁺³ м с ₆ н ₅ он	72	+39	100
• •			
10 ⁻³ M CH ₃ COOH	24	+15	100
10 ⁻⁴ н с _{12^н22} о ₁₁	12	0	100
-12-22-11		-	
sat'd CH4	15	-10	67

medium before it could be oxidized, a stainlesssteel coil was wrapped around the lamp and quartz coil. Ice water was pumped through the stainless-steel coil during irradiation in order to maintain the sample at a low temperature. Under these conditions, methane was oxidized completely to 002

In contrast, certain refractory compounds, such as acetic acid, were found to be incompletely converted to CO, in the cooled system. To achieve complete conversion of both volatile and refractory compounds, a two-stage oxidation system was tried. The sample passes first through an air-cooled irradiation chamber, and then through an uncooled chamber. Fig. 3 is a cross-sectional sketch of the two-step irradiation sequence. Both chambers employ dip-type 4-w mercury vapor lamps (Ultra-Violet Products, Inc., Model SC-1) powered by 36-w transformers (Ultra-Violet Products, Inc., Model SCT-1). In the "cold" chamber, the lamp is surrounded by an oversized quartz coil and housed in a 7.5-cm-dia polished aluminum cylinder. A 3.2-w fan (Rotron Manufacturing Co., Model Aximax 3) draws ambient air through the cylinder and between the lamp and quartz coil, and maintains the sample at about 1 K above ambient. In the "hot" chamber, the quartz coil fits snugly around the lamp and the assembly is housed in a 2.5-cmdia polished aluminum cylinder.

Inorganic Carbon Removal

Since the water quality monitor (WQM) measures TOC after oxidation to CO2, it is necessary to remove CO, from the sample prior to oxidation. CO2 may exist in water as the dissolved gas, as bicarbonate (HCO_{2}), or as carbonate (CO_{2}^{2}), depending on solution pH. In acidic solutions, CO, is present only as the dissolved gas; in alkaline

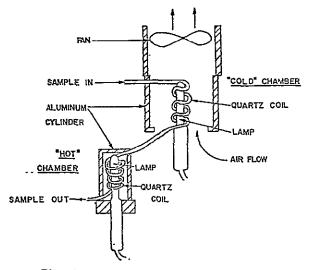


Fig. 3 Two-step exidation apparatus

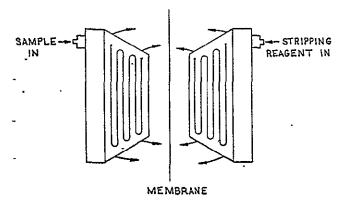
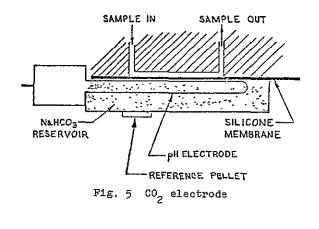


Fig. 4 Inorganic carbon stripper

species, HCO₂ or CO₂.

This difference in volatility between the queous and ionic forms is the basis of the method for inorganic CO2 removal before oxidation of the organic compounds. The removal is accomplished by means of a membrane stripper. The stripper (Fig. 4) consists of two acrylic plates, each with very shallow channels (0.10 mm) which are mirror images of each other. The plates are clamped together with a sheet of silicone rubber, GE type MEM-213 (0.025 mm thickness) sandwiched between them. The sample, which has been acidified by the addition of the 1 M H2SO4 - (NH4)2S208 reagent, passes through the channel on one side of the membrane. All of the inorganic carbon exists as CO2 on this side of the membrane. An alkaline solution is pumped through the other channel on the opposite side of the membrane. The CO, in



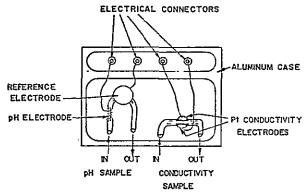


Fig. 6 Combination pH-conductivity module

the acidified sample diffuses through the membrane and is converted to CO_3^- ion in the alkaline stripping solution. The stripper removes 99.9 percent of the CO_2 from the sample in 30 sec. Thus, a sample which initially contains 1000 ppm of inorganic carbon as CO_2 , HCO_3^- , or CO_3^- contains only 1 ppm after passage through the stripper. Even the purest distilled water often contains about 1 ppm of organic carbon, so the residual inorganic carbon is negligible in nearly all conceivable cases.

In the WQM, the stripping reagent is made by addition of NaOH to a portion of the sample. This is done to prevent the loss of any volatile species, such as methane, which may be present in the sample. By using equal volumes of sample and equal volumes of reagent, the concentration of methane or other volatile, non-ionized species is the same on each side of the membrane, so none is lost from the acidified sample which is then used for the TOC measurement. The alkaline portion of sample flows to waste after passing through the stripper.

J.

100

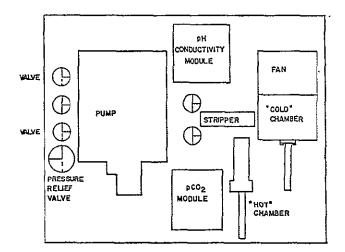


Fig. 7 Fluid handling package layout

CO2 Measurement

Once the inorganic carbon has been stripped from the sample and the organic carbon has been oxidized to CO2, the sample passes to the CO2 electrode. A miniature flow-through electrode was designed for this application. Fig. 5 is a schematic representation of the sensor. The CO, electrode is a miniature pH electrode in contact with a very small reservoir of NaHCO3 solution. This reservoir and electrode are separated from the sample by a silicone rubber membrane. CO in the sample equilibrates with the solution in the reservoir by diffusion through the membrane until the partial pressures of CO, are equal in the reservoir and sample. The diffusion of CO, into and out of the reservoir affects the pH of the reservoir in accordance with equation (1).

$$CO_2 + H_2O = HCO_3 + H^+$$
 (1)

The equilibrium expression for this reaction is shown in equation (2).

$$K_{eq} = \left[HCO_{3}^{2}\right] \left[H^{+}\right] / pCO_{2}\left[H_{2}O\right]$$
(2)

[] signifies the activity of the enclosed species and pCO₂ is the partial pressure of CO₂. Since K_{eq} is a constant at constant temperature and pressure, and $[H_2O]$ and $[HCO_2^-]$ are large enough to be unaffected by the value of pCO₂, $[H^+]$ varies linearly with pCO₂ according to equation (3).

$$pCO_2^{\circ} = constant \cdot [H^+]$$
 (3)

The electrode potential varies linearly

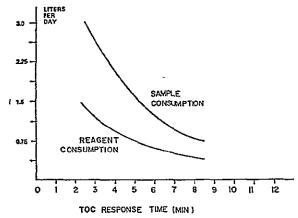


Fig. 8 Relationship between response time and sample/reagent consumption

with log $[H^+]$ and thus with log (pCO_2) . The antilog of the electrode potential is taken electronically, and displayed digitally as ppm carbon. The CO₂ sensor is housed in an aluminum block, the temperature of which is maintained electronically at 30 C. For replacement, the sensing module can be removed from the assembly by loosening a thumb screw. Fluid and electrical connections are made and broken automatically when the sensor is installed or removed.

pH and Conductivity

The pH and conductivity measurements are taken upstream of the TOC system. The sample stream is split equally by aspiration through a "T" fitting using two equal flow channels of the perstaltic pump. The pH and conductivity sensor are housed in the same module, and are attached to a temperature controlled block identical to the one used for the CO_2 sensor. The pH and conductivity measurements are made on the separate sample streams. Fig. 6 is a schematic of the combined module.

The pH electrode is a 1.5-cm length of 1-mm-dia pH sensitive glass capillary, backed with fused silver chloride and silver wire, resulting in a completely solid-state device. The sample passes through the capillary and then through a flow-through reference junction providing contact with a silver chloride reference electrode. The electrode signal is displayed digitally in pH units. After passage through the pH sensor, this sample stream is combined with NaOH and becomes the alkaline stripping reagent.

The conductivity cell consists of a cylindrical epoxy tube with platinum plates oriented 180 deg apart as electrodes. The electrodes are

4

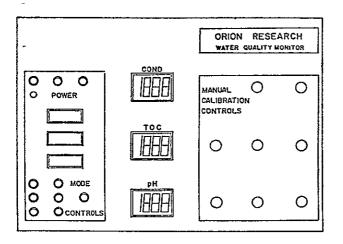


Fig. 9 Electronics package control panel

6.25 by 0.78 mm and the distance between them (the diameter of the flow path) is 8.88 mm. A 6-v, 800-Hz square wave signal is applied to the electrodes. The resistance measured across the fluid path is converted electronically to conductance, and displayed digitally as specific -conductivity in units of micromhos/cm.

SYSTEM DESCRIPTION

The WQM consists of three packages-reagents, fluid handling, and electronics.

The reagents package contains the two reagents, $H_2SO_4 - (NH_4)_2 - S_2O_8$ and NaOH, plus two standardizing solutions. All four solutions are contained in polyethylene-lined aluminum foil collapsible bags. The bags were developed under a previous contract with the NASA (10) specifically for operation under zero-G conditions. The quantities of solutins are sufficient for 30 days continuous operation of the monitor. The dimensions of the reagents package are height 15 cm, width 45 cm, depth 30 cm, and it weighs 20 kg.

The fluid handling package has the same dimensions as the reagents package and weighs 10 kg. Fig. 7 is a schematic of the fluid handling system. Sample, reagents and standardizing solutions enter from the left side. The reagents are aspirated directly into the pump. The sample and standardizing solution are pumped into miniature solenoid valves (General Valve, 1-57-90). A pressure relief valve maintains the sample inlet pressure between 0 and 250 mm Hg above ambient. The sample stream (or standardizing solution) is split in a "T." One stream passes through the conductivity cell and is then combined with the acid-peroxydisulfate reagent. It passes then

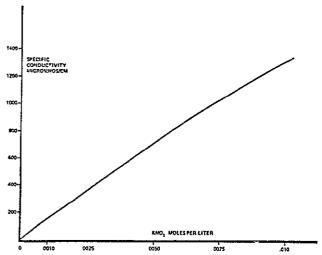


Fig. 10 Response of conductivity sensor to KNO_3 solution

through the stripper, the "cold" and "hot" UV chambers, the CO₂ sensor and then goes to waste. The other stream passes through the pH sensor, then is combined with the NaOH reagent before passing through the stripper and going to waste. Response times are 2 min. for pH and conductivity and 5 min. for TOC. Sample consumption is 40 ml/hr and reagent consumption is 8 ml/hr for each reagent. Response times can be shorter, but only at the expense of increased reagent consumption. The relationship between response time and reagent usage is shown in Fig. 8.

The dimensions of the electronics package are height 30 cm, width 34 cm, and depth 30 cm, and it weighs 23 kg. Fig. 9 is a drawing of the front panel. Three digital display meters are located in the center of the panel. Operational mode controls are located on the left, and manual calibration controls on the right. In automatic operation, all of the manual calibration controls and all operating controls, except for power and choice of mode, are concealed to prevent accidental changes of setting. The electronics are interfaced with the fluid-handling system by means of a multi-pronged connector.

During automation operation, a calibration cycle is invoked every 6 hr. A timer in the electronics section activates one of the solenoid valves, switching from sample to standardizing solution. After all of the sensors have stabilized on the standard (15 min.), the correct values are automatically set on each meter. Valve switching and automatic calibration can be activated manually with the controls on the left

5

102

	Tabl	e 2	рĦ	Results	on	Test	Solutions
Solu	ution	<u>.</u>					Observed pH
MTP	111	#1					9,85
							9.75 9.85
							9.85
MTP	111	#8					9.90
							9.80
							9.85
MTP	111	#10					9.80
MTP	111	# 7					10.10
							10.00 10.05
							10.02
MTP	111	#2					7.15
							7.15
MTP	111	₹6					7.15
							7.10
							7.15
MTD	111	ΞQ					7.00
****		u					7.05

panel. Calibration can also be accomplished entirely manually with the controls on the right panel.

RESULTS AND DISCUSSION

Conductivity

The response of the conductivity sensor to changes in solution composition is shown in a calibration curve in Fig. 10. Potassium nitrate solutions were used in this case, and a linear response was obtained from 0 to 1320 micromhos/cm.

рH

Table 2 shows some typical results of pH measurements on test solutions. The system requirements are plus or minus 0.1 pH units, and these are easily met. (Refer to Table 5 for the composition of the NASA Master Test Plan Solutions.)

Total Organic Carbon

A list of the compounds which have been quantitatively oxidized to CO_2 in the WQM using the dual UV lamp sequence is shown in Table 3. The compounds were selected to cover a wide range of molecular weights, organic functional groups and structures, and ease of oxidation.

To date, the only tested compounds that were not completely converted are thiourea and ethyl sulfide. The incomplete oxidation is probably due to the formation of COS (carbonyl Table 3 Summary of Organic Compounds Completely Oxidized by Two-Stage Irradiation System

			•
1.	Acetone	14.	Sucrose
2.	Acetic Acid	15.	Naphthol Yellow S
3.	Methanol	16.	Benzene
4.	Methyl Ethyl Ketone	17.	Ethyl Cyanoacetate
5.	Ethylene Glycol	18.	Ascorbic Acid
6.	1,4 Dioxane	19.	Aniline
7.	Phenol	20.	Phthalic Acid
8.	1-Octanol	21.	Kethane
9.	Ally1 Alcohol	22_	Mercaptoacetic Acid
10.	Urea	23.	Chloroacetic
11.	Glycine	24.	Nitrobenzene
12.	Oleic Acid	25.	Albumin
13.	Benzonic Acid	26.	Formaldehyde

sulfide) instead of CO₂ for the carbon which is attached to the sulfur atom.

This seems likely since carbonyl sulfide can be made by the reaction of related compounds in acid solution: for example, from ammonium thiocyanate, ethylthiocarbonate, or armonium thiocarbamate (<u>10</u>). This hypothesis is strengthened by the fact that organic sulfur compounds with other structures, such as mercaptoacetic acid and Naphthol Yellow S (also known as "Sulfur Yellow S"), are completely oxidized.

Table 4 gives typical results for TOC analysis on test solutions. (Refer to Table 5 for the composition of the NASA Master Test Flan Solutions.) The background level appears to be about 2-ppm carbon. There is no difficulty in detecting a 1-ppm increase above background; higher levels (up to 200 ppm) seem to work quite well.

FURTHER WORK

We are planning to continue our work on the WQM. Although the sensors were miniaturized for this first unit, much of the accessory hardware (such as pumps) was commercially available, off-the-shelf equipment, which can also be miniaturized to reduce the overall system size and weight.

For spacecraft applications, the use of mercury vapor lamps is not desirable. We plan to look at alternative UV sources, recognizing that changing to lamps of different efficiency may also require redesign of the heating and cooling stages of the present system.

ACKNOWLEDGMENT

Many helpful discussions with Robert Cusick,

	al Organic Carbon Results		Table 5
) ppm_expected ·		NASA Haster Test	Plan Solution Compositions
Solution	ppm Observed	MTP 111 #1	10 ⁻³ м к ₂ со ₃
HTP 111 #1	2 2 2		5 x 10 ⁻⁴ M HC1
		MTP 111 #2	10 ⁻³ M XHCO3
NTP 111 #2	2 2 2		5 x 10-4 M HC1
		MTP 111 #6	10 ⁻³ м кнсо ₃
4 ppm expected			5 x 10 ⁻⁴ M HC1
Solution	ppm Observed		5.2 x 10 ⁻³ м сн ₃ сос
MTP 111 #7	24 23 26 24	MTP 111 #7	10 ⁻³ н к ₂ со ₃ 10 ⁻³ н кнсо ₃
			•
15 ppm expected			2.0 x 10 ⁻³ M H ₂ NCON
Solution	ppn Observed	MTP 111 18	10 ⁻³ н к ₂ со ₃
MTP 111 #8	33		5 x 10-4 H HC1
	32 36 33		5 x 10 ⁻⁴ M C ₅ H ₁₁ O ₅ C
· · · · · · · · · · · · · · · · · · ·		MTP 111 #9	10 ⁻³ н кнсо ₃
7 ppm expected			5 x 10-4 M HC1
Solution	ppm Observed		10 ⁻⁴ M CH ₃ OH
MTP 111 #10	25 23		-
		MTP 111 #10	10 ⁻³ м к ₂ со ₃
MPT 111 411	25		5 x 10 ⁻⁴ M RC1
NTP 111 #17	25		5.2 x 10 ⁻⁴ M CH ₃ COC
			2.0 x 10 ⁻⁴ H H ₂ NCO
1.2 ppm expected			5.0 x 10 ⁻⁴ м сн _з он
Solution	ppm Observed		
MTP 111 #9	3	MTP 111 #11	10-3 M KHCO3
MTP 111 #16	3		5 x 10 ⁻⁴ H HC1
017 999 970	3		5.2 x 10 ⁻⁴ м сн _з со
91 ppm expected			2.0 x 10 ⁻⁴ M H ₂ NCO
Solution	ppm Observed		5.0 x 10 ⁻⁴ M CH ₃ OH
MTP 111 #6	155 140 15c of cold chamber	MTP 111 #16	10 ⁻² хнсо ₃
	125 J OF COLD CHANDEL		5 x 10 ⁻³ H HCL
	195 191		10-4 м сн ₃ он
		NTP 111 #17	10-2 M K2C03
			5 x 10 ⁻³ M HC1
Mashnical Monitor	r for the Breadboard Water		5.7 x 10 ⁻⁴ H CH ₃ COC
	gratefully acknowledged.		2.0 x 10 ⁻⁴ M H ₂ NCON
trans monthour, and b	Preveranta actionreafed.		

REFERENCES

1 Misselhorn, J. E., Witz, S., and Hartnung, W. H., "Development of a Laboratory Water Quality Monitoring System Suitable for Use in Zero Gravity," NASA CR-112267, Jan. 1973.

2 Goulden, P. D., and Brooksbank, P., "Automated Determinations of Dissolved Organic Carbon in Lake Water," Analytical Chemistry, Vol. 47, No. 12, Oct. 1975, pp. 1943-1946.

3 Armstrong, F. A. J., Williams, P. M.,

and Strickland, J. D. H., "Photo-oxidation of Organic Matter in Sea Water by Ultraviolet Radiation, Analytical and Other Applications, " Nature, No. 5048, July 30, 1966, pp. 481-483.

5.0 x 10⁻⁴ CH₃OH

4 Beattle, J., Bricker, C., and Garvin, D., "Photolytic Determination of Trace Amounts of Organic Material in Water," Analytical Chemistry, Vol. 33, No. 13, Dec. 1961, pp. 1890-1892.

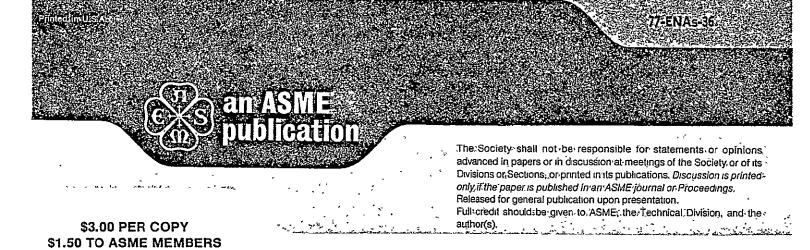
5 Ehrhardt, M., "A New Method for the Automatic Measurement of Dissolved Organic Carbon in Sea Water," Deep Sea Research, Vol. 16, 1969, pp. 393-397.

6 Grasshoff, K., "Results and Possibilities of Automated Analysis of Nutrients in Sea Water," <u>Technicon Symposium</u>, Vol. 1, 1966, pp. 573-579.

7 Baldwin, J. M., and McAtee, R. E., "Determination of Organic Carbon in Water with a Silver-Catalyzed Peroxydisulfate Wet Chemical Oxidation Method," Microchemical Journal, Vol. 19, 1974, pp. 179-190. 8 Kieselbach, R., "Continuous Recording of Concentration of Organic Matter in Waste Water," Analytical Chemistry, Vol. 26, No. 8, Aug. 1954, pp. 1312-1318.

9 Thompson, Kearton, and Lamb, Journal Chemical Society, <u>1935</u>, 1033, cited in Partington, J.R., "General and Inorganic Chemistry," Mac-Millan and Co., London, 1949, p. 487.

10 "Automated Potentiometric Electrolyte Analysis System," Contract NAS 9-12117, Dec. 14, 1973.



Preliminary Design of a Preprototype Water Quality Monitor

S. J. WEST

M. S. FRANT

S. H. FRANKS

Orion Research Incorporated, Cambridge, Mass.

As part of the Regenerable Life Support Evaluation (RLSE), which is being carried out at the NASA Johnson Space Center, a four-parameter Water Quality Monitor (WQM) is in the preprototype stage. Utilizing continuous chemical measuring techniques specifically developed for this application, the WQM will determine pH, specific conductance, ammonia concentration, and total organic carbon (TOC) content in water which has been recovered in the RLSE system. Minature components—valve manifold, peristaltic pump, inorganic carbon stripper, UV oxidation chamber, and sensors—have been designed for zero leakage, minimum volume hold-ùp, low volume weight and power, and maximum reliability. The system will respond within 5 min. to non-biological contamination of the water and consumes only 150 mi of expendable reagents per day.

Contributed by the Aerospace Division of The American Society of Mechanical Engineers for presentation at the Intersociety Conference on Environmental Systems, San Francisco, Calif., July 11-14, 1977. Manuscript received at ASME Headquarters April 4, 1977.

Copies will be available until April 1, 1978.

THE AMERICAN SOCIETY OF MECHANICAL ENGINEER

UNITED ENGINEERING CENTER, 345 EAST 47th STREET, NEW YORK, N.Y. 10017

Preliminary Design of a Preprototype Water Quality Monitor

S. J. WEST

M. S. FRANT

S. H. FRANKS

INTRODUCTION

New applications for automatic wet-chemical analysis systems in the industrial, biomedical, and environmental fields are being realized at an increasing rate. The reliability of these instruments must be very high in order that decisions of consequence can be based upon the information they generate. Use in manned space flights presents a uniquely challenging set of criteria for the design of such systems.

This paper describes the continuation of the design of a four-parameter Water Quality Monitor (WQM), a subsystem of the Regenerable Life Support Evaluation (RLSE) being conducted by NASA Johnson Space Center. This instrument will monitor the potability of reclaimed waste water in the self-contained RLSE payload. The instrument also has potential application on a manned orbiting space station which would utilize a regenerable water supply system.

The first phase of this effort generated a breadboard version of a continuous, automatically calibrating measuring system for pH, specific conductance, and total organic carbon (TOC). The primary aim of the breadboard work was to prove the feasibility of these wet-chemical analysis techniques within the specifications of the spacecraft environment.

¹ Misselhorn, J. E., Witz, S., and Hartung, W. H., "Development of a Laboratory Prototype Water Quality Monitoring System Suitable for Use in Zero Gravity," NASA CR-112267, Jan. 1973.

2 West, S. J., Frant, M. S., and Reich, D., "Interim Report on the Breadboard Water Quality Monitor," NASA Contract No. NAS9-14229, submitted by Orion Research Incorporated, Cambridge, Mass., 1976.

West, S. J., Frant, M. S., and Ross, J. W., "Development of a Water Quality Monitor for Spacecraft Application," Proceedings of Intersociety Conference on Environmental Systems, American Society of Mechanical Engineers, 1976. Having demonstrated feasibility of these measurements in the breadboard stage, a preprototype version of the instrument has been designed. The principal effort in the development of the preprototype WQM is directed toward increasing the mechanical integrity of the fluid handling system such that its reliability is high and that its response time, expendables consumption, volume and weight are low. The instrument contains caustic reagents, so the need to ensure against any possible leakage into the cabin atmosphere cannot be overemphasized.

The preprototype WQM development is described in two sections. The first describes the fluidic flow scheme and modifications in the chemistry which have been implemented since the breadboard. The second describes the engineering approach to flight-packaging and improving reliability.

CHEMICAL DESIGN

The chemical studies and design for the WQM were addressed with maximum priority in the development of the breadboard, and the preprototype development focuses chiefly on mechanical redesign and hardening. However, chemical testing and investigation has been an on-going process, and as a result, several modifications have been implemented. The preprototype WQM will be a four-parameter measurement system. In addition to the pH, specific conductance, and TOC measurements made in the breadboard WQM, ammonia will also be measured. Also, one of the two ultraviolet irradiation chambers of the breadboard has been eliminated, and the oxidizing reagent has been modified.

Plumbing Scheme

Fig. 1 is a schematic of the fluidic system. The plumbing logic is not different from the breadboard WQM since the incorporation of

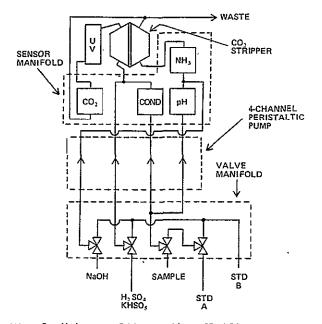


Fig. 1 Water quality monitor fluidic system

NH₅ sensor required no additional reagent. The sample, standardizing solutions, and reagents are aspirated by the peristaltic pump into the valve manifold. The incoming sample or standardizing solution is split and each stream pumped at 15 ml/hr into the measuring system. Conductivity and pH measurements are taken on the untreated sample streams, and then each is combined with separate reagents which are pumped into the sample streams at 3 ml/hr, increasing the flow in each leg to 18 ml/hr. The reagent added to the "conductivity leg" is 1 M KHSO₅ and 1 M H₂SO_L, and that added to the "pH leg" is 2 M NaOH.

The $\rm NH_3$ measurement is taken at this point on the alkaline sample. The two samplereagent streams then flow to the $\rm CO_2$ stripper, where dissolved $\rm CO_2$ is transferred from the acidic to the basic stream. After flowing through the stripper, the alkaline portion goes to waste, and the $\rm CO_2$ -free acid portion flows to the ultraviolet irradiation chamber. Here the organic constituents of the sample are oxidized to $\rm CO_2$ and the sample flows to the $\rm CO_2$ sensor and then to waste.

Ammonia Measurement

Incorporation of the NH₃ sensor into the WQM was straightforward since the NaOH reagent necessary for this measurement was already present in the system as the CO_2 suripping reagent. The NH₃ sensor, like the CO_2 sensor, is a gas-sensing electrode. Its response is

proportional to the log of the partial pressure of $\rm NH_3$ which, in turn, is linearly proportional to the concentration of free $\rm NH_3$ dissolved in the sample. The addition of NaOH to the sample prior to measurement assures that the ammonia, which can exist as ammonium ion ($\rm NH_4$), or as free ammonia ($\rm NH_3$), exists solely as $\rm NH_3$, the species sensed by the electrode.

The NH_3 sensor is mechanically identical to the CO₂ sensor. It consists of a miniature pH electrode which is in contact with an internal reference solution. This solution and the pH electrode are separated from the sample by an NH₃ permeable membrane. NH₃ in the sample equilibrates with this solution by diffusion, and this solution achieves a pH which corresponds to the sample NH₃ concentration. This electrode differs from the CO₂ sensor only in the type of membrane used and the composition of the internal reference solution. The miniaturized geometry of this type of electrode was optimized in the breadboard work.

Elimination of Room Temperature Irradiation

In the breadboard WQM, two UV chambers were used. One was maintained at room temperature since this was necessary to oxidize dissolved CH4. More detailed process information is now available, and NASA has indicated that oxidation of methane is not necessary in the preprototype WQM. As a result, the room temperature UV chamber has been eliminated in the preprototype. The present single UV chamber is allowed to be heated by the lamp to 60 C.

Elimination of the room temperature UV chamber affects the TOC response of the WQM to compounds with vapor pressures in aqueous solution that are in the same order as methane. With an uncooled UV chamber alone, compounds with water solubilities and vapor pressures of the same order as methane (e.g., ethane) are partially driven out of solution by the heat of the lamp, and into the oxygen bubbles which have been produced by the UV catalyzed decomposition of the oxidant. In this state, they fail to react. It was felt that the presence of such compounds was unlikely and that this limitation of the instrument was outweighed by the gains to be had in reducing size, weight, complexity, power consumption, and response time.

Reagent Design

Alternate oxidants for the TOC measurement were investigated in this work. The most powerful oxidant presently evaluated is ammonium persulfate, (NH4)25208, which was used in the breadboard WQM. Since that time, two other compounds, potassium monopersulfate, KHSO_c, and potassium peroxydiphosphate have become commercially available. These three compounds all combine the properties of good water solubility, strong oxidizing capability, and contain the peroxy-linkage which is readily activated by UV light. The disadvantage of the original $(NH_4)_2S_2O_8$ is its gradual thermal decomposition to the monopersulfate form and sulfuric acid. Evaluation of the potassium monopersulfate showed poorer oxidation of acetic acid, which is considered to be the most refractory organic compound." In experiments conducted under conditions suitable for 100 percent oxidation of acetic acid by ammonium persulfate, potassium monopersulfate oxidized only 85 to 90 percent. The change to the monopersulfate in the preprototype was justified by its performance with all other compounds tested and its greater stability.

Initial experiments with potassium peroxydiphosphate have been extremely encouraging; however, more testing is necessary to judge its suitability in comparison to monopersulfate.

MECHANICAL DESIGN

Both the reliability and safety of the WQM in the spacecraft environment depend primarily on engineering the system for zero leakage. Design for zero leakage must be accomplished within the constraints imposed by the functional optimization of the instrument -accurate data output, fast response time, longterm unattended operation; and also within the constraints imposed by its operating environment -- low volume, low weight, and low power and expendables consumption, and ability to operate in zero-G. In this section of the paper, the designs of the major subassemblies are described with reference to these criteria.

Valve Assembly

The preprototype WQM requires the use of valves in its calibration and flush-out modes. In the calibration mode, standardizing solutions are automatically substituted for the sample by

⁴ Hemer, C. G., Pringle, H. W., and Mauk, C. E., "Oxidation of Refractory Organic Materials by Ozone and Ultraviolet Light," DAAK-74-C-0239 Houston Research, Inc., Houston, Texas, 1974. means of a two three-way solenoid valves (Angar Scientific, Model 250). Each sensor requires a two-point calibration, so the two standardizing solutions (hereinafter designated STD A and STD B), have been designed to calibrate all four sensors simultaneously. In the flush out mode, STD B is substituted for the two caustic reagents, and the entire fluidic system is filled with this non-caustic solution for reasons of safety. This mode requires two additional three-way solenoid valves.

In ordinary usage, each of these four valves would require three fluid fittings and a complicated array of tubing. In striving for zero-leakage, these valves have been manifolded into one monolithic block which requires a total of nine fittings. In addition to the valving, this block effects the splitting of the sample stream, such that the fittings necessary for a "Tee" are also eliminated. Fig. 2 is a schematic representation of the valve manifolding concept. The two valves necessary for the introduction of STD A and STD B are shown as well as the plumbing for splitting the sample or standardizing solutions.

Peristaltic Fump

The peristaltic pump is the only component in the WQM where the fluid is contained in elastomeric tubing. This means that it is a high-risk area in terms of leakage. As a result, the pump designed for this application must contain any fluid which could be released in the event of pump tube rupture.

The pump is also the largest and most

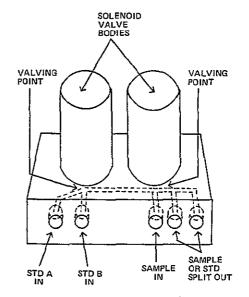


Fig. 2 Valve manifolding concept

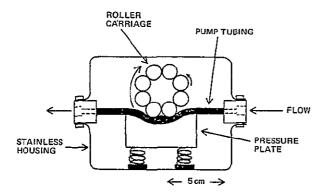


Fig. 3 Sealed peristaltic pump

mechanically complicated assembly in the WQM, and therefore the greatest gains in overall weight and volume reduction of the entire unit can be realized by proper pump design.

Fig. 3 is a schematic cross section of the four-channel peristaltic pump designed for the preprototype WQM. The pump mechanism is hermetically scaled in a stainless-steel housing. The roller carriage is driven by a planetary gear system which prevents mechanical abrasion of the tubing. The dimensions of the pump are 15 x 12.5 x 11 cm.

In order to continuously monitor the operational status of the WQM, four thermal flow sensors have been designed into the pump (not shown in Fig. 3). These sensors will measure the flow rate in each pump channel by a differential thermal technique. Pump tube rupture, leaks or blockages in the system, or exhaustion of reagent supplies can be indicated by these sensors.

Sensor Assembly

The design of the sensor assembly is based on the same concept of manifolding as the valve assembly. The pH, NH_3 , and CO_2 electrodes are similar in construction and amenable to the monolithic design philosophy. They are geometrically more complicated than the solenoid valves, however, and the base block of this assembly is, therefore, intricate.

Fluid paths are contained in the acrylic base block and lead to the surfaces at the points where the measurements are to be taken. The individual sensor blocks (acrylic) are bolted to the base block at these locations. Fig. 4 illustrates the concept in a simplistic way, and shows also the manner in which the reagents are combined with the sample without external "Tee" fittings.

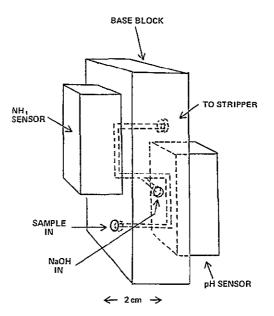


Fig. 4 Schematized sensor manifold

CO2 Stripper

In the stripper, the two sample streams pass through mirror-image spiral channels, separated by a 0.025-mm gas permeable, nonwetting membrane. In the acid stream, all the inorganic carbon exists as free CO_2 which diffuses through the membrane and reacts with the NaOH. There is no net transfer of volatile organics in the stripper due to the equal dilution of the sample streams. This is true even of volatile organic acids such as formic or acetic because the sample residence time in the stripper (40 sec) is not sufficient to allow measurable transfer of compounds with low vapor pressures.

In order that the CO₂ can be rapidly and efficiently removed from the sample, the geometry of the stripper has been optimized to promote rapid transfer across the membrane. The rate of diffusion varies with the inverse square of the channel depth so this depth is as small as will permit flow without excessive back pressure. The depth of the spiral channels is 0.2 mm, and each is 0.75 mm wide and 125 cm long. At the flow rates of 18 ml/hr through each channel, the stripping efficiency is 99.9 percent in 40 sec.

The plates, on which the channels are milled, are 316 L stainless steel, each 1.25 cm thick and 8.75 cm in diameter.

UV Oxidation Chamber

The design of the UV oxidation chamber

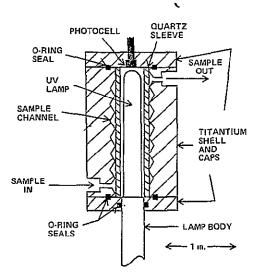


Fig. 5 UV chamber

presented the greatest difficulty in ensuring zero leakage. The chamber must contain the highly acidic oxidizing solution which is strongly activated by UV light, as well as the toxic mercury vapor which is contained in the UV lamp. Elastomers, epoxies, and many other common construction and sealing materials, which are compatible with the reagent or UV alone, are not acceptable in the presence of both.

A schematic cross section of the new UV chamber is shown in Fig. 5. The outer body of the chamber is a hollow titanium cylinder which has been threaded internally. The thread acts as the sample flow path. The titanium shell is heated to 400 C and slipped over a quartz sleeve, resulting in a 0.01- to 0.02-mm interference fit which mechanically seals the sample-reagent stream in the helical flow channel. The UV lamp fits into the quartz sleeve and is sealed in place with titanuum end caps and O-rings. Thus, the solution and lamp are individually sealed. A photocell is contained in the cap to monitor the operation of the lamp.

FURTHER WORK

The present WQM consists of integral subassemblies. The zero-leakage criterion has been applied to each sub-assembly by striving toward monolithic design. This state of design is a stepping stone to complete integration of the entire fluidic system. The diversity of chemical, mechanical, and electronic components which make up a continuous wet-chemical monitoring system necessitates that a rigorous design approach be taken to ensure maximum reliability, optimum system performance, and zero leakage.

We plan to continue our work on the WQM. The problems addressed in this work are common to a large field of chemical analysis techniques, and new technology deriving from this effort will find many applications.

ACKNOWLEDGMENT

We would like to gratefully acknowledge the help and collaboration of Eugene Winkler, cur NASA Technical Monitor. We also thank Bill Morris and Frank Samonski of NASA JSC for suggesting the monolithic approach.

