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DEVELOPMENT OF A LABORATORY PROTOTYPE WATER QUALITY MONITORING SYSTEM SUITABLE FOR USE IN ZERO GRAVITY

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CONTENTS

CONTENTS (Continued)

CONTENTS (Continued)

CONTENTS (Continued)

ILLUSTRATIONS

ILLUSTRATIONS (Continued)

ILLUSTRATIONS (Continued)

TABLES

TABLES (Continued)

SUMMARY

The development of a laboratory prototype water quality monitoring system has been completed. This system is intended for use in the evaluation of candidate water recovery systems and for study of techniques for measuring potability parameters. The monitoring system was designed to signal recovery system malfunction rather than measure absolute performance.

Sensors selected for specific ion measurement were an Orion (#94-17) solid state chloride electrode, a Corning (#476220) monovalent cation electrode for ammonium ion and an Orion (#91-01) pH electrode. The reference electrodes were Beckman Lazaran (#19033) electrodes. No particular problems were encountered with the Cl^- or pH electrodes. However, the NH_4^+ electrode had poor sensitivity at NH_4^+ ion concentrations <10 ppm. Alternate electrodes considered were a Beckman ammonium electrode (#39626), which failed mechanically when operated in flowing streams at a slight (approx. 2.5 psig) pressure above atmospheric, and a Beckman cation (#39137) electrode. Both cation electrodes were evaluated extensively and determined to have poor reproducibility at concentrations below 10 ppm, but would probably suffice as go-no-go indicators. Estimated errors in Cl^- measurement were about 10% at the alarm level (450 ppm). pH measurement errors were determined to be less than 5%.

Installation of the ion electrodes uncovered electrical problems related to ground loops and alarm techniques. Both were effectively solved by operating the ion meter readout from batteries and by sampling a single ion electrode at a time with a switching circuit rather than all simultaneously. Meter display for all electrodes remained continuous.

The specific conductance sensor is an epoxy flow through conductivity cell with a Beckman RI5 Solu Bridge indicator and is unmodified from its commercially available configuration.

A Beckman Model 915 Total Organic Carbon (TOC) analyzer was converted from manual to automatic operation. Automatic sample injection valves were installed and electronic circuitry was built to provide automatic signal processing. Additional circuitry was added, so that

degradation of the high temperature combustion tube (which is normal), could be periodically compensated for electronically. The TOC analyzer samples in the range from 0 to 200 ppm, alarming at 100 ppm organic carbon.

A bacteriological sensor has been developed and tested. The principle of detection is based upon measuring the increase in chemiluminescence produced by the catalytic action of bacterial porphyrins on a luminol-hydrogen peroxide mixture. The light emitted in the reaction, which was monitored by a photomultiplier tube, was proportional to the number of bacterial present. To permit differentiation between living and dead organisms, signals were obtained for both incubated and unincubated samples. The sensitivity of the biosensor toward E. coli (400 ml sample size) is 10 cells/ml total (viable and nonviable) and 5 cells/ml viable.

Sensing techniques for monitoring of the most desirable parameters is reviewed in terms of their sensitivities and complexities, and their recommendations for sensing techniques are presented. Rationale for selection of those parameters to be monitored (pH, specific conductivity, Cr^{+6}, I_2, total carbon, and bacteria) in a next generation water monitor is presented along with an estimate of flight system specifications (weight, 63 pounds; power, 77 watts; volume, ~ 1700 cu inches). A master water monitor development schedule is included.

INTRODUCTION

This is the final report submitted in accordance with the requirements of Contract NAS 1-10382, "Development of a Laboratory Prototype Water Quality Monitoring System Suitable for use in Zero Gravity."

The purpose of this contract was to adapt currently utilized techniques for measuring physical, chemical and bacteriological properties into a laboratory prototype of an inflight automatic water quality monitoring system. The contract covered:

1. A feasibility study devoted to the evaluation, development and/or perfection of suitable sensors that could ultimately be adapted to a zero-gravity environment. Sensors that were considered were those commercially available for monitoring specific conductivity, pH, total organic carbon, ammonium ion, chloride ion, plus an AMB developed biological sensor for E. coli.
2. The integration and testing of the above sensors as an automated prototype water quality monitoring system.
3. Additional effort related to the study of sensing techniques and a selection and recommendation for sensors to be incorporated in a next generation monitoring system.
4. Preparation of an operating and maintenance manual for the integrated water quality monitoring system.

All sensors were to be mounted in instrument racks so that the water monitor could be interfaced with potential water regeneration systems for evaluation. The selection of those parameters to be monitored was made based upon many diverse factors. Ammonium ion is monitored for an indication of a possible serious breakthrough of biological pollution and unpleasant flavor. Chloride is present in large quantities in urine, and excessive amounts in the reclaimed water would be indicative of possible system malfunction. pH is included because it will indicate acid carryover from any chemical pretreatment. Specific conductance is a measure of the total ionic species and, hence, an assessment of the total solids in the recovered water. A measurement of organic carbon is included to monitor compounds whether derived

from human functions, construction materials or reclamation system components, or materials associated with humans such as food or clothing. Monitoring of bacterial content is important since there are a number of pathogenic organisms of fecal origin which might appear as contaminants in a regenerated water supply.

SUBSYSTEM DEVELOPMENT

This section covers the evaluation of available sensing techniques, laboratory testing of various sensors, and selection of the most suitable methods. Development and description of the individual sensors follows.

Finally, performance data on the individual sensors is presented.

Study And Selection

Chloride Sensor. -

Two electrodes were evaluated for monitoring the Cl^- ion level; one was an Orion (#92-17) liquid ion exchange membrane electrode and the other an Orion (#94-17) solid state chloride electrode.

The liquid membrane electrode was selected initially because of no interference from Ag^+ and NH_3, two components which could be present in reclaimed water.* Apart from the interference expected from HCO^-_3, $SO^=_4$, Na^+ and OH^- ions, this electrode would require external pressure compensation for its filling solution when the sample stream is under pressure. The solid state electrode which has a solid membrane of silver chloride as an ionic conductor could be used in the presence of most common anions including sulfate, phosphate and bicarbonate ions. H_2S must be absent with this electrode, however, in the presence of dissolved oxygen, this sulfide is readily oxidized to water and free sulfur or sulfate, so it is high unlikely that interference from this source will be encountered. If significant levels of sulfide do occur, they could be scavenged by use of a silver mesh screen or insoluble silver chloride pellets placed in the path of the flowing stream. Dissolved ammonia could interfere, however, at the levels normally present in reclaimed water, the effect will probably be insignificant.

Apart from less interference from other anions, added advantages of the solid state over the liquid membrane electrode are (1) pressure compensation would not be required and (2) more readily adaptable to zero gravity operation (either by completely filling the electrode or using a packing of fine beads to wick the electrolyte to the membrane).

A comparison of the performance of the solid state and the liquid membrane electrode is given below.

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*Ag^+ has been used in one of the water regeneration systems as a bacteriostat.

Electrode Response -

The response of these electrodes to Cl^- ion at 1-1000 ppm is shown (Figure 1) to be virtually identical; the slight curvature observed is due to changing ionic strength of the test solutions. The alarm level is set at 450 ppm.

HCO_3^- or $SO_4^=$ Interference (Table 1) -

In contrast to what is observed for the liquid membrane electrode, interference from either HCO_3^- or $SO_4^=$ ions at concentrations up to 244 and 250 ppm, respectively, is seen to be nil for the solid state chloride electrode at Cl^- ion concentrations of 1 and 10 ppm.

No limit has been set for bicarbonate ion in drinking water since it does not present any health hazard; its presence in reclaimed water could be due to absorption from the atmosphere or to bacterial decomposition of organic matter. The maximum concentration of bicarbonate ion in reclaimed water is expected not to exceed 10 ppm (the HCO^-_3 concentration of water in equilibrium with CO_2 at 760 mm and 25°C is about 7 ppm).

Effect of pH -

1. Liquid Membrane Electrode (Figure 2)

   Negligible effect of pH 3 to 10.5 near alarm (450 ppm) level; significant interference above a pH of 9 at less than 100 ppm Cl^-.

2. Solid State Electrode (Figure 3)

   Virtually unaffected by pH of 3 to 10.5 from 710 ppm down to less than 10 ppm Cl^- ion.

The data indicate that the solid state chloride electrode exhibited less interference toward $SO_4^=$, HCO^-_3 and OH^- than the liquid membrane electrode. Because of the additional advantages of the solid state electrode (external pressure compensation and periodic membrane replacement are not required and more readily adapted to zero-gravity operation) no further testing was done on the liquid membrane electrode.

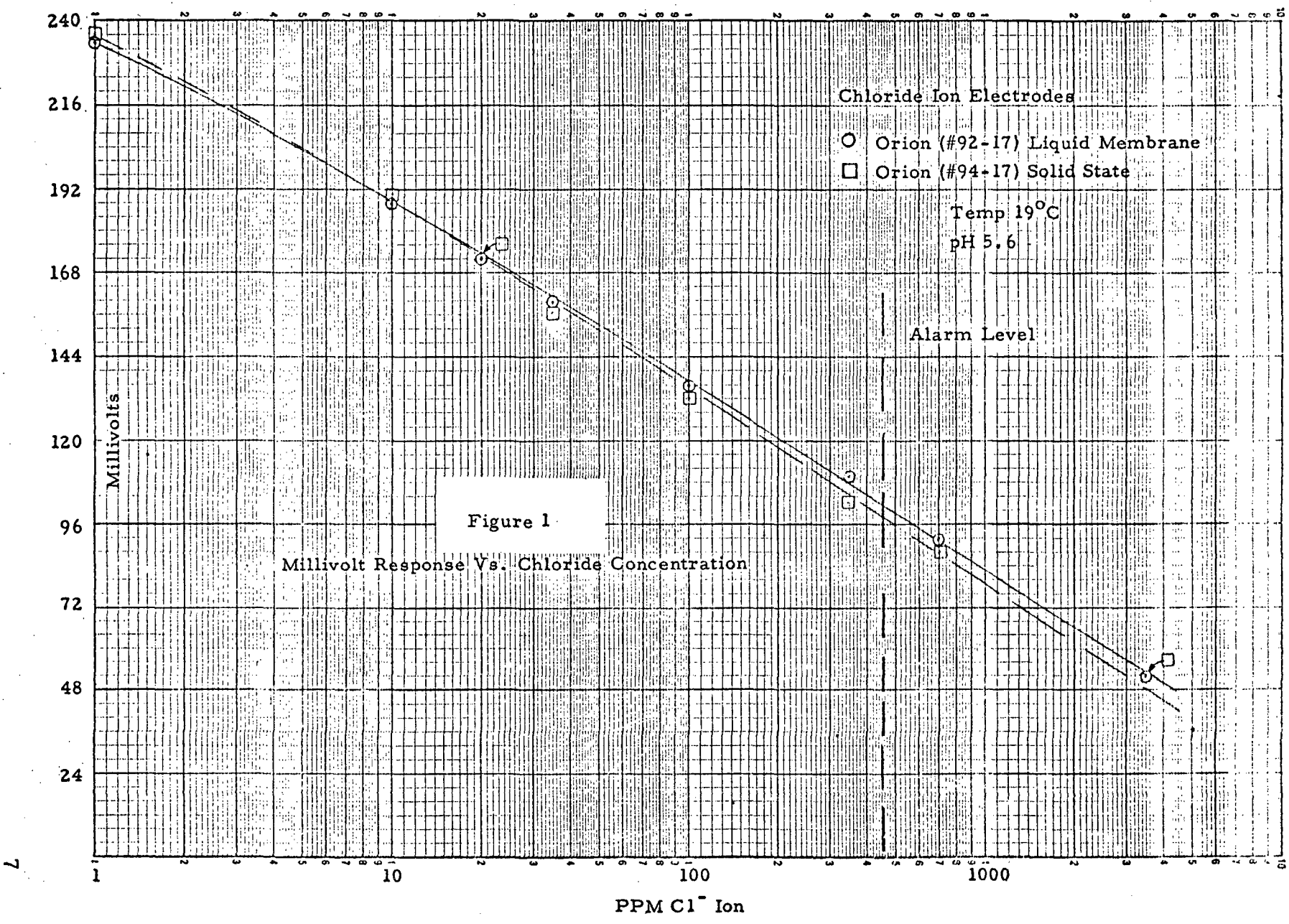


Figure 1

Millivolt Response Vs. Chloride Concentration

Table 1

Effect of HCO_3^- and $SO_4^=$ on Response of Orion Solid State and Liquid Membrane Chloride Electrodes*

	#94-17 (Solid State)		#92-17 (Liquid Membrane)	
Impurity	1 ppm (Cl^-)	10 ppm (Cl^-)	1 ppm (Cl^-)	10 ppm (Cl^-)
None	+238	+190	+238	+200
1.22 ppm HCO_3^-	+238	+190	+226	+195
13.4 ppm HCO_3^-	+238	+190	+205	+190
62.2 ppm HCO_3^-	+238	+190	+181	+178
122 ppm HCO_3^-	+238	+190	+171	+169
244 ppm HCO_3^-	+238	+190	+160	+158
None	+235	+188	+225	+188
5.0 ppm $SO_4^=$	+235	+188	+209	+182
10 ppm $SO_4^=$	+235	+188	+199	+179
25 ppm $SO_4^=$	+235	+188	+176	+165
50 ppm $SO_4^=$	+235	+188	+160	+155
125 ppm $SO_4^=$	+235	+188	+146	+145
250 ppm $SO_4^=$	+235	+188	+138	+135

*Orion Double Junction Reference Electrode (#90-02)

Figure 2

Effect of pH on Response of Orion (#92-17) Liquid Membrane Chloride Ion Electrode

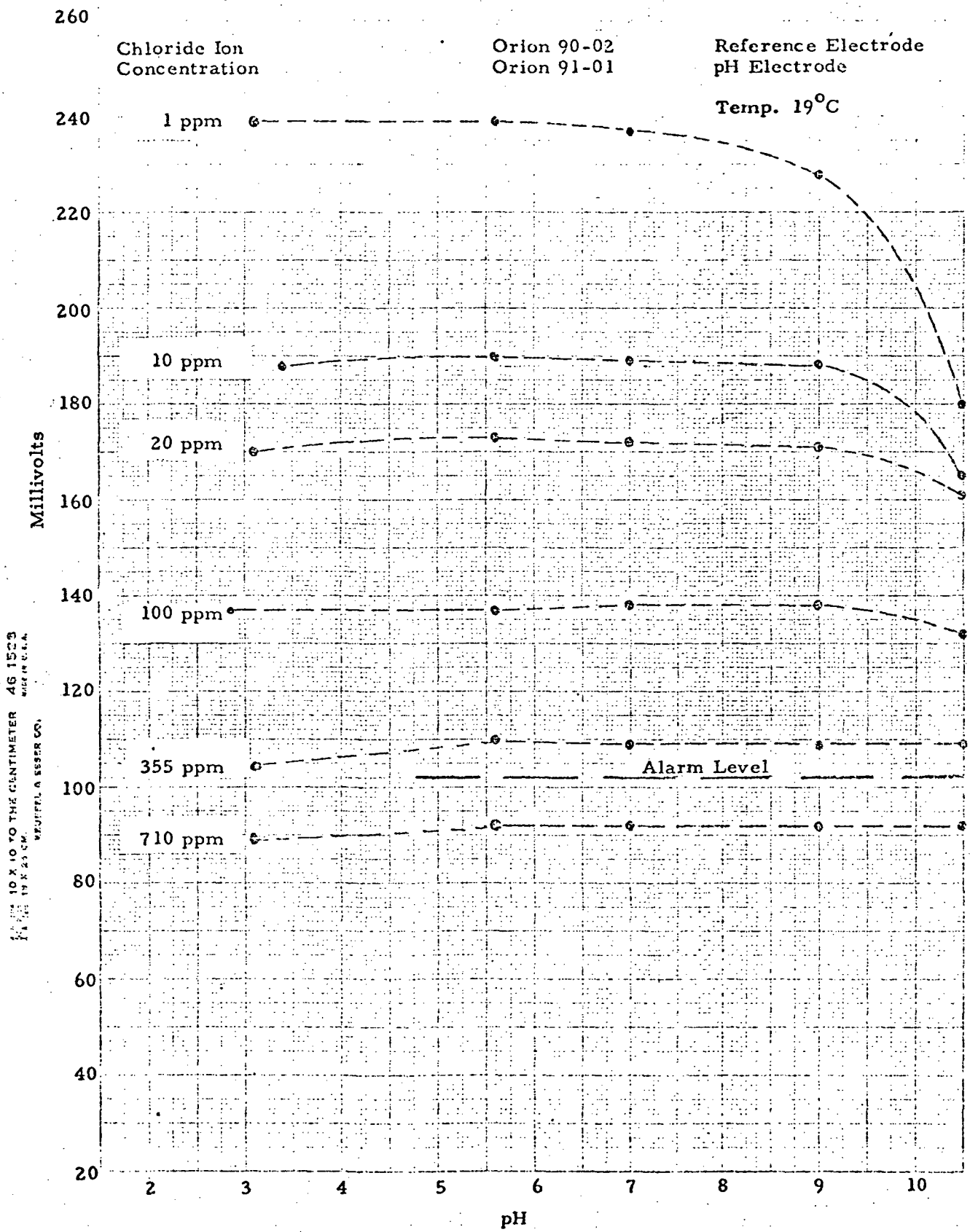
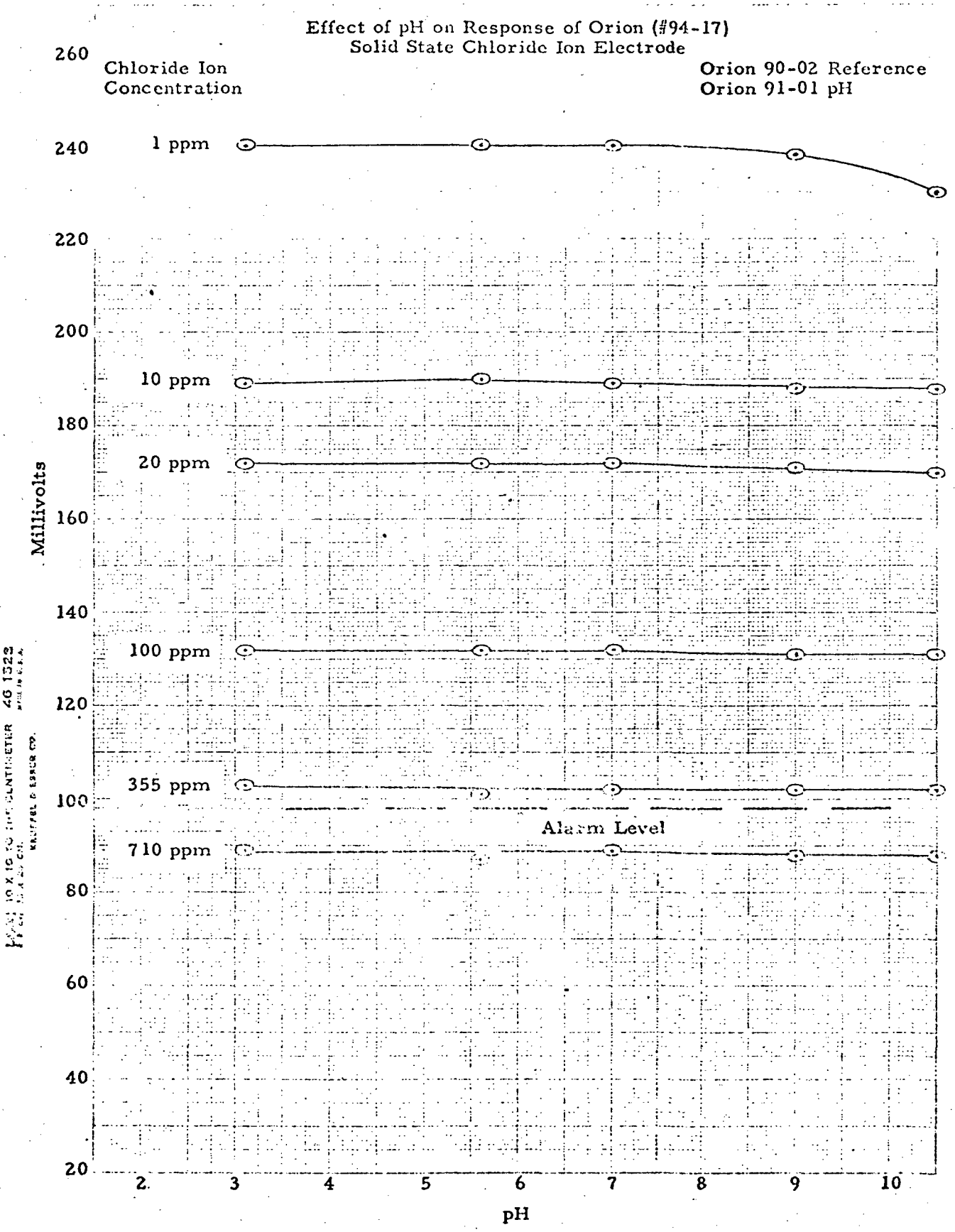


Figure 3


Effect of pH on Response of Orion (#94-17)
Solid State Chloride Ion Electrode
Chloride Ion
Concentration
Orion 90-02 Reference
Orion 91-01 pH
1 ppm
10 ppm
20 ppm
100 ppm
355 ppm
710 ppm
Alarm Level
Millivolts
pH
260
240
220
200
180
160
140
120
100
80
60
40
20
2
3
4
5
6
7
8
9
10

Drift -

The short term drift of the system comprising the Orion solid-state chloride (#94-17) - Lazaran reference and the Orion 401 meter was evaluated with the results shown in Table 2. Some data is included in which the Lazaran reference was replaced by an Orion double-junction reference electrode. The data indicate that within a 4-hour period, the drift was random in either a positive or negative direction; however, the drift 20 hours after calibration tended to be positive. The maximum deviation from the standard value observed at any one time is summarized by the following data.

	Maximum Deviation 450 ppm Calibration
4 hours	-3.8%, -4.8%
6 hours	-
20 hours	+7.3%

Ammonium Ion Sensor. -

The electrodes initially evaluated for monitoring NH_4^+ ion were (1) a Corning Monovalent Cation Electrode (#476220) and a (2) Beckman Ammonium Electrode (#39626).

The Corning electrode responds with varying sensitivity to most monovalent cations with a greater selectivity being exhibited toward $H^+ > K^+ > NH_4^+ > Na^+$ ions (in descending order of sensitivity). The working concentration range is claimed to be 10^0 to 10^{-5} moles/liter (or 0.18 to 18000 ppm NH_4^+). Being a glass electrode, a sample pressure of a few psi should not affect the reading; it should also be readily adaptable to zero-gravity operation.

The Beckman electrode utilizes a solid organic sensing element and although responding to most monovalent cations to varying degrees, the order of selectivity is $NH_4^+ > K^+ > Na^+$. It is also supposed to exhibit less H^+ interference than the Corning monovalent cation electrode. The

Table 2

Chloride Ion Electrode (Orion 94-17) Drift

Δ Time, Hrs.	ppm Cl^- Beckman Lazaran - #94-17 Chloride Electrodes	ppm Cl^- Orion Double Junction #94-17 Chloride Electrodes
Run No. 1		
0 (calibrate)	450	450
1.00 hrs	440	430
1.50 hrs	433	430
2.00 hrs	438	430
2.50 hrs	438	425
3.08 hrs	440	425
3.58 hrs	440	425
4.25 hrs	445	430
20.0 hrs	483	440
Run No. 2		
0 (calibrate)	420	-
0.42 hrs	423	-
1.67 hrs	400	-
2.17 hrs	417	-
2.90 hrs	425	-
3.92 hrs	400	-
4.25 hrs	410	-
Run No. 3		
0 (calibrate)	45	45
0.50 hrs	44	45
1.00 hrs	43.9	45
1.50 hrs	43.7	45.3
2.75 hrs	42.5	45
3.50 hrs	43	45.9
4.00 hrs	43	45.9
5.00 hrs	43	45.9
6.00 hrs	42	46
Run No. 4		
0 (calibrate)	45	-
2 hrs	46	-
4 hrs	47	-
20 hrs	57	-
24 hrs	54	-
27 hrs	52	-

working range of both electrodes are supposed to be comparable (1 to 10^{-5} moles/liter or 0.18-18000 ppm NH_4^+).

Electrode Response -

Data in Table 3 and Figure 4 show the response of the Beckman electrode compared to that of the Corning electrode at NH_4^+ concentration up to 89 ppm (at a pH of 6.2). Since the Orion Double Junction Reference electrode used in these measurements contains a concentrated KNO_3 solution which is slowly discharged through the junction and which could act as an interferent (NH_4^+ electrode responds to K^+), the effect of isolating the double junction electrode through a salt bridge containing a solution which does not interfere with NH_4^+ ion was evaluated.

The data indicated the following:

- The response for the Beckman electrode was fairly linear over the concentration range of interest whereas the Corning electrode showed a more pronounced curvature.
- The difference in the values obtained with and without the salt bridge was insignificant indicating that K^+ ion interference from the leaking double junction reference electrode was negligible.

Effect of pH -

a. Corning Electrode

Referring to Table 4, and Figure 5, from 1.8 to 1800 ppm NH_4^+, the decrease in ionization of NH_3 with increasing alkalinity is clearly evident at pH > 8 (the percent ionization of NH_3 as a function of pH is 99.5% NH_4^+ at pH = 7, 94.8% at pH = 8 and 64.5% at pH 9).

Interference from H^+ becomes more pronounced, the lower the NH_4^+, with no significant change from the plateau evident down to pH 3 for 180 and 1800 ppm NH_4^+, but significant below pH 5.4 for 18 ppm and below pH 7 for 1.8 ppm NH_4^+.

Table 3

Response of the Beckman NH_4^+ Electrode and the Corning Monovalent Cation Electrode to NH_4^+ Ion*

	Beckman NH_4^+ Electrode		Corning Monovalent Cation Electrode
PPM NH_4^+	90-02 Reference	90-02 Ref. + Salt Bridge	90-02 Reference
0.18	---	-160 mv	---
0.36	---	-145	---
0.54	---	-137	---
0.89	-126 mv	-121	-131 mv
1.8	-108	-105	-120
3.6	-90	-90	-110
8.9	-68	-68	-93
18	-50	-50	-79
36	-41	-41	-70
89	-15	-15	-40

*at a pH of 6.2

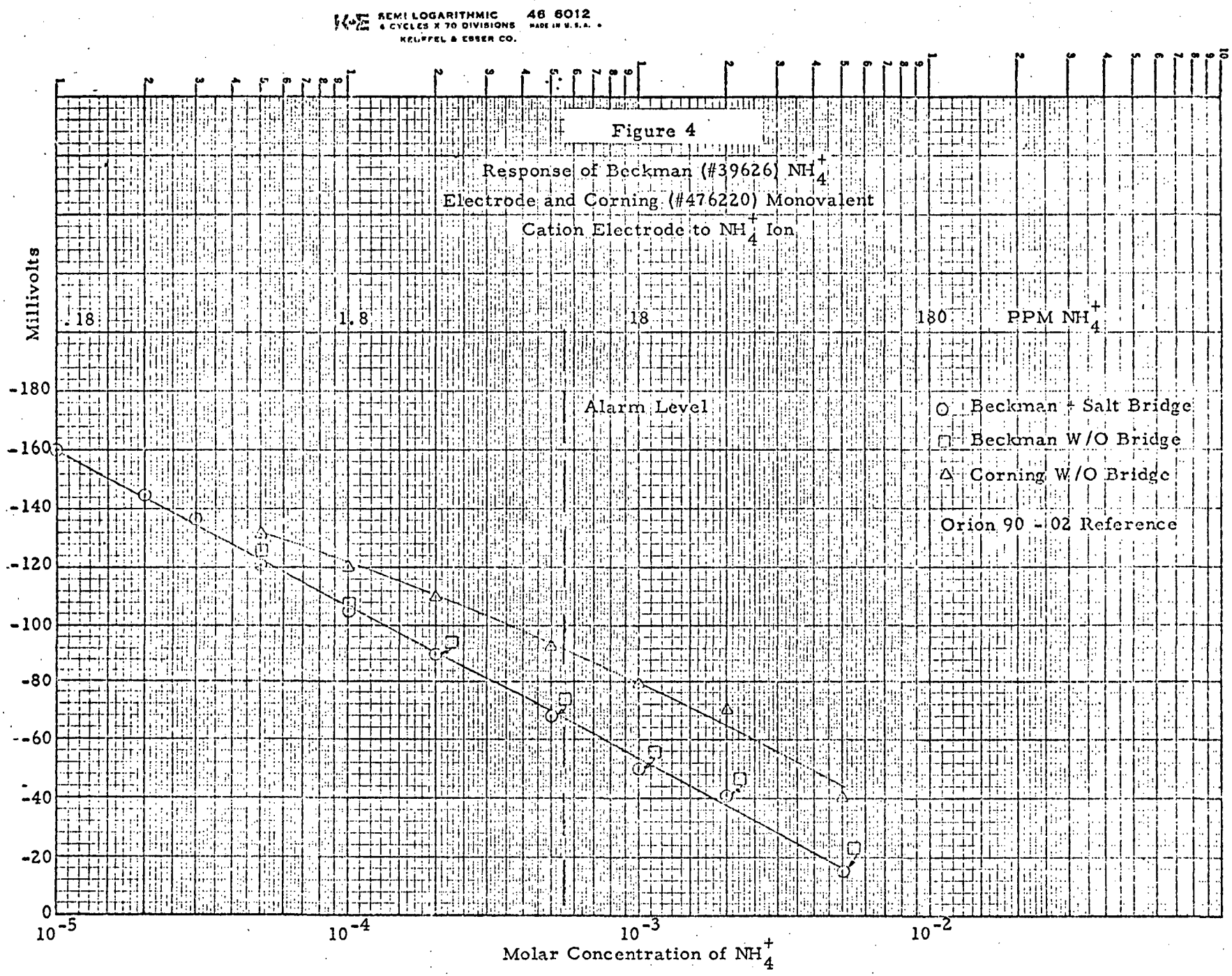

SEMI LOGARITHMIC 46 6012
6 CYCLES X 70 DIVISIONS MADE IN U.S.A.
KEUFFEL & ESSER CO.
Figure 4
Response of Beckman (#39626) NH_4^+ Electrode and Corning (#476220) Monovalent Cation Electrode to NH_4^+ Ion
Millivolts
.18
1.8
18
180
PPM NH_4^+
Alarm Level
Beckman + Salt Bridge
Beckman W/O Bridge
Corning W/O Bridge
Orion 90 - 02 Reference
-180
-160
-140
-120
-100
-80
-60
-40
-20
0
10^{-5}
10^{-4}
10^{-3}
10^{-2}
Molar Concentration of NH_4^+

Table 4

Effect of pH on Response of NH_4^+ Electrode*

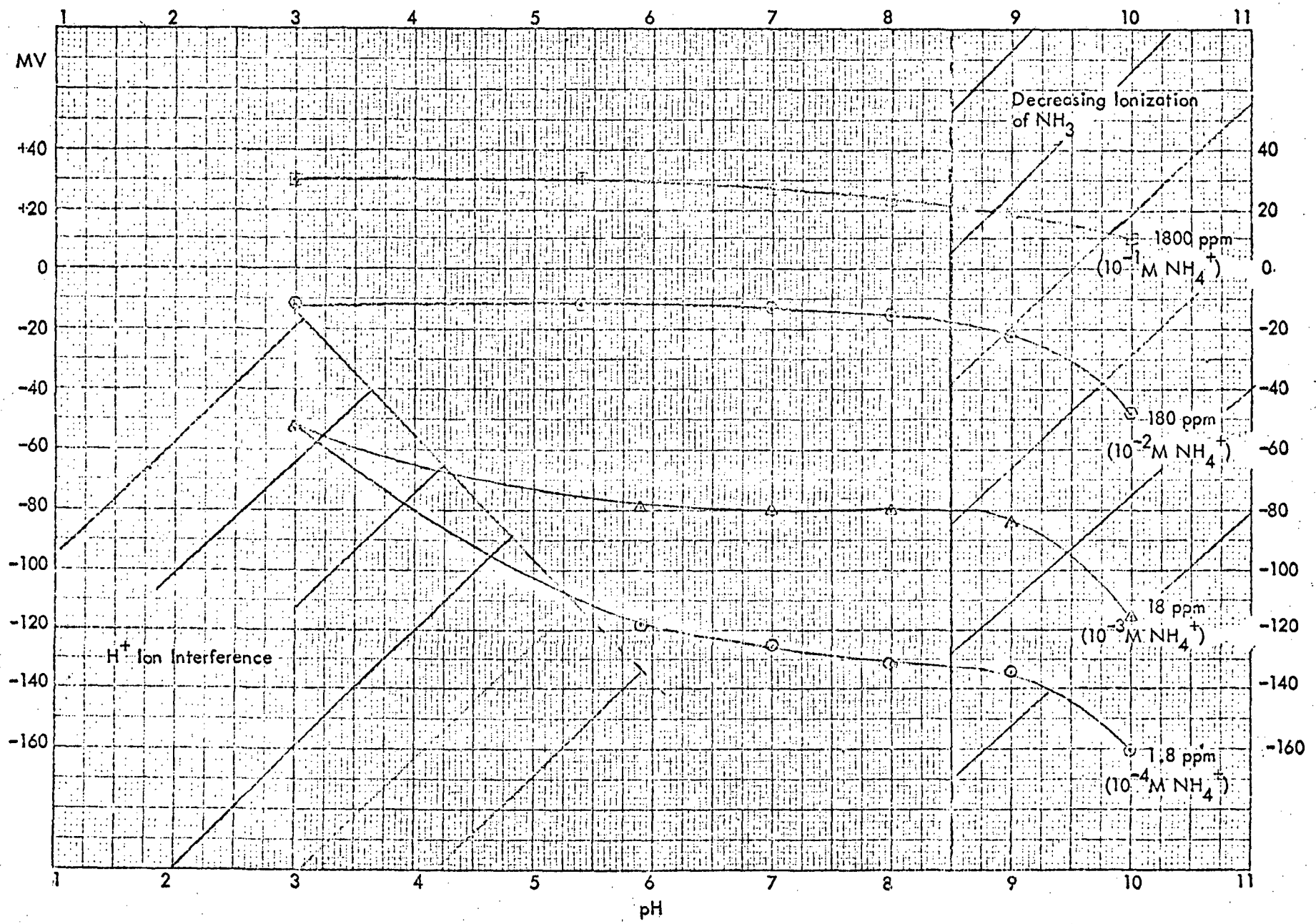
pH	M.V. Readings			
	1.8×10^3 ppm NH_4^+	180 ppm NH_4^+	18 ppm NH_4^+	1.8 ppm NH_4^+
3.0	+30	-12	-53	-53
5.4	+30	-12	-79 (pH 5.9)	-118 (pH 5.9)
7.0	+27	-13	-80	-125
8.0	+24	-15	-80	-132
9.0	+20	-22	-84	-134
10.0	+10	-48	-115	-160

*Monovalent Cation Electrode, Corning #476220; 90-02 Orion Double Junction Reference Electrode; Orion 401 Meter

K&E 10 X 10 TO ½ INCH 46 1322
7 X 10 INCHES MADE IN U.S.A.
KEUFFEL & ESSER CO.

Figure 5

MV READING VS SOLUTION pH (Corning Monovalent Cation Electrode #476220)



For the concentration range of interest (i.e., 1-20 ppm)*, the electrode response is not appreciably affected by pH at a pH of 7 to 8. Two alternatives present themselves for permitting measurement over the full pH range of interest (i.e., pH 3 to 10); either add an appropriate buffer to the sample stream to adjust the pH to the desired value (i.e., pH of 7) or to determine empirically, as illustrated by the data in Table 4, family of signal response-concentration curves covering the pH range of interest. It is evident from the data in the table that for concentrations of 1.8 and 18 ppm, the M.V. reading is fairly constant (< 10% variation) for pH between 7 and 9, and could be represented by a single response-concentration curve.

The marked interference from H^+ at the lower NH_4^+ ion concentrations (i.e., at 1.8 ppm) underscores the difficulty in making accurate measurements in this region. This is further complicated by the comparatively long periods required to reach equilibrium in low ionic strength solutions (e.g., 4 to 5 minutes required at 1.8 ppm NH_4^+ compared to 30 seconds or less at the higher concentrations; see Table 5 for specific conductivity of test solutions).

b. Beckman Ammonium Electrode

The effect of pH on performance of the Beckman NH_4^+ ion electrode is summarized in Figure 6. In contrast to the results obtained with the Corning monovalent cation electrode which showed marked H^+ ion interference below a pH of 6 at 1.8 ppm NH_4^+, the effect of acid pH on the Beckman electrode is decidely less pronounced. For both electrodes, the effect of decreasing ionization of NH_3 is evident above a pH of 8.5.

Interferences from Na^+ and K^+ -

Two other ions which could interfere in measurement of NH_4^+ with the Corning monovalent cation electrode are Na^+ and K^+ ions. Based on the data shown in Table 6, one should be able to read NH_4^+ from 1.8 to 18 ppm without interference from Na^+ or K^+ if they do not exceed 2 ppm. The maximum observed values in the 60-day tests at McDonnell Douglas for Na^+ and K^+ were 0.90 and 0.21 ppm, respectively.

*Maximum observed value for NH_3 in reclaimed water samples in 60-day test at McDonnell Douglas in 1968 was 12.5 ppm; mean observed value was 4.8 ppm.

Table 5

Specific Conductivity of $(NH_4)_2 SO_4$ Test Solutions

	μ mho/cm
	pH 5.5
Distilled Water Only	1.21
0.89 ppm NH_4^+	10.7
8.9 ppm NH_4^+	82
89 ppm NH_4^+	700

Figure 6

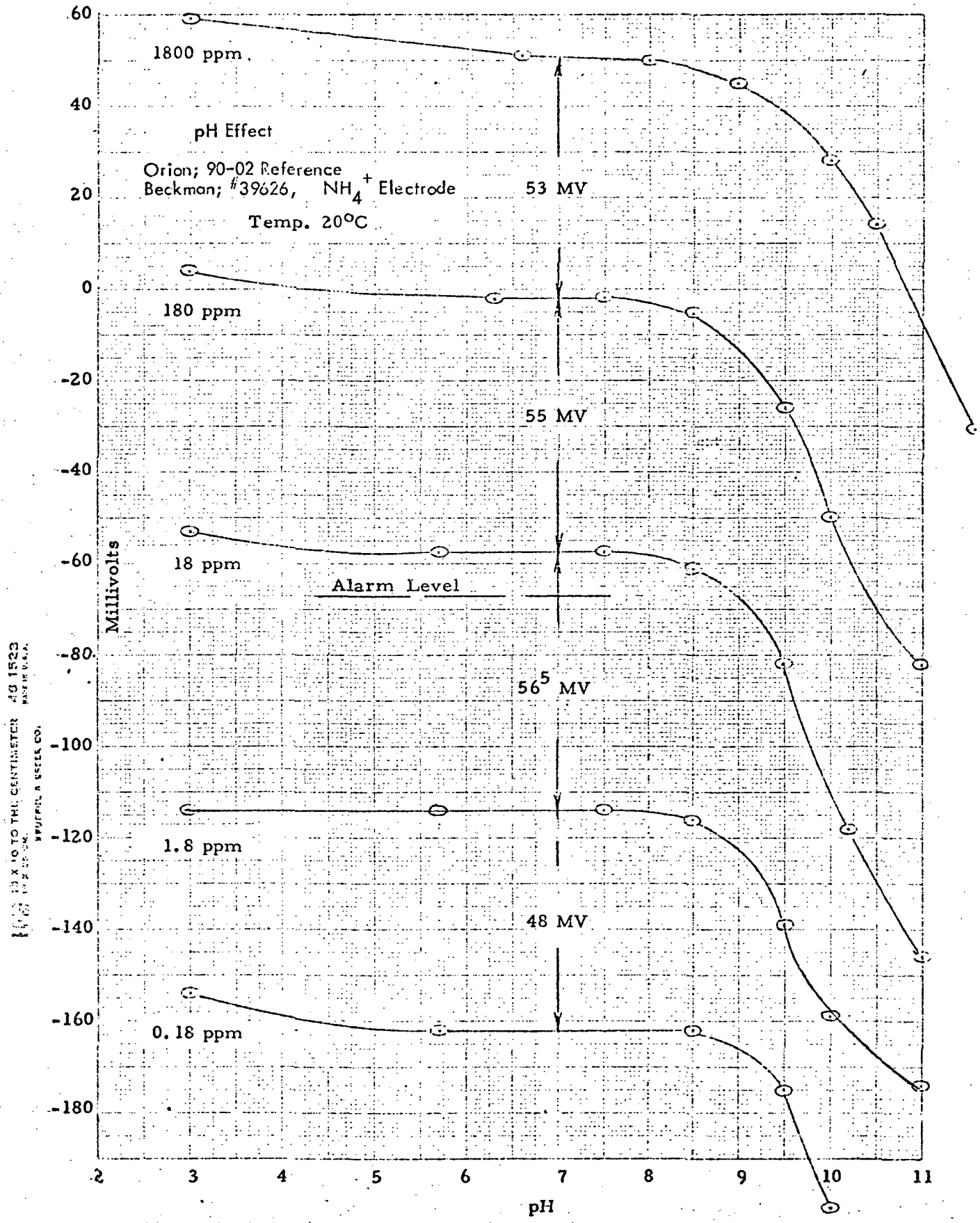

60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
Millivolts
1800 ppm
pH Effect
Orion; 90-02 Reference
Beckman; #39626, NH_4^+ Electrode
Temp. 20°C
53 MV
180 ppm
55 MV
18 ppm
Alarm Level
56.5 MV
1.8 ppm
48 MV
0.18 ppm
2
3
4
5
6
7
8
9
10
11
pH

Table 6

Effect of Na^+ and K^+ on Response of NH_4^+ Electrode*

	Added	M.V.	pH
1.8 ppm NH_4^+	0 ppm Na^+	-120	5.6
	1.3 ppm Na^+	-119	5.6
	2.5 ppm Na^+	-117	5.6
	13.5 ppm Na^+	-102	5.6
	25 ppm Na^+	-96	5.6
18 ppm NH_4^+	0 ppm Na^+	-70	5.5
	1 ppm Na^+	-70	5.5
	12 ppm Na^+	-69	5.5
	24 ppm Na^+	-68	5.5
3.6 ppm NH_4^+	0 ppm K^+	-110	5.5
	0.7 ppm K^+	-108	5.5
	1.4 ppm K^+	-101	5.5
	2.1 ppm K^+	-100	5.5
	3.5 ppm K^+	-92	5.5
	7.0 ppm K^+	-80	5.5
18 ppm NH_4^+	0 ppm K^+	-68	5.5
	0.7 ppm K^+	-68	5.5
	1.4 ppm K^+	-68	5.5
	3.5 ppm K^+	-64	5.5
	7.0 ppm K^+	-60	5.5

*Corning #476220; Orion 401 Meter; 90-02 Double Junction (Orion) Reference Electrode.

Since the Beckman Ammonia electrode has its greatest sensitivity toward NH_4^+ (not the case with the Corning electrode) similar tests were not made for the Beckman electrode.

Drift -

The extent of variation observed in the millivolt readings over a 3-day period with the Beckman NH_4^+ ion electrode and either the Orion double junction or Beckman Lazaran reference electrodes is summarized by the data in Table 7. The observed variation is due mainly to instrument drift* and could be minimized by periodic standardization with solutions of fixed concentration. For standardization of the three sensors (pH, Cl^-, NH_4^+), a single standard solution containing a Tris buffer (pH 7.1) and NH_4^+ and Cl^- ions at the alarm levels (i.e., 10 ppm NH_4^+ and 450 ppm Cl^-) would be flowed through the electrode well.

Day-to-day reproducability of a particular series of tests with the Corning electrode is shown in Figure 7.

pH Electrode. -

The drift observed for the Orion pH electrode - Lazaran reference combination with an Orion 401 meter is summarized by the data in Table 8. The drift is seen not to exceed 0.1 pH unit within 24 hours after calibration.

Reference Electrode. -

The Orion 90-02 double junction reference electrode was originally selected because it was non-mercury containing and had a slow bleed of KNO_3 through a sleeve junction thereby permitting measuring low levels of Cl^- ion without interference**. One disadvantage of this type of electrode is that daily filling of electrolyte is required as well as the necessity to supply pressure compensation for the electrolyte filling solution when operating with pressurized samples.

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* Instrument drift includes that due to meter + electrodes.

** Standard calomel reference electrodes bleed KCl solution through a junction.

Table 7

Response of Beckman NH_4^+ Ion Electrode*

Millivolt Readings

A. With Orion Double Junction Reference

Date	pH	.18	.89	1.8	18	89 ppm NH_4^+	Comment
5.5-71	6.0	-167	-128	-111	-54	-14.5	Double Junction Reference with Salt Bridge
5-5-71	6.2	-160	-122	-105	-50	-15	" " " "
5-5-71	6.2	-	-126	-108	-50	-15	Double Junction Reference without Salt Bridge
5-7-71	6.0	-162	-	-114	-57.5	-	" " " "

B. With Lazaran Reference

5-5-71	6.2	-100	-74	-60	-6	32	No Salt Bridge
5-6-71	6.0	-108	-80	-66	-13	-	" "
5-7-71	6.0	-120	-	-67	-17	-	" "

*Standard solution was $(NH_4)_2SO_4$ in distilled water. Measurements normalized to 20°C.

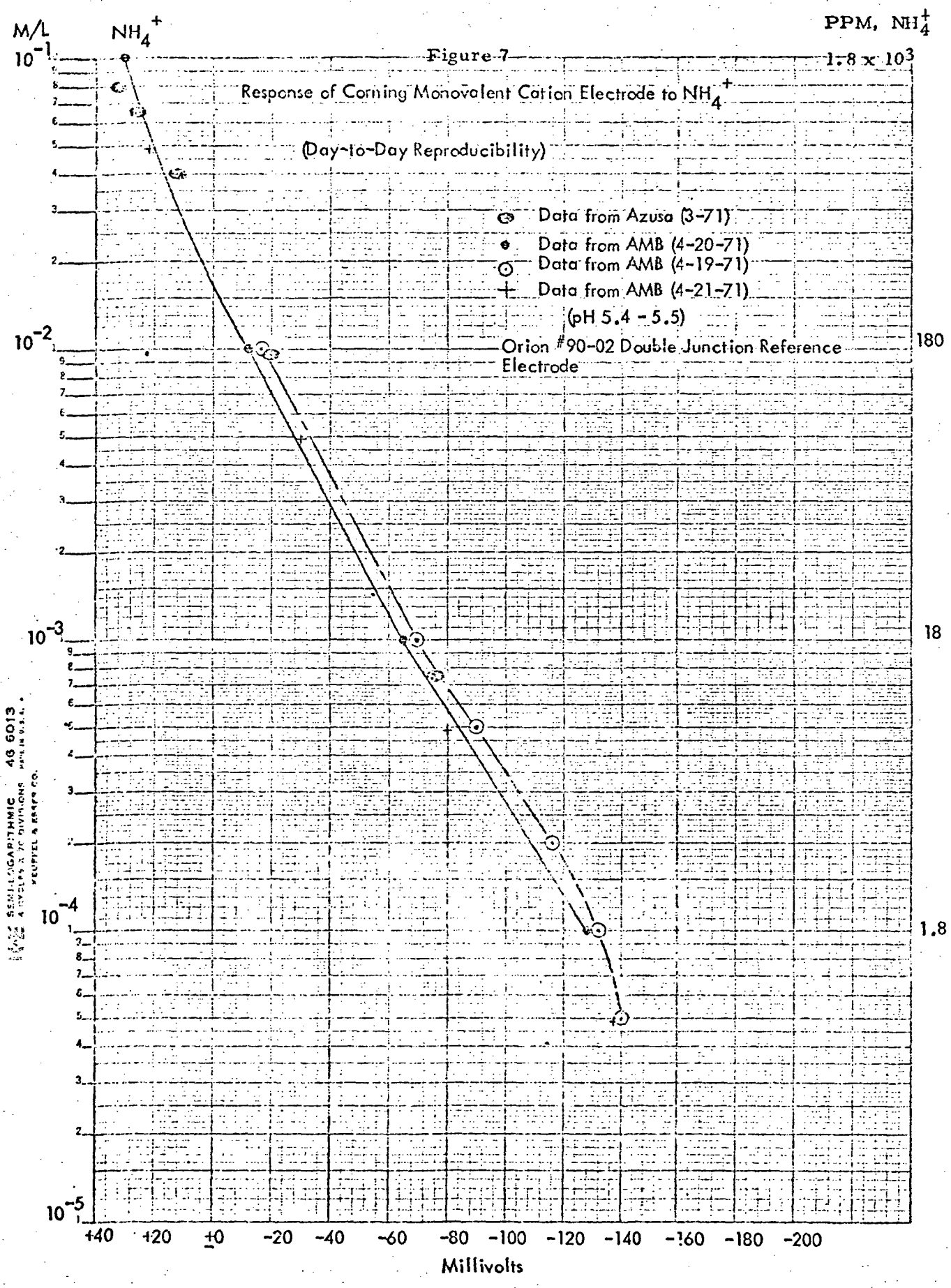


Figure 7

Response of Corning Monovalent Cation Electrode to NH_4^+

(Day-to-Day Reproducibility)

Table 8

pH Electrode (Orion #91-01) Drift

Δ Time, Hrs	Beckman Lazaran Reference	Orion Double Junction (90-02) Reference
0 (calibrate)	7.00	7.00
0.50 hrs	7.05	7.01
1.00 hrs	7.00	7.03
1.50 hrs	7.00	7.00
2.50 hrs	7.00	7.01
3.00 hrs	7.00	7.00
4.00 hrs	7.00	7.00
0 (calibrate)	7.03	-
2 hrs	6.97	-
4 hrs	6.95	-
6 hrs	6.95	-
21 hrs	6.95	-
24 hrs	6.94	-

To overcome these problems, a Beckman Lazaran reference electrode which uses a gelled KCl electrolyte which does not require replenishment (for at least 6 months) and usable up to 100 psi without external pressure compensation was examined. The bleed rate of KCl is claimed to be sufficiently low as not to cause interference with measurement of small quantities (i.e., 1 ppm) of either Cl^- or NH_4^+ ions. The results of measurements made with the electrode in combination with the Beckman ammonium ion electrode are shown in Figure 8. Except for a shift of scale, the response of this electrode appears to be comparable with that of the Orion double junction reference electrode (compare Figures 6 and 8).

Specific Conductance Sensor. -

The sensor selected for measurement of the ionic content of the sample water was a Beckman Type RI5 Solu Bridge Conductivity Indicator with a temperature compensated flow through cell. This sensor did not require any modifications from its commercially available configuration.

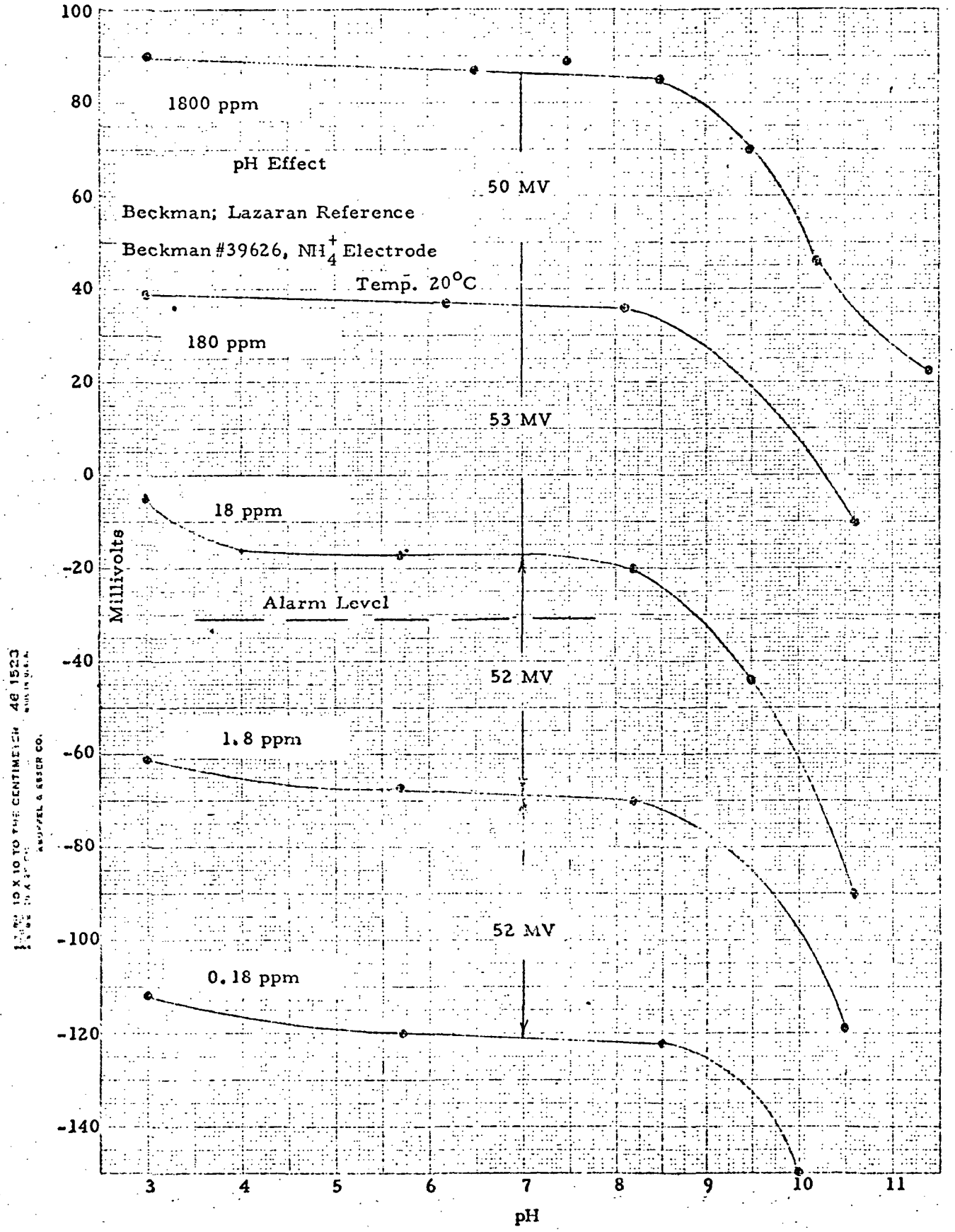
Total Organic Carbon Sensor. -

The instrument originally selected was a Precision Scientific Aquarator for measurement of chemical oxygen demand. LARC expressed a desire for a direct measurement of organic carbon. Only two commercially available instruments appeared to fit this requirement; a Beckman Model 915 TOC, and an Envirotech (Dohrmann) TOC. The Envirotech device is more complicated and since LARC has had experience with the Beckman 915 TOC, it was selected for this sensor.

Biosensor. -

The technique selected for monitoring the bacteriological quality of the water sample determines the presence of bacteria by chemiluminescence. The principle of detection is based on measuring the increase in chemiluminescence produced by the catalytic action of bacterial porphyrins, specifically hematin, on a luminol-hydrogen peroxide mixture (called Premix). Hematin, which occurs either in the free state or in combination

Figure 8


1800 ppm
pH Effect
50 MV
Beckman; Lazaran Reference
Beckman #39626, NH_4^+ Electrode
Temp. 20°C
180 ppm
53 MV
18 ppm
Millivolts
Alarm Level
52 MV
1.8 ppm
52 MV
0.18 ppm
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
3
4
5
6
7
8
9
10
11
pH

with a protein, is a substance found in most organisms, living or dead. The reaction is virtually instantaneous and occurs immediately on mixing the bacterial suspension with the aqueous reagents. Mixing is carried out within view of a photomultiplier tube which monitors the light emitted by the reaction. The signals generated are directly proportional to the number of bacteria present. To permit differentiation between living and dead organisms, chemiluminescent signals are obtained for both incubated sample indicates the presence of viable organisms.

The biosensor samples and concentrates (by filtration) the bacteria. This concentrate is then resuspended and further concentrated by filtration. (For measurement of the number of viable organisms, an incubation step is inserted between the concentration steps). The concentrate is then washed to remove any soluble matter that would interfere with the chemiluminescence. The concentrate is once more resuspended in aqueous reagent and reacted with Premix. Finally, several cleanup steps are performed to reduce cross-contamination between samples and inhibit the growth of bacteria within the sensor.

Development

Ion Sensors. -

Effect of Flow and Pressure -

The effect of sample flow and pressure on the response of Cl^-, NH_4^+ and pH electrodes in combinations with a Beckman Lazaran Reference electrode were evaluated using the test setup shown in Figure 9. The results summarized in Tables 9 through 11 indicate the following:

1. Orion (#92-01) pH - Beckman Lazaran Reference Electrode Combination (Table 9).

   Neither flow or pressure have an appreciable effect on electrode response except for very low conductivity solutions (i.e., of less than 100μmho). High resistance systems of this type are subject to capacitative pickup from body movements or the presence of charged objects (e.g., nylon lab coats) in their vicinity and is reflected by a wandering or erratic behavior by the pH meter. This can generally be minimized by adequate screening (with an earth ground) of the electrode cable and an electrode design which incorporates screening around the inner reference electrode right down to the region of the pH-sensitive membrane. An alternative approach would be to enclose the entire system (electrodes, leads and meter) in a Faraday cage to eliminate capacitative pick-up. A further approach is to reduce the electrical resistance of the fluid path between the pH and reference electrodes by placing the sensing tips closer together or by metering an electrolyte into the sample stream (final concentration $\sim$0.001 Molar) to bring the conductivity of the system above 100μmho/cm . (More discussion in section on installation). The addition of an electrolyte may entail separating the pH electrode from the NH_4^+ and Cl^- sensors because of possible interferences.

2. Orion (#94-17) Solid State Chloride - Beckman Lazaran Reference Electrode Combination.

   As indicated by the data in Table 10, sample flows up to 2 ml/min had a negligible effect at Cl^-ion concentrations ranging from 45 to 450 ppm at solution conductivities of less than 100μmho/cm indicate the same interference problems of capacitative pick-up as experienced with the pH electrode, only to a somewhat lesser extent. Since the Cl^-ion electrode will have a buffered

Figure 9

PRESSURE AND FLOW TEST FIXTURE

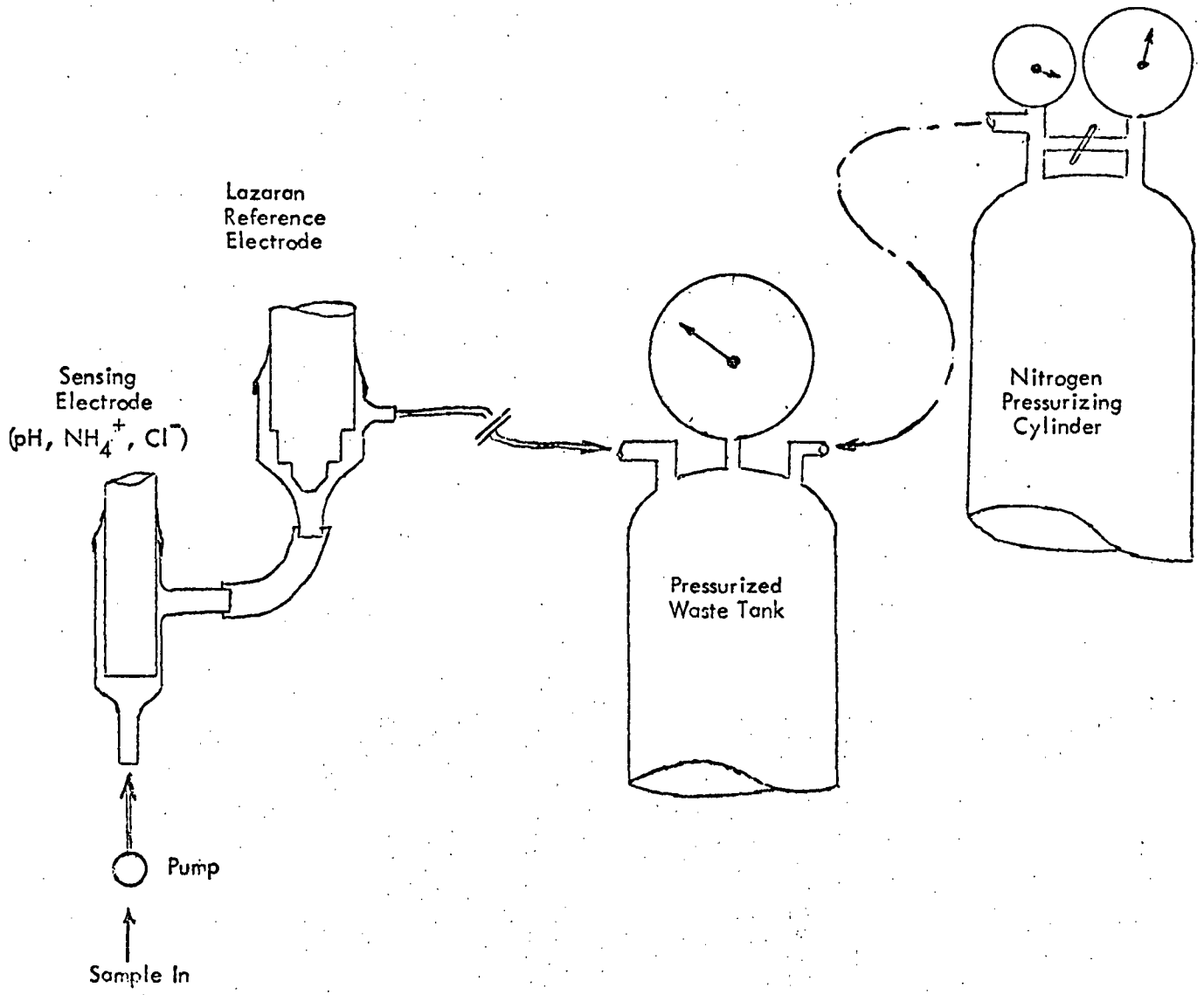


Table 9

Effect of Sample Flow and Pressure on Response of Orion pH Electrode

Condition: Beckman Lazaran Reference Electrode
Orion - 401 Meter

		pH Readings			
		Zero Flow	2 ml/min		
	Pressure	Zero psig	Zero psig	2.5 psig	5.0 psig
Run	Sample				
1	Standardizing Solution (Conductivity 1150 μmho/cm) (after 15 min)	6.9	6.9	6.9	6.9 6.85
2	1:5 Dilution of Std Solution (270 μmho/cm) (after 10 min)	6.85	6.85	6.85	6.85 6.80
3	5.9×10^{-4} M NH_4Cl (81 μmho/cm)	5.7	5.7	-	-
		Both readings slightly affected by operator movement near meter. Steady without movement.			
4.	Water Only (3.5 μmho)	5.7	5.7	5.7	5.7
			Flow readings sensitive to operator movement near meter.		

Table 10

Effect of Sample Flow and Pressure on Response of Orion Solid-State Chloride Ion Electrode (No. 94-17)

Condition: Beckman Lazaran Reference Electrode; Orion No. 401 Meter

		Meter Reading, ppm Cl^-			
		Zero Flow	2 ml/min		
	Pressure	Zero psig	Zero psig	2.5 psig	5.0 psig
Run	Sample				
1	450 ppm*	450	450	450	440
2	450 ppm*	450	450	445	430
3	45 ppm**	45	45	45	45

*System calibrated with standardizing solution (1150 μmho/cm) before test.

**System calibrated with 1/10 dilution of standardizing solution (134 μmho/cm) before test.

Table 11

Effect of Sample Flow and Pressure on Response of Corning Monovalent Cation Electrode* Toward Ammonia

Conditions: Beckman Lazaran Reference Electrode
Orion No. 407 Meter

		Meter Reading, ppm NH_3			
		Zero Flow	2 ml/min		
	Pressure	Zero psig	Zero psig	2.5 psig	5.0 psig
Run	Sample				
1	** 10 ppm NH_3 (initial)	10	10	10	10
	(after 45 min)	-	-	-	9.3
2	** 10 ppm NH_3 (initial)	10	10	10	10
	(after 40 min)	-	-	-	9.6
3	*** 2 ppm NH_3 (initial)	2.0	2.01	2.05	2.1
	(after 15 min)	-	-	-	2.15

* No. 476220

** System calibrated with standardizing solution (1150 μmho/cm specific conductivity) before initial reading.

*** System calibrated with 1/5 dilution of standardizing solution before initial reading.

environment (see Figure 12) with a conductivity of $> 100\mu$mho, this should not present a problem with this electrode.

The effect of sample pressures up to 5 psig can be considered to be small or negligible with the maximum deviation not exceeding 5%. In order not to over strain the membrane and to prolong electrode life, it would probably be best to limit the chloride electrode to sample pressures not exceeding 2.5 psig.

The time required to displace the liquid volume in the electrode pair* with a new solution of a different composition was found to be about 15 minutes for a liquid flow of 2 ml/min. This was the interval of time required to reach an equilibrium value on displacing distilled water with standardizing solution (containing 450 ppm Cl^-, 10 ppm NH_3, pH 7.0 and a specific conductivity of 1160μmho/cm). This number will vary depending on volume and geometry of the final electrode well design.

3. Ammonium Electrode - Beckman Lazaran Reference Electrode Combination (Table 11).

The two electrodes evaluated for monitoring NH_4^+ ion were (1) a Corning Monovalent Cation electrode (#476220) and (2) a Beckman Solid Organic Ammonium electrode (#39626).

Although initial tests indicated the Beckman electrode showed greater specificity toward NH_4^+ ion than the Corning electrode, further testing indicated two serious shortcomings for the former; namely, (1) after approximately 100-200 hours of operation in a flowing stream, the organic sensing element begins to dissolve and spurious readings are obtained and (2) displacement of the sensing element (resulting in false readings) when sample pressure reaches 2.5 psig. In contrast, pressures up to 5 psig have a negligible effect on the response of the Corning Monovalent Cation electrode (Table 11). The data in Table 11 also indicate that flow conditions of up to 2 ml/min do not affect the readings; as with the other electrodes, steady state operation (i.e., freedom from capacitance interference) is best achieved at solution conductivities greater than 100μmho/cm. Since this electrode is to be in a buffer environment at conductivities greater than 100μ mho/cm (see Figure 12), this does not present a problem with this electrode.

*Holdup volume for electrode pair = 9 ml.

Installation of Ion Sensors -

One of the designs that was considered for adding a flow-through feature to the present electrodes is shown in Figure 10. This attachment would be made of plastic (e.g., polypropylene or polyvinyl chloride), with a minimum holdup volume, to permit easy flushing of contents and capable of use at elevated sample pressures. A prototype configuration that was tested in the laboratory is shown in Figure 11, glass construction was used initially for convenience.

To allow for buffering of the NH_4^+ ion sensor (to eliminate pH interferences) without affecting the pH sensor, the electrodes were arranged as shown in Figure 12. A non-interfering buffer (i.e., Tris - H_2SO_4, pH $\sim$ 7) is mixed with the incoming sample stream feeding into the well containing the Monovalent Cation, the Orion Solid State Chloride and the Lazaran electrodes. A standardizing solution containing the alarm levels of Cl^- (450 ppm) and NH_3 (10 ppm) at a pH 7 will be used periodically for adjusting for system drift.

The problem of erratic meter behavior mentioned earlier in connection with pH measurement of low conductivity ($< 100 \mu$mho/cm) solutions was eliminated by placing the pH and reference electrodes close together in the same electrode well. Stable operation was achieved for flowing solutions (2 ml/min) with conductivities of $< 25 \mu$mho/cm. Narrow constrictive connections between sensing and reference electrodes are to be avoided when dealing with low conductivity solutions.

The final configuration is shown in Figure 13. Some difficulty was experienced, in machining the unmodified polypropylene material, however, these were only related to a familiarization of the machining characteristics of the material and subsequently no problems were encountered.

Total Organic Carbon Analyzer (TOC). -

Modifications to Provide Automatic Operation -

The Beckman Model 915 TOC Analyzer is basically a laboratory instrument to be operated manually on an intermittant basis. For the present

Figure 10

CONCEPT FOR ION ELECTRODE WELL

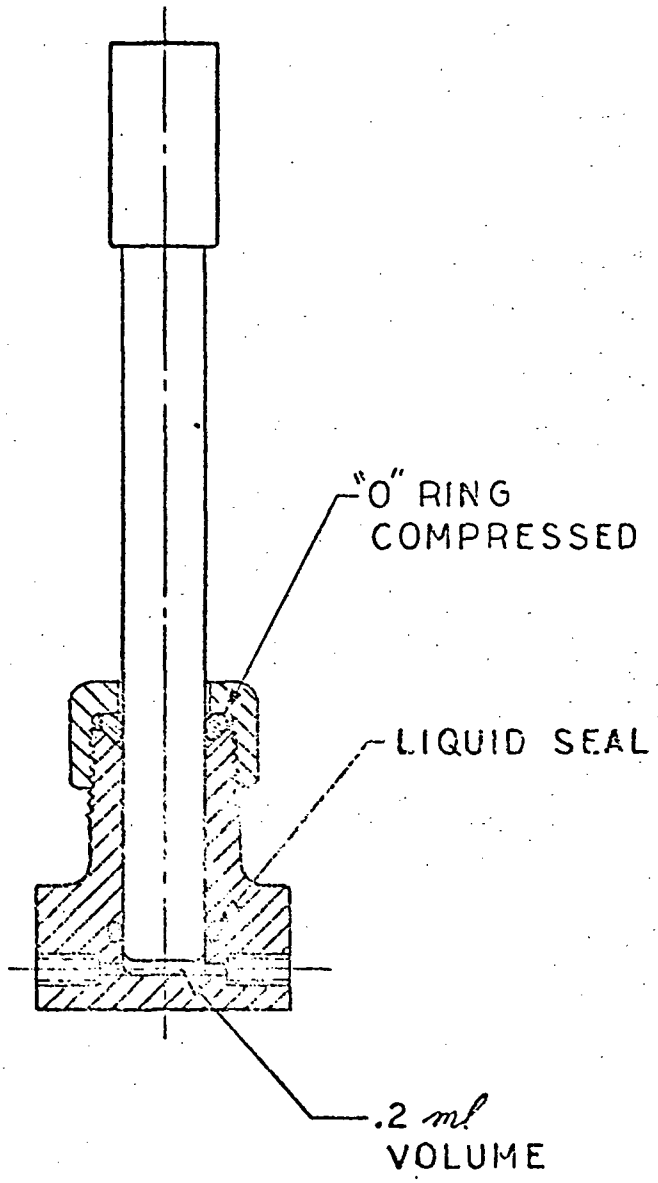
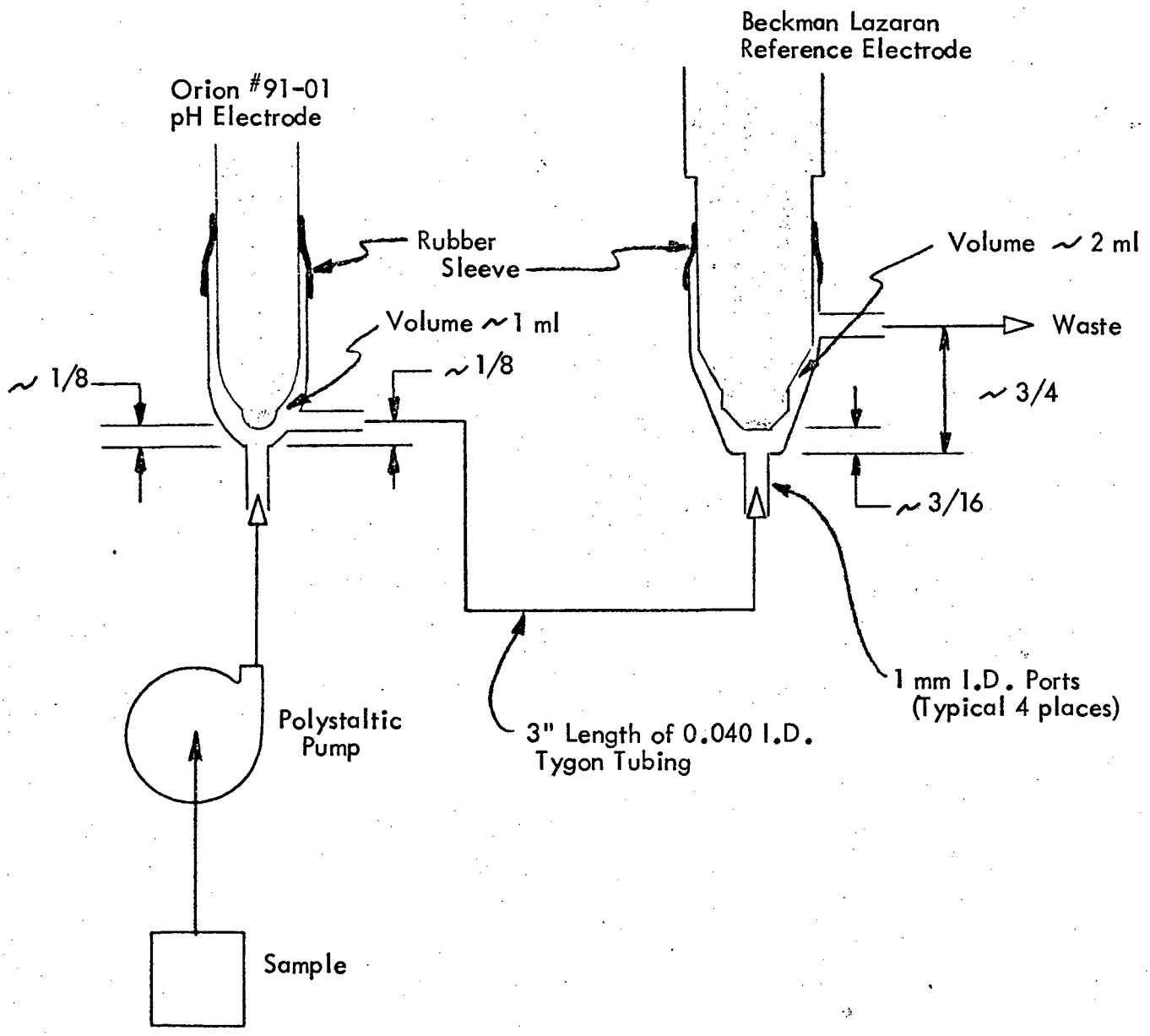


Figure 11

Laboratory Prototype Flow Configuration



ELECTRODE ARRANGEMENT

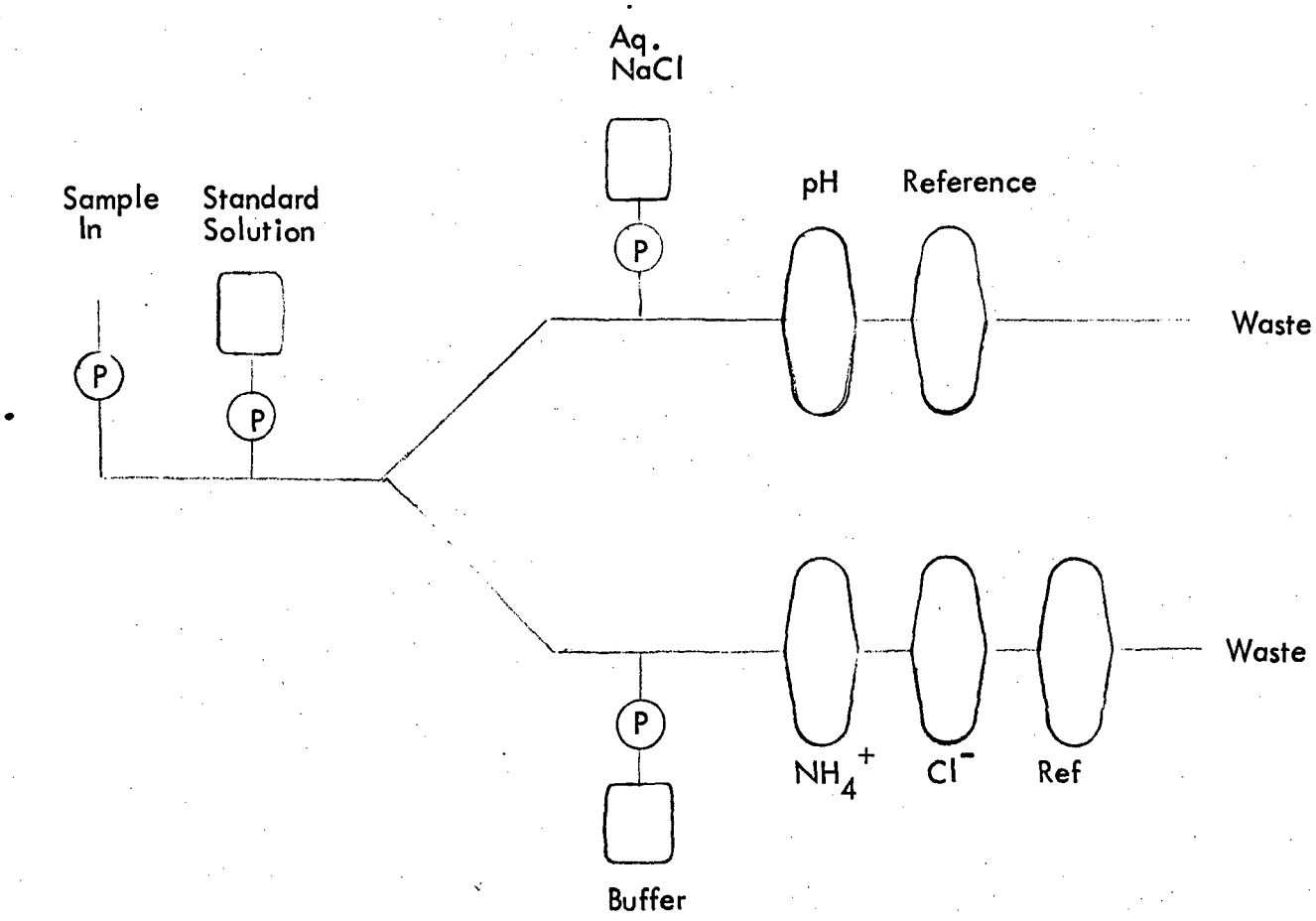


Figure 12

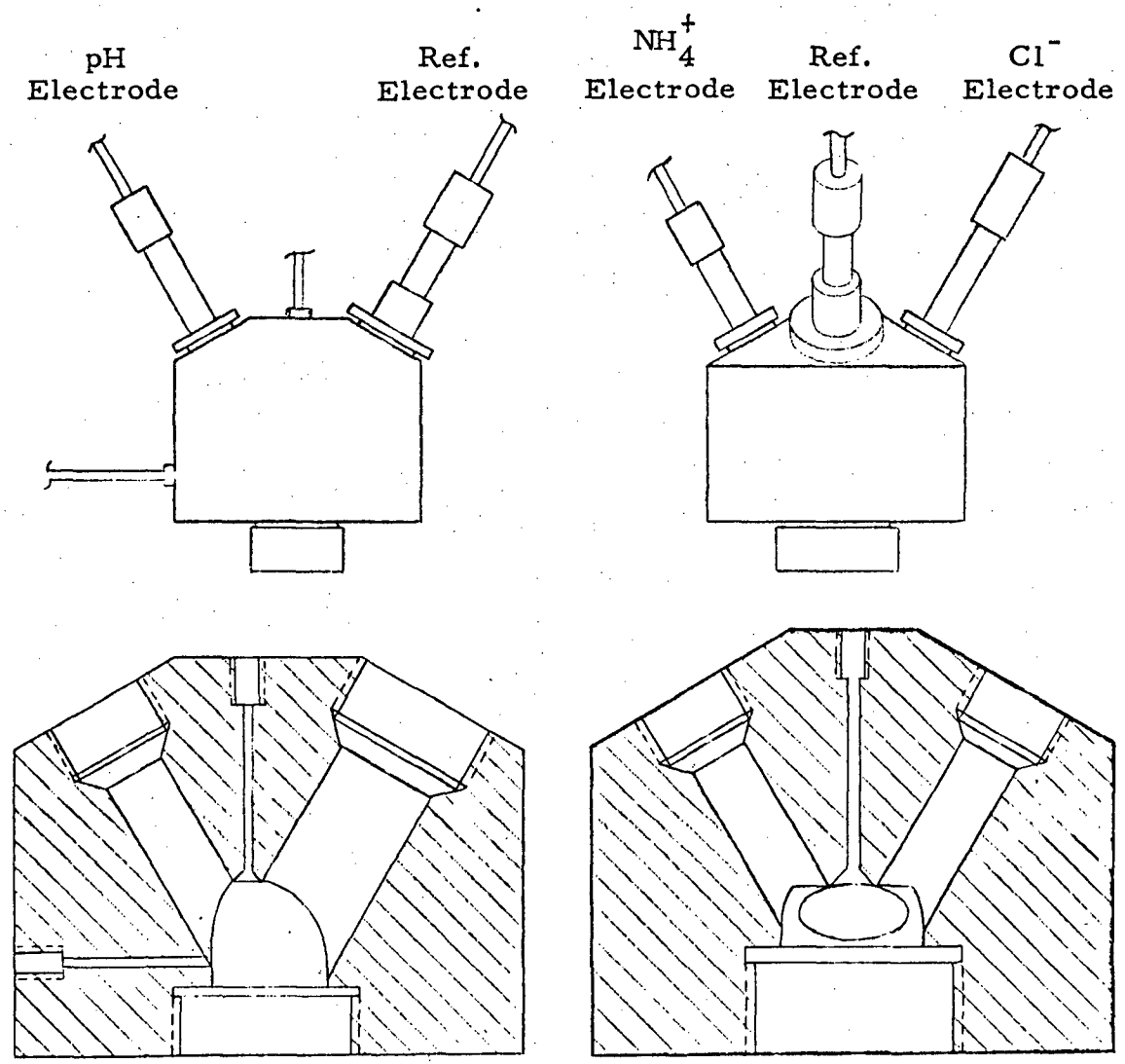


Figure 13. Polypropylene Electrode Wells

application it was necessary to provide automatic injection of water samples. In addition, since a single Infrared Analyzer is used to monitor the response from both the total carbon and inorganic carbon channels, some means had to be provided for selecting and processing each signal separately and finally, to subtract the inorganic carbon signal from the total carbon signal.

Chromatromix Rotary Sample Injection Valves (No. R60SVAS) with sample loops for automatic injection of water samples into the TOC were installed. Carrier gas was used to force the water sample from the pre-calibrated sampling loops into the combustion furnaces. Data for the total carbon furnace was compared between this automatic mode of operation and manually injected samples using a hypodermic syringe. The results showed some variation, depending on whether the gas stream used to purge the sample loop was kept flowing for a short time or long enough to reduce the sample signal to baseline value. The most consistently repeatable results were obtained using a sample loop carrier gas pressure of 6 psig for a duration of about 2 seconds.

Modifications to the TOC to achieve this automation are:

a. Two Chromatronix sample injection valves have been installed.

b. Two Teflon Mace valves have been installed to replace the manual valve used to divert either the inorganic or total carbon sample to the IR Analyzer.

c. Automatic operation of the above valve modification is controlled by a cam-type timer/programmer.

d. Injection of the liquid sample is accomplished by forcing the sample through the injection valve with 6 psig carrier gas for approximately 2 seconds.

A complete description of the automated Total Organic Carbon sensor is found in the Operating and Maintenance Manual.*

*Operating and Maintenance Manual, No. 1101 OM, For A Laboratory Prototype Water Quality Monitoring System Suitable For Use in Zero Gravity, Contract NAS 1-10382, 28 July 1972, Aerojet Medical and Biological Systems.

Problems With High Temperature Furnace Packing -

During the data gathering effort on the TOC anomolous operation of the instrument was observed. The automatic injection technique was checked and found to be satisfactory. The difficulty was finally traced to the high temperature furnace. Beckman had been recommending a packing procedure which deviated from the method outlined in their instruction manual. This procedure, which AMB had been using, involved the use of 25 gms of cupric oxide as a catalyst. AMB was experiencing erratic results which were apparently due to the catalyst.

Conversations with Beckman confirmed the erratic results AMB had been experiencing and they recommended abandoning the cupric oxide catalyst and returning to the method listed in the TOC operating manual, which employs a cobalt nitrate treatment of long-fiber asbestos.

Since both the total carbon and the inorganic carbon signals are processed through the same IR analyzer electronics, this imposes a requirement that the calibration, for automatic operation of the two carbon channels be the same if instrument accuracy is to be within about 10%. This level of accuracy is probably obtainable, but several attempts at repacking the high temperature tube would be necessary, and success would not be apparent until furnace operation was resumed. This being an undesirable mode of operation, an alternative method employing the signal processing electronics was incorporated.

Signal Processing -

The signals from the IR analyzer are sent to the processing electronics where the inorganic carbon signal is subtracted from the total signal. Because the high temperature furnace packing is subject to deterioration with use, an additional gain control (external to the IR analyzer) has been provided for the total carbon signal. Signals from the inorganic channel are relatively stable and are not modified. The net effect of the gain control has been to shift the calibration of the total carbon signal up or down as necessary, due to either combustion tube packing degradation and/or repacking, so that inorganic standards gave essentially the same response on both channels.

Biosensor. -

Development of the biosensor progressed in two steps. First a biosensor was fabricated and tested for sampling and reading the total (viable and nonviable) level of E. coli from two sources. Subsequently, this biosensor was modified so that one of the processed samples could be monitored for viable coliform bacteria by incorporating incubation in the processing sequence.

A fluid flow schematic showing all valving and pump connections is shown in Figure 14. A brief explanation of the processing steps follows. (see Figure 14).

Total Count Sample Processing:

1. Samples are collected on F1 and F2.

2. Samples are backwashed from F1 and F2 to the filter-concentrator using urea from P2.

3. Samples are washed at the filter-concentrator using H_2O from P5 (low speed).

4. Filter-concentrator is indexed once placing sample A in position to be backwashed with urea from P2 into the reactor cell where it is mixed with Premix from P3 to yield a chemiluminescence reaction.

5. Filter-concentrator is indexed again to position sample B for backwash and reaction as in 4. At this time P4 starts to clean up F1 and F2 and the related fluid lines and also the filter-concentrator filter that had sample A on it.

6. Filter-concentrator is indexed again to clean up the filter-concentrator filter that had sample B on it. Also continue cleaning F1 and F2 with urea.

7. Urea flow from P4 is stopped and P5 (high speed) is started to flush remaining urea from F1 and F2 and the related fluid lines.

8. Process repeats.

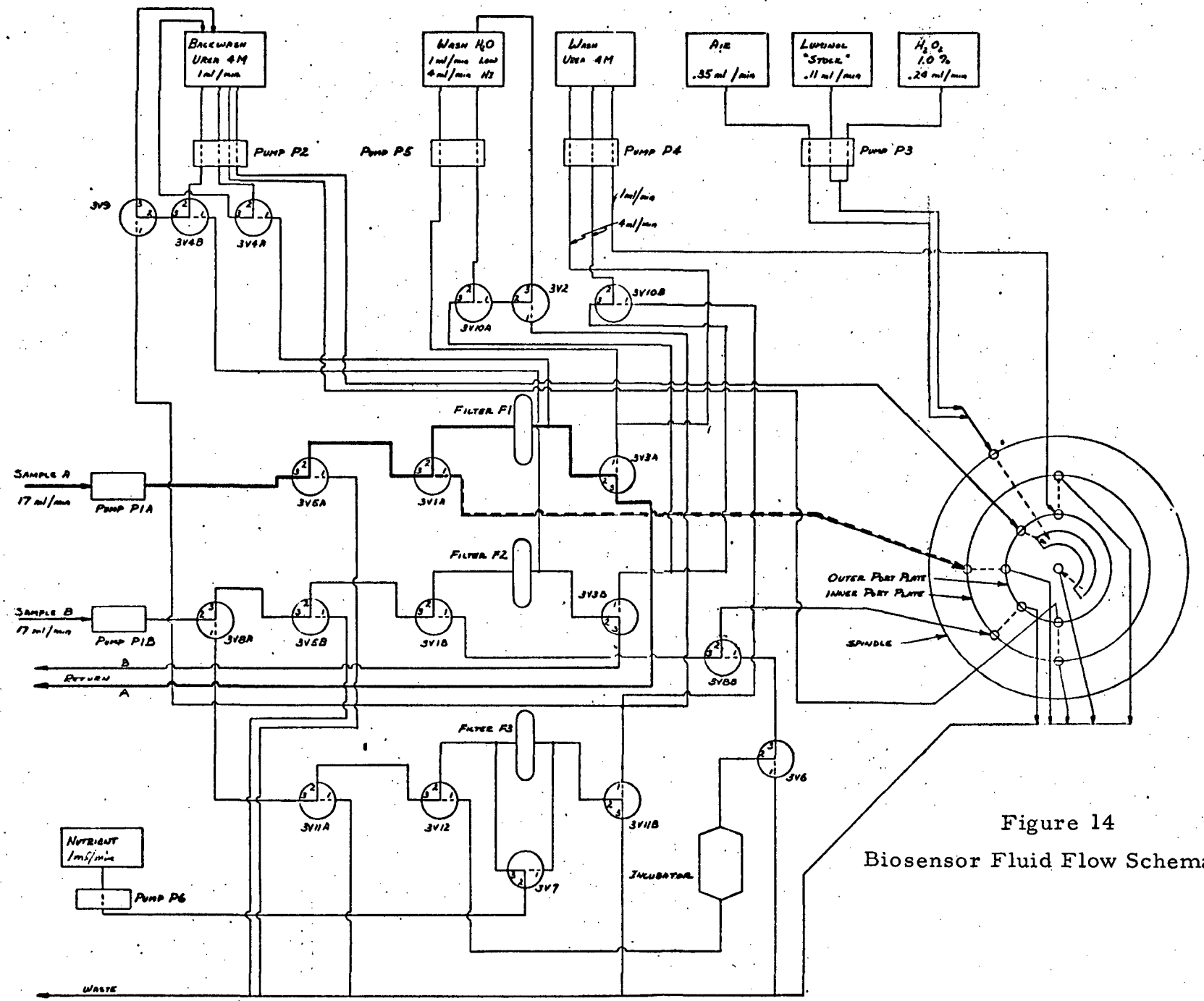


Figure 14

Biosensor Fluid Flow Schematic

Viable-Count Sample Processing:

The processing of sample A for total count remains unchanged from the above sequence. Filter F2 is not used in this operating mode. The steps which follow are for the viable count.

1. Sample B is diverted and collected on F3.
2. Sample B is washed at F3 using nutrient from P6.
3. Incubator is filled with nutrient.
4. Sample B is backwashed with nutrient into incubator.
5. Sample B is incubated for 136 minutes. During the approximately two hours of incubation the biosensor continues to process two total cell counts.
6. The incubated sample is washed from the incubator to the filter-concentrator using urea from P2.
7. Filter-concentrator is indexed once placing sample A in position to be backwashed with urea from P2 into the reactor cell where it is mixed with Premix from P3 to yield a chemiluminescence reaction.
8. Filter-concentrator is indexed again to position sample B (incubated) for backwash and reaction as in 7. At this time P4 starts to clean up F1 and F3 and the related fluid lines (including the incubator) and also the filter-concentrator filter that had sample A on it.
9. The filter-concentrator is indexed again to clean up the filter-concentrator filter that had sample B on it. Also continue to clean F1, F3 and incubator with urea.
10. Urea flow from P4 is stopped and P5 (high speed) is started to flush urea from F1, F3, the incubator and the related fluid lines.
11. Process repeats.

Sample and Reagent Pumps -

Peristaltic pumps are used for all fluid transport. The desired flow rates are achieved by varying the pump speed and/or the diameter of the Tygon tubing passing through the pump rollers. When the peristaltic action of the pumps is properly adjusted, effective isolation of the water monitor from the water regeneration system pressure range of 0-30 psig is obtained. Tygon tubing is the best material available for use in the pumps and is compatible with the reagents. After approximately 200 hours of service, the tubing should be replaced. Eventual breakdown of the Tygon causes flaking, and the release of particles results in spurious signals in the chemiluminescence process. Also continued usage of Tygon at fluid temperatures above 90-100°F shortens the life of the tubing. The recommended upper limit on the sample water temperature is 90°F.

The two sampling pumps require tubing replacement after about 50 to 100 hours of use, as both the tube size and the flow rates utilized are near the upper limit of the pump, and the tubing is subjected to considerable flexing. Eventually, the tubing takes a set and the required flow rates cannot be maintained.

Reagent requirements are shown in Table 12.

Concentration Filters -

Initial sample concentration is accomplished by passing the recovered water through 47 mm filters (Gelman Acropor AN-450, 0.45 micron pore). The large filter is necessary to collect a 400 ml sample in a reasonable length of time. The filter holders are stainless steel Gelman holders which have been modified by the addition of inserts. The purpose of the inserts is to provide a uniform distribution of the fluid to be filtered and also to reduce the holdup volume to about 0.5 ml. A minimum holdup is desirable so that the bacterial concentrate has a relatively high density during the backwash cycle. This minimizes processing time and more importantly insures that the bacterial challenge is centered in the incubator.

Table 12

Biosensor Reagent Usage (ml/hour)

	Nutrient	4M Urea	Distilled-Filtered H_2O	Luminol	H_2O_2
Viable Mode	2.2	190	60	6.6	14.4
Total Mode	0	178	78	6.6	14.4

During checkout of the biosensor some difficulty was experienced with leaks in the reagent feed portion of the system. This difficulty was traced to insufficient flow through the 47 mm filter holders (see F1, F2, and F3 on schematic in Figure 14). Plugged and slightly misaligned porting in the filter holders caused excessive back pressure resulting in leaks at some reagent pumps. Correction of this problem also resulted in better recovery of bacteria from these filters when backwashing (see Section on Biosensor Performance).

Filter Concentrator/PMT Housing -

The concentrated samples on the initial filters (47 mm) are resuspended in backwash media (urea for total counts and dextrose broth for viable counts) and eventually reconcentrated at the filter concentrator. The purpose of the filter concentrator is to provide a small volume ($\sim$ .1 ml) highly concentrated challenge as close to the face of the PMT as possible so that the bacteria are in a "clump" when reacted with the premix rather than being strung-out. This insures that almost all of the chemiluminescence takes place in view of the PMT for a maximum signal.

The filter concentrator consists of 8 filters 13 mm in diameter equally spaced around the circumference of a circle. It is made from a single 102 mm filter membrane (Gelman Acropor AN 450, 0.45 micron pore) which is supported on both sides using cutdown Millipore 90 mm stainless steel support screens. The membrane and screens are sandwiched between two Teflon cavity disks and supported by two stainless steel pressure plates. The filter-holder assembly is rotated in 45 degree increments by a pneumatic mechanism. In use the filter holder assembly is sandwiched between two Teflon port plates. Two samples are concentrated simultaneously and washed free of any soluble components that might interfere with the chemiluminescence reaction. When the filter holder is advanced 45 degrees, the first sample is backwashed using 4M urea into the reactor cell (mounted underneath the filter concentrator against the face of the PMT) where it is mixed with Premix. Further advance of the filters places the second sample in position for backwash and

reaction with Premix. The backwash cycle is followed by two cleanup steps which remove residual material from the collection side of the filter that might lead to clogging with extended operation.

While the biosensor was being operated in a viable count mode using nutrient as a backwash media, excessively large signals were observed. These large signals were traced to small amounts of nutrient in the reactor cell. (They could also have been due to contamination, however, contamination was systematically checked and discounted as a possible cause.) It was finally determined that the nutrient was being passed through the filter-concentrator (which is normal) but that the nutrient was not being washed out before the F/C was indexed and nutrient was consequently being "smeared" between sliding surfaces. On subsequent washes it proved to be impossible to remove the trace amounts of nutrient. The "smearing" was traced to an error in programming the operation of the biosensor. It was concluded also that additional washing (cleanup) of the biosensor was desirable and an additional urea line was added to pump 2.

Incubator -

The incubator design was changed from a straight enlarged glass tube to a coil of 6 mm ID glass tubing about 18 inches long with a holdup volume of 4.5 ml (large enough to contain the backwashed bacterial suspension). The reason for the configuration change was to insure that the backwashed bacterial challenge (to be incubated) would remain in the incubator. During the backwash operation using the straight tube design it was observed that channeling of the challenge was occuring and that a portion of the challenge was passing through the incubator (not mixing with the nutrient) and being lost. This resulted in a low sensitivity. Changing the configuration resulted in nearly plug flow through the incubator with a minimum loss of bacteria. The incubator is maintained at 37^{o}C by a heater/controller.

Biosensor Electronics -

The electronics module performs two basic functions.

1. Control of all functions that pertain to processing of the water sample.

   The 18-step programmer performs most of the process control. Each step on the programmer has an adjustable dwell time ranging from about 5 seconds to 10 minutes. For most of the sample processing, the dwell at any step is less than 10 minutes. Incubation, which is 136 minutes, and the sampling step (25 minutes) are the only exceptions. Up to 20 functions (load switches) are controlled during each program step.

2. Processing and displaying the electronic signals which are indicative of the bacterial level.

   The photomultiplier tube (PMT) detects the amount of light generated in the reactor cell. The PMT signal is transmitted to the processing electronics where it is compared to a preset threshold valve. Signals exceeding the threshold turn on an alarm light which remains on until reset manually. Direct readout from the PMT is also displayed on a strip chart recorder for permanent record and analysis of data.

Results

Error in Ion Sensor Measurement. -

A study was performed to determine the error that would be introduced into a measurement if a one solution calibration procedure was employed. More specifically, if a system was calibrated only at the alarm level (e.g., 450 ppm Cl^- ion or 10 ppm NH_3), what would the error be at the lower concentration levels? Figure 15 shows calculations derived by Dr. Ross of Orion for their solid state chloride electrode (#94-17) taking into consideration both ionic strength effects and the solubility of silver chloride (the sensing element in this electrode). Comparing the real chloride ion concentration with the value that would appear on the meter using the best straight line fit of the data, the maximum error in the range of 1 to 450 ppm is seen to be 18% at a sample temperature of 25°C. The slope of the best straight line fit is 92% of the theoretical Nernst slope* and is the setting used on the meter. To achieve greater accuracies at the lower levels, it would be necessary to use more than one calibrating solution and adjust the meter to the slope corresponding to the straight line between the calibration points.

The error actually observed in our laboratories with meter settings of 92% and 100% respectively, using the Orion (#94-17) solid state chloride electrode in combination with either a Lazaran or double junction reference electrode is summarized by the data in Table 13. It is apparent that better agreement is achieved at the 92% slope setting.

An additional source of error could be introduced by a temperature fluctuation in the interval between calibration and sample measurement. In a series of five separate determinations designed to evaluate the

*For a system exhibiting a true Nernst response, the electrode potential changes 59.16 mv at 25°C for each tenfold change in ionic activity. The activity of an ion is equal to the concentration of that ion multiplied by the activity coefficient of that ion. The latter depends on the total concentration of all the ions in the sample and can be estimated from the sample conductivity.

Figure 15

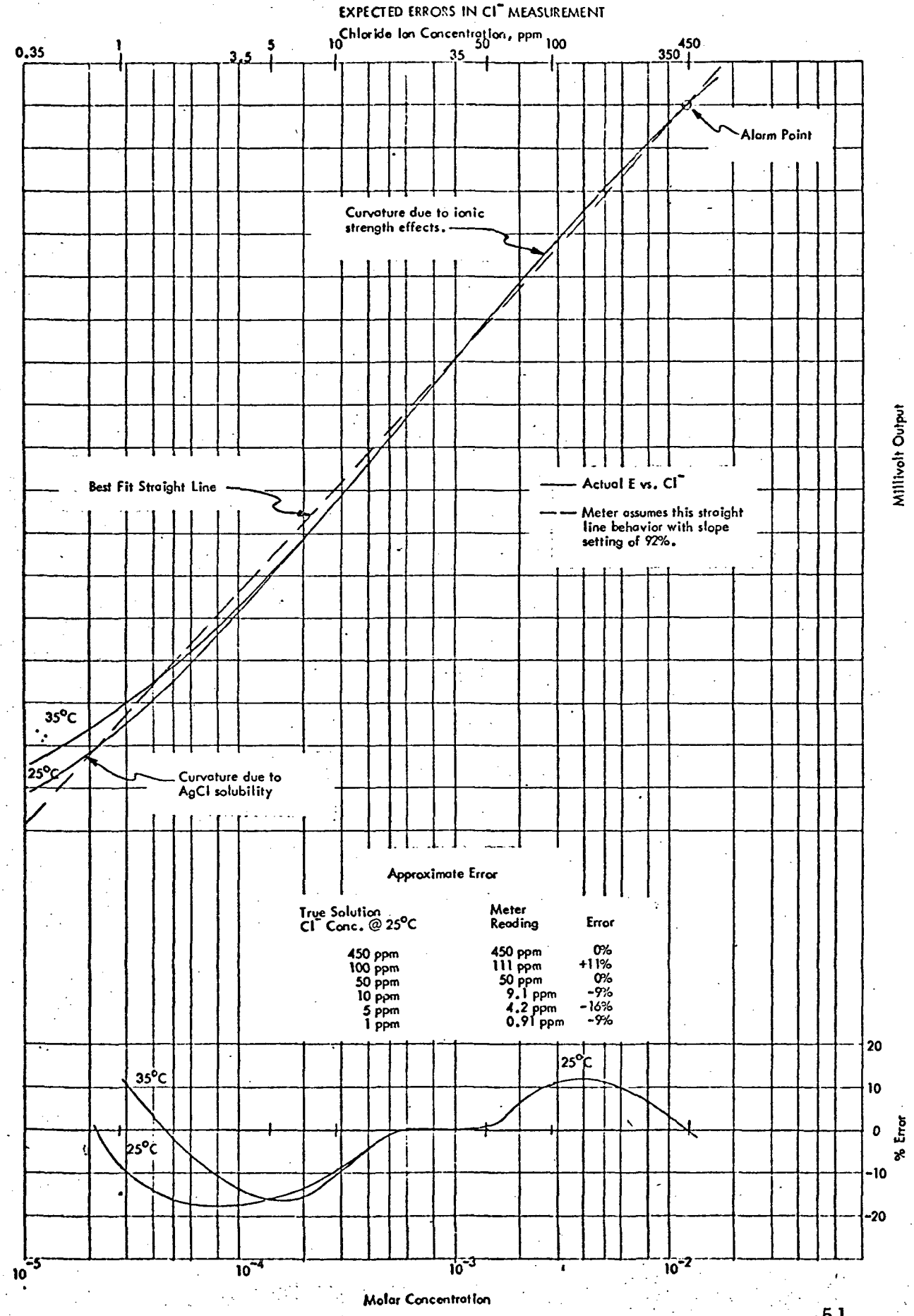

EXPECTED ERRORS IN Cl⁻ MEASUREMENT
Chloride Ion Concentration, ppm
0.35
1
3.5
5
10
35
50
100
350
450
Alarm Point
Curvature due to ionic strength effects.
Best Fit Straight Line
Actual E vs. Cl⁻
Meter assumes this straight line behavior with slope setting of 92%.
35°C
25°C
Curvature due to AgCl solubility
Millivolt Output
Approximate Error
True Solution Cl⁻ Conc. @ 25°C
Meter Reading
Error
450 ppm 450 ppm 0%
100 ppm 111 ppm +11%
50 ppm 50 ppm 0%
10 ppm 9.1 ppm -9%
5 ppm 4.2 ppm -16%
1 ppm 0.91 ppm -9%
35°C
25°C
20
10
0
-10
-20
% Error
10⁻⁵
10⁻⁴
10⁻³
10⁻²
Molar Concentration

Table 13

Slope Determination of Orion Chloride Ion Electrode (#94-17)

Run No. 1 - 92% Slope - Reference, Beckman Lazaran

	True Soln. Conc. at 25°C	Meter Reading, ppm	% Error
Calibrate*	450 ppm Cl^-	450 ppm Cl^-	0
	45 ppm Cl^-	40 ppm Cl^-	-11.1
	22.5 ppm Cl^-	21.5 ppm Cl^-	-4.4

Run No. 2 - 100% Slope - Reference, Beckman Lazaran

Calibrate	450 ppm Cl^-	450 ppm Cl^-	0
	45 ppm Cl^-	37.5 ppm Cl^-	-16.5
	22.5 ppm Cl^-	16.9 ppm Cl^-	-25.0

Run No. 3 - 92% Slope - Reference, Orion 90-02**

Calibrate	450 ppm Cl^-	450 ppm Cl^-	0
	45 ppm Cl^-	42 ppm Cl^-	-6.7
	22.5 ppm Cl^-	22.5 ppm Cl^-	0

Run No. 4 - 100% Slope - Reference, Orion 90-02

Calibrate	450 ppm Cl^-	450 ppm Cl^-	0
	45 ppm Cl^-	48 ppm Cl^-	+6.7
	22.5 ppm Cl^-	26 ppm Cl^-	+15.5

Run No. 5*** - 100% Slope - Reference, Beckman Lazaran

Calibrate	450 ppm Cl^-	450 ppm Cl^-	0
	225 ppm Cl^-	219 ppm Cl^-	-2.7
	50 ppm Cl^-	35.5 ppm Cl^-	-29.0
	15 ppm Cl^-	10 ppm Cl^-	-33.0

*Set slope and temperature indicator. Then calibrate with standard solution.

**Double junction reference electrode.

***Run on a different day from Runs 1-4.

magnitude of this effect, an average value of -2.5% $\pm$0.8 (1σ) was obtained for the error introduced per ^{o}C rise in temperature.*

For the Cl^- electrode the estimated measurement error is less than 5% at Cl^- alarm level (450 ppm) and less than 20% at low levels using a slope setting of 92%. Drift can add another 5% to 8% (4 hours and 20 hours respectively) at the alarm level.

Similar experiments were performed with the Orion pH electrode (with Lazaran reference) to define the error introduced by (1) standardizing at a pH of 7 and making sample measurements at a pH of 4 or 9** and (2) a fluctuation in temperature between calibration and sample determination.

An evaluation of the first parameter (Table 14 indicates that readings are lower at a pH of 4 and pH of 9 than the actual solution would dictate, whether one were operating at a slope setting of 95% or 100%.

In an evaluation of the temperature effect, an increase of $1^{o}C$ will produce an error corresponding to -0.01 pH*** unit at pH 7, -.03 pH at pH of 4 and -.04 pH at a pH of 9. The temperature effect can be seen to produce a small to negligible error in the sample measurement.

For the pH electrode the estimated measurement errors due to electrode sensitivity and temperature effects are about 2.5% to 3.5% over the pH range from 9 to 4 respectively with a slope setting of 100%. The error due to drift is less than 0.1 pH unit over 24 hours.

Similar tests were conducted on the Corning monovalent cation (NH_4^+) electrode (with Lazaran reference) to estimate measurement errors.

a) Slope Setting

The percentage error introduced into measurements made at concentrations lower than the alarm level of 10 ppm NH_3 (the point of system calibration) is shown by the data

---

*Meter reads 2.5% lower than actual solution concentration.

**Reclaimed water samples are expected to fall mainly in this pH range.

***Increasing temperature produces decreasing pH.

Table 14

Slope Determination for Orion 91-01 pH Electrode (Beckman Lazaran Reference)

		pH Reading	% Error
Calibration	pH 7.03 @ 23°C Slope 100%		
	pH standard 4.00	3.90	-2.5
	pH standard 9.21	9.00	-2.3
Calibration	pH 7.03 @ 23°C Slope 95%		
	pH standard 4.00	3.78	-5.5
	pH standard 9.21	9.13	-0.9

in Table 15. The maximum error from the best straight line fit (85% of the theoretical Nernst slope) of the experimentally determined points is seen to be about 8%.

b) Drift

The data in Table 16 indicate that system drift was approximately 10% (at 10 ppm) over a four-hour period and 25% over a 25-hour period.

c) Temperature Coefficient

The data in Table 17 indicate that the effect of fluctuating temperature (occurring between calibration and sample measurement) is small, amounting to an error of only 0.3%/^{o}C at 10 ppm and 1.1%/^{o}C at 1 ppm.

The estimated measurement error due to electrode sensitivity and temperature is about 8% to 9% around 2 ppm and about 1% at the alarm level of 10 ppm (calibration done at 10 ppm). At the alarm level, drift over a four-hour period could add another 10% error (over 24 hours, 25%).

Conductivity Cell (Beckman CEL-VDJ-2). -

The epoxy flow through conductivity cell (with SOLU bridge conductivity indicator, Type RI5, and automatic temperature compensator) was evaluated with the following results.

a. Holdup Volume - approximately 25 ml

b.

Sensitivity	Reading @ 23^{o}C	Literature	Error
5×10^{-4} M KCl	74	74	0
1×10^{-3} M KCl	141	147	-4.1%
5×10^{-3} M KCl	690	710	-2.8%

c. Temperature Compensator

	@ 23^{o}C	@ 43^{o}C
5×10^{-4} M KCl	74	73 (5 min for equilization)
1×10^{-3} M KCl	141	143
5×10^{-3} M KCl	690	690

Table 15

Meter Slope Setting Evaluation

Monovalent Cation (NH_4^+) Electrode (Corning #476220)
Beckman Lazaran Reference Electrode
Orion Model 407 Meter

NH_3, ppm*	Meter Reading Mv.	% Error**
10	-24	0
5	-37.5	+6.2
3.3	-48	-1.5
2	-60.5	-7.5
1	-73	+2.5

*In Standardizing Solution.

**Based on slope of best straight line fit through data points (50.19 Mv/decade = 84.8% of Nernst slope).

Table 16

System Drift

Monovalent Cation (NH_4^+) Electrode (Corning #476220)
Beckman Lazaran Reference Electrode
Orion, Model 407 Meter

Time, Hrs	Meter Reading ppm, NH_3
0 (calibrate)	10.0
4	11.0
18	12.6
24	12.5
40	13.1

Table 17

Temperature Coefficient

Monovalent Cation (NH_4^+) Electrode (Corning #476-220)
Beckman Lazaran Reference Electrode
Orion Model 407 Meter

t°C	Meter Reading ppm, NH_3
22°C	10.0
39°C	10.5
22°C	1.35
39°C	1.60

d. Effect of Flow

A comparison of the conductance reading under flow (2 ml/min) and no flow conditions indicated no significant difference in the readings.

Total Organic Carbon Analyzer. -

The responses of the automated version of the TOC were found to be linear with challenge (Table 18 and Figure 16). However, the total carbon and inorganic carbon responses were not the same when challenged by equivalent inorganic solutions. The efficiencies of the two channels differ due primarily to differencies in combustion tube designs and packing techniques for the high temperature furnace. The slope and the intercept of the total carbon curve are sensitive to the tube repacking procedure. In addition, as the packing degrades, the curve (calibration) will shift. Compensation for this shift is done electronically by means of a gain control on the total carbon signal.

If the resultant organic carbon signal corresponds to more than 100 ppm an alarm is activated. At the present time, a full scale reading from the IR analyzer corresponds to 200 ppm. Fully automatic sample handling and signal processing is controlled by a cam-type timer/programmer which provides organic carbon readings once every 30 minutes.

Water sample size is 45.5 μl for the inorganic channel and 41.5 μl for the total channel.

Biosensor. -

Effects of Reagent Composition -

The response of the instrument to a fixed bacterial challenge (recovered off the filter-concentrator) was evaluated in order to permit better assessment of operation with a more complete system employing both filters.

In this determination a water sample containing a fixed bacterial challenge was concentrated on a single port of the filter-concentrator, indexed to the next position, and then backwashed with 4M urea (1 ml/min).

Table 18

Automatic* Sample Injection Into Total Carbon and Inorganic Carbon Furnaces

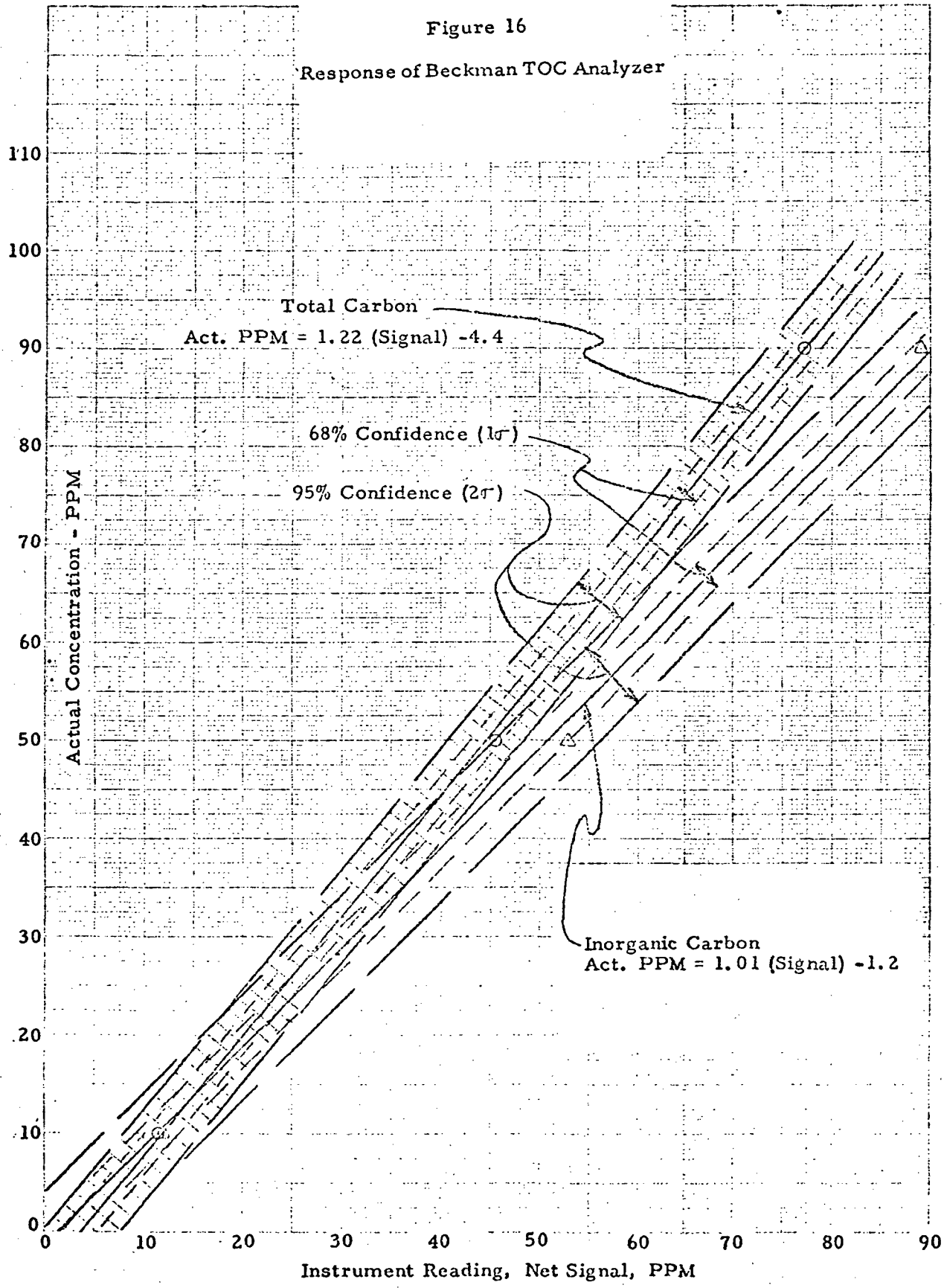
	Number of Samples	
Total Carbon		
Water blank	6	3.67 ± 0.96**
10 ppm	9	15.22 ± 0.84
50 ppm	9	49.22 ± 1.40
90 ppm	9	80.78 ± 2.05
Inorganic Carbon		
Water blank	8	2.9 ± 0.99
10 ppm	9	14.9 ± 0.60
50 ppm	9	55.8 ± 1.30
90 ppm	9	92.0 ± 1.73

* Carrier gas through sample loop at 6 psig for 2 seconds.

** Standard deviation

Figure 16

Response of Beckman TOC Analyzer



The net signal obtained as a function of luminol/H_2O_2 ratio is summarized in Table 19. This latter parameter was briefly examined since the sensitivity of a system is markedly affected by the mixing pattern as determined by reactor cell geometry.

The results shown in the table indicate that net signals of about 21 volts were observed with 2 reagent formulations designated No. 1 and No. 3. While No. 3 may be preferred since it produced a lower reagent baseline voltage (i.e., 4 vs 8 volts), No. 1 formulation employing the more concentrated H_2O_2 would probably exhibit a better shelf life. Subsequent testing was done using formulation No. 1.

Performance -

The preliminary response of the biosensor, (i.e., before modification to do viable cell counts) was evaluated for bacterial challenges (of E. coli) down to a level of 4000 cells (10 cells/ml, 400 ml sample). The results presented in Table 20 show that:

1) For total challenges of 1×10^5 cells of E. coli, the effects of sample size, flow rate, and challenge level are considered to be small.

2) A comparison of net signal against challenge is non-linear. Linear response is obtained at challenges below about 50 cells/ml. Above this level the response is non-linear. The reactor cell concept used in the biosensor was originally designed and optimized for systems where total challenges were about 10^4 cells (50 cells/ml for 400 ml sample). For larger challenges a portion of the chemiluminescence reaction has probably passed outside of view of the PMT resulting in reduced efficiency and non-linear signal response. It is also probable that variable recovery from the filters occurs at high challenges due to saturation of the filters.

3) The biosensor is capable of detecting challenges as low as 10 cells/ml (400 ml sample) within 1σ probability.

Subsequent to biosensor modifications to incorporate viable capability (and rework of the 47 mm filter holders), the biosensor was retested at challenge levels of 10 cells/ml (400 ml sample). The biosensor was subjected to bacterial challenges while operating in a total count mode and in a

Table 19

Effect of Reagent Composition on Signal Response Toward *E. coli*[1]

Formulation No.	Luminol Composition	Conc. of H_2O_2 Stream, %	S-N Net Signal (volts) av	Reagent Baseline Signal (N) (volts)
1	Stock Luminol[3]	1.0	21	8
2	Stock Luminol	1.3	12	14
3	Stock Luminol:H_2O 1:1 Dilution	0.6	21.5	4
4	Stock Luminol:H_2O 1:1 Dilution	1.0	15	6
5	Stock Luminol:H_2O 1:1 Dilution	1.4	12	8
6	Stock Luminol:H_2O 1:1 Dilution	1.0	15[2]	4

(1) Bacterial challenge (except where noted) was unknown but fixed level of *E. coli*; net signals represent mean average of 2 to 6 points.

(2) Challenge for this formulation: 1.36×10^4 *E. coli*/ml, 10 ml sample.

(3) Stock luminol contains 1 mg/ml luminol, 15 mg/ml Disod-EDTA, 60 mg/ml NaOH; luminol and H_2O_2 flows were 0.11 and 0.24 ml/min, respectively.

Table 20

PRELIMINARY DATA ON BIOSENSOR RESPONSE TO BACTERIAL CHALLENGES of *E. coli*

(Unincubated Challenges)

Flow Rate (ml/min)	Sample Size (ml)	Challenge Level (E. coli/ml)	Total Challenge (E. coli)	Net Signal (S-N) (volts)	S*
17	10	1×10^5	1×10^6	25.0(1)	±0.6
17	10	1×10^4	1×10^5	15.1(2)	±3.2
17	100	1×10^3	1×10^5	17.5(3)	±0.7
17	400	2.5×10^2	1×10^5	16.8(3)	±1.8
10	400	2.5×10^2	1×10^5	17.8(3)	±0.4
17	400	5×10^1	2×10^4	9.8(4)	±2.1
15	360	5×10^1	1.8×10^4	6.9(1)	±2.6
17	400	2×10^1	8×10^3	3.4(5)	±1.7
17	380	1×10^1	3.8×10^3	1.8(6)	±0.6

Reagents: 1% H_2O_2 and Stock Luminol

* S = Standard Deviation

(1) Average of 4 Data Points

(2) Average of 8 Data Points

(3) Average of 2 Data Points

(4) Average of 6 Data Points

(5) Average of 12 Data Points

(6) Average of 10 Data Points

viable count mode (but without nutrient) to check operation and compare results with previous data. Results at levels of 10 E. coli per ml show an average response of 4.6 volts compared with about 2 volts from the biosensor before the 47 mm filter holders were reworked. The standard deviation of this data (22 data points) is ±2.1 volts.

Operation in a viable mode showed a response to a challenge of 10 E. coli/ml (400 ml sample) of 12.3 volts ±3.3 (1σ).

A summary of all response data for the biosensor is shown in Figure 17. Typical recorder traces are shown in Figures 18 and 19. Samples are collected simultaneously and processed (and read) sequentially from right to left.

SYSTEM INTEGRATION

This section covers the major problems associated with interfacing of the various sensors with each other and a description of the total integrated water monitor.

Figure 17

BIOSENSOR SIGNAL RESPONSE TO E. COLI

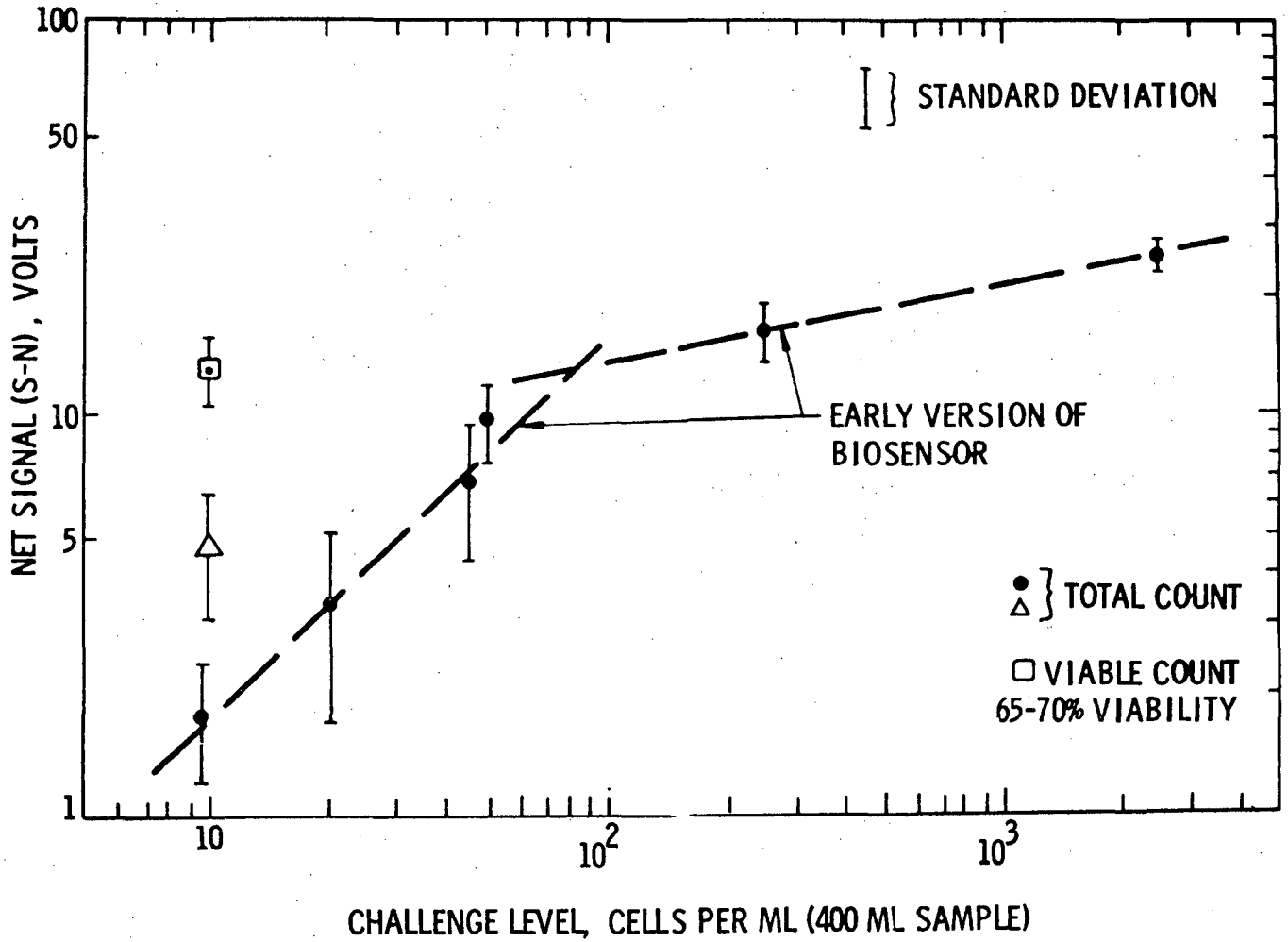
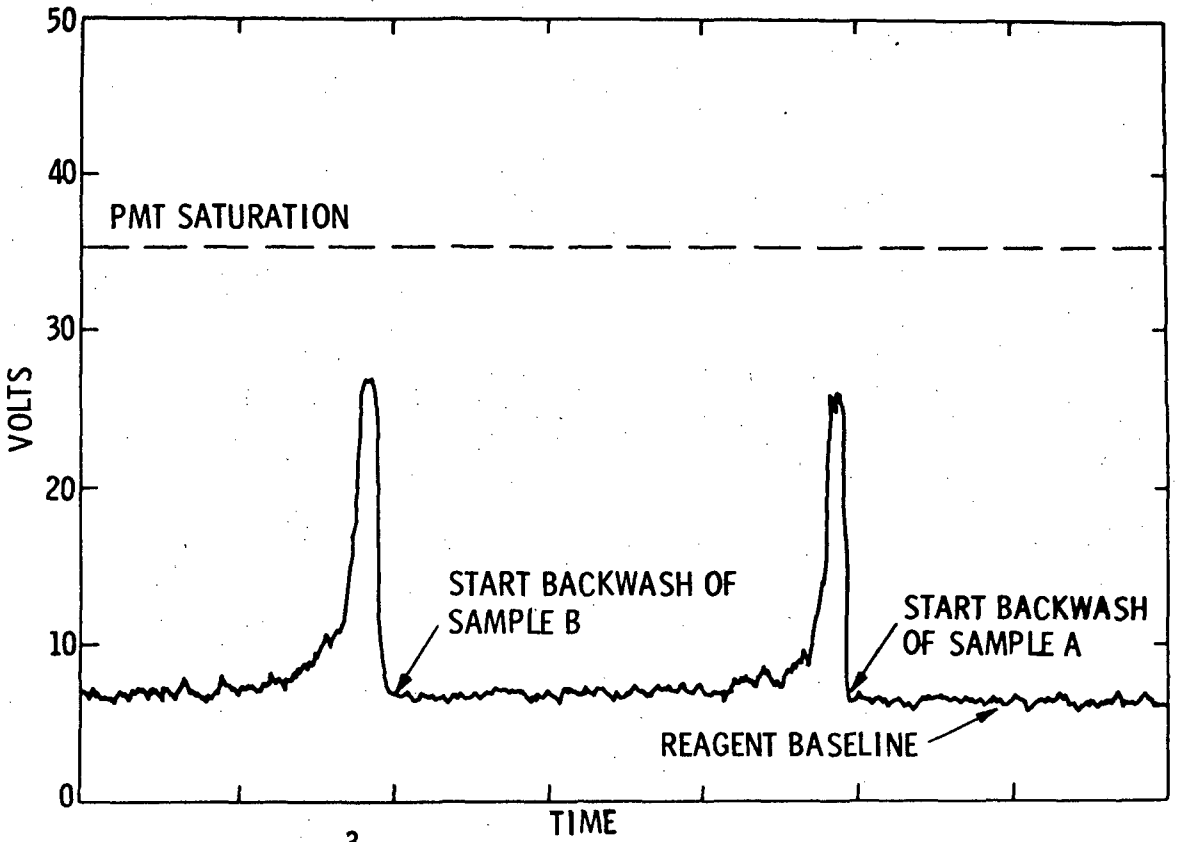


Figure 18

TYPICAL BIOSENSOR RESPONSE DATA (TOTAL COUNT)



CHALLENGE: 1×10^3 E. COLI/ML (100 ML SAMPLE AT 17 ML/MIN)

REAGENT BASELINE: ~6 VOLTS

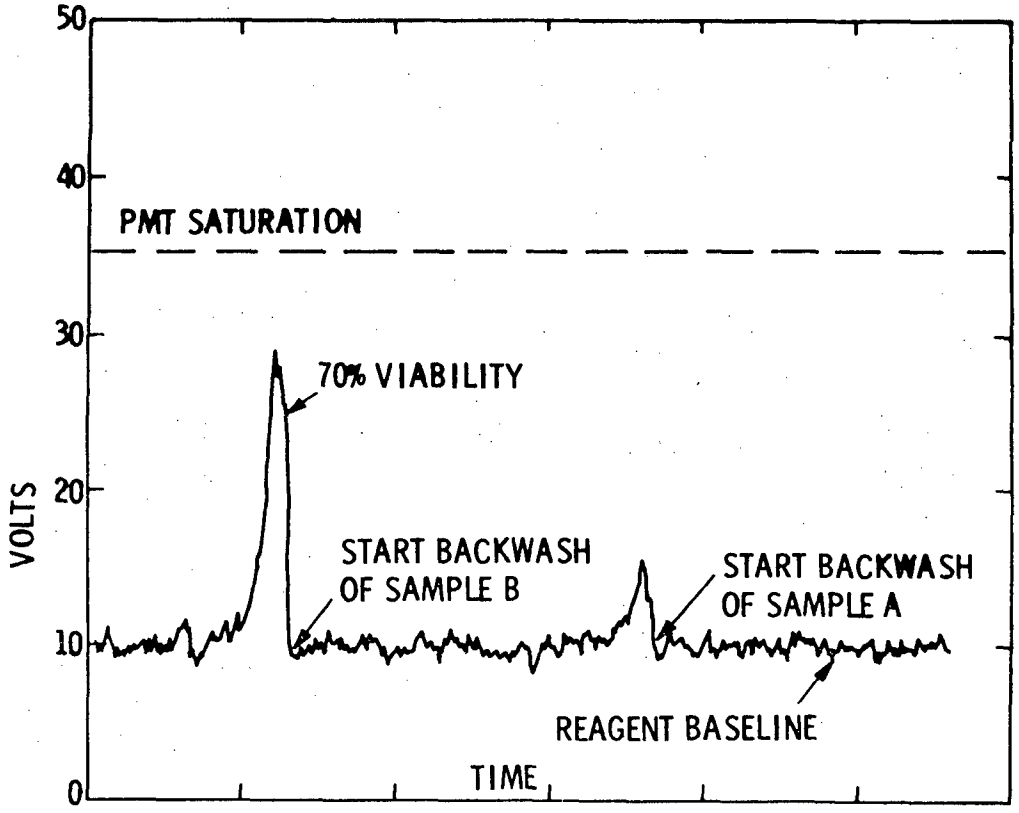
WATER BLANK SIGNAL (N) (NOT SHOWN): 9 VOLTS (AVE. OF 4 DATA POINTS)

NET SIGNAL (S-N) FOR SAMPLE A = (26 - 9) = 17 VOLTS

NET SIGNAL (S-N) FOR SAMPLE B = (27 - 9) = 18 VOLTS

Figure 19

TYPICAL BIOSENSOR RESPONSE DATA (TOTAL AND VIABLE COUNT)



CHALLENGE: 10 E. COLI/ML (400 ML SAMPLE AT 17 ML/MIN)

REAGENT BASELINE ~ 10 VOLTS

WATER BLANK SIGNAL (N) (NOT SHOWN): 13 VOLTS (AVE. OF 2 DATA POINTS)

NET SIGNAL (S-N) FOR SAMPLE A: (15.5 - 13) = 2.5 VOLTS

NET SIGNAL (S-N) FOR SAMPLE B: (29 - 13) = 16 VOLTS (70% VIABILITY)

Ground Loops in Electrode Installation

The ion electrodes were installed in their respective wells. Solutions of known ion concentration were passed through the wells to obtain sensor response under conditions representative of the final installation. Two separate electrical problems were observed; one associated with spurious pickup of 60 Hz noise at the remote output connectors, and the other an electrical interaction between ion electrodes.

Shielded wire is used for transmitting electrode signals from the meters to the remote output connectors and also to the alarm circuitry. Providing a common ground for the shields eliminated 60 Hz interference on all outputs except the NH_4^+. The monovalent cation (NH_4^+) electrode uses an Orion 407 meter, while the Cl^- and pH electrodes use Orion 401 meters. It has been concluded that a slight AC signal (approx. 0.4 mv peak-to-peak) will exist on the recorder output from the 407 meter. AMB discussed this with the Orion representatives. They stated that the shielding in the 407 meter is not as good as that on the 401 meter. Orion offered possible corrective procedures; however, none have reduced the AC pickup. It is undesirable to have AC pickup, since the alarm set points will have to provide an additional allowance so as not to give false alarms. It is anticipated that the $\pm$0.2 mv AC signal on the 407 meter will not cause any difficulties. It should be noted, however, that the 407 meter will have to operate on batteries. The 401 meters (Cl^- and pH) may operate off of the line converters with no difficulty.

The second problem of electrical interaction between electrodes was solved by providing a switching circuit on the output electronics. It is not permissible for the ion meters to have more than one common ground (the processing electronics have one ground and the sample solution serves as a second common ground for all electrodes). This was corrected with a switching circuit in the processing electronics so that only one electrode output could be read at a time. Each electrode is set to read for a one-minute interval every three minutes.

Effect of Specific Conductance Cell on Ion Electrodes

A check was made to determine whether the electrical potential or current in the flow cell would have any effect upon the ion electrode readings. Measurements with solutions of 1275 μ mhos and $< 10 \mu$ mhos gave no perceptable change in electrode readings. This was the case whether or not a peristaltic pump was inserted between the conductance cell and the electrode wells.

Problems With Monovalent Cation (NH_4^+) Electrodes

During the contract the original Corning (#476220) monovalent cation electrode was broken. A replacement was obtained, however, it was returned because of lack of response to NH_4^+ solutions. Another replacement was obtained. This electrode worked all right for awhile, but then began to behave erratically; day-to-day reproducibility was poor with variations of 30 to 50 percent at concentrations of 10 ppm and below being common. AMB discussed the problem with both technical and quality control personnel at Corning who admitted to having production problems with the monovalent cation electrodes so that it would perform well for NH_4^+. Alternate electrodes to the Corning electrode were considered.

A Beckman cation electrode (No. 39137) was obtained as a possible replacement for the Corning (No. 476220). About the same time Corning sent AMB a monovalent cation electrode (No. 476220) which they had hand-selected and felt would provide adequate response to NH_4^+. The response of these electrodes (Table 21) showed that with the Orion double junction reference electrode the Corning electrode gave a response nearer the theoretical Nernst response (59.2 mv) than did the Beckman electrode. In combination with the Lazaran reference electrode, both sensing electrode responses were on the order of half the theoretical. The data seemed to indicate that at least some of the past difficulties had not been with the specific ion electrode, but with the Lazaran reference electrode. Data taken with a second Lazaran (designed as #2) showed essentially identical response. The response of the Lazaran electrodes with the pH and Cl^- electrodes was satisfactory.

Table 21

Response of NH_4^+ Electrodes

	Orion Double Junction Ref.		Lazaran #1*	
	Corning	Beckman	Corning	Beckman
20 ppm	-92 mv	+108 mv	-19 mv	+190 mv
2 ppm	-149	+ 60	-53	+160
	Δ = 57 mv	Δ = 48 mv	Δ = 34 mv	Δ = 30 mv

*The system used 2 Lazaran Reference Electrodes; the one used in this evaluation is designated as #1. This electrode has been exposed to NH_4^+ solutions for about 4-5 months.

Since the Lazarans had been subjected to extended usage (4 or 5 months) in NH_4^+ solutions, the question arose as to whether or not the Lazaran electrodes could have been poisoned toward NH_4^+. When the Lazaran was first received and tested, the response was about 50 mv per decade of NH_4^+ concentration over the range from 1 ppm to 10 ppm. Short term (25 hours) resoaking of a Lazaran electrode in 4 M KCl resulted in improvements in NH_4^+ response, but after another 24-hour use in NH_4^+ solution, performance degraded. A new Lazaran electrode was ordered for tests to determine whether the poisoning theory was correct.

The third Lazaran reference electrode was compared against one of the other Lazarans when used in combination with a monovalent cation electrode. These results are presented in Table 22. It appeared that the poisoning theory was incorrect, since Lazaran #3 had never been exposed to NH_4^+ solution prior to this test. The consistency of the Δ mv between the two Lazaran electrodes was remarkable. The data did show a significant drop in response at low NH_4^+ concentrations particularly below 10 ppm NH_4^+. Above 10 ppm the response was good.

Additional investigations and tests were performed to determine whether the poor response at low NH_4^+ concentrations could be traced to the Lazaran or whether this was representative of most monovalent cation electrodes.

Both the Beckman (No. 39137) and Corning (No. 476220) Monovalent Cation Electrodes were used in combination with a Beckman Lazaran (No. 19033) reference electrode for the determination of NH_4^+ concentrations from 1-1000 ppm. Both cation electrodes exhibited poor reproducibility at concentrations below 10 ppm NH_3. In agreement with the observations of other investigators* the response of the Beckman electrode was found to be markedly affected by the type of pretreatment, with the electrode exhibiting a faster and better response if soaked for several days in distilled water

*G.G. Guilbault et al, Anal. Chem. 41, No. 4, 600 (1969).

Table 22

Comparison of Lazaran Reference Electrodes

Conditions: Using Orion 401 Meter and distilled water
pH to 6.9 with Tris Buffer and HCl.

	Lazaran #1	Δ mv	Lazaran #3	Δ mv
Water pH 6.9 Cond. 6300 μmhos/cm	-123		-133	
		11		11
1 ppm NH_4^+	-112		-122	
		40		40
10 ppm NH_4^+	- 72		- 82	
		51		51
100 ppm NH_4^+	- 21		- 31	
		54		55
1000 ppm NH_4^+	+ 33		+ 24	

rather than in (NH_4^+) solutions before use. The sensitivity of the cation electrode was also found to vary from electrode to electrode, also in agreement with that reported by other workers.*

In an effort to establish that the observed variability was due to the cation electrode and not the reference electrode, a number of different reference electrodes (double junction, calomel, Lazaran) were used in combination with a single cation (Beckman) electrode. The results summarized in Tables 23 and 24 indicate that all three reference electrodes behave similarly in combination with Beckman's monovalent cation electrode, and that the reliability of the latter drops off below 10 ppm NH_3. The observation that consistent and reliable data were obtained in the last series of experiments in the 1-10 ppm concentration range (Table 24) when a fresh 1 ppm NH_3 solution was prepared just prior to measurement suggests that at least part of the problem lies in preparing 1.0 ppm NH_3 without trace contamination by other cations, particularly, K^+ or Na^+ to which the monovalent cation electrodes are decidedly more sensitive. In conclusion, the poisoning theory has been discounted, and the difficulty in making measurements at NH_4^+ concentrations less than 10 ppm seems typical of monovalent cation electrodes and seems to be due in part to preparing the test solutions.

Adjustment of Ion Electrode Alarm Threshold

During system operation, the millivolt output from the electrodes is converted by the Orion meters to a ppm concentration and displayed. The meters have an output jack with a signal level from -10 mv to +10 mv. The meter output is directly proportional to the meter needle position with a mid-scale output value of 0 mv. Figures 20 through 22 and Table 25 present this calibration data. For a given ion concentration, the proper alarm threshold value may be read directly from the above curves. Alternately, the meter may be adjusted manually to the desired alarm level (in ppm or pH units) and the appropriate alarm cards adjusted to just trigger the alarm. The meter output (in mv) is sent directly to the alarm circuits for processing.

*J. Montalvo and G.G. Guilbault, Anal. Chem. 41, No. 13, 1897 (1969).

Table 23

Response of Beckman Cation Electrode with Several Reference Electrodes

Conditions: Dried NH_4Cl dissolved 0.1 M Tris Buffer (pH 6.9) to yield following concentrations of NH_3. Readings were made with a Beckman (76008) Digital pH meter. Readings were run in duplicate in the order shown below:

a) Electrode Combination: Beckman Monovalent Cation + Beckman Lazaran Reference

	M.V. Reading	Δ mv
1.0 ppm NH_3	64.5	
		37
10.1 ppm NH_3*	101.5	
		57
100.9 ppm NH_3*	158.5	
1.0 ppm NH_3	76.5	
		29
10.1 ppm NH_3	105.5	
		53
100.9 ppm NH_3	158.5	

b) Electrode Combination: Beckman Monovalent Cation + Orion Double Junction Reference

1.0 ppm NH_3	66.5	
10.1 ppm NH_3	64.5	51
100.9 ppm NH_3	115.5	
1.0 ppm NH_3	65	1.5
10.1 ppm NH_3	66.5	48
100.9 ppm NH_3	114.5	

c) Electrode Combination: Beckman Monovalent Cation + Beckman Calomel Reference

1.0 ppm NH_3	69.5	
10.1 ppm NH_3	65.5	50
100.9 ppm NH_3	115.5	
1.0 ppm NH_3	64.5	2.0
10.1 ppm NH_3	66.5	49
100.9 ppm NH_3	115.5	

*About 1 minute to reach equilibrium.

Table 24

Response of Beckman Cation Electrode with Several Reference Electrodes

Conditions: Same as Table 23 Beckman Monovalent Cation Electrode was used in combination with the various reference electrodes shown below.

Reference Electrode	Millivolt Reading			
	1.0 ppm NH_3	10.0 ppm NH_3	99.9 ppm NH_3	999.2 ppm NH_3
Beckman Calomel	64.5	64.5	114.5	169.5
Δ m.v.		0	50	55
Beckman Lazaran	108.5	106.5	156.5	211.5
Δ m.v.		--	50	55
Orion Double Junction	66.5	64.5	114.5	168.5
Δ m.v.		--	50	54
Prepared fresh 1.0 ppm NH_3 and rechecked.				
Beckman Calomel	9.5	65.5	114.5	167.5
Δ m.v.		56	49	53
Beckman Lazaran	51.5	107.5	156.5	209.5
Δ m.v.		56	49	53
Orion Double Junction	9.5	64.5	114.5	166.5
Δ m.v.		55	50	52

10 X 10 TO ½ INCH 46 1322
7 X 10 INCHES MADE IN U.S.A.
KEUFFEL & ESSER CO.

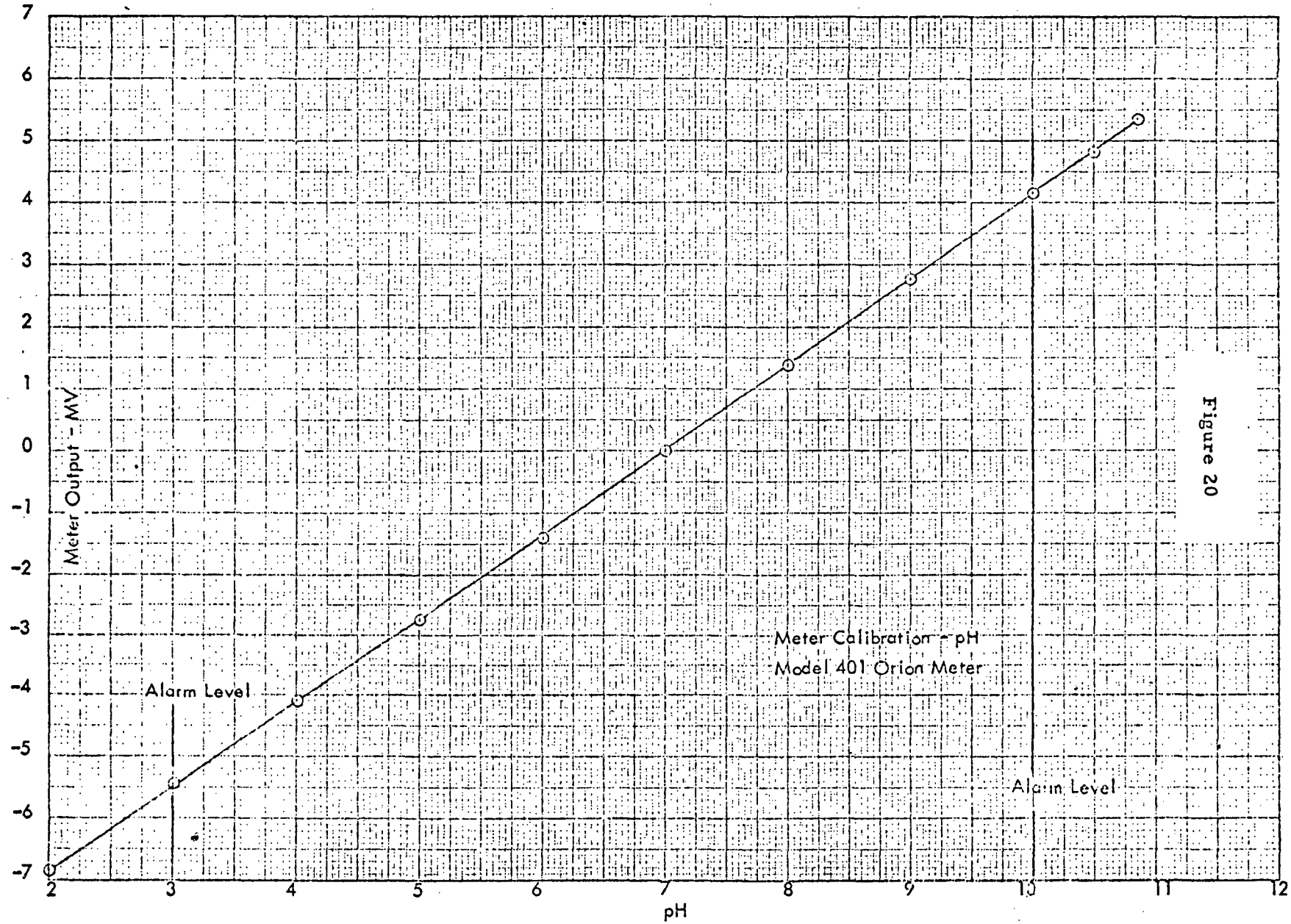


Figure 20

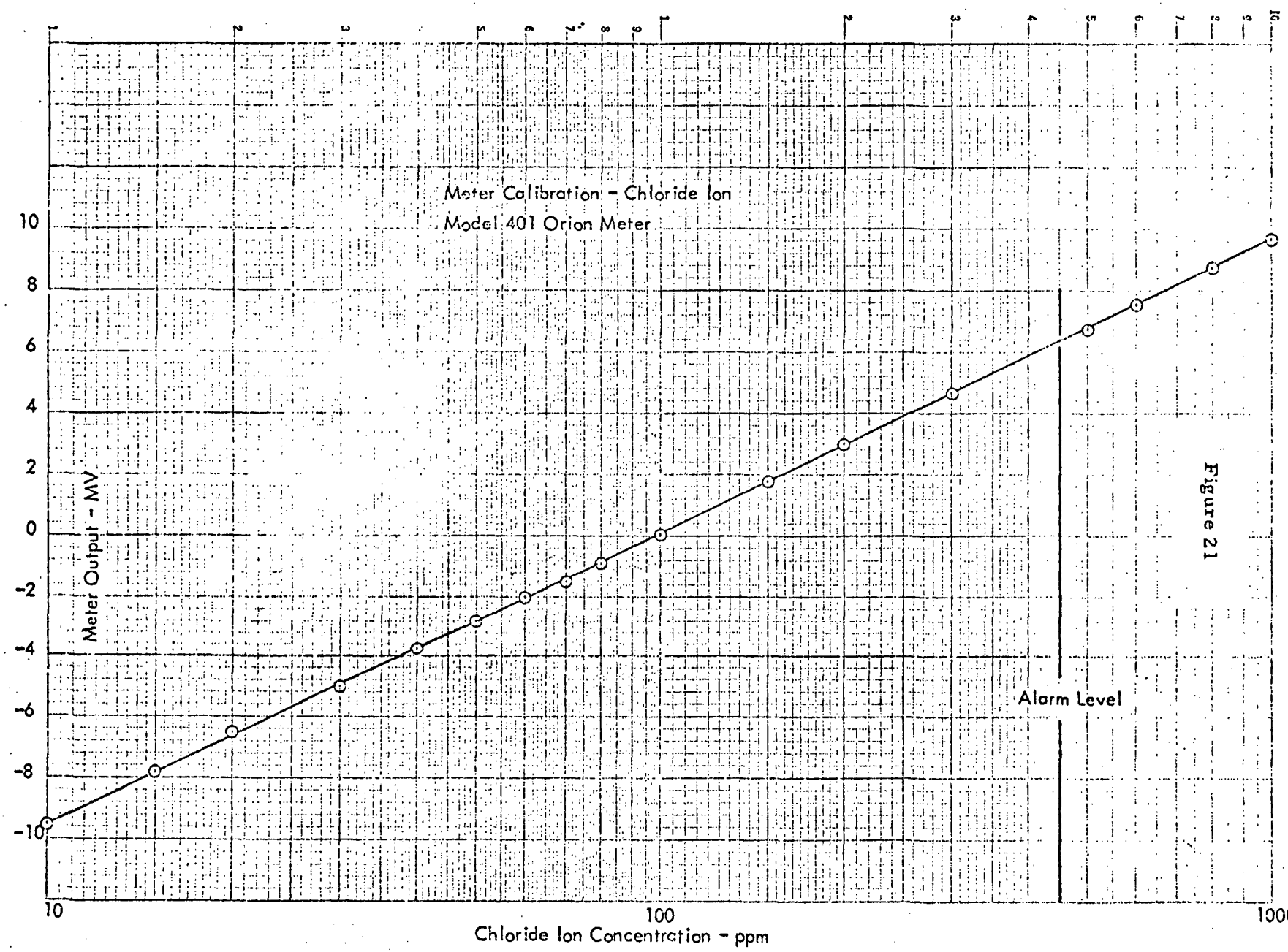

Meter Calibration - Chloride Ion
Model 401 Orion Meter
Meter Output - MV
10
8
6
4
2
0
-2
-4
-6
-8
-10
Alarm Level
10
100
1000
Chloride Ion Concentration - ppm

Figure 21

Figure 22

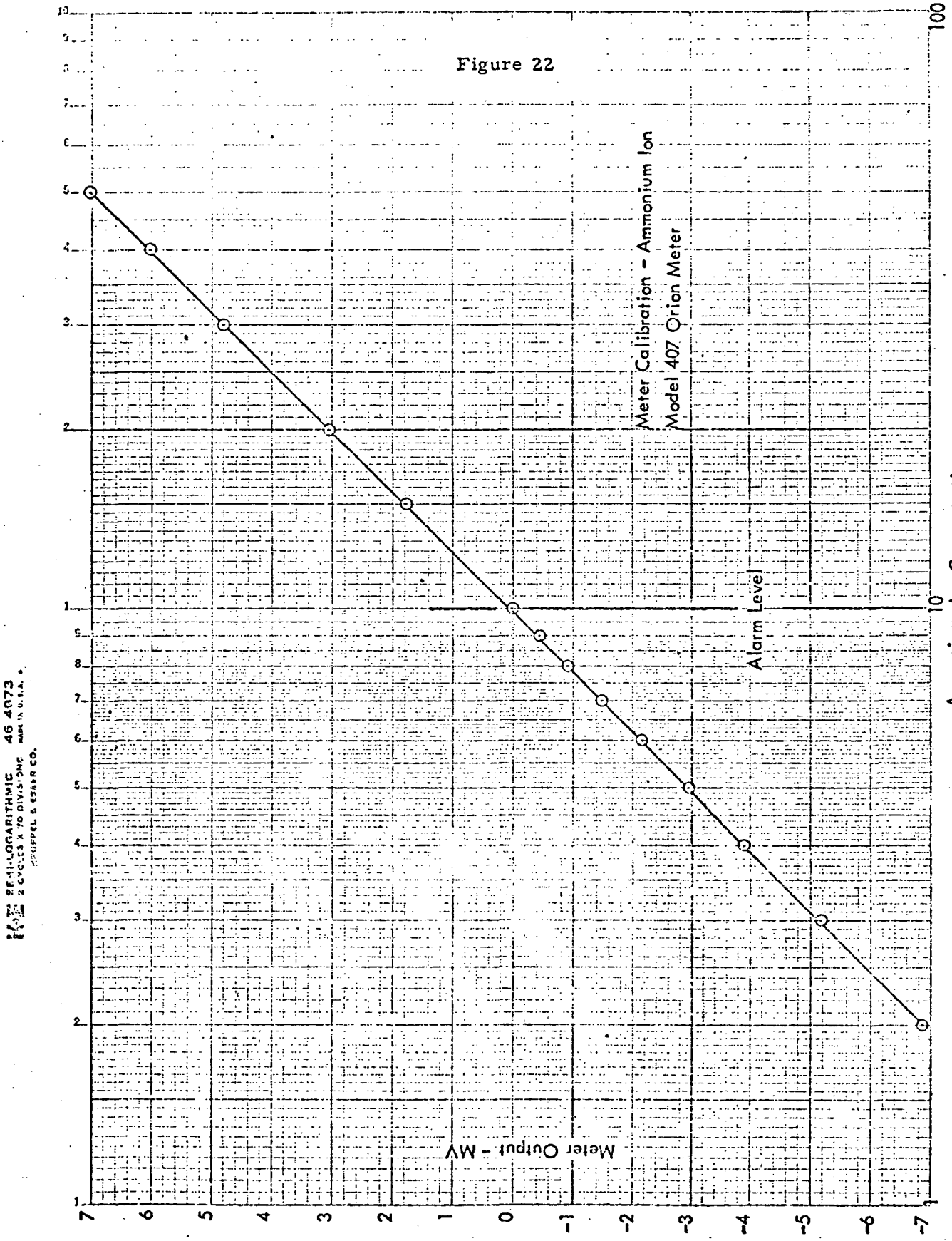

Meter Calibration - Ammonium Ion
Model 407 Orion Meter
Alarm Level
Meter Output - MV
Ammonium Ion Concentration - ppm
100
10
1
7
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
-6
-7

Table 25

METER CALIBRATION

Orion 401 pH	Meter Output Millivolts	Orion 407 NH_4^+, ppm	Meter Output Millivolts	Orion 401 Cl^-, ppm	Meter Output Millivolts
10.58	5.34	80	9.10	1000	9.64
10.5	4.82	70	8.50	800	8.75
10.0	4.15	60	7.85	600	7.58
9.0	2.77	50	7.02	500	6.78
8.0	1.40	40	6.05	300	4.65
7.0	0.01	30	4.80	200	2.97
6.0	-1.38	20	3.06	150	1.77
5.0	-2.72	15	1.79	100	0.06
4.0	-4.09	10	0.02	80	-0.87
3.0	-5.45	9	-0.44	70	-1.43
2.0	-6.83	8	-0.91	60	-2.07
		7	-1.47	50	-2.78
		6	-2.17	40	-3.75
		5	-2.94	30	-4.96
		4	-3.91	20	-6.55
		3	-5.18	15	-7.78
		2	-6.85	10	-9.53
		1	-9.95		

Total System Configuration

All sensors have been installed into two instrument racks. The racks are 38 1/4 inches wide by 31 inches deep. One rack is slightly under 79 inches high and the other about 37 inches high. This installation is shown in Figure 23. A comprehensive description of the water monitor system is contained in the Operating and Maintenance Manual.* A specification for overall system is shown in Table 26. An overall system schematic is shown in Figure 24.

The Total Organic Carbon Analyzer is placed upstream of the peristaltic pump in order to avoid sample contamination by the plasticizer from the Tygon pump tubing.

The flow-through conductivity cell is shown installed in one of the sample lines to the biosensor. The holdup volume of the present conductivity cell is about 25 ml and requires a relatively large flow rate to equilibrate to changes in sample solution conductivity. The sample flow rate through the biosensor satisfies this requirement, however the biosensor sampling pump operates only 24 minutes during each hour. Consequently, conductivity measurements are available only part of the time. The alternate location shown is the preferred installation for conductivity cells whose holdup volume does not exceed 2 - 3 ml. Continuous readings are obtained at that location.

Block diagrams for the various sensor subsystems are shown in Figures 25 through 29.

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*Operating and Maintenance Manual, No. 1101 OM, For A Laboratory Prototype Water Quality Monitoring System Suitable For Use In Zero Gravity, Contract NAS 1-10382, 28 July 1972, Aerojet Medical and Biological Systems.

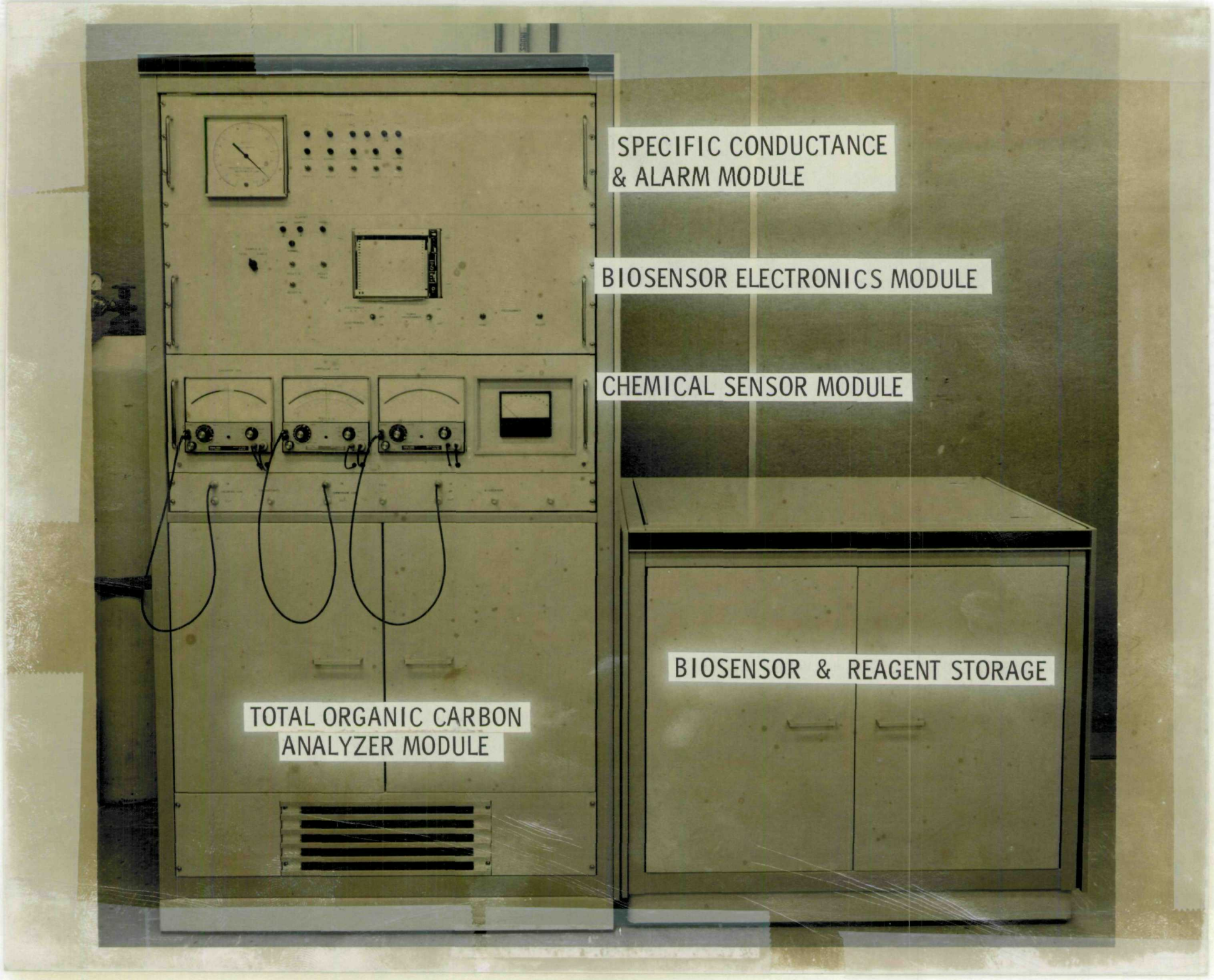
SPECIFIC CONDUCTANCE
& ALARM MODULE
BIOSENSOR ELECTRONICS MODULE
CHEMICAL SENSOR MODULE
BIOSENSOR & REAGENT STORAGE
TOTAL ORGANIC CARBON
ANALYZER MODULE

Table 26

WATER QUALITY MONITOR SPECIFICATIONS

General

Size		3'7"W x 6'7"H x 3'9"D
	and	3'7"W x 3'2"H x 3'9"D
		(both cabinets on casters)
Weight		913 lb. (est.)
Power		115V, 60 Hz 2535 Watts Maximum (est.)
Sample H_2O Head Pressure		0-30 psig
Air Supply		Standard Lab Supply 95 psig (min.)

All sensor outputs have connectors for remote monitoring.

Biosensor

In total count operating mode--

Sample H_2O Size	Sample A (total)	400 ml
	Sample B (total)	400 ml
Time between readings	Sample A (total)	68 min.
	Sample B (total)	68 min.
Sensitivity*	10 cells/ml	
Reagent Usage		
Dextrose Broth	0 ml/hr	
Urea (4M)	178 ml/hr	
Distilled Filtered H_2O	78 ml/hr	
Luminol	6.6 ml/hr	
H_2O_2 (1%)	14.4 ml/hr	
Incubation	None	

*Tests run with E. coli

Table 26 (Continued)

In viable count operating mode--

Sample H_2O Size	Sample A (total)	400 ml
	Sample B (viable)	400 ml
Time between readings	Sample A (total)	68 min.
	Sample B (viable)	204 min.
Sensitivity*	10 cells/ml (total)	
	5 cells/ml (viable)	
Reagent Usage		
Dextrose Broth	2.2 ml/hr	
Urea (4M)	190 ml/hr	
Distilled Filtered H_2O	60 ml/hr	
Luminol	6.6 ml/hr	
H_2O_2 (1%)	14.4 ml/hr	
Incubation	136 min. @ 37°C	

Strip chart recorder for display of chemiluminescence signals.

Alarms (red lights with manual reset).

Alarm level adjustable.

Chemical & Physical Sensors

Total Sample H_2O Size	96 ml/hr (continuous)
Alarms (red lights with manual reset)	
Alarm level adjustable.	

Total Organic Carbon Analyzer (Modified and automated Beckman Model 915 TOC)

Programmed Sample Injection	(43 µl nominal sample size)
Automatic Signal Processing	
Range	Total Carbon 0-200 ppm
	Total Organic Carbon 0-200 ppm
Alarm	@ 100 ppm TOC (adjustable)
Zero Grade Air Required	300 cc/min. (max.)
Time Between Readings	~ 30 min.

*Tests run with E. coli

Table 26 (Continued)

Specific Conductance

Beckman Type RI5 Solu Bridge Indicator

Beckman CEL-VDJ-2 KF Epoxy Flow Through Cell, 25 ml holdup volume

Range	0-1000 μ mhos
Alarm	@ 990 μ mhos (adjustable)
Time Between Readings	36 minutes

Specific Ion Sensors

Orion Meter Readout for pH, NH_4^+, Cl^-

Automatic switching circuitry for sequential signal processing.

Polypropylene electrode wells (2) with holdup volumes of ~6 ml each.

NH_4^+ sensor uses buffered sample to prevent H^+ interference.

Ranges

pH	2 to 11
Cl^-	10 to 1000 ppm
NH_4^+	1 to 100 ppm

Alarms (adjustable)

pH		@ 3.2 and below
	and	@ 9.8 and above
Cl^-		@ 385 ppm and above
NH_4^+		@ 8.2 ppm and above

Reagent Usage

Standardizing Solution	~ 64 ml/standardizing cycle
Buffer Solution	48 ml/hr
Time Between Readings	Each sensor reads for a 1 min. interval every 3 min.

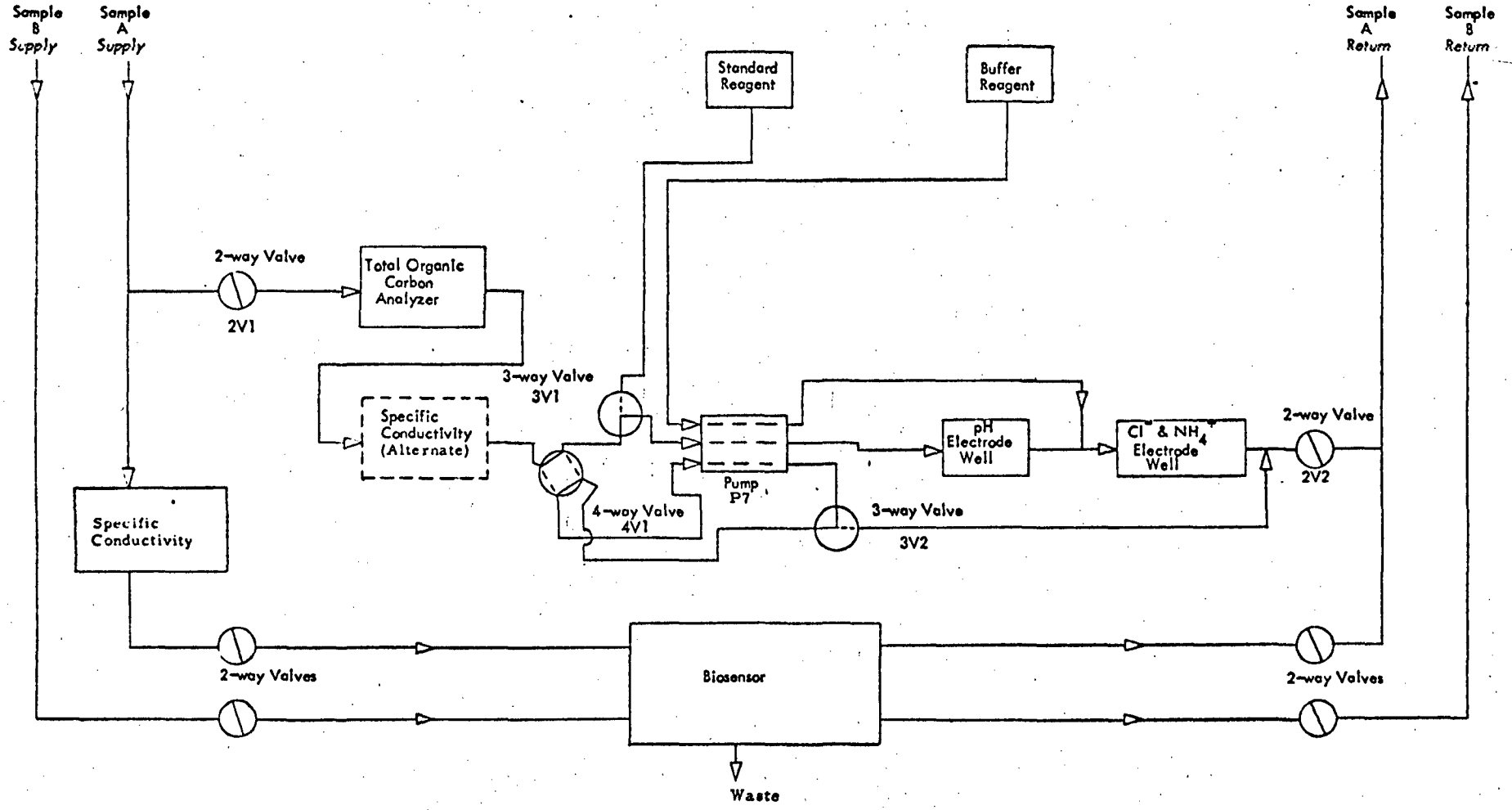

Figure 24. Water Monitor Flow Schematic

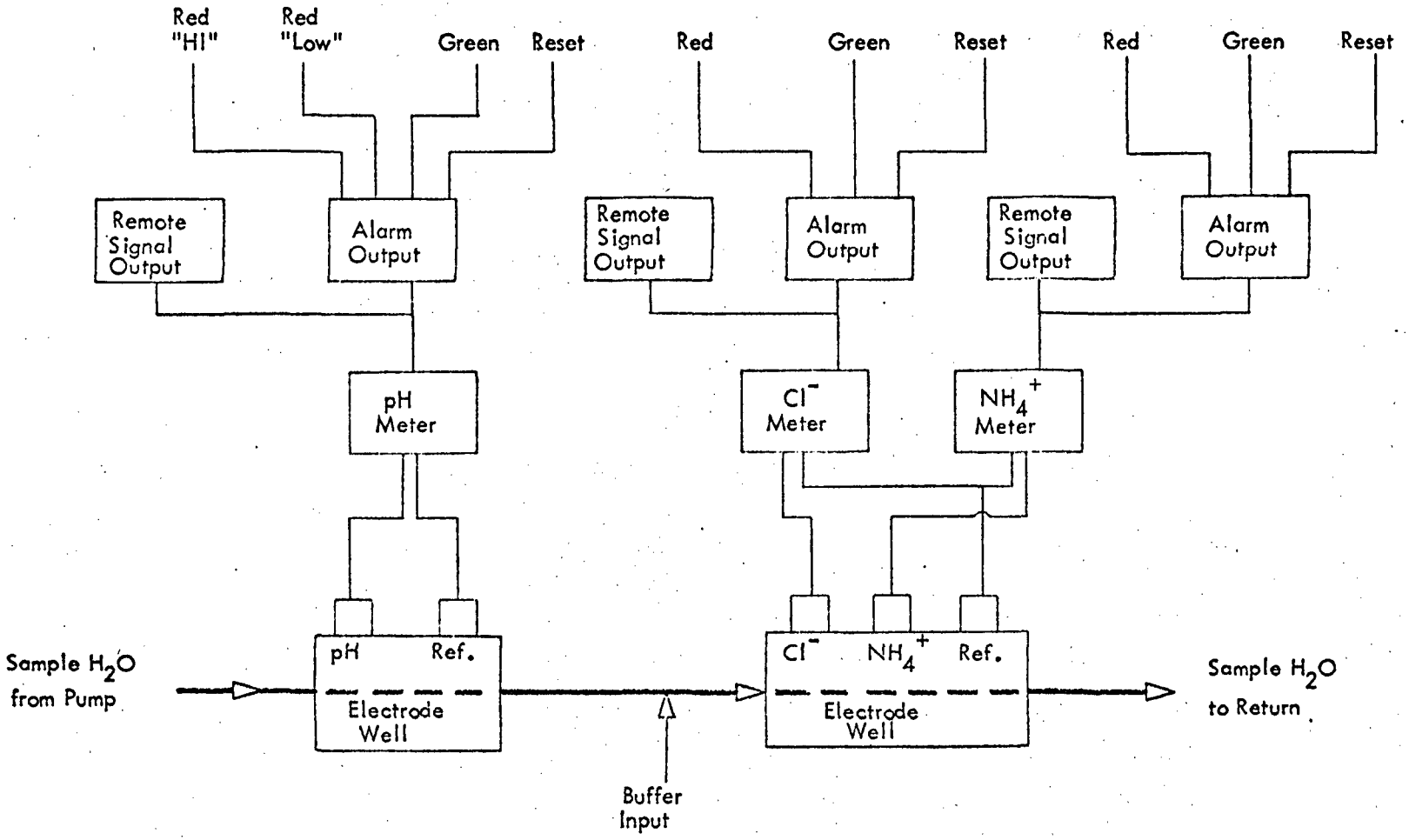

Figure 25. Ion Electrode Block Diagram

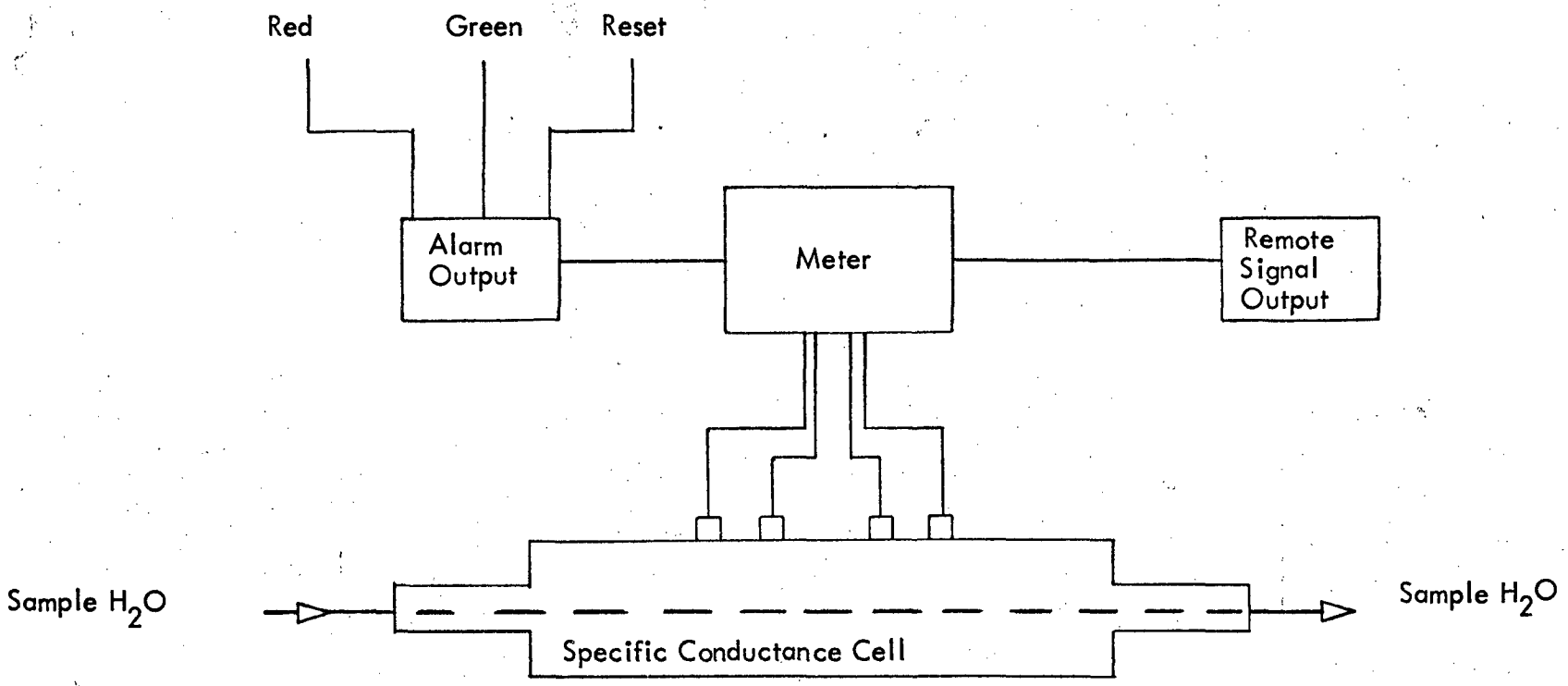

Figure 26. Specific Conductance Block Diagram

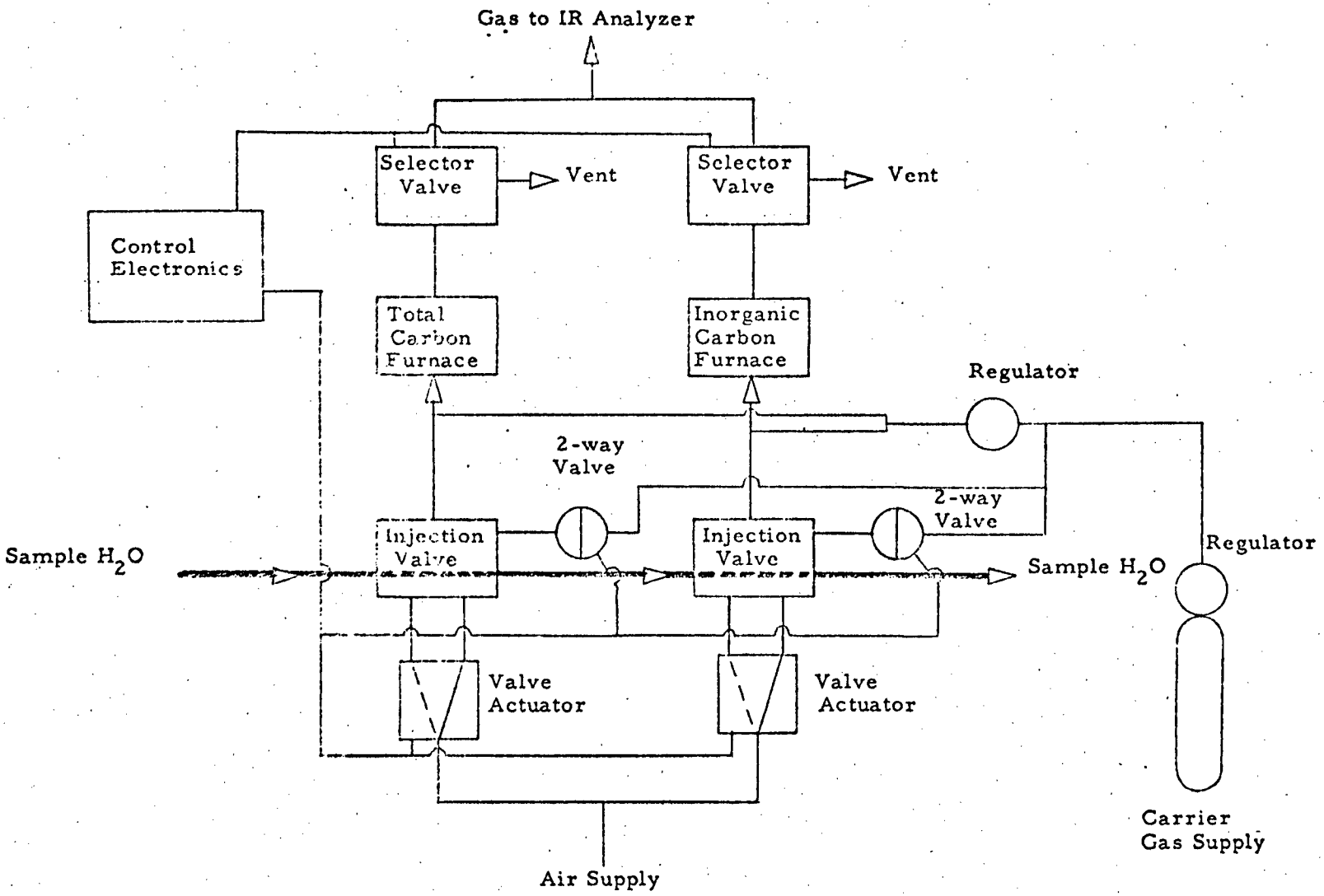

Figure 27. Total Organic Carbon Analyzer Block Diagram

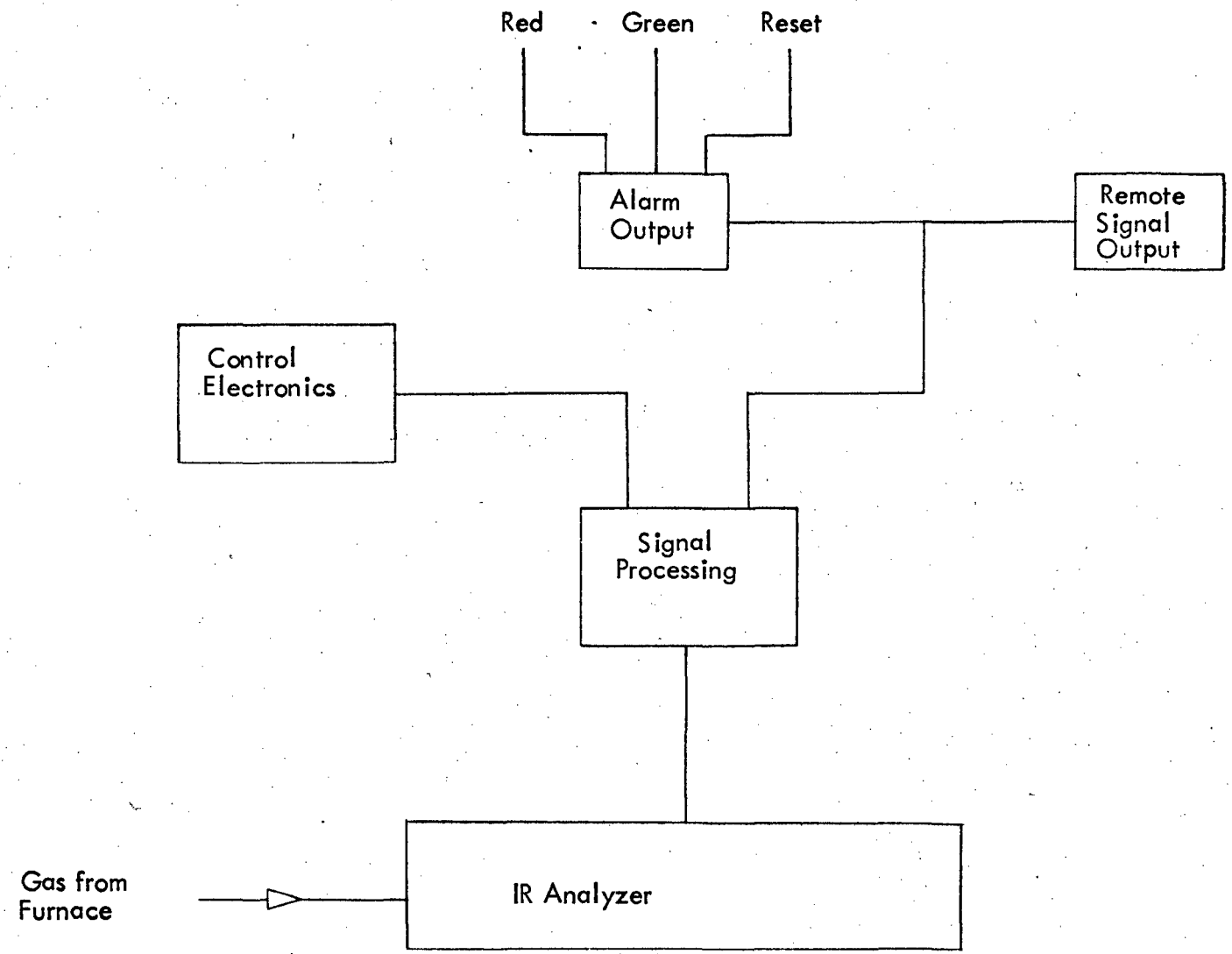

Figure 28. Total Organic Carbon Analyzer Block Diagram

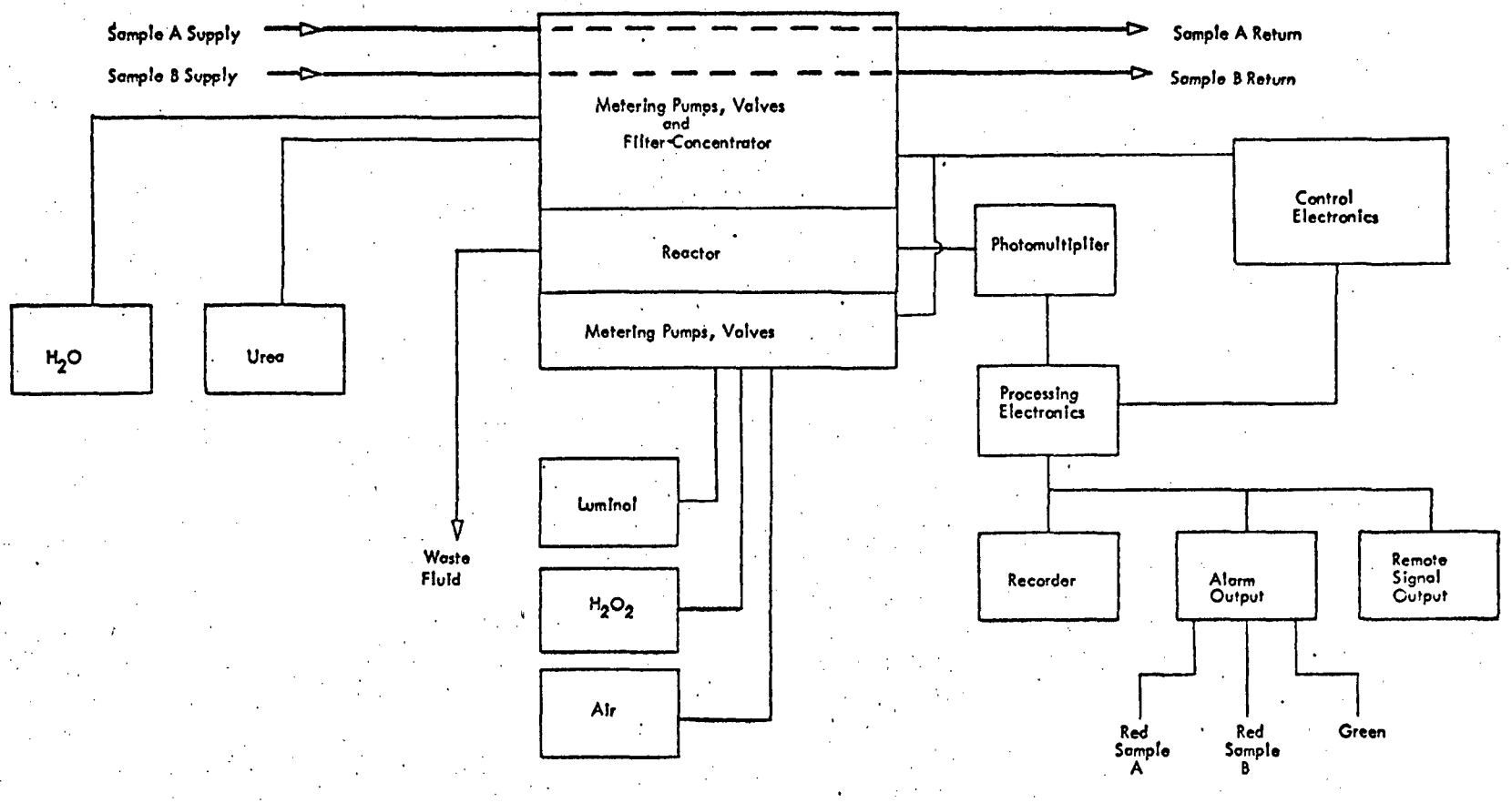

Figure 29. Biosensor Block Diagram

SYSTEM RECOMMENDATIONS FOR FLIGHT WATER QUALITY MONITOR

This section covers an in-depth review of techniques for sensing those parameters incorporated in the present water monitor and also additional parameters which are important in assessing the operation of a water regeneration system and the quality of the recovered water. Recommendations are made regarding the techniques which would probably have the most successful "flight" development and have the desired sensitivity.

Finally, rationale is presented for selecting and recommending those sensors to be included in a next generation water monitoring system along with estimates of the development time required to reach flight-rated status.

Review of Sensing Techniques

pH Sensor. -

Discussion -

The present system (Orion pH glass electrode plus Beckman Lazaran Reference Electrode) is adequate for the present application. The range of pH values reported elsewhere for regenerated water samples in two separate studies were pH 6.3 to 8.7* (average 7.2) and 4.3 to 7.0** (average 5.3). The ion electrode technique is an acceptable method of measurement, however, the holdup volume in the present pH sensor system is ~6 ml which is somewhat large for rapid system response to pH changes. In order to achieve a rapid response it is necessary to reduce the volume of liquid in contact with the electrode to about 1 ml. Large electrodes are not compatible with minimum sample size requirements.

Recommendations -

The recommended areas for further improvement of the present system include (1) reducing the holdup volume to improve response time, (2) temperature regulation, (3) reduction in system drift in order to decrease standardization interval, and (4) automatic chemical standardization at regular intervals and automatic compensation for any amplifier zero and/or electrode drift.

With respect to the first feature (i.e., miniaturization), it is doubtful whether the current system can be reduced below a 3 ml sample volume. Reduction to 0.5 ml is possible with the Beckman Microblood pH assembly*** (Figure 30) which includes a glass electrode and calomel reference separated by a salt bridge. Modifications required to adapt this

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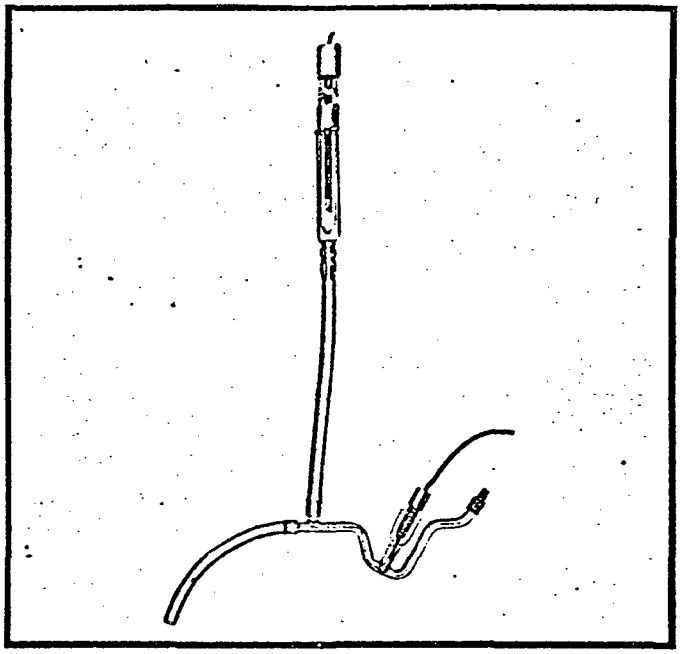
*MACDAC-60 day test of a Regenerative Life Support System, Dec., 1968 NASA CR 98500.

**Symposium, Langley Research Center, Nov. 17-18, 1970, NASA SP-261.

***Beckman #46850.

Figure 30*



46850 Micro Blood pH Assembly

* Extracted from Beckman Scientific and Process Instruments Division, Bulletin 780A

unit to the present application are: (1) replacement of the calomel reference by a silver-silver chloride reference; pressure compensation (with bladder arrangement for zero-g) will also be required for the reference electrode, (2) electrodes must be clamped down to permit operation at 2-5 psig, and (3) temperature compensation by water jacket controlled to $\pm 2^{\circ}C$ when sample is $\pm$ $10^{\circ}C$ of water bath temperature.

With respect to the problem of system and/or electrode drift, the major drift in the present system is mainly due to the Lazaran reference. Less electrode drift should be observed with the silver-silver chloride reference electrode. System drift reported for several commercial on-stream pH analyzers designed to operate with non-pressurized systems (i.e., Ecologic Instrument Corp., Model 400-12 or Enviro Control Inc., Model 1001) is less than 0.01 pH in 24 hours. These commercial units, however, require large sample throughputs (i.e., generally several hundred ml/hr).

Because of its cell geometry (i.e., sensor and reference separated by narrow bore tubing), one of the problems that may be encountered with the Microblood pH Assembly is erratic readings for water samples with specific conductivities of less than 100 μmho/cm. A specially designed electrode well placing the sensing electrode close to the bridge junction could solve this problem just as was done on the present contract.

Chloride Sensor. -

Discussion -

The reported chloride content of regenerated water samples has ranged from 0 to 30 ppm. The NAS/NRC recommended maximum is 450 ppm Cl^-.

The present system which utilizes an Orion Model 94-17 solid state electrode with a Lazaran reference is satisfactory for accurate sensing at the alarm level. Materials such as OH^- or NH_3 which may interfere at the lower levels, have no significant effect at 450 ppm Cl^- in the pH range of 3 to 11 or at NH_3 levels of 10 ppm (the recommended maximum).

For accurate measurements below the alarm level the following considerations are a factor.

The solid state chloride electrode can be used for measurements at 1-450 ppm in the pH range of 3 to 11 (i.e., system does not have to be buffered, as it is being done at present). At a pH of 11, however, water which contains dissolved ammonia at 10 ppm, means that virtually all (98%) of it is present as free NH_3. The latter does interfere and produces malfunctioning of the electrode if the Cl^-/NH_3 ratio drops below 8/1. Thus in an unbuffered system containing 10 ppm NH_3, accurate measurements can theoretically only be made down to 80 ppm Cl^-. In a system containing 10 ppm ammonia buffered to a pH of 7, the free NH_3 content is only ~ 0.06 ppm permitting accurate measurements down to $8 \times .06 = 0.48$ ppm Cl^-.

Recommendations -

At the present time the technique currently used (i.e., ion electrode) is considered satisfactory, however it suffers from the same low response time as the pH sensor. Miniaturization is the best approach to reducing the time lag to chloride ion changes.

The recommended approach to miniaturization is to use a configuration similar to the Beckman Microblood pH assembly (see Figure 30 for general configuration) which uses a 0.5 ml sample. The electrode is a silver billet type electrode (virtually solid state) not requiring refilling of electrolyte. The reference however, is a calomel reference electrode which should be replaced by a silver-silver chloride reference. This should provide interference free operation at pH 3-11 and NH_3 levels of 10 ppm at 1-450 ppm Cl^- with the waters normally encountered in regenerated systems. Modifications that would be required are: (1) pressure regulation (with bladder) for pressurized systems operable at zero-g; (2) temperature regulation, and (3) relocate the sensing electrode close to the bridge junction to prevent erratic readings in water samples with specific conductivities of less than 100 μmho/cm.

Ammonia Sensor. -

Discussion -

In the bacterial decomposition (both aerobic and anaerobic) of nitrogenous organic matter, ammonia is produced. Monitoring of this parameter could therefore be used either as an indication of bacterial build-up or breakthrough of organic pollution in the regeneration system.

Under the current program, monovalent cation electrodes from two sources (Beckman and Corning)* were utilized for determination of ammonium ion (NH_4^+) concentration since these electrodes can be used without modification for measurement of flowing streams under pressure. Several problems encountered with these electrodes, however, included:

(1) Poor reproductibility at ammonium ion concentrations below 10 ppm,

(2) a variable response (i.e., time to reach equilibrium) depending on prior history,

(3) considerable variability in sensitivity and selectivity from electrode to electrode from a single manufacturer.

With water at pH 7, interference can come from $Ag^+ > K^+ > Na^+$, in that order. The concentration ranges reported for each of these in NASA regenerated waters are shown below:

	ppm
Ag^+	0.0007 to 0.03
K^+	0.1 to 0.6
Na^+	0.05 to 0.9

The selectivity of these ions relative to NH_4^+ varies somewhat depending on manufacturer, thus:

*Beckman No. 39137 or Corning No. 476220 monovalent cation electrodes used in combination with Beckman Lazaran reference electrode.

	Beckman No. 39137	Corning No. 476220
Ag^+/NH_4^+	10/1 (+3%)	Not available
K^+/NH_4^+	1/1 (+6%)	3/1 (+18%)
Na^+/NH_4^+	1/10 (+1%)	1/3 (+3%)

At 10 ppm NH_4^+, the respective errors introduced into the readings at the maximum concentration are seen to be smaller (figures in parenthesis) for the Beckman than for the Corning electrode. The errors would be proportionately higher at lower concentrations of NH_4^+ ion. For use as a sensing device to alarm at levels in excess of 10 ppm ammonia, these monovalent cation electrodes would be adequate, assuming fairly frequent standardization ($\sim$4 hour intervals).

Improved response time is also desirable and this could be achieved with a smaller holdup volume assembly. The Beckman Microblood Cationic Assembly #77447 with a holdup volume of $\sim$0.5 ml would be suitable. This assembly also contains a calomel (mercurous chloride) reference electrode (separated by a salt bridge from the sample stream) which should be replaced by a relatively non-toxic silver-silver chloride reference (i.e., Beckman #40249). Modifications that would be required to adapt this unit for the present application include:

(1) pressure regulation of the reference electrode for use at 2-5 psig (bladder arrangement would be required for zero-g application),

(2) electrodes must be clamped down to permit operation at 2-5 psig,

(3) temperature control ($\pm 1^{\circ}C$) -- this may be provided by a constant temperature aluminum block (i.e., the Beckman #28505 or, more preferably, one can be fabricated to accommodate the three miniature sensors (microblood pH, chloride and ammonia). For maximum flexibility in operation, it would be desirable to keep the pH, ammonia, and chloride sensors separate (i.e., each with their own reference electrode).

It is quite probable that this modified Microblood assembly would still require frequent standardization (i.e., 4 hour intervals). Standardization at short time intervals is undesirable, and experience on the present Contract (NAS 1-10382) has shown that at the low levels of NH_4^+ being monitored, no two electrodes will possess the same selectivity. This problem has plagued Corning for more than a year as AMB has found out in performance of the present contract.

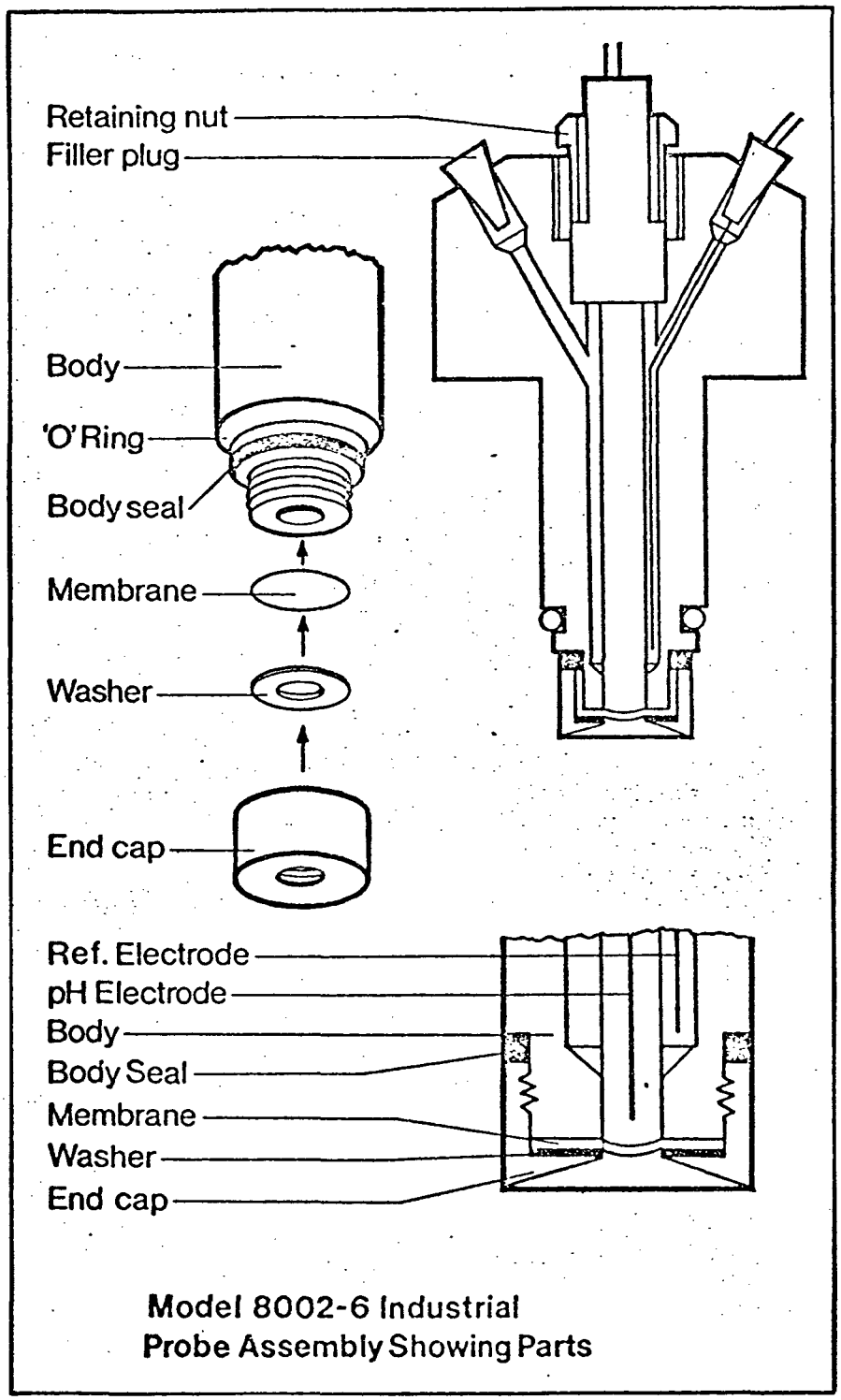
An alternative method that might be considered for ammonia monitoring is a specific ion electrode which responds to ammonia rather than ammonium ion. Ammonia electrodes are currently available from two sources, Orion Research Corp. and Electronic Instruments Ltd. Both operate on the same principle; namely, when ammonia gas is dissolved in water the following equilibrium is set up:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Since the probe responds to NH_3 rather than NH_4^+, the sample solution is made alkaline (pH $>$ 11) to shift the equilibrium to the left and assure that the ammonia is present almost entirely ($>$98%) as free ammonia. The probe, shown schematically in Figure 31, consists of an internal pH electrode (and internal reference electrode) immersed in an ammonium chloride solution and separated from the sample by a gas permeable hydrophobic membrane. When the probe is in contact with a solution which contains ammonia, the internal solution between the pH electrode membrane and the gas permeable membrane gains or loses ammonia gas through the latter until an equilibrium concentration is established on both sides. The pH of this internal filling solution is proportional to this free ammonia concentration in the sample.

Ammonia levels of regenerated samples from NASA tests have run to a maximum of 12.5 ppm (average 4.8) and 0-19 (average 2.0) in two recent test series of regenerated water. The recommended maxima by NAS/NRC are 1 ppm NH_3 pH $>$ 7 and 10 ppm NH_3 pH $<$ 7.

Figure 31*



Ammonia Electrode

*Electronic Industries Ltd.

The specific ion electrodes available from Orion or Electronic Industries Ltd. are reported to provide accurate measurements below 10 ppm without interference from Na^+, K^+ or Ag^+. Apart from requiring constant buffering (pH > 11) of the sample stream, other shortcomings include the need for pressure compensation (i.e., since the electrode has an internal reference electrode, it requires pressure regulation for operation in the 2-5 psig range), periodic replacement of the external membrane and addition of (2) liquid fillings of the electrode. These electrodes may also be subject to frequent standardization. Clearly some other alternative seems desirable.

Recommendations -

For accurate readings in the 0.01 to 20 ppm range, the accepted method and the method recommended is a wet chemical colorimetric procedure which has been widely automated (see Figure 32). One possible drawback to the method is the use of sodium nitroprusside ($Na_2Fe(CN)_5NO$) which is poisonous. The function of this component is to increase sensitivity and speed of color formation. However, the method is feasible without it and the sensitivity would still be of the order of 0.1 ppm although it would require the use of higher processing temperatures (90°C vs. 60°C) and a longer delay time (20-30 min. vs < 5 min). Several fully automated on-stream monitoring systems utilizing this reaction are commercially available (i.e., Ecologic Inst. Corp. Model 503; Technicon Monitor IV; Enviro Control Inc., Enviro Monitor Series 1000; Ratheon, Inc.).

The unit from Ecologic Instruments is typical of those commercially available.

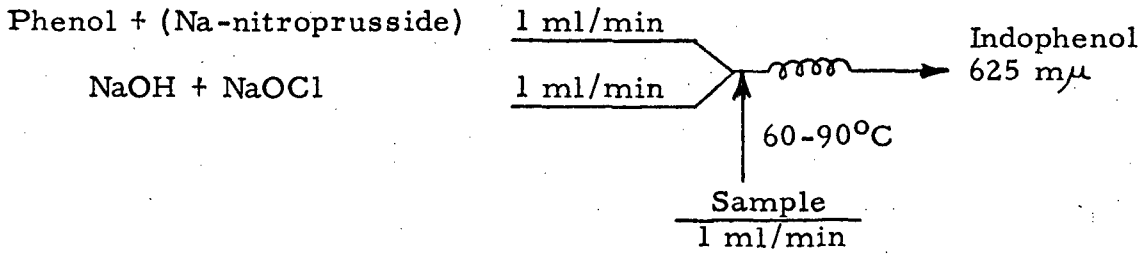
- Flow rates required for continuous on-stream monitoring are 200 ml/hr.
- 15 minute response time.
- Dual beam colorimeter used to measure (at 650 mμ) the intensity of the blue complex formed.

Figure 32

Colorimetric Measurement of Ammonia

Desired Range	Sensitivity	Processing Time	Reagent Stability	Sample Volume
0-20 ppm	< 0.1 ppm	5-15 min	2 months at 4°C	0.5 - 1.0 ml/min

Detection Technique



- o 1 gallon each of two reagents for a one week supply
- o Weight is 55 pounds
- o Size is 20" H x 16" W x 8" D

This unit is too large, weighs too much, and uses too much reagent and sample water for space application. It should be possible to design a miniaturized system based on this principle with an overall holdup volume of 5 ml or less.

Specific Conductivity Sensor. -

Discussion -

The present measuring technique uses a standard Beckman flowthrough conductivity cell and direct reading meter. It is more than adequate for measurements in the range of interest. (The specific conductivity for a series of regenerated water samples ranged from 3 to 420 μmho cm^{-1} with a mean value of about 30 μmho cm^{-1}).

The holdup volume of the present flowthrough conductivity cell is much larger (25 ml) than is necessary. In fact, experience with the present cell has demonstrated that the large holdup is detrimental to obtaining accurate real time readings because of the time necessary to equilibrate to new concentration levels. When the present sensor is connected in series with other sensors (in particular specific ion electrodes) their response time is also affected.

An alternate approach which responds to dissolved ionic and nonionic (i.e., organic) species is to measure freezing point depression. Advanced Instruments Model 3R (sample volume < 1 ml, processing time < 2 minutes) Osmometer has a sensitivity of 5 ppm NaCl (10 ppm ethyl alcohol). It can be automated and is adaptable to zero-g.

Recommendations -

The approach which is recommended is to miniaturize the present technique in two areas:

- o Replace the present flow-through cell with one whose holdup volume does not exceed 1 ml.
- o Reduce the size of the readout unit.

Chromatronix has a microflow conductivity cell (MCC-75) with a holdup volume of < 0.1 cc and which is temperature compensated. Leeds and Northrup had indicated that they could also develop a microcell of this volume capacity. There should be no problem minimizing the sample size.

There is no reason why the readout unit must be as large as that currently used (i.e., Beckman RI5 SoluBridge). The present unit has much wasted space. With current technology it should be possible to reduce the size of the readout unit by about 75%.

Nitrite/Nitrate Sensor. -

Discussion -

Nitrites and nitrates are generally formed by the action of bacteria upon ammonia and organic nitrogen. Their presence are often indicative of pollution.

The NO_2/NO_3 content of regenerated water has run from 0 to 8.7 ppm (as Nitrogen) with a maximum total Nitrogen recommended by NAS/NRC at 10 ppm.

There are two methods which might be used to monitor these parameters: (1) specific ion electrodes and, (2) a colorimetric procedure. The least complex method is the use of ion electrodes. Two suppliers of nitrate specific ion electrodes are Beckman (Model 39618) and Orion (Model 92-07). The recommended reference electrode for Beckman's electrode is a single-junction reference. The Beckman nitrate electrode has a replacable sensor tip which is guaranteed for 100 hours in static solutions (probably less for flowing streams). Similar in construction to the Beckman ammonia electrode (with organic sensor) which was evaluated on the present contract and which failed in operation with pressurized liquids, it is probable that the nitrate sensor would behave similarly. Pressure compensation and electrolyte refill would also be required for the reference electrode. The Orion electrode uses a liquid ion exchange membrane and

would also be subject to electrolyte refill and pressure compensation. Both electrodes are not considered reliable below about 10 ppm.

The colorimetric method shown in Figure 33 is more complex and has the desired sensitivity. Several variations of this procedure have been automated by others. The method is adaptable to zero-g, the materials are not hazardous and the reagents are stable, at least for the periods indicated.

Recommendations -

The method which is recommended for measurement of nitrites and nitrates is the colorimetric method. The sensitivity of about 0.1 ppm is more than adequate for the intended usage whereas the ion specific electrodes do not possess sufficient sensitivity. Also, with minor modification, the colorimetric readout could be shared with another measurement, for example, the ammonia sensor. The only additional hardware required would be that associated with the reagent system.

Hexavalent Chromium Sensor. -

Discussion -

Monitoring of Cr^{+6} is desirable because of its toxicity and the possibility of its carryover from the pretreatment chemicals used in the reclamation procedure. Cr^{+6} is introduced into the water on pretreating the urine with dichromate-sulfuric acid solution. The Cr^{+6} content of recovered water has ranged from 0.001 to 1.0 ppm (average $< .001$ and 0.1 ppm in separate series) with a NAS/NRC recommended maximum of 0.05.

Recommendations -

The method recommended is the colorimetric procedure shown in Figure 34 and is based on reaction of the sample with diphenylcarbazide to form a reddish-purple color in acid solution. The only interference is from iron in concentrations greater than 1 ppm. Fe^{+} in regenerated water, except in rare instances, runs well below 0.1 ppm.

Figure 33

Colorimetric Measurement of Nitrate/Nitrite

Desired Range	Sensitivity	Processing Time	Reagent Stability	Sample Volume
0-10 ppm	< 0.1 ppm	10 min	4-5 weeks at ambient	1-3 ml/min

Detection Technique

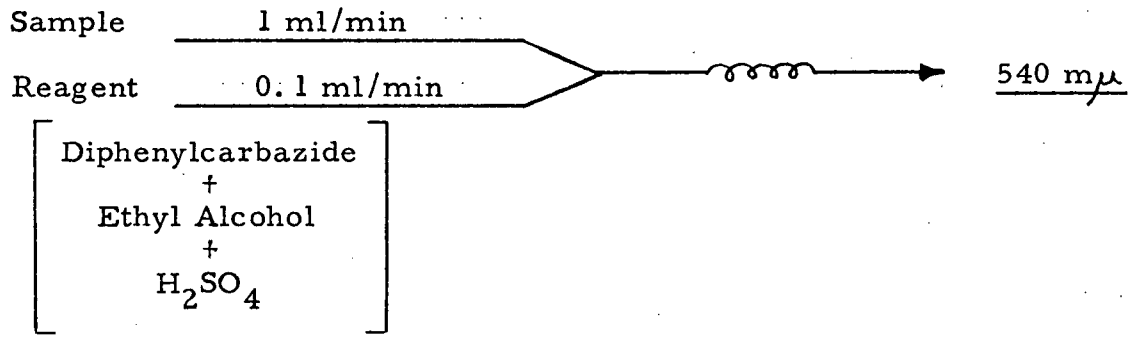
$$\text{Nitrate} \xrightarrow[67^{\circ}C]{N_2H_4 \text{ Hydrate}} \text{Nitrite} \xrightarrow{\text{Sulfanilic acid}} \text{Diazo} \xrightarrow{\alpha\text{-naphthyl amme}} \underline{\text{color (520 m}\mu\text{)}}$$

Figure 34

Colorimetric Measurement of Hexavalent Chromium

Desired Range	Sensitivity	Processing Time	Reagent Stability	Sample Volume
0-1 ppm	.005 ppm	6-7 min	1 month at refrigeration	1 ml/min

Detection Technique



This sensor could also be combined with measurements of ammonia and NO_2/NO_3 so as to share the same readout device thus minimizing size, weight and power.

Turbidity Sensor. -

Discussion -

Turbidity is caused by the presence of suspended matter. The standard procedure is the candle method -- the measurement is based on the light path through a suspension which just causes the image of the flame of a standard candle to disappear (that is to become indistinguishable against the general background illumination). The longer the light path, the lower the turbidity. Turbidity is reported in Jackson units. Regenerated waters have ranged from 0-5 Jackson units. The NAS/NRC recommended maximum is 10 units. Turbidity measurements at levels less than about 5 JTU employ scattered light (nephelometers) rather than transmitted light. Forward scattering measurements are more sensitive than 90^{o} scattering and correlate better with suspensions standardized on a candle turbidimeter. Calibration against the candle turbidimeter is necessary.

Continuous turbidity systems have been automated. One such system is manufactured by Ecologic Inst. Corp., Model 204-1 -- temperature compensated with a response time of two minutes.

Recommendations -

The method which is recommended for measurement of turbidity is the scattered light (nephelometer) technique. The commercially available unit above (Ecologic Instrument) would require miniaturization to be suitable for space application. The electronics has to be repackaged or redesigned and the sensing unit should be redesigned to reduce the holdup volume to about 1 ml or less. The operating range from 0-15 JTU is satisfactory however the accuracy of $\pm 2\%$ (± 0.3 JTU) should be improved to $< 1\%$ or about ± 0.1 JTU.

Color Sensor. -

Discussion -

Color may result from presence of metallic ions or carryover of certain organic materials. The unit of color is that produced by 1 mg/liter of platinum (in the form of the chloroplatinate ion) containing cobaltous ion at a specific concentration. Regenerated waters have ranged from 0 to 8 (Platinum-cobalt units) with a NAS/NRC recommended maximum of 15.

Interferences to color measurements are caused by turbidity and pH; increases is either result in apparent color values which are higher than the true color.

Recommendations -

The procedure recommended is color comparison in a dual beam photometer. If go-no-go indications are desired, a single comparison is sufficient. Measurements of actual color values would require the use of a color wheel containing a series of pre-calibrated glass color disks. Response times should be on the order of less than 2 minutes.

In view of the complexity associated with removal of the interferents (turbidity is generally removed by centrifugation of the sample and pH is corrected by determining the color response of a given water sample over a range of pH values) it is probable that this sensor should be a go-no-go sensor which measures apparent color.

Carbon Sensor. -

Discussion -

Three conventional approaches which have been used for monitoring the degree of organic pollution in water include:

- Determining the amount of oxygen (or other oxidant) required to convert the organic impurities to a stable oxidation state.
- Monitoring the CO or CO_2 produced on oxidation of the organic carbon present.

- Monitoring the methane formed on pyrolysis of the sample in an oxidizing atmosphere and subsequent reduction over a hydrogen enriched nickel catalyst. A flame ionization detector is used for monitoring the methane.

Alternate methods which may be used to detect the presence of dissolved organics include measurement of surface tension and freezing point depression. Both of these methods are adaptable to zero-g operation, have a rapid response (< 2 minutes) and require minimal sample volumes for analysis. Both methods, however, are non-specific in the sense that they respond to both organic and inorganic contaminants without being able to distinguish between the two.

Oxygen Determination

This approach is normally determined by conventional biochemical (BOD) and chemical (COD) oxygen demand tests. The BOD is defined as the amount of oxygen required by bacteria while stabilizing decomposable organic matter under aerobic conditions. Originally the test involved measuring the oxygen content of a sample of diluted waste water, before and after incubation at 20°C for 20 days. The test was gradually reduced to 5 days with test results for the 5 day period ranging from 70-90% of the 20 day BOD test.

Apart from the fact that the BOD test is too slow for real time control, there are a number of substances which interfere. Included among these are: (1) oxidizable nitrogen derived from nitrite, ammonia and organic nitrogen which serve as food for nitrifying bacteria, and (2) oxidizable components such as ferrous iron, sulfites and sulfides. All of these materials tend to produce high BOD values. Low results might be caused by toxic materials (i.e., copper ions which inhibit action of bacteria) or refractory organic materials (e.g., common "hard" detergents) which are only slowly degraded by bacterial action.

The COD test was designed to provide a more rapid method of determining carbon in waste water by application of chemical oxidizing agents such as a boiling mixture of chromic and sulfuric acids. Excess dichromate is titrated with standardized ferrous ammonium sulfate, the

amount of oxidizable organic matter, measured as oxygen equivalents, being proportional to the potassium dichromate consumed. Although requiring only two hours instead of five days, the COD does not produce the same answer as the BOD. One of the problems of the COD test is that organic pollutants such as acetic acid, straight chain aliphatic compounds and aromatic hydrocarbons (i.e., pyridine, benzene) as well as ammonia are not oxidized appreciably. Chlorides tend to produce high results unless the chloride ion is complexed with mercuric sulfate. An automated COD analyzer is commercially available from Technicon Instruments Corporation (see Figure 35).

Some of the objections of the COD and BOD were overcome by the Total Oxygen Demand (TOD) method developed by Dow and commercially instrumented by Ionics, Inc. The TOD method produces a value which is a measure of the amount of oxygen required during the high temperature combustion of a water sample. In a typical analysis a 20 μl water sample is introduced into a carrier gas (N_2 containing 200 ppm O_2) and passed over a platinum catalyst at 900°C. Two reactions occur. The oxidizable components in the liquid sample are converted to their stable oxides by partially depleting the oxygen on the platinum surface. Following this, the oxygen equilibrium on the catalyst surface is restored by the oxygen in the carrier gas stream. The momentary depletion of the oxygen concentration in the carrier gas is detected by a silver-lead fuel cell and is recorded as a negative oxygen peak on a potentiometer recorder. The TOD for the sample is determined by comparison of the recorded peak height with a standard calibration curve.

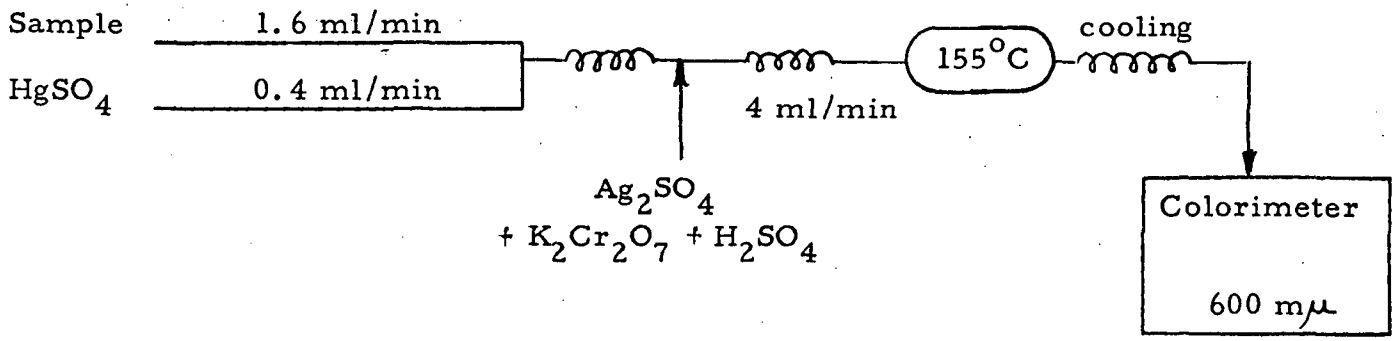
The primary advantage of the TOD analyzer is that organics (including aromatics) as well as ammonia, are completely oxidized. As in the case of BOD and COD measurements, carbonates and dissolved CO_2 do not interfere. However, dissolved oxygen in the water sample reduces the oxygen demand determined by the TOD analyzer; with water which had been saturated with oxygen, this would correspond to 28 ppm carbon. Although the instrument has a relatively narrow dynamic range of 200 ppm carbon

Figure 35

Colorimetric Measurement of COD

Desired Range	Sensitivity	Processing Time	Reagent Stability	Sample Volume
0-200 ppm	1 ppm	~15 min	months	1-2 ml/min

Detection Technique — Technicon Autoanalyzer



full scale, this is adequate for the present application. As with any high temperature platinum catalyzed system, catalyst poisoning by heavy metals can be a problem.

CO or CO_2 Determination

One of the other approaches for determining the presence of organic carbon in a sample is by monitoring the CO or CO_2 formed by high temperature oxidation. In this category are the TC, CO_2D and TOC analyzers.

In the TC (Total Carbon) device developed by Dow Chemical and marketed by Beckman Instruments, a 20 μl water sample is injected into a high temperature (950°C) combustion tube where the organic matter is oxidized to carbon dioxide (oxygen carrier gas). The CO_2 is quantitated by passage through a non-dispersive infrared analyzer. The sensitivity of the instrument is 2 ppm carbon. Virtually complete oxidation of carbon in any form (including acetic acid) is claimed to take place on passage through the combustion furnace. The data in Table 27 shows that conversion to carbon dioxide is virtually complete for a number of representative carbon-containing materials. In carbonaceous compounds containing halogen, sulfur, nitrogen and phosphorus, only carbon is determined (see Table 28). For water samples containing inorganic carbonates and dissolved CO_2 it would be necessary either, (1) to remove these by acidifying the sample (to convert carbonates to carbonic acid) and purging it with nitrogen for about five minutes to drive off the dissolved CO_2 or, (2) to determine the inorganic carbonates (and dissolved CO_2) by passage through a second combustion tube ($\sim$150°C) containing quartz chips wetted with 85% H_3PO_4, where combustion to CO_2 takes place. The latter is quantitated by passage through an infrared analyzer. Subtracting the value for inorganic carbon from total carbon yields the organic carbon. A manual laboratory TOC (Total Organic Carbon) analyzer is marketed by Beckman Instruments based on this procedure. The second method is preferred since sparging after acidification (as in (1) above) could result in loss of volatile organics.

Table 27*

ANALYSES OF STANDARD SOLUTIONS

Compound	Carbon, ppm				Std. dev. (±)[a]	Av. % recovery
	Calcd.	Found				
		Max.	Min.	Av.		
Benzoic acid	68.8	69.0	67.4	68.2	0.66	99.1
Phenol	76.6	77.2	76.5	76.9	0.30	100.4
Sucrose	104.8	105.1	104.3	104.5	0.40	99.7
Glycine	100.7	101.2	99.5	100.3	0.69	99.6
Pyridine	105.6	104.4	103.6	104.2	0.40	98.7
Urea	100.0	100.9	99.1	99.8	0.86	99.8
Sodium cyanide	122.5	122.1	119.5	120.5	1.11	98.4
Acetanilide	75.4	76.0	75.0	75.4	0.48	100.0
p-Nitroaniline	106.2	105.8	104.9	105.4	0.52	99.2
4-Aminoantipyrine	111.5	110.6	108.9	110.2	0.85	98.8
Sulfanilic acid	89.3	90.5	88.6	89.3	0.90	100.0
Diphenylaminesulfonate, Ba salt	87.8	87.6	86.8	87.4	0.40	99.5
dl-Methionine	103.0	102.7	101.8	102.5	0.45	99.5
2, 4, 6-Trichlorophenol	75.4	76.0	74.0	75.0	0.84	99.5
Sodium carbonate	99.5	100.0	99.2	99.4	0.40	99.9
Acetic acid in 20% NaCl	100.0	101.0	99.0	100.0	0.82	100.0
Acetic acid in 20% $CaCl_2$	100.0	100.0	98.1	99.1	0.78	99.1

[a] All results based on 4 determinations. Calibration made with standard solutions of acetic acid in water.

*C.E. Van Hall et al., Anal. Chem. 35, 315-319 (1963).

Table 28*

EFFECT OF FOREIGN IONS ON DETERMINATION OF CARBON IN ACETIC ACID**

Anion (1% Solution)	Carbon, mg. per liter	
	Calcd.	Found[a]
NO_3^-	100.0	100.9
Cl^-	100.0	100.1
SO_4^{-2}	100.0	100.0
PO_4^{-3}	100.0	99.0

[a] Average of four determinations.

*C. E. Van Hall et al., Anal. Chem. 35, 315-319 (1963).

**Test solution contained a known quantity of acetic acid plus a 1% concentration of either sodium nitrate, sodium chloride, sodium sulfate or sodium phosphate.

The CO_2D analyzer is an adaptation of the total carbon analyzer with CO_2 being used as the carrier gas instead of oxygen or air. In this laboratory device, referred to as a Precision Aquarator and manufactured by Precision Scientific, a 20 μl water sample is injected into a stream of dry CO_2 and swept over a platinum catalyst (at 900°C) which oxidizes the organics to CO and H_2O. After stripping out the water in a drying tube,* the CO content of the gas stream is determined by passage through an infrared analyzer. The CO produced can be directly related to the chemical oxygen demand determined by the classical wet chemical method. Since the infrared analyzer responds only to CO, carbonate or dissolved CO_2 do not interfere. As with the TOD system, dissolved O_2 (in addition to sulfates, phosphates and nitrates) tend to produce low values for the oxygen demand (see Table 29).

Monitoring of Methane Formation

In the last considered approach for monitoring organic carbon, a detector (i.e., flame ionization) which responds only to C-H bonds (formed on sample pyrolysis or reduction of CO or CO_2) is utilized. Two devices fall in this category; one is in the developmental stage (Rocketdyne Corp.) and one is commercially available (through Envirotech Corporation).

1) Rocketdyne System

The system developed by Rocketdyne, consists of a pyrolysis chamber, a chromatographic column and a hydrogen flame ionization detector. The sample is injected into the pyrolysis chamber (in a N_2 atmosphere) and cracked to form organic fragments rather than being converted to CO_2. The C-H fragments pass through a short column and then to the flame ionization detector. If the column contains an inert packing such as glass beads, all of the fragments are eluted simultaneously and the resultant readout is of total organics (total processing time less than 2 minutes). If a longer column is used, separation of the various fragments occur and the instrument could then be used for qualitative determinations. The prime advantage of the Rocketdyne Organic Analyzer (ROA) is that it is specific for C-H bonding. The sensitivity of the

*Drying tube has to be replaced daily

Table 29*

THE EFFECT OF DISSOLVED OXYGEN ON TOD

Sample		PPM Dissolved Oxygen	PPM TOD Found	No. Detn.	Rel. Std. Dev.
170	ppm KHP**	0	200	8	±1.07%
170	ppm KHP	8.2	191	8	±1.84%
85.1	ppm KHP	0	100	8	±0.94%
85.1	ppm KHP	8.2	91	8	±1.09%

*A. L. Goldstein et al, "Total Oxygen Demand - A New Automatic Instrumental Method For Measuring Pollution and Loading on Oxidation Processes". Paper presented at Am. Chem. Soc. Meeting, Altantic City, N. J. on Sept. 12, 1968.

**KHP is an organic standard solution.

instrument to hydrocarbons varies, however. Thus the relative response for a series of 2-carbon hydrocarbons containing ethyl alcohol, acetic acid, acetaldehyde and dimethyl ether are 2:1, 1.7:1, 1:1, respectively.

2) Envirotech (Total Organic Carbon Analyzer)

The other device which can be used to monitor total or organic carbon by conversion of carbonaceous pollutants to methane (and quantitation of the latter by flame ionization) is commercially available from the Dohrman Division of Envirotech Corporation (California).

For determining the organic carbon content, an acidified water sample (30 μl) is injected into a sample boat which contains CuO oxidation catalyst. The CO_2 (from both dissolved CO_2 and carbonates) is removed by vaporization at 90°C by passage through a by-pass valve. The residual organic carbon left in the boat reacts with the CuO in a heated zone at 850°C to produce CO_2. The latter is then reduced to CH_4 by passage (in a helium carrier gas) through a nickel reduction catalyst at 300°C. The methane formed passes through a flame ionization detector for quantitation.

To determine total carbon with this device, an unacidified sample is passed through the vaporize and pyrolyze cycles.

Unique features of the Dohrmann device are:

- Volatile organics which might be lost on initial vaporization of the sample to expell CO_2 are caught on a column and then recovered for reduction to CH_4.
- Pyrolysis of carbonaceous materials in an inert atmosphere to CH_4 or other volatile organic fragments (as in the Rocketdyne device) has the disadvantage that nonvolatile coke may be formed thereby lowering the measured carbon value. The Dohrmann device eliminates this problem by pyrolyzing any carbonaceous residue in the presence of an oxidation promoter (i.e., copper oxide). The latter has to be replaced weekly.
- Since the detector is specific for methane, chlorides, sulfates, ferrous ion and ammonia in the sample do not interfere.

Measurement of Surface Tension

Water has a surface tension greater than that of most common liquids and for many organic substances the values are of the order of 20 to 30 dynes per cm at ordinary temperature compared to a value of about 72 for water (see Table 30). In contrast to dissolved organics, electrolytes generally increase the surface tension of water. However, at the levels likely to be encountered in regenerated water, their contribution (i.e., the electrolytes) is apt to be negligible. When two liquids, whose surface tension do not differ very greatly are mixed, the surface tension of the mixture is roughly a linear function of their respective concentrations.

The surface tension of a liquid can be correctly evaluated by measuring the maximum pressure required to release a bubble from the end of a tube immersed in that liquid. The relation between the maximum pressure, P_m (measured by a suitable manometer) and the surface tension (γ) of the liquid is given by

$$P_{max} = xg\rho + \frac{2\gamma}{r}$$

Where x is the depth to which the tube is immersed in the liquid, g, the gravitational field, ρ the density of the liquid and r, the radius of the bubble. For use in a zero-g environment, the unit would have to be incorporated into a small centrifuge to fix the position of the liquid-air interface. Since the surface tension of a liquid is affected by temperature (i.e., generally decreases with increasing temperature) control of the latter would be required.

In spite of these limitations measurement of surface tension provides a simple and rapid measurement of the presence of organics in a drinking water supply. Other advantages include small sample size, as well as minimal reagent, power and volume requirements. One advantage of surface tension over specific conductivity as a measure of water quality is that the former is less affected by dissolved CO_2, which in itself, is not considered a contaminant. Thus whereas purified water saturated with CO_2 exhibited an increase in specific conductivity from 0.2 to 47 μmho cm^{-1}, the

Table 30

SURFACE TENSIONS OF LIQUIDS AT 20°C. IN DYNES CM.$^{-1}$

Water	72.8
Nitrobenzene	41.8
Carbon disulfide	33.5
Benzene	28.9
Toluene	28.4
Acetic acid	27.6
Chloroform	27.1
Carbon tetrachloride	26.8
Acetone	23.7
Methyl alcohol	22.6
Ethyl alcohol	22.3
Ethyl ether	17.0

surface tension (measured by four different methods) remained unchanged.*

Measurement of Freezing Point Depression

Another technique for monitoring the presence of organics, which is adaptable to zero-g operation is one based on measuring the freezing point depression.

In this method, the presence of any solute (i.e., solid or liquid dissolved in water) will reduce the freezing point, compared to that of pure water, in direct proportion to its concentration. One mole of a non-ionic solute added to 1 kg. of water will yield Avogadro's number (6×10^{23}) of molecules in solution and depress the freezing point 1.86°C. The depression is almost twice as great if an ionic solute (e.g., NaCl) is dissolved in water since it yields twice as many particles in solution (e.g., Na^+ and Cl^-). Thus a measure of the freezing point depression could be used to detect the presence of both inorganic and organic components. In effect, this type of monitoring combines the functions of the conductivity and TOC measurements, without however being able to distinguish between the two.

Commercial instruments are currently available which can be adapted to fully automatic on-line monitoring of freezing point depression. These are rapid (< 2 minutes sample processing time) and require only a 0.2 ml liquid volume for analysis. An unautomated version** weighs about 60 lbs., occupies 3.2 cubic ft. of space and requires less power (350 watts vs. 1700 watts) to operate than a TOC device. Further reductions in these requirements are possible.

In the commercial instrument, the sample is cooled down rapidly (~1 minute); then the rate of cooling is reduced before crystallization is reached so that the sample is relatively isothermal throughout. A one-second pulse nucleates the entire sample producing a fast liberation of heat of fusion. This thaws some ice and the sample hangs at isothermal equilibrium between thawing and freezing. The instrument senses this plateau and

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*G. Schwen, Tenside 1970, 7 (1) 21-2.

**Model 3R Osmometer from Advanced Instruments Inc. (Massachusetts).

makes its reading when it is constant. The whole process takes less than two minutes to complete.

Based on published data, the current detection thresholds of these instruments toward such materials as sodium chloride and ethyl alcohol are about 6 and 9 ppm, respectively (the sensitivity toward higher molecular weight materials would be less). This sensitivity is somewhat less than either the TOC ($\sim$1 ppm) or specific conductivity ($<$1 ppm NaCl).

Recommendations -

With exception of the classical BOD or COD tests, the major drawbacks with all of the conventional methods described are the high power, weight and volume requirements (see Table 31), making them less desirable for space application.

The indirect methods for measurement of 1) surface tension, or 2) freezing point depression do not suffer as severely from power, weight, and volume. They are however, non specific, and being unconventional they may pose an additional problem of acceptance, and then only after very extensive testing.

A summary of the various techniques which could be used to monitor carbonaceous materials in regenerated water is shown in Table 32. Also shown are other materials to which the respective techniques respond. In determining the best method for the present application one would have to consider the following:

1) the contaminants likely to be present which might interfere in the determination of organic carbon

2) the interest in detecting other contaminants beside carbonaceous materials.

As can be seen by the data in Table 32, none of the techniques respond exclusively to organic carbon of the type generally associated with polluted water. However, since the interferents (i.e., NH_3, Fe^{++}, sulfides, sulfates, etc.) lead to high values, these techniques are beneficial in that they do indicate the presence of other objectionable contaminants beside organic carbon. Ammonia, chlorides, sulfates, nitrates, nitrites and iron

Table 31

INSTRUMENT REQUIREMENTS

Instrument	Weight lbs. *	Power Watts	Volume cu ft.
Beckman's TOC Analyzer	155	1660	8
Model 915	(195)**	(1700)**	(9)**
Dohrman's TOC Analyzer	--	--	--
Model OC-50	(95)	(1400)	5.4
Precision Scientific's			
Precision AquaRator	90	1500	4.8
TOD Device (Ionics, Inc.)	(125)	(1700)	(5.6)

*Excludes weight of gas cylinders (which may be optional).

**Figures in parenthesis include recorder or digital readout (which may be optional).

Table 32

CARBON ANALYSIS TECHNIQUES

Material detected (in water)	Method					
	BOD[1]	COD	TOD	CO_2D	TCA	TOC[2]
Organic carbon	Yes	Yes	Yes	Yes	Yes	Yes
Organic nitrogen	Yes	No	Yes	Yes	No	No
Aromatics	Yes[3]	No	Yes	Yes	Yes	Yes
ABS plastic	No[3]	Yes	Yes	Yes	Yes	Yes
Cellulose	No	Yes	Yes[6]	Yes	Yes[6]	Yes
Ammonia	*Yes*	*No*	*Yes*	*Yes*	*No*	*No*
Nitrites	Yes	Yes	Yes	No	No	No
Carbonate	No	No	No	No	Yes	No
CO_2	No	No	No	No	Yes	No
Ferrous iron	Yes[4]	Yes	Yes	No	No	No
Sulfides	Yes[4]	Yes	Yes	No	No	No
Sulfites	Yes[4]	Yes	Yes	No	No	No
Halides	No	Yes[5]	No	Yes[7]	No	No
Sulfate	No	No	No	8	No	No
Phosphate	No	No	No	8	No	No
Nitrate	8	No	No	8	No	No
Oxygen	9	No	8	8	No	No

[1] 5-day *BOD test.*

[2] Obtained either by (1) preacidifying sample and sparging to remove dissolved CO_2 or (2) subtracting inorganic carbon from total carbon determination.

[3] Oxidized slowly, but eventually degraded.

[4] Included only if test based on initial dissolved oxygen demand (IDOD).

[5] Can be partially eliminated by complexing with mercuric sulfate.

[6] Provided particles are small enough to be decomposed during short contact time.

[7] Partially oxidized

[8] Reduces oxygen demand

[9] Not applicable.

have been found in significant amounts in regenerated water. If other chemical sensors are being utilized for detecting these inorganic contaminants, then an organic carbon sensor which exhibited minimal interference would be desirable. The greatest specificity in this regard is shown by either Beckman's or Dohrmann's TOC Analyzers.* For the present application the technique used in the Beckman device is preferred since, (1) the reaction sequence is more easily automated** and, (2) the open hydrogen flame component of the flame ionization detector used in the Dohrmann device presents a hazard (which would have to be eliminated by appropriate shielding).

One obvious simplication of the Beckman device would be to determine Total Carbon (TC) rather than Total Organic Carbon. This would require the use of only one furnace rather than two. Monitoring TC rather than TOC is permissable if the level of carbonates or dissolved CO_2 in the regenerated water is insignificant, as it is in the present case. Considering the method of regeneration (i.e., distillation combined with an exchange treatment) the carbon attributable to dissolved carbonates or CO_2 should be less than 2 ppm. (More likely less than 0.5 ppm since inorganic carbonates would be decomposed at distillation temperature and dissolved CO_2 would be minimized by storing reclaimed water at pasteurization temperature.)

In attempting to miniaturize and reduce the power requirements of the TOC device, attention is of necessity, centered on the combustion process. The method used for detecting and quantitating the products of combustion is also important, but a secondary consideration in terms of the parameters of interest. With only one combustion tube instead of two, the power requirement could be reduced to about 700 watts with the standard equipment.

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*Rocketdyne's Organic Analyzer is not considered since it per se is not commercially available.

**Beckman's Model 915 TOC Analyzer has been automated in the current program.

To achieve a more radical reduction in the power requirements, redesign of the combustion train is required. Two alternatives might be considered; namely, (1) a hot wire technique or (2) a modified catalyst bed technique. The feasibility of both, in terms of combustion efficiency, have been adequately demonstrated by other investigators. These methods differ in two major respects. In order to get efficient combustion with the (Pt) hot wire method, temperatures of the order of 950°C are required whereas with some catalyst bed reactors, temperatures as low as 600°C may be employed*.

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* A third approach, the wet chemical method (i.e., oxidation of organic carbon by a chromic acid-sulfuric acid mixture) which requires even lower temperatures for oxidation (e.g., 250°C for 2.5 minutes) was not considered because of; (1) variable susceptibility of some organic compounds to oxidation by this procedure, (2) hazards in handling the concentrated acids, (3) complexity of equipment and difficulty in adapting to zero-G, and (4) high reagent volume requirements. In a continuous automatic prototype analyzer developed by DuPont, the procedure (overall processing time of 10 minutes) involves filtration of the sample, precipitation of carbonates, oxidation of organic carbon to CO_2 by chromic acid - H_2SO_4 acid, stripping the reaction mixture of CO_2 in a small falling-film column, removal of chlorine (formed by oxidation of chloride) and water vapor by passage through an antimony scrubber and Drierite, respectively. The purified gas (i.e., CO_2) is measured in a differential thermal conductivity analyzer (R. Kieslback, Anal. Chem. 26, No. 8, 1312 (1954)).

Catalyst Bed Combustion Approach

A number of combustion catalysts* have been utilized for conversion of organic carbon to carbon dioxide. Other than the use of platinum, the more common catalysts include copper (II) oxide, cobalto-cobaltic oxide or a copper oxide - ferric oxide mixture, (Arneil catalyst). In cases where a thermal conductivity detector is used for measuring the CO_2 formed on combustion, silver or silver vanadate have been used in combination with these catalysts to remove halogens, SO_2 and SO_3, which would interfere in the determination. With exception of the Arneil catalyst, which is used at temperatures of 600°C, the other catalysts mentioned have to be heated in excess of 750°C to effect complete oxidation of organic carbon to carbon dioxide. Palladium catalysts, which are less commonly used, can convert saturated-hydrocarbons (i.e., methane and ethane) to carbon dioxide at temperatures of 200°C.

A brief description of each of these catalysts is given below:

a. Platinum Catalysts

One of the most effective catalysts is pure platinum used in the form of platinum balls prepared by rolling small pieces of 80-mesh platinum gauze into balls 3 to 4 mm in diameter.** The extent of conversion of hydrocarbons in an oxidizing atmosphere increases with temperature, and above 750°C the incremental change is relatively small. The sensitivity is also related to the length of the packing, the nature of the material being oxidized and the flow rate. A packing length of 5" of platinum balls (in a silica combustion tube 16" long) is generally sufficient to effect complete oxidation of most organics, except for such volatile compounds as methanol, ethanol and acetone. If a longer packing length is employed, the steam pressure developed when the aqueous sample reaches the combustion zone, forces the sample vapor back into the cooler portion of the tube. The delayed reaction causes a lowering of the peak height. The peak height also increases with increasing flow rates up to 50 ml/min. and remains faily constant between 50-100 ml/min.

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* One other catalyst not covered in this discussion was used in the 90-day test at McDonnell Douglas. It is designated Ardox (R), by Arde Co., of Mahwah, New Jersey, and is usable at temperatures of 115-140°C. This catalyst is of proprietary composition, but has good usable life (30-90 days) without replacement at high throughput.

** V. A. Stenger and C. E. Van Hall, Anal Chem. 39, 207 (1967).

Apart from the expense of using this catalyst, it is also subject to poisoning by a number of materials (i.e., SO_2, Cl_2, NH_3, P, As, Sb). Highly carburetted gases react with platinum to form a carbide which causes brittleness and general deterioration.

Platinized asbestos or quartz chips coated with a thin film of platinum were found to be not as effective as pure platinum.

b. Cobaltous - Cobaltic Oxide Catalyst

This catalyst has been used by itself in combination with CuO. Investigators * report good results initially with cobalto-cobaltic oxide (supported on pumice) at 700°C; however, some good batches lost their activity after three or four determinations (due possibly to poisoning of the catalyst by an alkaline impurity). Satisfactory combustion was achieved with a variety of organic compounds (containing B, N, P and S as well as only C, H and O), using the arrangement shown graphically in Figure 36.

Silver gauze extends beyond the furnace so that its temperature decreases to 300 - 400°C; within this temperature range, the silver will absorb halogens and sulphur (removal of these interferents is required only if a thermal conductivity detector is being utilized).

c. Cupric Oxide Catalyst

Though reportedly ** less active than the cobaltic oxide catalyst, cupric (II) oxide, is commercially available, requires less conditioning and produces more consistent results -- even after six months use. This catalyst oxidizes hydrogen to water at 250°C and CO to CO_2 at 280 - 295°C. However, for complete oxidation of hydrocarbons temperatures of 850 - 900°C are required.

Although, CuO is an effective oxidizing agent, studies by Gustin *** showed that CO_2 dissociated in its presence above 600°C. This problem was resolved by providing a second combustion tube of Cu - CuO at 400-500°C downstream. ****

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* J. A. Kuck et al, Anal Chem. 34, 403 (1962).

** H. A. C. Montgomery and N. S. Thom, Analyst, 87, 689 (1962).

*** G. M. Gustin, Microchem. J. 4, 43 (1960).

**** The length of the CuO packing in the first combustion unit was ~27" (silica combustion tube 25 cms x 7 mm bore). The second combustion tube (Pyrex, 8 mm I. D., 10 mm O. D., 6" long) contained a CuO packing ~3" in length and ~3" length of Cu wire (20-60 mesh). The CuO combustion tube can be used in a vertical position .

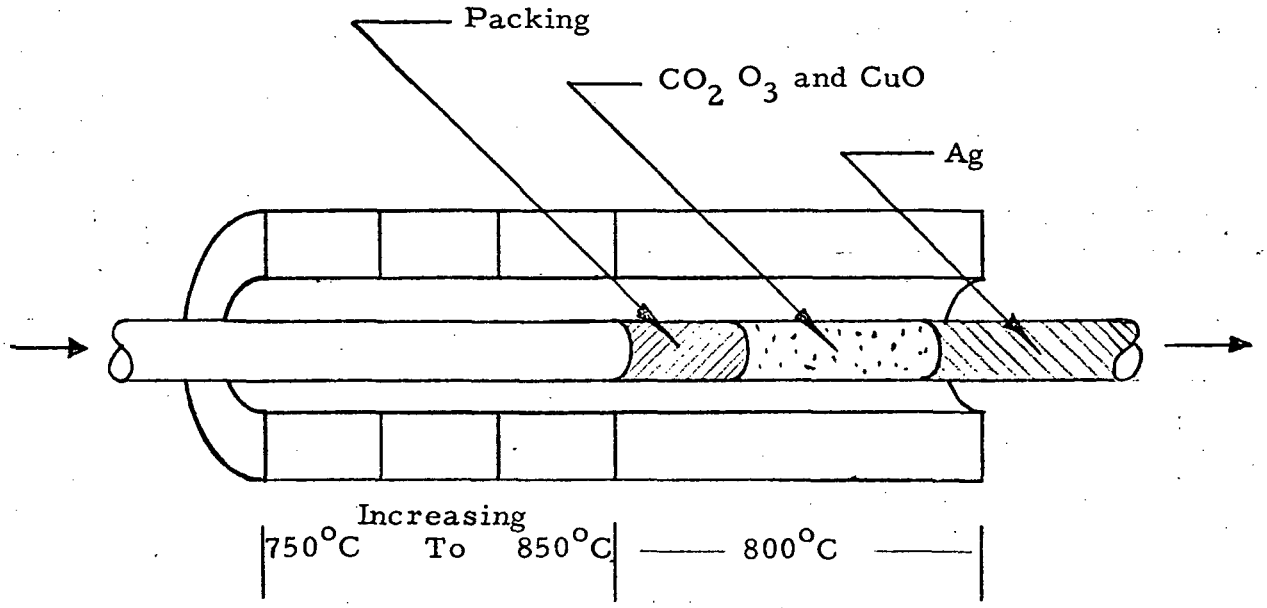

Figure 36. Combustion Furnace

This second unit provided both a reducing and oxidizing medium and no CO_2 dissociation was detected in the presence of copper when heated as high as 800°C. The life of the packing of the second unit exceeded several hundred analyses. The CuO catalyst can be easily regenerated by passage of air over the heated catalyst.

d. CuO - Fe_2O_3 Mixture (Arneil Catalyst)

This combustion catalyst operates effectively at 600°C. It is readily prepared by grinding together 99% by weight of CuO with 1% weight of Fe_2O_3. To 80 parts by weight of this mixture, 20 parts by weight of finely ground Kaolin are added, mixed to a stiff paste with water and squeezed through a suitable sized tube to form threads. After drying and firing at 600°C, the catalyst is ready for use. This catalyst can be reactivated periodically by heating in an oxygen atmosphere (at 600°C).

e. Palladium Catalyst

Palladium in the form of the pure metal or as a coating on various insert substrates (i.e., asbestos, alumina, molecular sieve) has been used as a combustion catalyst for saturated hydrocarbons (e.g., methane and ethane) at temperatures of 200 - 600°C.* Although, oxidation takes place readily, the results of several investigators have not been consistent principally because of catalyst poisoning (i.e., by carbon formed in the reaction of equation (1))and oxidation of the palladium at temperatures of ~400°C.

$$CH_4 \xrightarrow[Pd]{} C + 2\,H_2 \qquad (1)$$

The extent to which either of these occur is dependent on the CH_4/O_2 ratio in the gas stream (i.e., oxidation of Pd occurs more readily the higher the partial pressure of O_2 relative to methane). Even at low CH_4/O_2 ratios, some carbon (according to equation (1) above) always forms and is deposited on the palladium.

The equilibrium mixture of Pd/PdO which results from the partial oxidation of the palladium catalyst would be expected to be a function of the CH_4/O_2 ratio in the gas phase. To achieve consistent combustion efficiencies from one run to the next pretreatment of the catalyst bed with a reducing atmosphere (i.e., H_2) would be required to convert the palladium oxide back to palladium.

The expense of the catalyst and the aforementioned shortcomings have prevented its widespread use as a combustion catalyst for hydrocarbons.

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* C.F. Curtis et al. Trans Far Soc., 67 , 864 (1971).
J.G. Firth, Trans Far Soc., 62 , 2566 (1966).
G.M. Schwab and A.M. Watson, J. Catalysis, 4, 570 (1965).

Platinum Hot Wire Combustion Method

In the presence of oxygen, all combustible gases are oxidized in contact with platinum wire at about 900°C. The most convenient way of heating the wires is by electrical means. One method commonly used for achieving complete oxidation of methane or ethane by this technique is to leave the reaction mixture (hydrocarbon, plus excess oxygen in a 150 ml reaction volume) in contact with a platinum spiral coil* heated electrically to a bright yellow for a two-minute period.

For use in the present application, vaporization of the liquid sample might be achieved by passage through a preheated zone or by evaporation and pyrolysis from an electrically heated platinum boat. The efficacy of achieving complete oxidation of the organic compound in the presence of the water vapor would have to be established with representative organic standards.

Hot wire platinum filaments are available commercially** in a variety of configurations.

Detection of Combustion Products

Two techniques which might be used for sensing the products of combustion are a thermal conductivity detector or a nondispersive infrared detector.

The differential thermal conductivity detector is based on a differential measurement in which the thermal conductivity of one gas is compared with that of another in a single apparatus.

The principle is illustrated schematically in Figure 37. Two filaments of matched dimensions and resistance are mounted in similar cavities in the cell block. The filaments are connected as adjacent arms in a Wheatstone Bridge, the other two arms consist of fixed resistors. The bridge contains a potentiometer for balancing any slight

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* Platinum spiral coil - 90% Pt + 10% I r alloy, 20 cms of wire, O. 16 - 0.17 in diameter.

** Leeds and Northrup is one source.

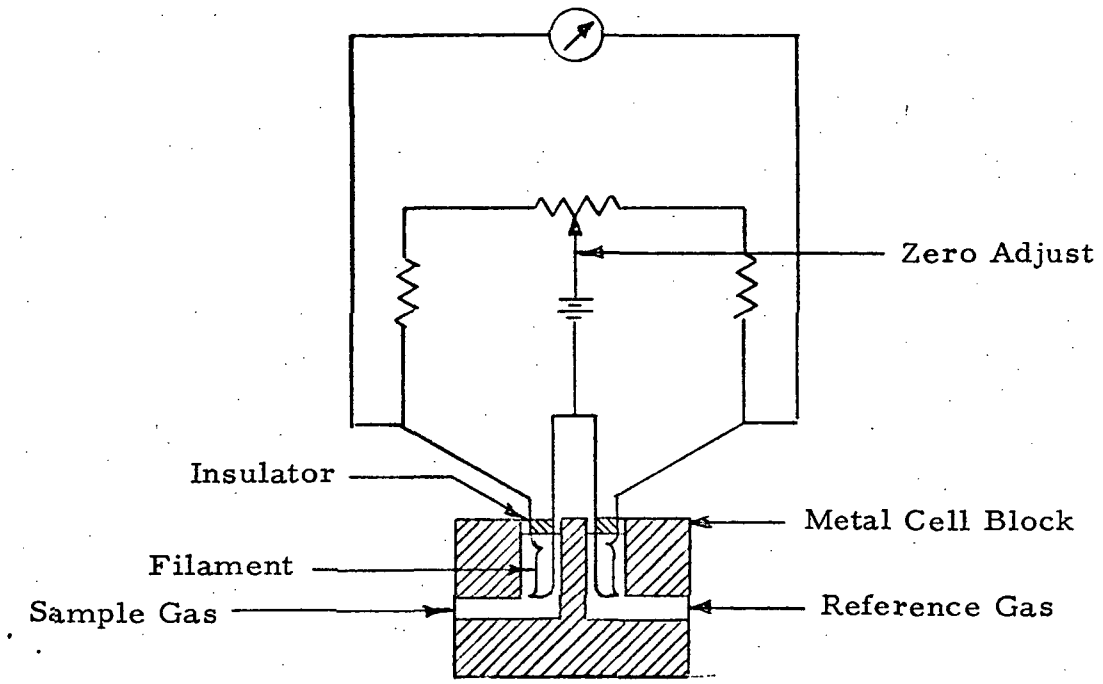

Figure 37. Simple Thermal Conductivity Cell and Bridge

inequalities in the bridge arms. Sufficient potential is applied to the bridge to heat the filaments, and bridge unbalance is detected with the meter. Initial "zeroing" of the instrument is accomplished by filling both cavities of the cell with the same gas and adjusting the potentiometer for zero bridge output. When different gases fill the cavities, the bridge output reflects the difference in their thermal conductivities. The bridge output voltage is calibrated empirically in terms of concentration. This is accomplished by maintaining a gas of fixed composition (i.e., the reference gas) in one cavity of the cell and noting the bridge output produced by various known mixtures of sample and reference gas placed in the other cell cavity.

Unlike the nondispersive infrared analyzer, which responds only to CO_2 molecules, the thermal conductivity detector is not specific for CO_2 and consequently interferring gases generated on combustion (other than CO_2) must be removed. The products of combustion can be separated by physical (i.e., gas chromotography) or chemical means.

An example illustrating the use of both detectors is the work of Kuck et al. * In this study, involving the analyses for carbon and hydrogen in organic compounds containing a variety of chemical elements (N, S and halides beside carbon, hydrogen and oxygen), the combustion tube shown in Figure 36, was used. The CO_2 generated on combustion was determined in the presence of the other gases using a nondispersive infrared gas analyzer. The hydrogen content was determined using a thermal conductivity detector. Since the conductivity detector was not specific for hydrogen, all interfering gases had to be removed. The SO_2, SO_3 and Cl_2, formed on combustion were removed by the hot silver in the combustion tube. The CO_2 (after passage through the infrared analyzer) was removed by Ascarite. Nitrous oxide, could interfere in the hydrogen determination, however, its presence was unlikely (since it decomposes into its elements on heating (in the combustion tube). The most likely interferent would be nitrogen dioxide (NO_2) and could be removed by passage through a tube containing a reducing agent, such as pyrophoric copper or zinc.

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* J.A. Kuck et al, Anal. Chem. 34, 403 (1902).

The prime advantage of the nondispersive infrared analyzer over the thermal conductivity detector is the specificity of the former toward CO_2. This eliminates the need for separating interferring gases and thus simplifies the combustion train. The infrared analyzer would also require less maintenance and attendance. The advantage of the thermal conductivity sensor, is its smaller volume and lower weight and power requirement.

Conclusions

For space application, the requirements for a system which possess minimum weight and power requirements have to be balanced against the requirements for a system which needs minimal attendance and component replacement. The most attractive approach in this regard appears to be the use of an electrically heated platinum spiral (in which the water sample is vaporized and preheated) for effecting combustion of the organic carbon. The low temperature catalyst, Ardox(R), looks attractive and would be competitive with the hot wire approach and should be investigated further. The detector should be a nondispersive infrared analyzer, which has been miniaturized for space application, for the CO_2 measurement. Since neither of these items are off-the-shelf items, development efforts are required.

Chlorine Sensor. -

Discussion -

In addition to the expected effects of concentration and temperature, the bactericidal action of chlorine is highly dependent on pH, showing an inverse function with respect to the latter (i.e., a decrease in pH increases the biocidal activity of chlorine in pH range of 6-13). At constant pH, an increase in either concentration or temperature increases the antibacterial activity. Reduced bactericidal capacity of chlorine solutions are observed in the presence of trace metal ions (copper, nickel, cobolt) or organic materials which serve to decompose or consume available chlorine. Apart from the chlorine consumed in the above processes, available (active) chlorine may exist either as free or combined chlorine. Combined chlorine refers to that portion of the total residual (available) chlorine that combines with ammonia and other nitrogenous compounds present in natural water to form chloramines or N-chloro compounds. These are generally much less active in their bactericidal activity than free chlorine. Municipal potable water supplies are generally maintained at the 0.2 - 0.3 ppm free chlorine level while that in swimming pools at 0.6 to 1 ppm. In the present application a method is desired for measuring chlorine in the 0-2 ppm with a sensitivity of 0.01 ppm. Those methods, which can be used in the present application include: 1) a colorimetric method involving o-tolidine, 2) an amperometric method and 3) a specific ion electrode.

The advantages and disadvantages of each are described below:

a. Colorimetric Method (Figure 38)

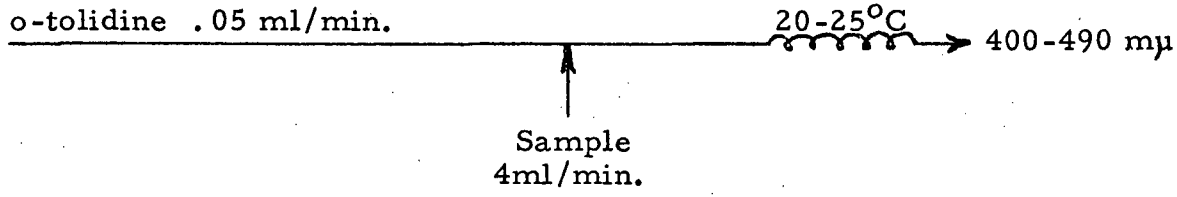
In the orthotolidine method for determination to total residual chlorine, the colorless o-tolidine reagent when added to a chlorine solution turns a yellow-orange-red color, depending on the chlorine concentration. Color intensity can be measured spectrophometrically

Figure 38

Colorimetric Measurement of Chlorine

Desired Range	Sensitivity	Processing Time	Reagent Stability	Sample Volume
0-2 ppm	.01 ppm	2 - 3 min.	6 Months at Ambient	4 ml/min.

Detection Technique



(at 400 - 490 mμ). Color development is influenced by temperature, with the maximum color being achieved in 2 - 3 minutes at ambient temperature (20 - 25°C). Reagent requirements are small; a flow system would require reacting reagent and water sample in a 1:100 ratio. Thus, for continuous monitoring, at a 4 ml/min. sample flow rate, the reagent requirements would be 0.05 ml/min. or only 72 ml for a 24-hour day. The reagent has at least a 6-month stability at ambient temperature. Interferring substances which may also give rise to the characteristic yellow color with o-tolidine reagent are >0.3 mg/l iron, >0.01 mg/l manganic manganese and >0.10 mg/l nitrite nitrogen. The level of these contaminants in NASA regenerated water generally falls below these limits. (Some exceptions*).

The o-tolidine method is best suited for measuring total (free and combined) residual chlorine. For measuring free residual chlorine, colorimetric tests are available but these generally involve the use of toxic ingredients (i.e., arsenite in the o-tolidine - arsenite method or mercury in the leuco crystal-violet (Black-Whittle) procedure.

b. Amperometric Method

The method commonly employed for continuous on-line monitoring of residual chlorine in potable water supplies involves an amperometric measurement.

The principle of operation involves passing the sample streams to be analyzed through a cell containing two concentric electrodes (i.e., an inner (gold) measuring electrode and an outer (copper) reference electrode). A small d-c potential is then applied across the electrodes. This causes the electrodes to become polarized, thereby, preventing current flow in the circuit. In the presence of a strong oxidizer (i.e., free chlorine), the polarizing layer becomes oxidized, thereby, permitting a current to flow.

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* NASA SP-261, "Preliminary Results from an Operation 90-Day Manned Test of a Regenerative Life Support System." NASA Symposium at Langley Research Center, Nov 17 - 18, 1970.

The amplitude of the self-generated depolarization current is proportional to the concentration of strong oxidizing agent. The current is measured by a series connected microammeter. The instrument can be calibrated to read directly in ppm of free or total chlorine. When measuring total residual chlorine, buffered (pH4) KI reagent is mixed with the sample prior to measurement. This reacts with the free and combined chlorine to liberate iodine in an amount equal to the total chlorine. The iodine behaves in an identical manner to the chlorine and a current directly proportional to the total residual is generated.

Amperometric systems commercially available for continuous monitoring generally require minimum sample flow rates of 125 ml/min. (reaction cell volume of 25 ml). Below this flow rate, the current generated becomes flow dependent, with also some loss in sensitivity. The commercial systems also utilize a gravity sample feed and a vented electrode chamber, which would require adaptation for a zero-g application. In principle, a system can be built which would utilize smaller flow rates or a smaller sample size (permitting a static measurement to be made on an intermittent basis).

c. Specific Ion Electrode

Although, specific ion electrodes are not available for measuring chlorine directly, it can be measured indirectly by adding the sample to a reagent containing a known concentration of iodide. In the presence of chlorine the following occurs:

$$Cl_2 + 2KI \longrightarrow 2K\,Cl + I_2$$

Specific ion electrodes for measuring iodide (I^-) ions in the concentration range of interest are available and can be used to measure the loss of iodide on reaction with chlorine. Chloride ion would not interfere in this determination.

Recommendations -

If measurement of total residual (free + combined) chlorine would suffice, the recommended method would be the colorimetric o-tolidine precedure since this would require less of a development effort to adapt it for space application. If "free" chlorine is the parameter to be measured, the amperometric approach with appropriate modifications would be the recommended approach. The amperometric system would be more trouble-free once the system is developed.

Iodine Sensor. -

Discussion -

Iodine, as a disinfectant for water has two distinct advantages over chlorine, namely:

1. The concentrations necessary to disinfect, do not vary greatly with different species of organisms.

2. I_2 exerts its effectiveness over a wider pH range than chlorine.

Because of the limited solubility of I_2 in water, a solubilizing agent or "carrier" is used. The resulting complex or combination slowly releases free iodine. The solubilizing agent which has been used by NASA is potassium iodide:

$$KI + I_2 \rightleftharpoons KI_3$$

The concentration of I_2 used for disinfecting drinking water is generally 5 - 6 ppm of residual iodine.

The method commonly used for monitoring residual iodine in this range involves the use of the leuco crystal-violet. The latter is oxidized from a colorless to a colored form by I_2 and monitored spectrophometrically. However, in view of the fact, that this reagent contains a toxic component (i.e., mercury derivative) it would not be recommended for the present application. An alternative approach would involve titrating the iodine solution with standard thiosulfate in accordance with the following reaction:

$$2S_2O_3^{=} + I_2 = S_4O_6^{=} + 2I^-$$

The end point is generally determined by use of starch as an indicator. Starch reacts with iodine in the presence of iodide to form an intensely blue-colored complex.

Recommendations -

While the titration of iodine solutions with standard thiosulfate and monitoring of color formation could be automated, a simpler approach would be the amperometric method to monitor I_2 directly without the use of reagents. The amperometric system described for monitoring chlorine would apply here.

By far, the simplest approach for iodine would be a colormetric approach utilizing the intense yellow-to-brown color developed by solutions of iodine in aqueous iodide. As little as 15 ppm I_2 is known to produce a perceptible yellow colored solution. The feasibility of this direct approach would have to be investigated, particularly, with regard to determining possible interference from other metal ions generally found in regenerated water.

Silver Sensor. -

Discussion -

The presence of chlorides and sulfides can interfere with the bactericidal action of silver. Organic material does interfere with silver disinfection, but not to the extent that it does with chlorine.

The recommended limit for silver in drinking water* is .05 mg/l (or 0.05 ppm). Prolonged exposure to silver does give rise to cosmetically objectional argyria, (permanent blue-grey discoloration of skin, eyes, and mucous membranes). The NAS/NRC recommended maximum ** is 0.5 ppm. Silver ion concentration of regenerated water has ranged from 0.0002 to 0.03 ppm.

Two procedures are available for measuring Ag^+ ion concentrations: 1) solid-state membrane electrodes from Orion (No. 9476) or Beckman (No. 39610); or 2) a fluorescent-quenching technique based on quenching of fluorescence of eosin-phenanthroline by Ag^+. (Figure 39).

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* Public Health Service Drinking Water Standards, 1962.
** NASA SP-261, "Preliminary Results from an Operation 90-Day Manned Test of a Regenerative Life Support System." NASA Symposium at Langley Research Center, Nov 17 - 18, 1970.

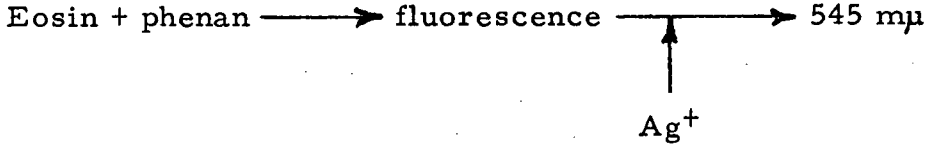
Figure 39

Colorimetric Measurement of Silver

Desired Range	Sensitivity	Processing Time	Reagent Stability	Sample Volume
0 - 500 ppb	4 ppb	5 sec.	Stable Months	1 ml

Detection Technique

Fluorescent Quenching



Recommendations -

The electrode approach would certainly be suitable for the 0.1 to 0.5 concentration range: below that, down to 0.01 ppm Ag^+ (its detection limit) the response time is slow (10 - 20 minutes for equilibrium).

If accuracy and speed of response is required in the ppb range, the fluorescent quenching procedure is the method of choice.

Biosensor. -

Discussion -

The principle of detection in the sensor being used to monitor the bacteriological quality of the recovered water is based on measuring the increase in chemiluminescence produced by the catalytic action of bacterial porphyrins, specifically hematin, on a luminol-hydrogen peroxide mixture (called Premix). Hematin, which occurs either in the free state or in the combination with a protein, is a substance found in most organisms, living or dead. The reaction is virtually instantaneous and occurs immediately on mixing the bacterial suspension with the aqueous reagents. Mixing is carried out in a reaction chamber within view of a photomultiplier tube (PMT) which monitors the light emitted by the reaction. The signals generated are directly proportional to the number of bacteria present. To permit differentiation between living and dead organisms, chemiluminescent signals are obtained for both incubated and unincubated bacterial samples. A higher signal for the incubated sample indicates the presence of viable organisms.

The present techniques for processing total and viable samples perform well but are complex. Great care has been exercised in setting up the processing steps to insure that all sample processing paths (incubated and unincubated samples) which have been exposed to bacteria are flushed with a bactericide (4M Urea) and filtered-distilled water to minimize the possibility of contamination. The biosensor is

designed to independently monitor water from two sources (either or both may be monitored). A water sample from one source is processed for total bacterial content only. The other may be processed for total bacterial content or for viable content.

Two separate processing paths are provided for total cell counts and a third for viable cell counts. Normally, two samples are processed together; either as total/total or as total/viable. The third path which processes only viable samples was included in an effort to keep nutrient interference and the possibility of contamination to a minimum. The object was to be able to switch from total cell counts to viable counts almost on demand. In reality, this demand capability is not quite realized. (No matter how clean a processing path may be initially, if it is not used for about an hour, the next sample that is processed will contain particles and substances that have been leached from the fluid lines and this gives an erroneous signal. Only after processing several samples (a sort of self-cleaning operation) will the reading be accurate).

In addition to the above, another complexity associated with sample processing is that of the filter-concentrator. The purpose of the filter-concentrator (F/C) is to provide a small volume highly concentrated bacterial challenge in close proximity to the reactor chamber so that the bacteria are in a "clump" when reacted with the reagents rather than being strung-out. This maximizes the chemiluminescence that takes place within view of the PMT for maximum signal. In operation, a filter holder subassembly is rotated in 45 degree increments by a pneumatic mechanism. Two samples are concentrated simultaneously and washed free of any soluble components that might interfere with the chemiluminescence reaction. Then the filter holder is advanced 45 degrees and the first sample is backwashed using 4M Urea into the reactor cell (mounted underneath the filter-concentrator against the face of the PMT) where it is mixed with Premix. Further advance of the filters places the second sample in position for backwash and reaction with Premix. The backwash

cycle is followed by two cleanup steps which remove residual material from the collection side of the filter that might lead to clogging with extended operation. Because operation of the filter-concentrator requires the use of rotating fluid seals, it is susceptible to leaks and mechanical malfunction.

A third drawback of the existing biosensor is the method of metering sample water and reagents. Flow rate requirements range from a low of 0.1 ml/min. for reagents to about 20 ml/min. for sample water. The reagent flow must be fairly free of pulsations and the pumps must provide a positive shut-off of fluids when not operating. At the present time the only pumps which effectively meet all the requirements are peristaltic. Being peristaltic, the tubing (Tygon) requires replacement at periodic intervals (no more than 200 hours) because as the tubing degrades, flexing causes flaking, and the release of particles results in spurious signals in the chemiluminescence reaction.

The goal of the present contract (NAS 1-10382) was to develop a biosensor capable of detecting as little as 10 cells E. coli per ml of sample water (using a 400 ml sample), both viable and nonviable organisms. This goal has been achieved, but at the expense of complexity, reduced reliability and additional maintenance. The goal of the next generation biosensor should be to attain the same level of detectability but with a simpler, more reliable and maintainable system. Development of the next generation system should also be toward reduced size, weight and power.

Recommendations -

A simple modification which reduces biosensor complexity is to eliminate all fluid lines, valves and filters associated with the second total cell count path (i.e., the one containing filter F2) and to use the third path for processing either total or viable counts. Nutrient would be introduced and the incubator activated only for those samples for which viable counts are desired; otherwise, the path would operate to process total counts. This modification does little toward achieving a flight worthy

biosensor however, since it is still too complex, requires excessive maintenance (and too much reagent) and does not have the level of reliability desireable for a flight system. Biosensor sensitivity is not degraded by this modification.

The recommended approach for the next generation biosensor is to pursue development of a system similar to that being done on Contract NAS 9-12548.* This system uses disposable capsules for processing of all bacterial samples. Current development is in the breadboard stage. The reagent requirements for the capsule system are about 25 ml/hr. or less compared to about 170 ml/hr. for the present biosensor. The possibility of cross-contamination is minimized with a disposable capsule. The area requiring the most attention in the capsule approach is improving the sensitivity: currently, about 60 to 100 cells E. coli/ml compared to 10 cells/ml for the biosensor on this contract.

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* Tape Cassette Bacteria Detection System, NASA Manned Spacecraft Center, Contract NAS 9-12548, Aerojet Medical & Biological Systems.

Projections of Prototype Flight System

Discussion. -

In selecting parameters which provide criteria for establishing the potability of regenerated water, prime consideration should be given to monitoring those contaminants which are toxic and have a good probability of being present during normal operation or through malfunction of the regeneration system. In addition, the water must not contain any impurity which offends the sense of sight, taste or smell.

A list of impurities which could prove harmful is given in Table 33.

Some of the impurities indicated, need not be monitored if the regeneration system is first subjected to an extensive qualifying test series using actual urine to establish that none of the fittings or plumbing contain metal impurities which could be leached out under normal operating conditions. Apart from the monitoring of cadmium, copper, lead and zinc, careful scrutiny would be given to the presence of other metal contaminants (i.e., Al, Be, Bi, Ca, Co, Fe, Li, Mg, Mn, Hg, Ni, Na, K, Si, Sn, P and Mo), excessive amounts of which could affect either the appearance or physiological acceptability of the water. The absence of these contaminants in the regenerated water supply during this pretrial qualification test period would establish that the regeneration system does not contain structural components which could contaminate the water under normal operating conditions. Once this has been established, the subsequent daily monitoring for these components in actual use would not be necessary.

The source of some of the contaminants shown in Table 33, are foods consumed by the astronaut. The source of contamination of these foods could be the ground waters used for irrigation, the soil in which the plant food is grown or the insecticide used for spraying the food. Contaminants which would fall into this category include arsenic, barium, boron, fluoride, selenium and organic phosphorus. Once it is shown that the food contains acceptable levels of each of these contaminants,

Table 33

POSSIBLE WATER CONTAMINANTS

Contaminant	Recommended Maximum	Agency	Source of Contaminant	Hazard
Arsenic	0.5 ppm	NAS/NRC	Food Insecticides	Cumulative poison; carcinogenic
Barium	2 ppm	NAS/NRC	Mineral Waters, Foods	Toxic effects on heart, blood vessels, nerves.
Boron	5 ppm	NAS/NRC	Foods	Excessive amounts cause nausea, cramps, convulsions, coma.
Cadmium	0.05 ppm	NAS/NRC	Impurity of zinc-galvanized iron	Toxic - anemia liver damage, death
Chlorides (Cl^-)	450 ppm	NAS/NRC	Urine, foods, disinfectants	Corrisive to metals; imperts saline taste to water in excess of 450 ppm.
Chromium (Hexavalent)	0.05 ppm	NAS/NRC	Used for pre-treating urine	Skin irritant, ulcers, carcinogenic
Copper	3 ppm	NAS/NRC	Copper and brass plumbing in water system; foods	Gastrointestinal catarrh; imparts disagreeable taste to water (>1 ppm)
Fluoride	2 ppm	NAS/NRC	Mineral waters, foods (meat, fish, peas, tea)	Toxic at high concentrations (>8 ppm); causes crippling fluorisis, death.
Lead	0.2 ppm	NAS/NRC	Mineral waters, foods, plumbing	Cumulative poison

Table 33 (Continued)

POSSIBLE WATER CONTAMINANTS

Contaminant	Recommended Maximum	Agency	Source of Contaminant	Hazard
Selenium	0.05 ppm	NAS/NRC	Water, foods cereals and grains	Highly toxic - impairment of vision, weakness and respiratory death.
Sulfates (SO_4=)	250 ppm	NAS/NRC	Mineral waters; sulfuric acid used for pretreating urine	Cathartics at high concentration; corrisive to plumbing; effects taste 250 ppm.
Zinc	5. ppm	U.S. Public Health	Zinc galvanizing on plumbing	Imparts astringent taste to water; produces turbidity in alkaline waters.
Ammonia (NH_3)	1, pH >7 10, pH < 7	NAS/NRC	Bacterial decomposition of nitrogenous organic matter; from decomposition of urea in urine; from space cabin atm.	Presence evidence of organic pollution or malfunctions of water regeneration system; affects taste and odor of water at higher concentrations.
Nitrates (NO_3-), Nitrites (NO_2-)	10 ppm (Total as N)	NAS/NRC	Urine, foods	Toxic - nitrites convert hemoglobin to methemoglobin in the blood; dangerous in high concentrations (500 ppm or more).
Acids, Alkalis (pH)	pH 4-10	NAS/NRC	Acid pretreatment of urine; alkali salts in food and urine	Lime-like taste to water at pH 11; High pH (up to 10.8) accelerates corrosion of aluminum, tin, lead. Water with pH 4 used safely in municipal water supplies but corrosive to plumbing.

Table 33 (Continued)

POSSIBLE WATER CONTAMINANTS

Contaminant	Recommended Maximum	Agency	Source of Contaminant	Hazard
Organic Phosphorus	0.1 ppm	No std.	Agricultural pesticides	Highly toxic - affects nervous system.
Total Dissolved Solids (Specific Conductivity)	1000 u mho/Cm	NAS/NRC	Dissolved salts in urine, food; urine pretreatment.	If maximum levels exceeded - could indicate malfunction in water regeneration system; teaste, color, odor could be affected.
Organic Carbon	100 ppm	NAS/NRC	Food insecticides, urine, space cabin atmosphere, refreshments.	Some are highly toxic.
Turbidity	10 Jackson Units	NAS/NRC	Metal hydrocides, or other suspended matter.	Offend the senses may indicate presence of toxic component.
Odor	None Objectionable	NAS/NRC	Bacterial decomposition products, urine.	Offend the senses may indicate presence of toxic component.
Color	15 Pt-Co Units	NAS/NRC	Iron, margarine salts, organics, urine	Offend the senses may indicate presence of toxic component.
Taste	None Objectionable	NAS/NRC	Dissolved salts urine	Offend the senses may indicate presence of toxic component.
Foaming	None Persistent 15 sec.	NAS/NRC	Dissolved surfactants (principally organics, salts to a lesser degree	Offend the senses may indicate presence of toxic component.

Table 33 (Continued)

POSSIBLE WATER CONTAMINANTS

Contaminant	Recommended Maximum	Agency	Source of Contaminant	Hazard
Silver Ion (Ag+)	0.5 ppm	NAS/NRC	Water Disinfectant	Discoloration of skin, eyes and mucuous membrances (Hrgyria)
Iodine (+ iodides)	No std.		Water Disinfectant	Iodide in excess causes hyperactivity of of thyroid in some individuals.
Radiosotopes (Plutomum)	No std.		Heating source for VD-VF water recovery system	Radiation harzard

further monitoring of the regenerated water supply for these components would not be required.

The breakdown of some step in the regeneration process could give rise to excessive levels of ammonia, nitrates (and nitrites), as well as hexavalent chromium. The pH, organic carbon, conductivity and total organic carbon values could also exceed the recommended maximum.

With respect to hexavalent chromium it would appear that the limit of 0.05 mg/l originally established in 1946, may have been established more on the basis that this was the lowest amount that was analytically determinable. Based on the experiments of some investigators * it would appear that man could drink water with a hexavalent chromium content of 5 ppm without deleterious physiological effects. The total chromium content (Cr^{+2}, Cr^{+3}, and Cr^{+6}) of regenerated water in the last 90-day test series ranged from .001 to 1.0 ppm. The high figure occurred during acceptance pretesting of the system. The results of the biweekly analysis during the 90-day test ranged from .001 to 0.01 ppm. Assuming that the 0.05 ppm limit for Cr^{+6} were to be retained, then a separate sensor for this contaminant would have to be utilized since Cr^{+6} at the alarm level of 0.05 ppm would not exceed the acceptable limits of pH (3 to 11) established by NAS/NRC.

With reference to ammonia, its presence above the tolerable limits would also not be picked up by a pH sensor and so, a separate sensor would be required if the specified limits are to be maintained. At only one point in the 90-day test series mentioned earlier, did the ammonia level (19 ppm) rise above the allowable 10 ppm (pH 6.7).

With respect to Nitrates/Nitrites, their combined presence, according to NAS/NRC should not exceed 10 ppm (as N). These limits were established because of infant nitrate poisoning (methemoglobinema)

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* Water Quality Criteria, prepared by California Institute of Technology for California State Water Pollution Control Board, Second Edition, 1960.

associated with waters containing excessive amounts (70 ppm) of this component. Its presence in the present application would arise from aerobic oxidation of organic nitrogen by bacteria or a breakdown in the regenerative system. In no instance in the last 90-day series, did the combined level of nitrate/nitrite exceed 10 ppm. Since nitrate/nitrite at this level would not necessarily be detected by any of the other sensors (i.e., pH, biosensor), a separate sensor would be required for this parameter if this standard is to be maintained.

With respect to the other parameters indicated in Table 33; Cl^- is present in large quantities in urine and excessive amounts would be indicative of a possible system malfunction. Excessive chloride would also enhance corrosion of system components and this could cause leaching of toxic metal impurities at a more rapid rate. Excessive amounts do affect the taste. Monitoring of this parameter would be of interest (Cl^- levels at the alarm limit are not necessarily toxic) to indicate possible malfunctioning of the system. The upper limit (450 ppm) of Cl^- would cause the specific conductance to alarm (exceed 1000 μ mhos/cm).

The principle source of $SO_4^=$ is from sulfuric acid used in urine pretreatment - monitoring of this parameter is not really required if the Cl^- is being monitored, since excessive amounts of the latter in regenerated water would indicate system malfunction.

pH indicates acid carry-over from chemical pretreatment - simple parameter to measure.

Specific conductance is a measure of the total ionic species and is an overall assessment of the total solids in the recovered water and can be conveniently monitored.

Excessive amounts of organic carbon may be due to the presence of simple hydrocarbons present in the urine (aldehydes, ketones, alcohols, etc.) or to organics picked up from the food, clothing or extraneous equipment in the space cabin. Since some of these can be toxic, monitoring of this parameter is recommended as an overall assessment

of the water quality. Since inorganic carbon is expected to be less than 2 ppm, the parameter to be monitored should be total carbon.

Taste, color and turbidity are of secondary concern; off-color, off-taste could be caused by presence of iron and managese in the water - neither of which is particularly harmful. $Cr^{+6} > 1.5$ ppm does affect taste and color. Monitoring of these (taste and color) parameters can be done by utilizing the senses of the astronaut. This would apply to turbidity (suspended solids) as well, which might indicate breakdown of the filtering system.

Foaming could be caused by the presence of cleansing agent in wash water or certain organics. This might be readily performed by astronaut (manually and visually).

Odor could be caused by the presence of organics or excessive amounts of ammonia. This could be checked out by the astronaut, (i.e., sense of smell).

The water disinfectants Ag^{+}, I_2 can be toxic in excessive amounts, and bacterial buildup can occur if certain minimum level is not maintained. These parameters should be monitored if Ag^{+} or I_2 are used as water disinfectants.

Radioactivity should be monitored only if a radioisotope is utilized for thermal source in VD-VF, Water Regeneration System.

Recommended Sensors. -

The system which is recommended for a next generation water monitor should contain sensors for pH, specific conductance, total carbon, bacteria, Cr^{+6}, and I_2 (or Ag^{+} or Cl_2 depending on the bactericide used). A sensor for NH_3 is not recommended at this time because presumptive evidence from the 90-day test indicates that excessive (>10 ppm) levels of NH_3 would also be reflected in abnormally high readings (although, not at alarm level) of other included sensors (see Figure 40). In this instance, TOC and specific conductivity were abnormally high. Further analysis of probable recovery systems would be necessary to determine

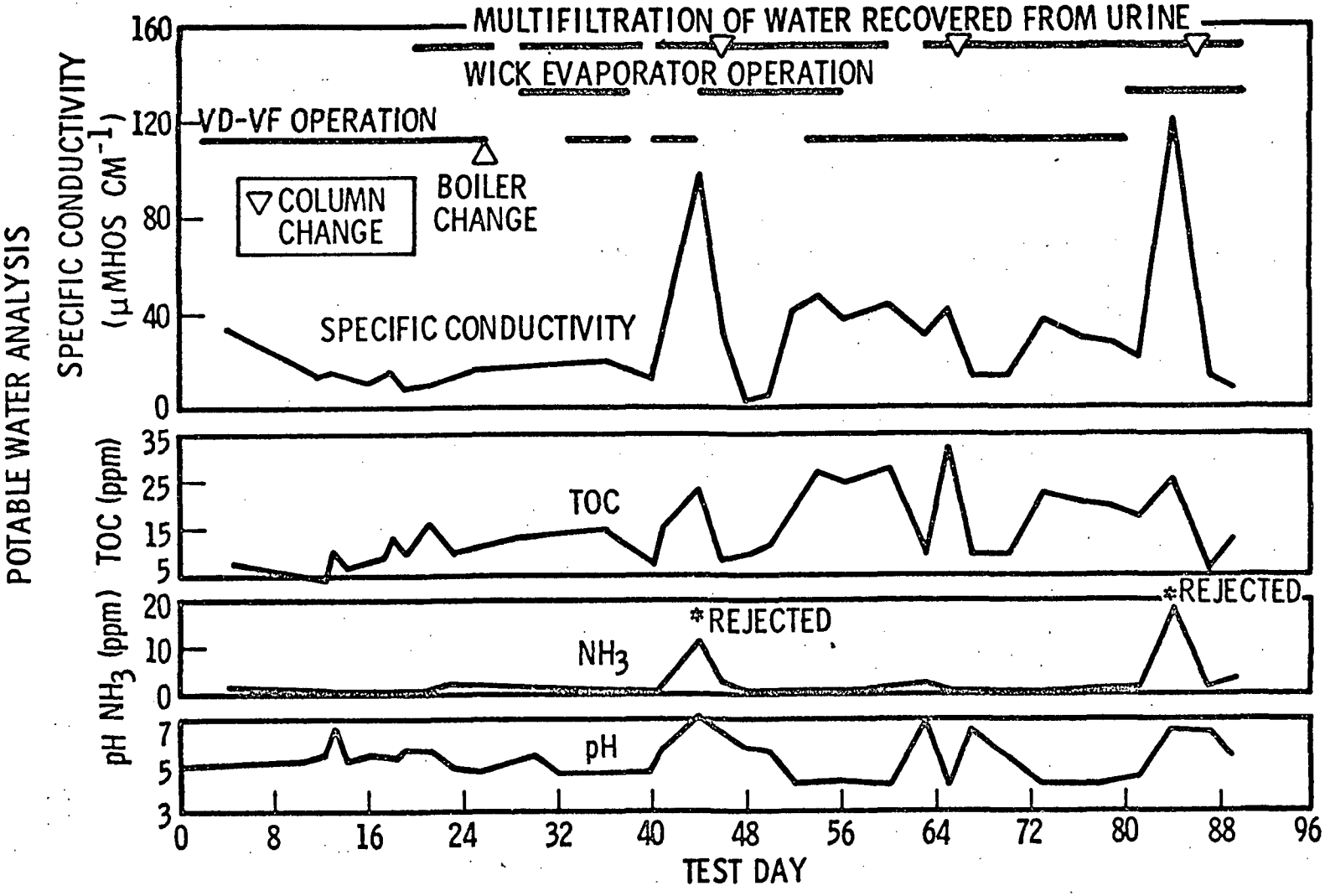


Figure 40. Reclaimed potable water analysis.

* Extracted from Preliminary Results from an Operational 90-Day Manned Test of a Regenerative Life Support System, NASA SP-261, Nov. 17-18, 1970.

whether or not this theory is correct. In the event it is not, then monitoring of NH_3 would be required. A sensor for total nitrogen (NO_2/NO_3) is not recommended by the same reasoning (i.e., levels exceeding 10 ppm did not occur).

Preliminary projections of the weight, power and size of a flight system are shown in Table 34.

A few comments on the rationale at arriving at the estimated weights are most appropriate in the case of the total carbon sensor and the biosensor.

Carbon sensor:

The miniature CO_2 sensor developed by Perkin Elmer (Contracts NAS 9-1191 and NAS 9-2255) weighs 2.6 pounds and requires about one-watt power and a volume of 40 cu in. This sensor does not have sufficient sensitivity. Development of a satisfactory CO_2 sensor should be possible with characteristics of three pounds, <2 watts and a volume of 50 cu in.

The power necessary to raise a 50μl water sample and carrier gas (150 cc/min) from ambient to 900°C is about six watts. With careful furnace design and selection of insulation, the total power requirement should not be more than about 30 watts.

Biosensor:

Based on reagent usage of 20 ml/hr (~4000 ml/wk), the reagent package should weigh about eight pounds and occupy ~250 cu in.

The use of microelectronics should permit the manufacture of flight-weight electronics weighing about two pounds, and requiring no more than five watts in a space of about 3 x 5 x 4 inches.

The processing module is the most difficult to estimate. In its present configuration (laboratory test bed), it weighs about 60 pounds (without pumps). An estimated flight weight of 20 pounds does not seem unreasonable. The biggest users of power in the processing module are the reagent and the sample pumps. Whether or not the estimate of 20 watts is correct will ultimately depend upon pump technology and the possibility of using gas-driven positive displacement pumps.

Table 34

Estimated Flight System Specifications

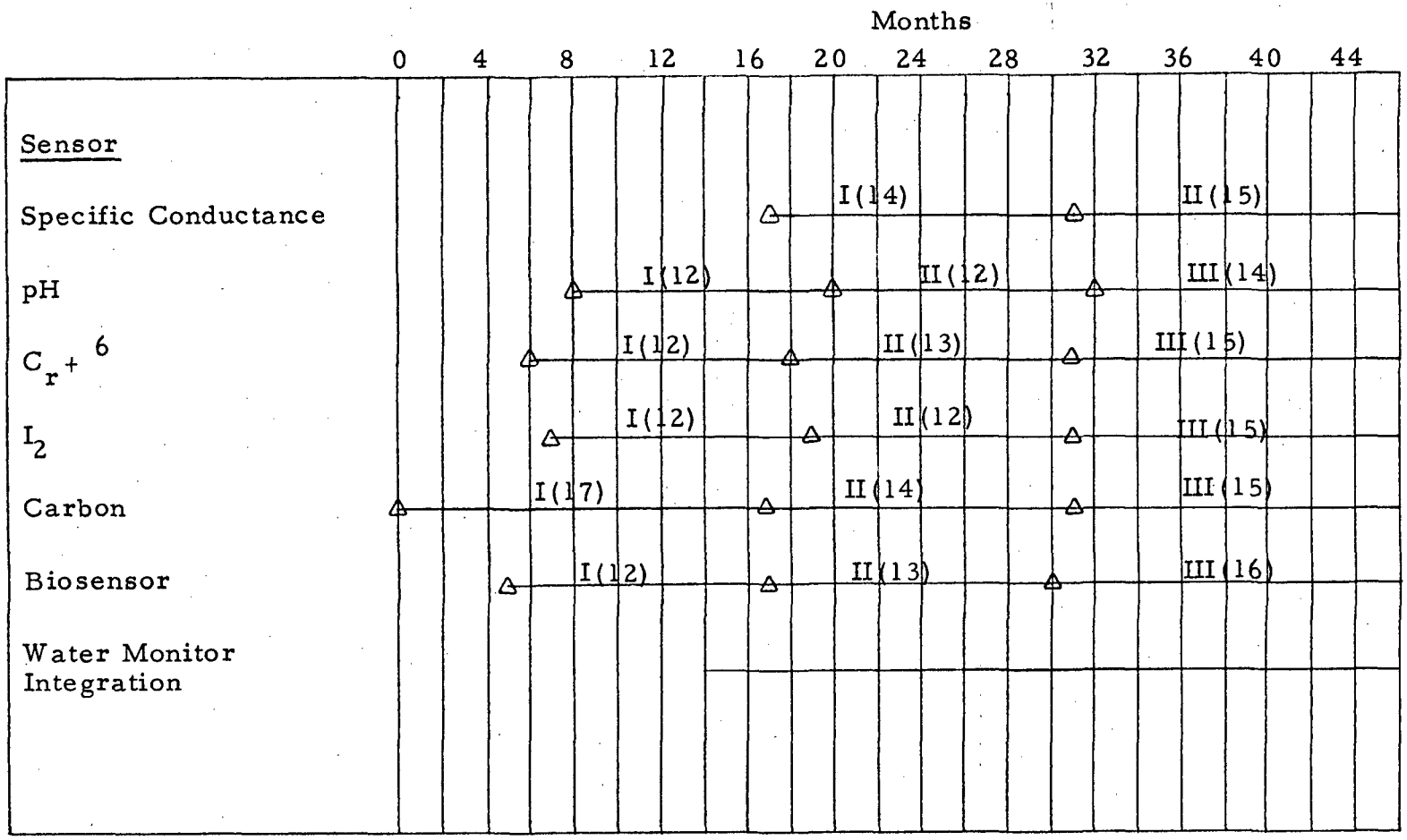
Sensor	Weight	Power	Size
pH	2 lbs.	1 Watt	40 cu. in.
Conductivity	2 lbs.	3 Watts	60 cu. in.
TC			
CO_2 Sensor	3 lbs.	< 2 Watts	50 cu. in.
Furnace	7 lbs.	30 Watts	240 cu. in.
Biosensor			
Reagents	8 lbs.	--	250 cu. in.
Processing Module	20 lbs.	20 Watts	600 cu. in.
Electronics	2 lbs.	5 Watts	60 cu. in.
C_{r+}^{6}			
Processing Module	4 lbs.	5 Watts	200 cu. in.
Colorimeter	5 lbs.	5 Watts	160 cu. in.
I_2 Shares Colorimeter with C_{r+}^{6}	2 lbs.	2 Watts	40 cu. in.
Integrating Hardware and Electronics	8 lbs.	4 Watts	
TOTAL	63 lbs.	77 Watts	1700 cu. in.

Development Schedule. -

Program projections are presented below for a water monitor system incorporating the following sensors: Specific Conductance, pH, Hexavalant Chromium, Iodine, Total Carbon and a Bacterial Sensor. Schedules/Tasks are presented for each sensor. In addition, an overall schedule for the water monitor system is shown in Figure 41.

Figure 41

Program Schedule
Water Monitor System



Specific Conductance Sensor -

Phase 1 - 14 Months (Figure 42)

Objective: Design, fabricate and test a miniaturized sensor system. Tasks to be performed include:

1. Design, fabrication and checkout of miniaturized flow through cell.
2. Design, fabrication and checkout of miniaturized readout.
3. Sensitivity and reliability testing of sensor system.
4. Field testing of sensor system.
5. Optimization and redesign of system.
6. Additional sensitivity tests.

Phase 2 - 15 Months (Figure 43)

Objective: Testing of flight-rated units. Tasks include:

1. Design, fabrication and checkout of flight-rated prototype.
2. Sensitivity and reliability testing.
3. Qualification tests; shock, vibration and other tests to achieve flight-rated status.
4. Fabrication of flight-rated units for acceptance tests.
5. Acceptance tests.

Figure 42

Program Schedule
Specific Conductance Sensor

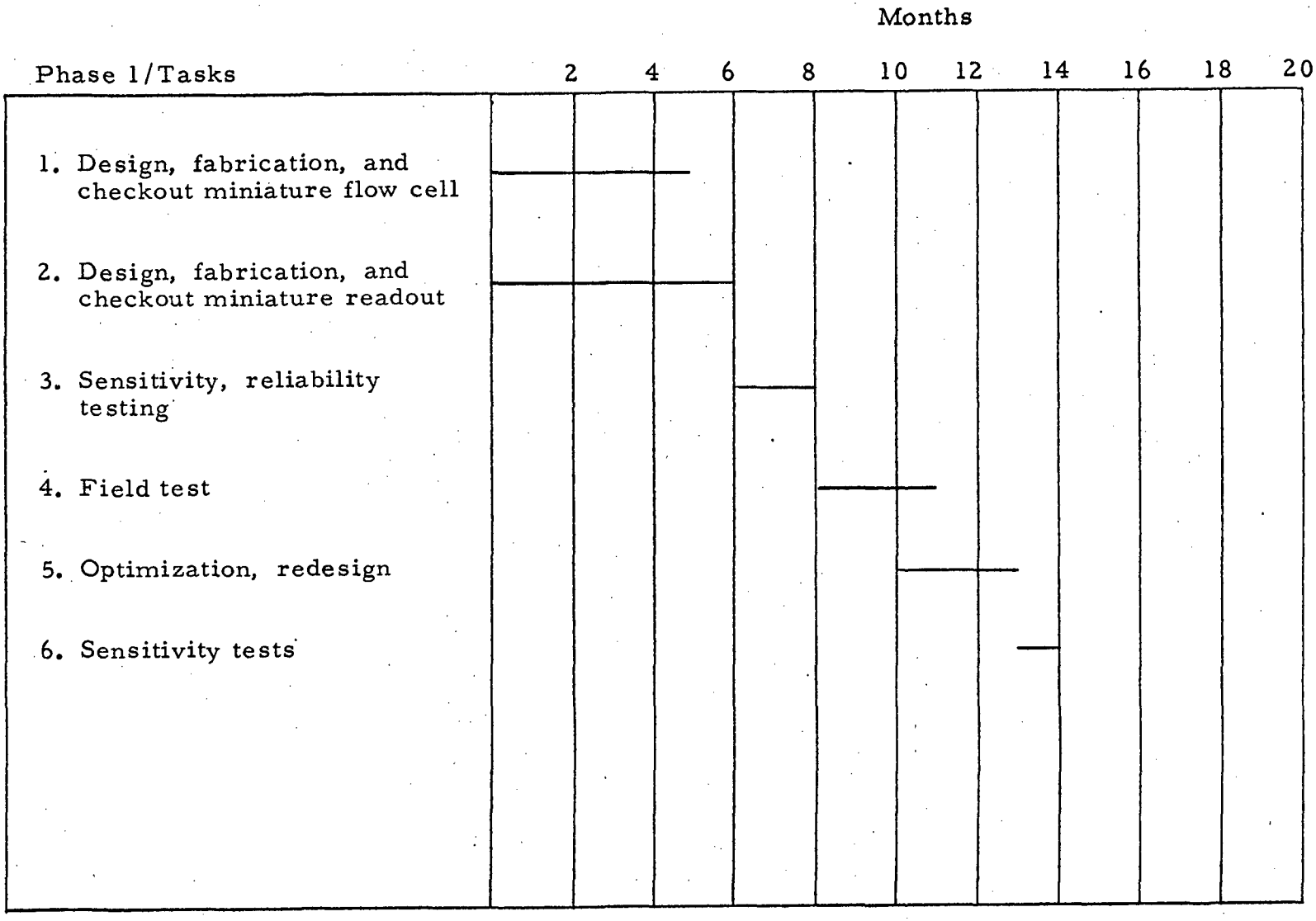
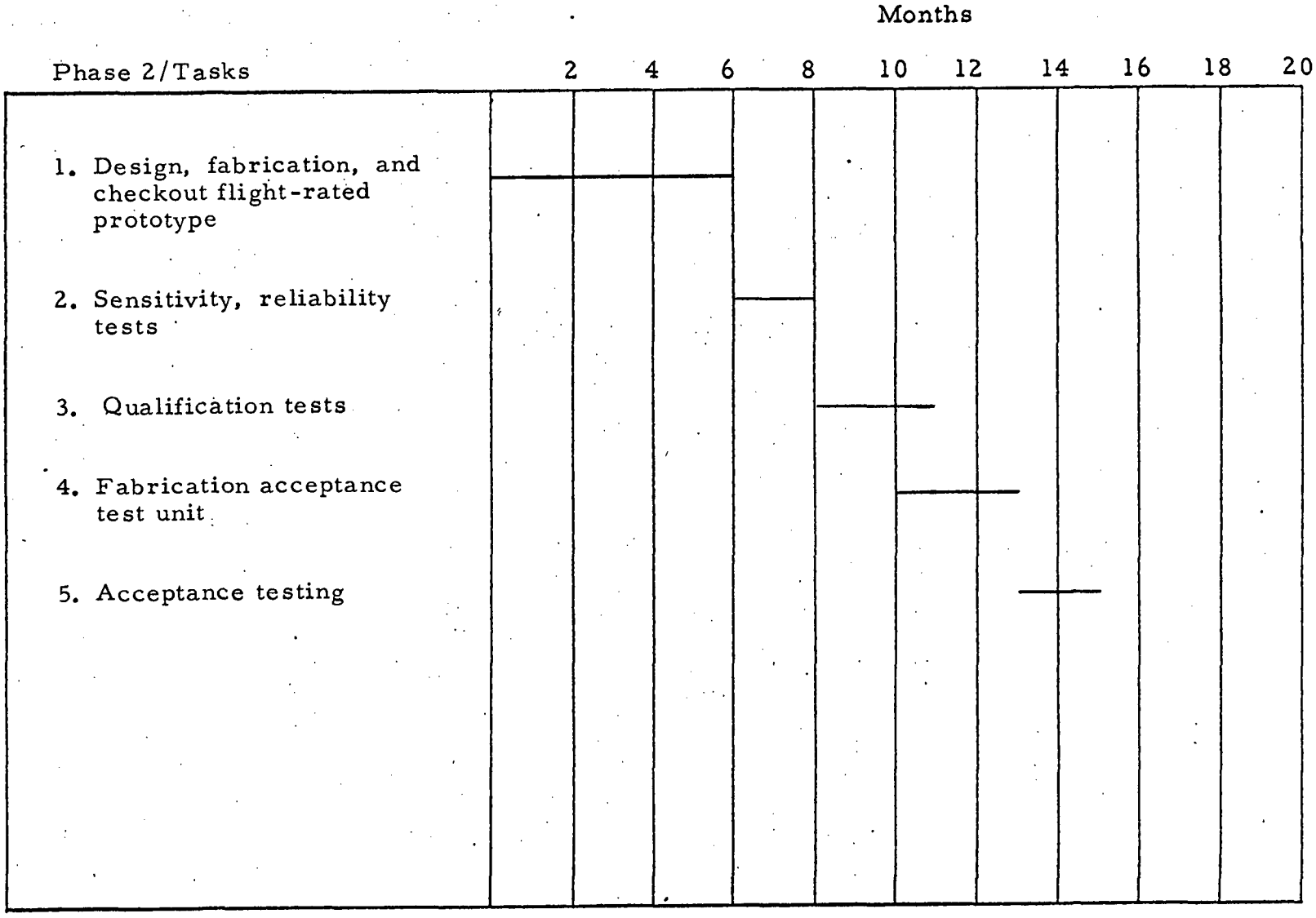


Figure 43

Program Schedule
Specific Conductance Sensor



pH Sensor -

Phase I - 12 Months (Figure 44)

Objective: Design, fabrication and testing of Zero-g compatible electrode sensor (subsystem). Tasks include:

1. Laboratory testing of sensing and reference electrodes.
2. Design, fabrication and checkout of miniaturized electrode well and pressure compensating hardware.
3. Sensitivity testing and optimization redesign.

Phase 2 - 12 Months (Figure 45)

Objective: Design of miniaturized readout and field testing of sensor system. Tasks include:

1. Design, fabrication and checkout of miniaturized readout unit.
2. Field testing of sensor system.
3. Redesign and optimization.
4. Sensitivity and reliability tests.

Phase 3 - 14 Months (Figure 46)

Objective: Testing of flight-rated units. Major tasks to include:

1. Design, fabrication and checkout of flight-rated prototype.
2. Sensitivity and reliability tests.
3. Qualification testing; shock, vibration and other tests to achieve flight-rated status.
4. Fabrication of flight-rated units for acceptance tests.
5. Acceptance tests.

Figure 44

Program Schedule
pH Sensor

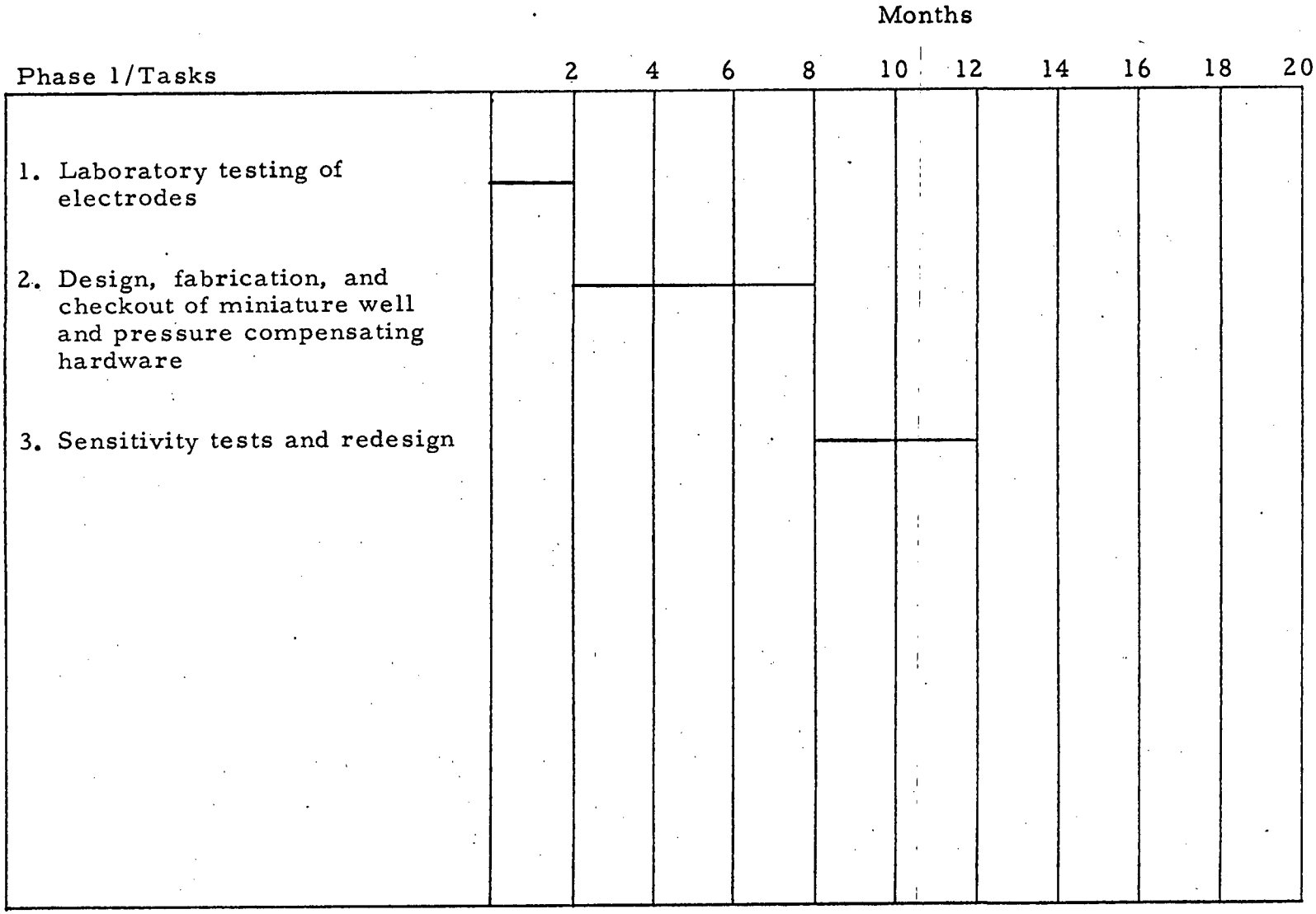


Figure 45

Program Schedule
pH Sensor

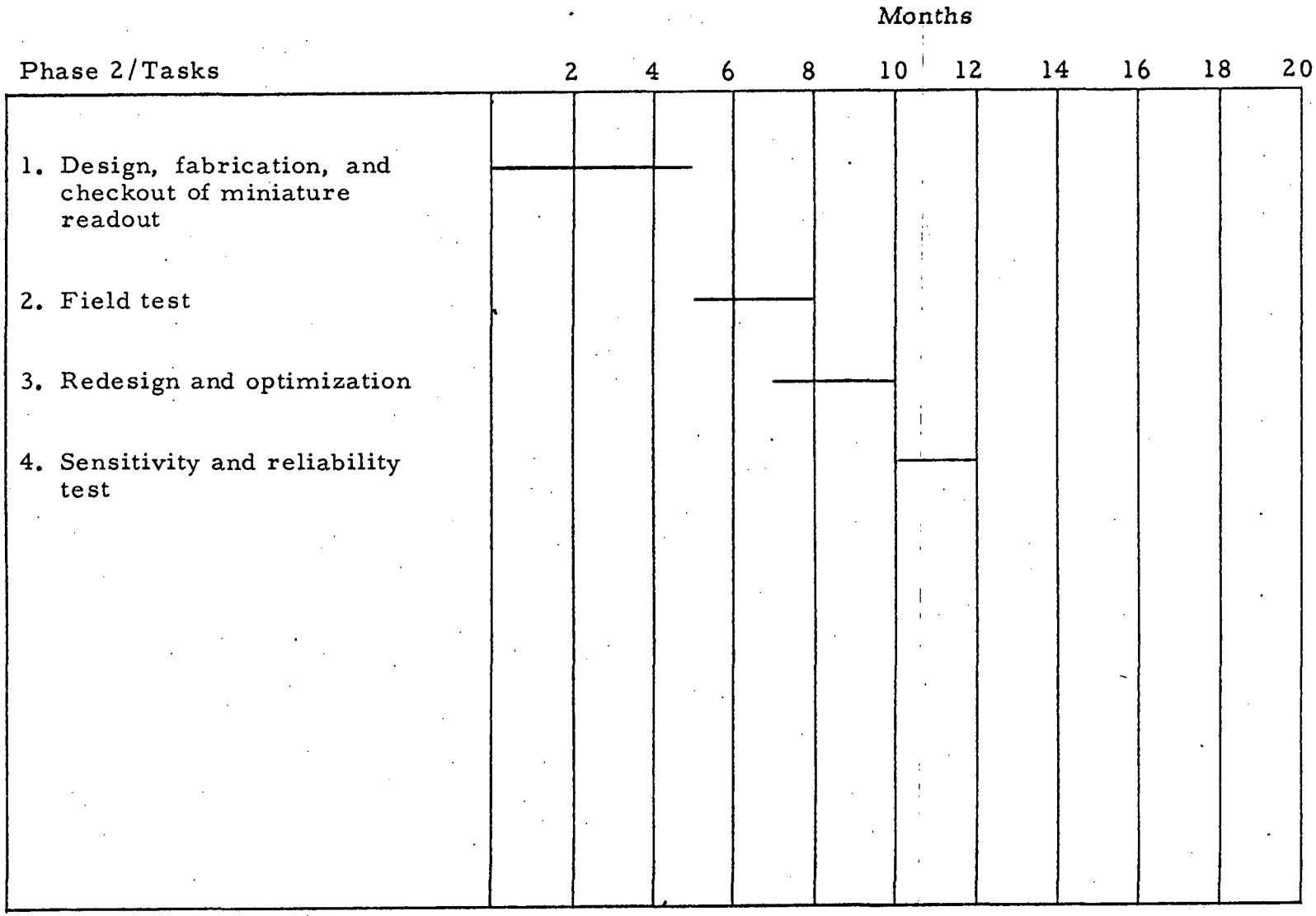
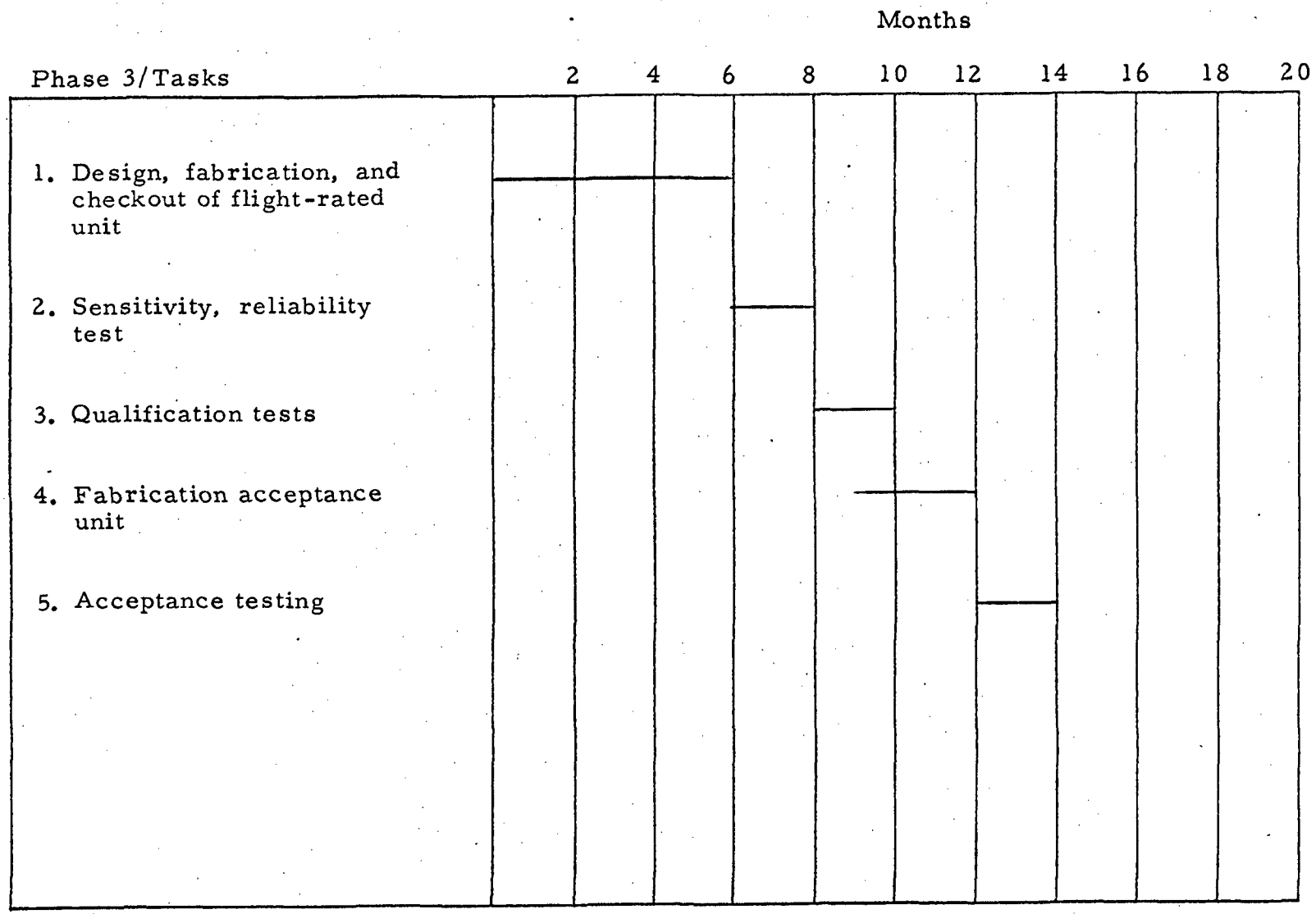


Figure 46

Program Schedule
pH Sensor



Hexavalent Chromium Sensor -

Phase 1 - 12 Months (Figure 47)

Objective: Design, fabrication and testing of reagent and sample handling subsystem. Major tasks to include:

1. Laboratory studies to demonstrate feasibility (wet-chemistry) of approach.
2. Design, fabrication and checkout of an automated subsystem.
3. Evaluation and testing, and redesign of subsystem for optimum performance.

Phase 2 - 13 Months (Figure 48)

Objective: Miniaturization of reagent subsystem and miniaturization of colorimeter. Tasks include:

1. Design, fabrication and checkout of miniaturized reagent and sample handling subsystem.
2. Design, fabrication and checkout of miniaturized colorimetric readout.
3. Sensitivity and reliability system testing.
4. Field test the system interfaced to a water recovery system.
5. Optimization of system design and retesting for sensitivity and reliability.

Phase 3 - 15 Months (Figure 49)

Objective: Testing of flight-rated units. Tasks include:

1. Design, fabrication and checkout of flight-rated prototype.
2. Sensitivity and reliability tests.
3. Qualification testing; shock, vibration and functional.
4. Fabrication of flight-rated units for acceptance tests.
5. Acceptance testing.

Figure 47

Program Schedule
Hexavalent Chromium Sensor

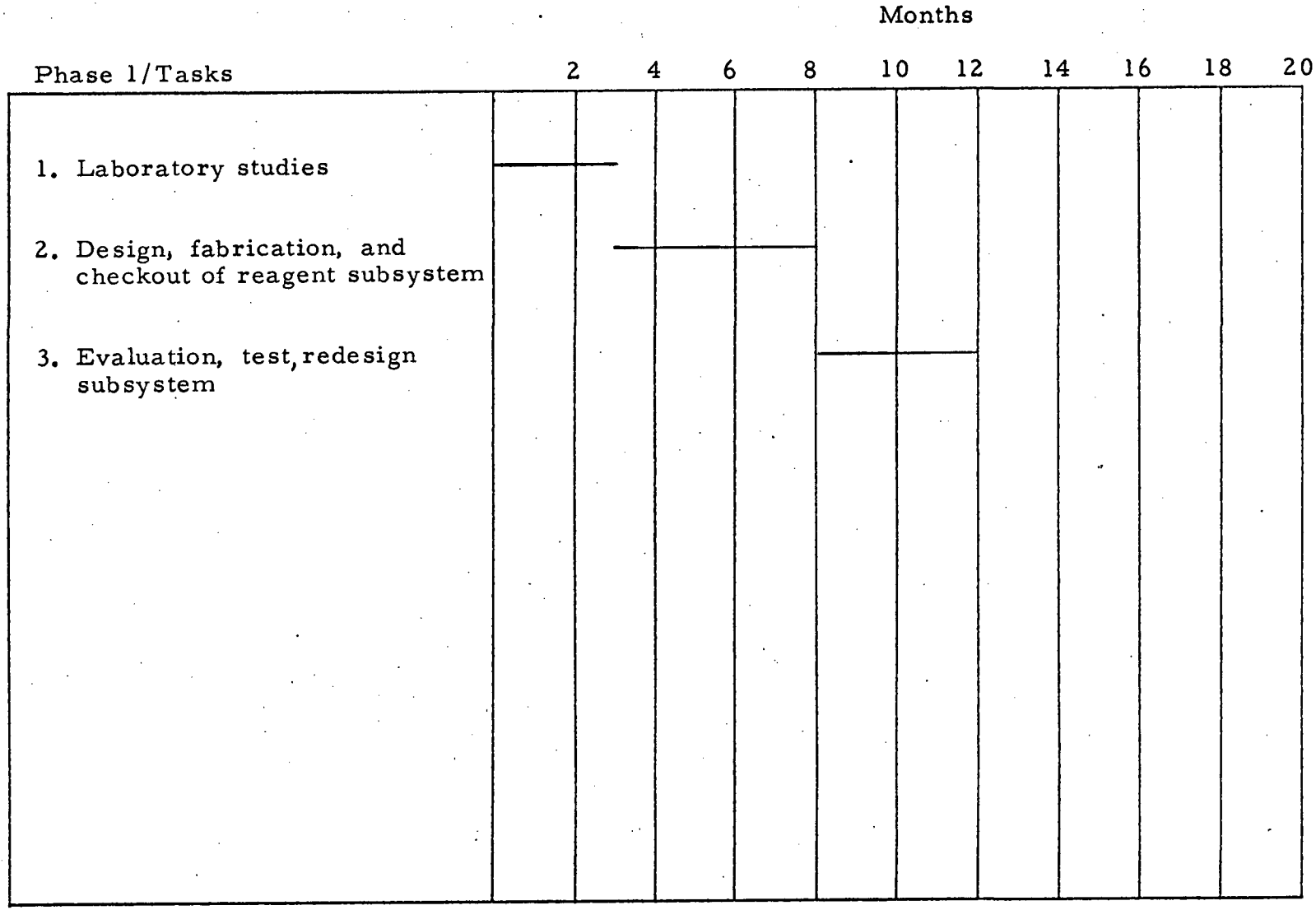


Figure 48

Program Schedule
Hexavalent Chromium Sensor

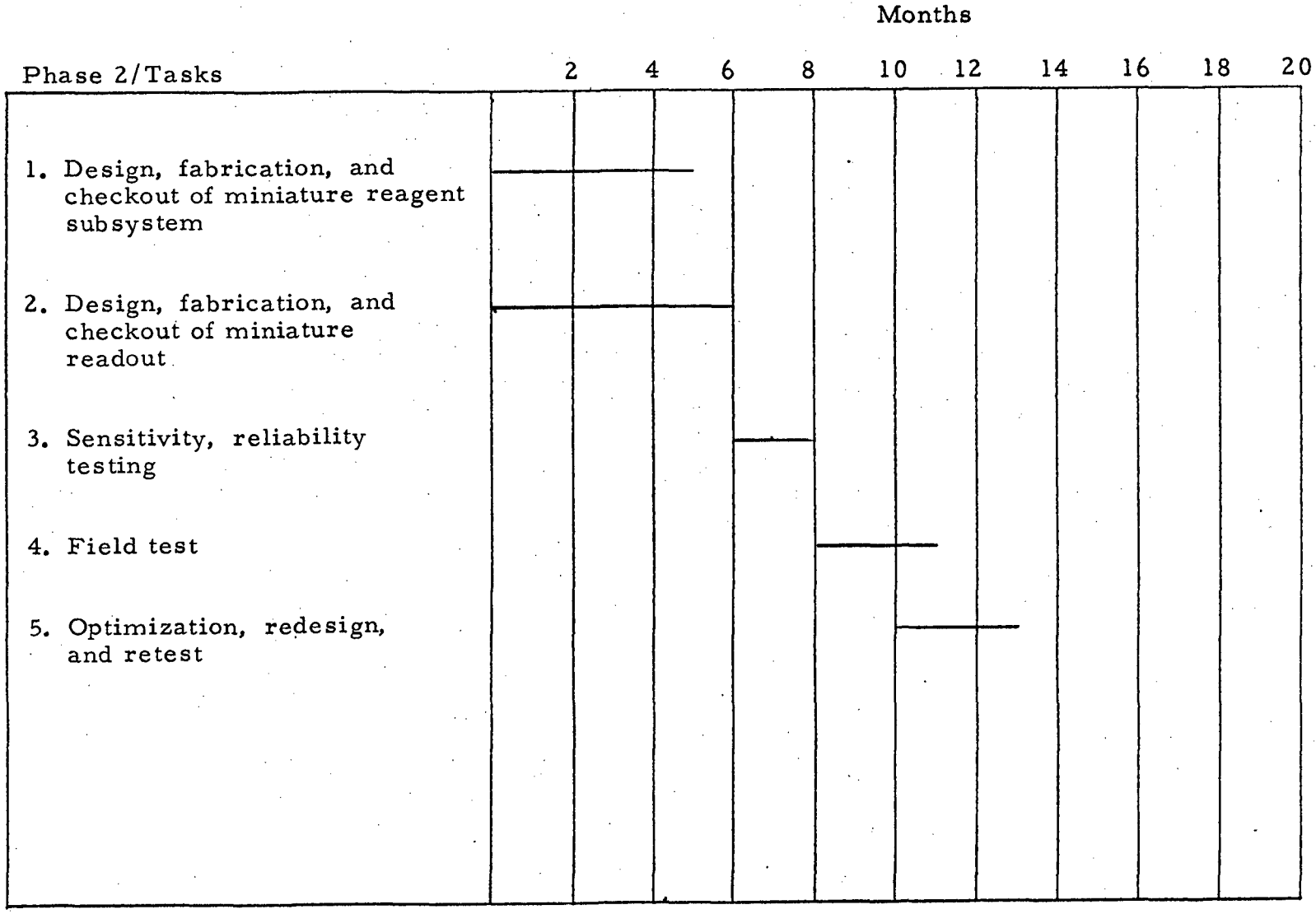
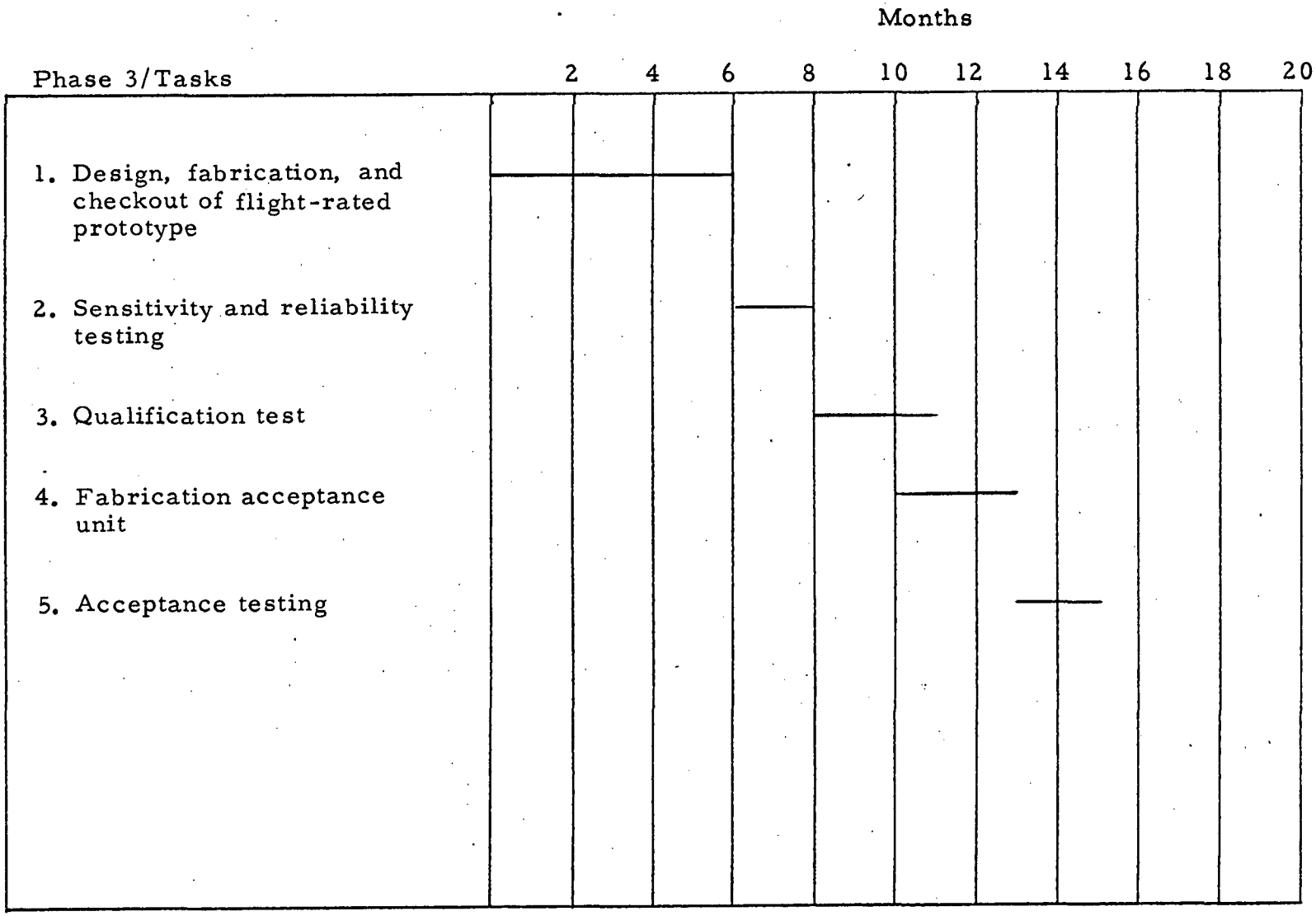


Figure 49

Program Schedule
Hexavalent Chromium Sensor



Iodine Sensor -

Phase 1 - 12 Months (Figure 50)

Objective: Design, fabrication and evaluation of sensing techniques and selection of best method. Tasks include:

1. Laboratory studies to evaluate colorimetric and amperometric approaches.
2. Design, fabrication and checkout of colorimetric sensor.
3. Design fabrication and checkout of amperometric sensor.
4. Comparative sensitivity testing and evaluation of sensors. Selection of one sensor method.

Phase 2 - 12 Months (Figure 51)

Objective: Miniaturization of sensor and field testing. Tasks include:

1. Design, fabrication and checkout of miniaturized sensor system.
2. Sensitivity and reliability testing.
3. Field testing of sensor.
4. Optimization of design and retesting for sensitivity.

Phase 3 - 15 Months (Figure 52)

Objective: Testing of flight-rated units. Tasks include:

1. Design, fabrication and checkout of flight-rated prototype.
2. Sensitivity and reliability tests.
3. Qualification testing; shock, vibration and other tests to achieve flight-rated status.
4. Fabrication of flight-rated units for acceptance tests.
5. Acceptance testing.

Figure 50

Program Schedule
Iodine Sensor

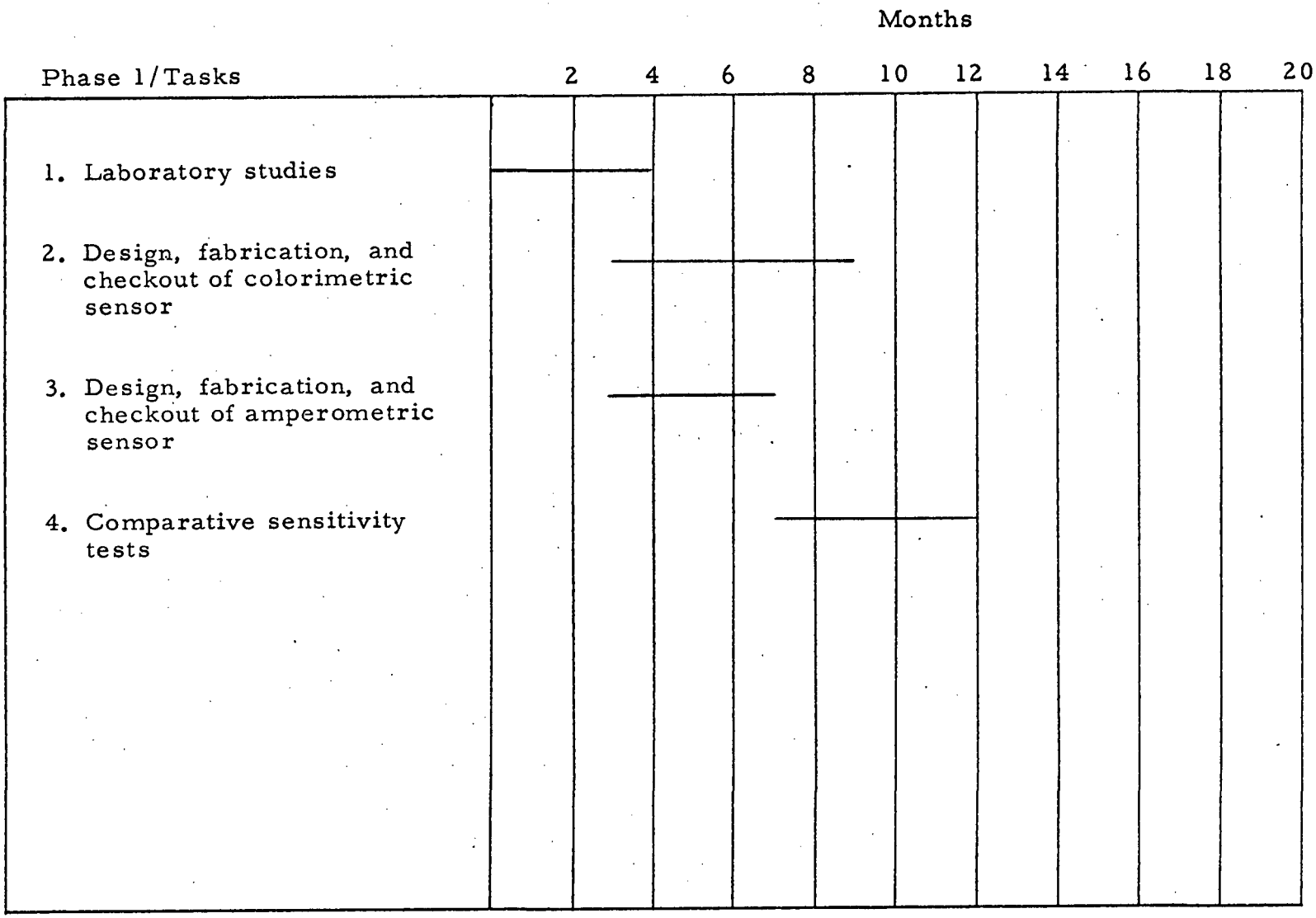


Figure 51

Program Schedule
Iodine Sensor

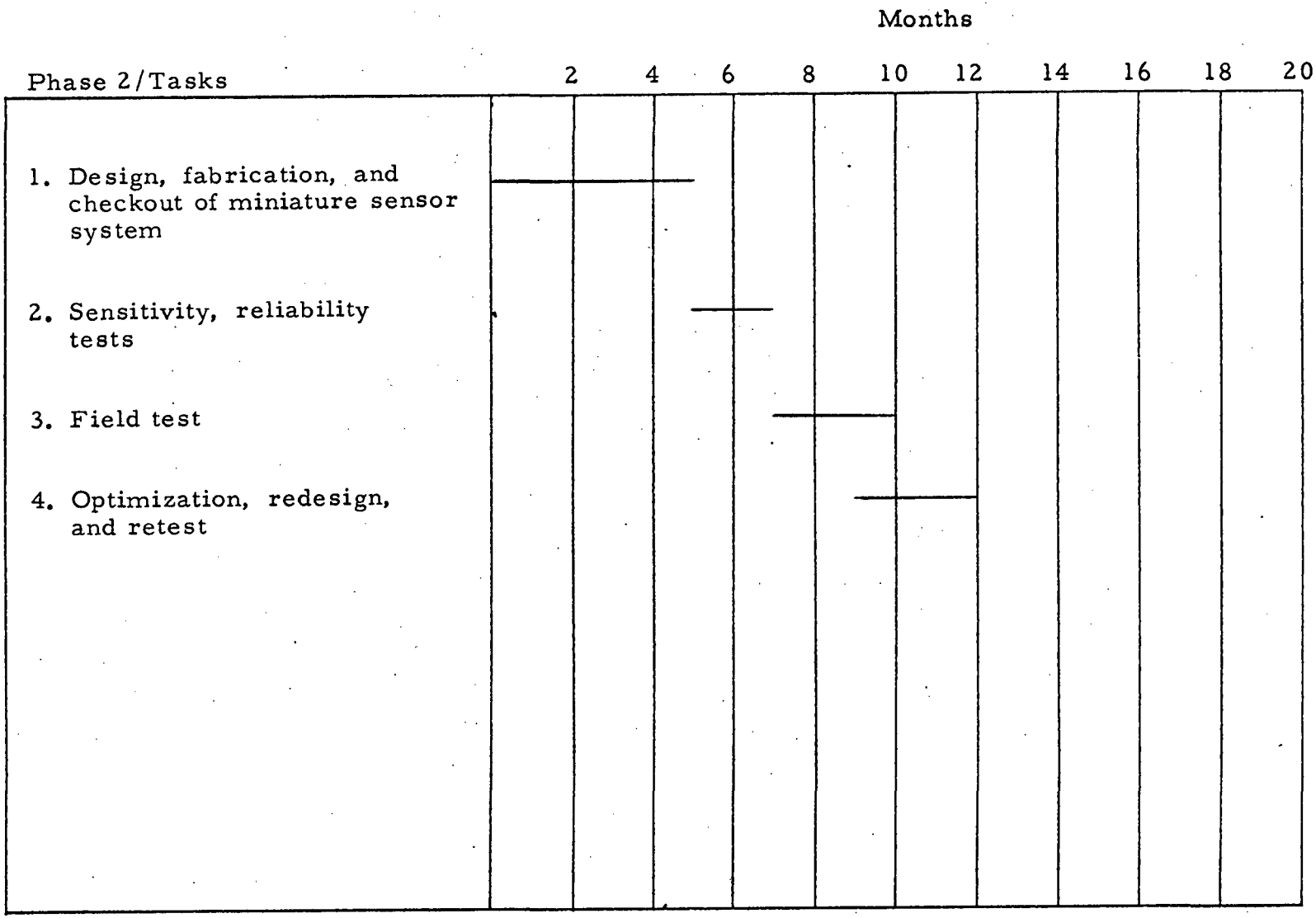
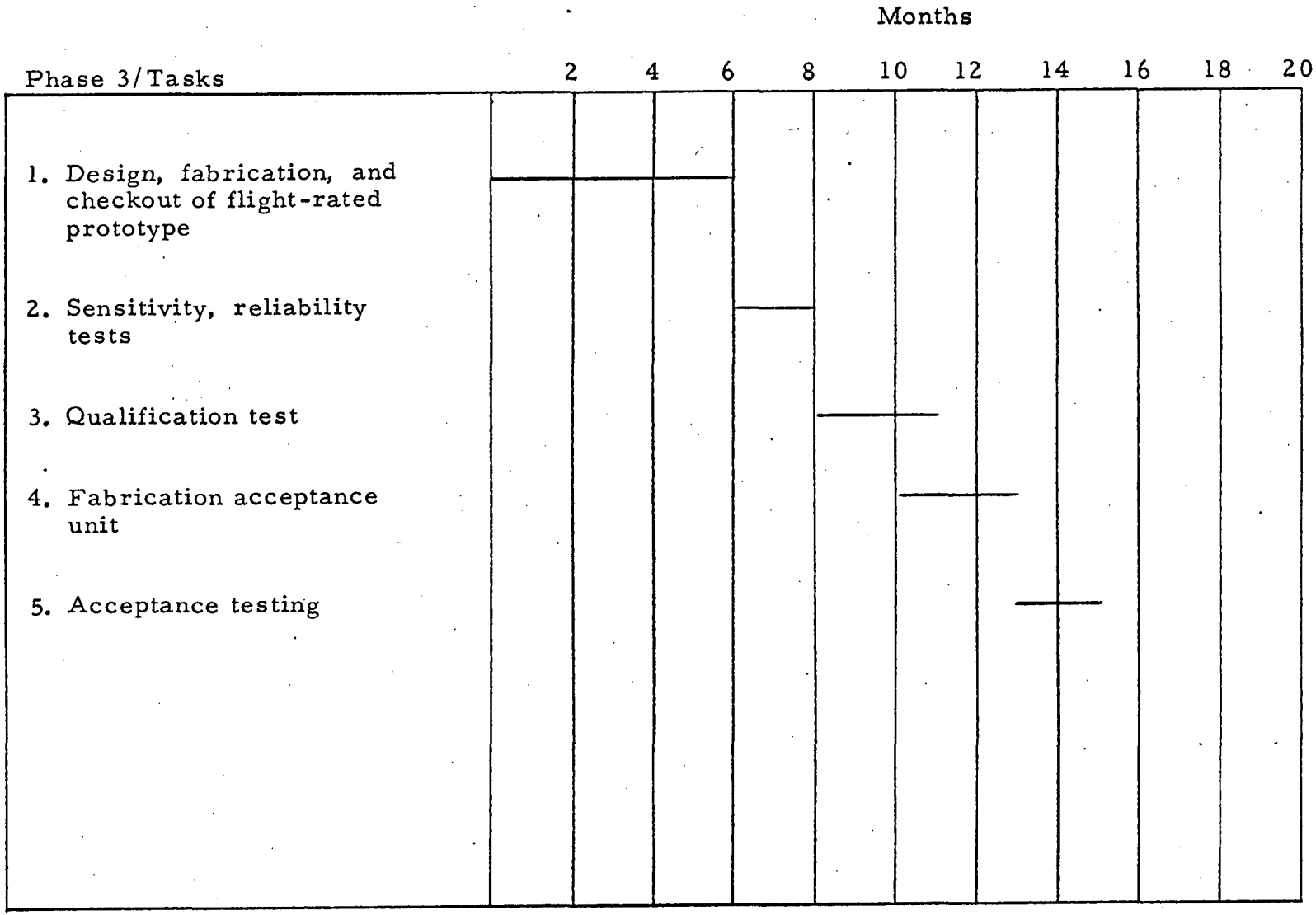


Figure 52

Program Schedule
Iodine Sensor



Carbon Sensor -

Phase 1 - 17 Months (Figure 53)

Objective: To develop a flight-rated combustion train suitable for determination of the organic carbon content of regenerated water. Tasks include:

1. Design and Fabrication

   Construct manually operated miniaturized combustion tubes (i.e., low weight, power and volume requirements) utilizing the Ardox combustion catalyst and the platinum spiral approach.

2. Evaluation

   a. Optimize reaction conditions (temperature, flow rates, etc.) for achieving maximum combustion efficiency of each of the systems (nondispersive IR used to monitor the CO_2).

   b. Evaluate the combustion efficiency of each of these systems toward water samples containing representative hydrocarbons (saturated hydrocarbons, alcohols, aldehydes, ketones, etc.). Extend the evaluation to hydrocarbons containing other elements besides C, H and O (i.e., N, P, and S). Evaluate the effect of interferents (i.e., Cl^-, NH_3 and $SO_4^=$) in the water on the combustion efficiency.

   c. Establish the usuable life of the respective catalysts (i.e., Pt wire vs. Ardox catalyst).

3. Automation and Integration

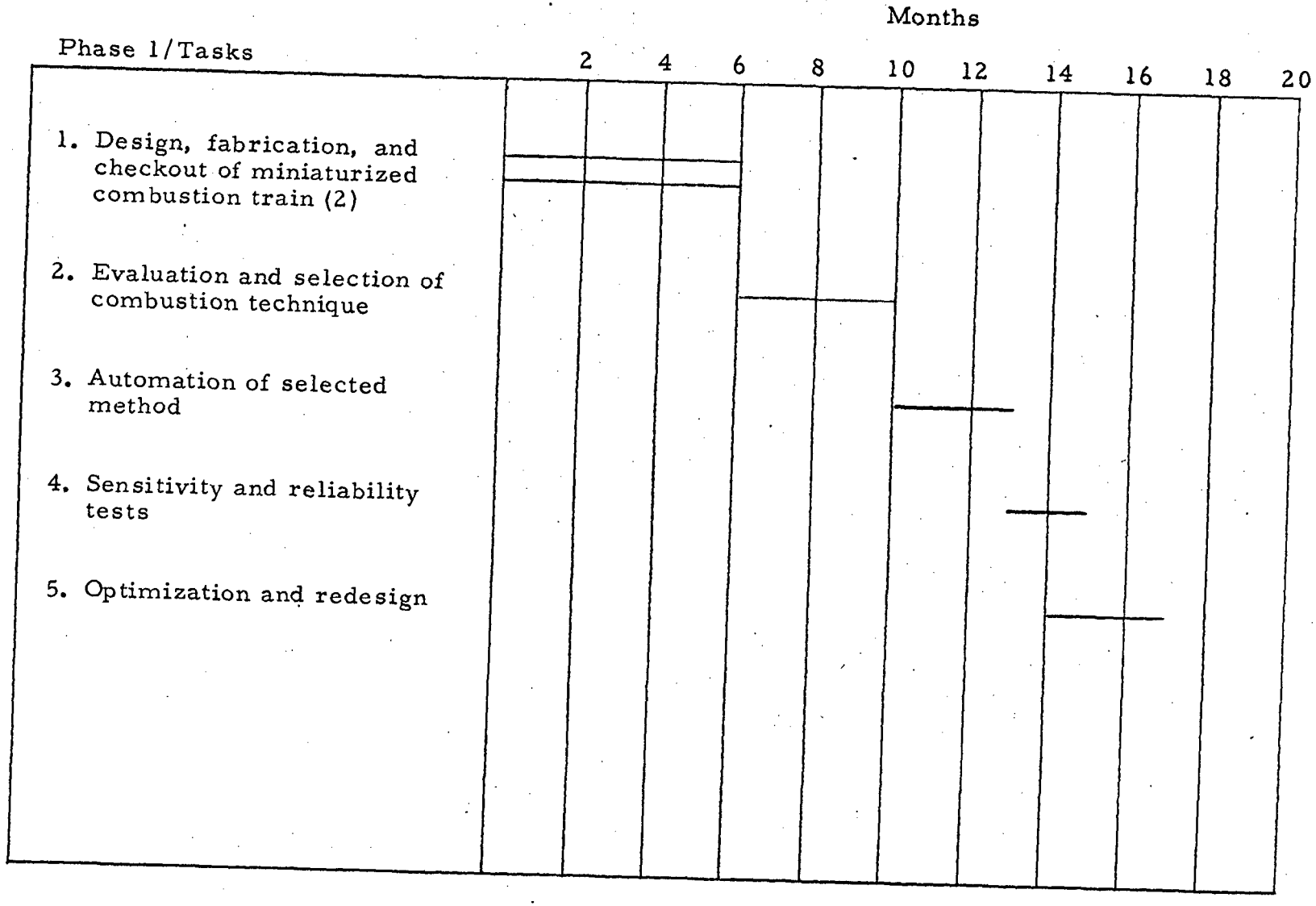
   The optimum method will be selected, automated and checked out.

4. Sensitivity and reliability tests.

5. Optimization and redesign of combustion train.

Figure 53

Program Schedule
Carbon Sensor



Phase 2 - 14 Months (Figure 54)

Objective: Design, fabrication and testing of miniaturized combustion train and detector. Tasks include:

1. Design, fabrication and checkout of miniaturized prototype combustion train.
2. Design, fabrication and checkout of miniaturized nondispersive infrared (CO_2) detector.
3. System sensitivity and reliability testing.
4. Field testing of system interfaced with water regeneration system.
5. System optimization and redesign.

Phase 3 - 15 Months (Figure 55)

Objective: Testing of flight-rated units. Tasks include:

1. Design, fabrication and checkout of flight-rated prototype sensor system.
2. Sensitivity and reliability tests.
3. Qualification tests; shock, vibration and other tests to achieve flight-rated status.
4. Fabrication of acceptance test unit.
5. Acceptance testing.

Figure 54

Program Schedule
Carbon Sensor

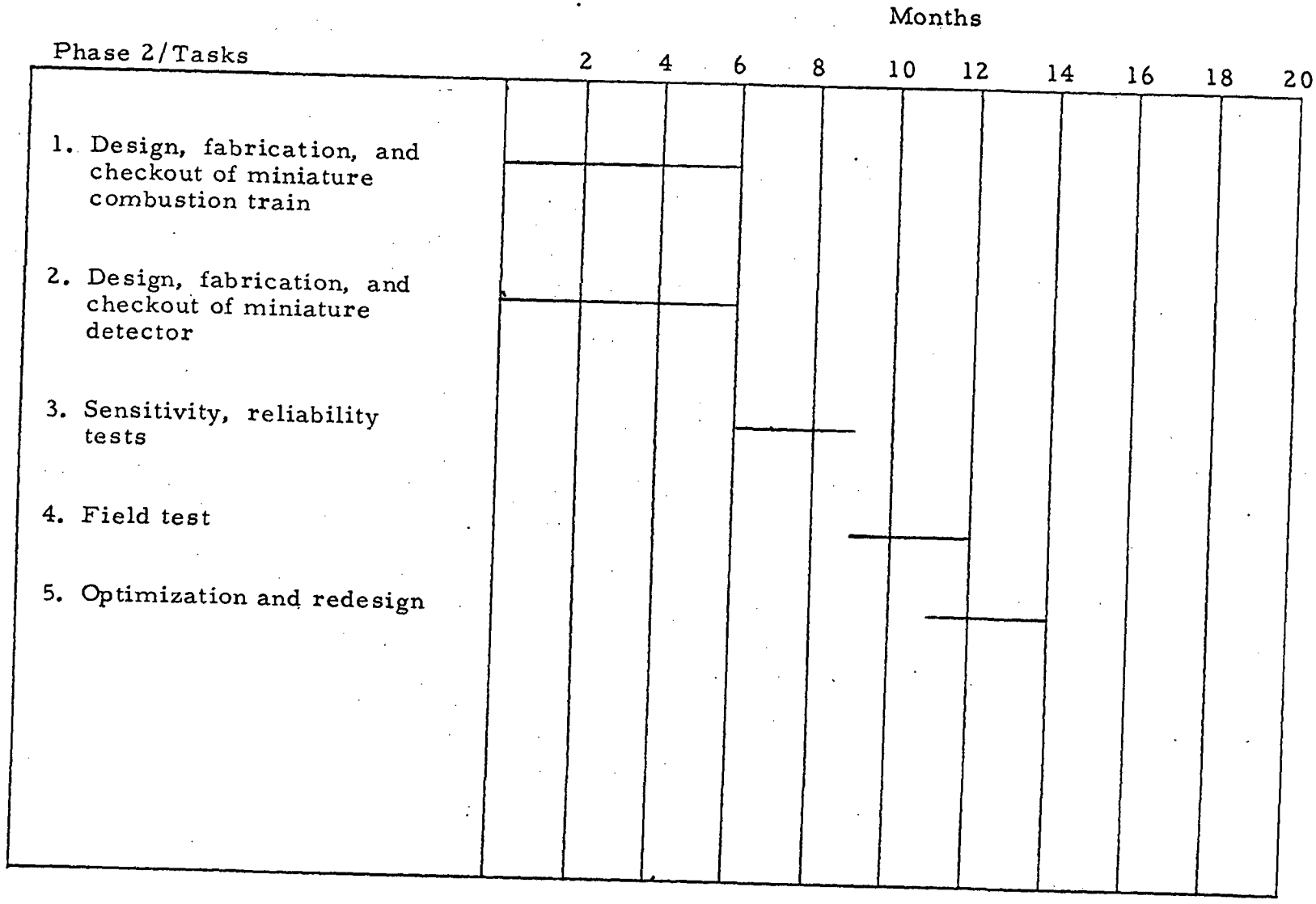
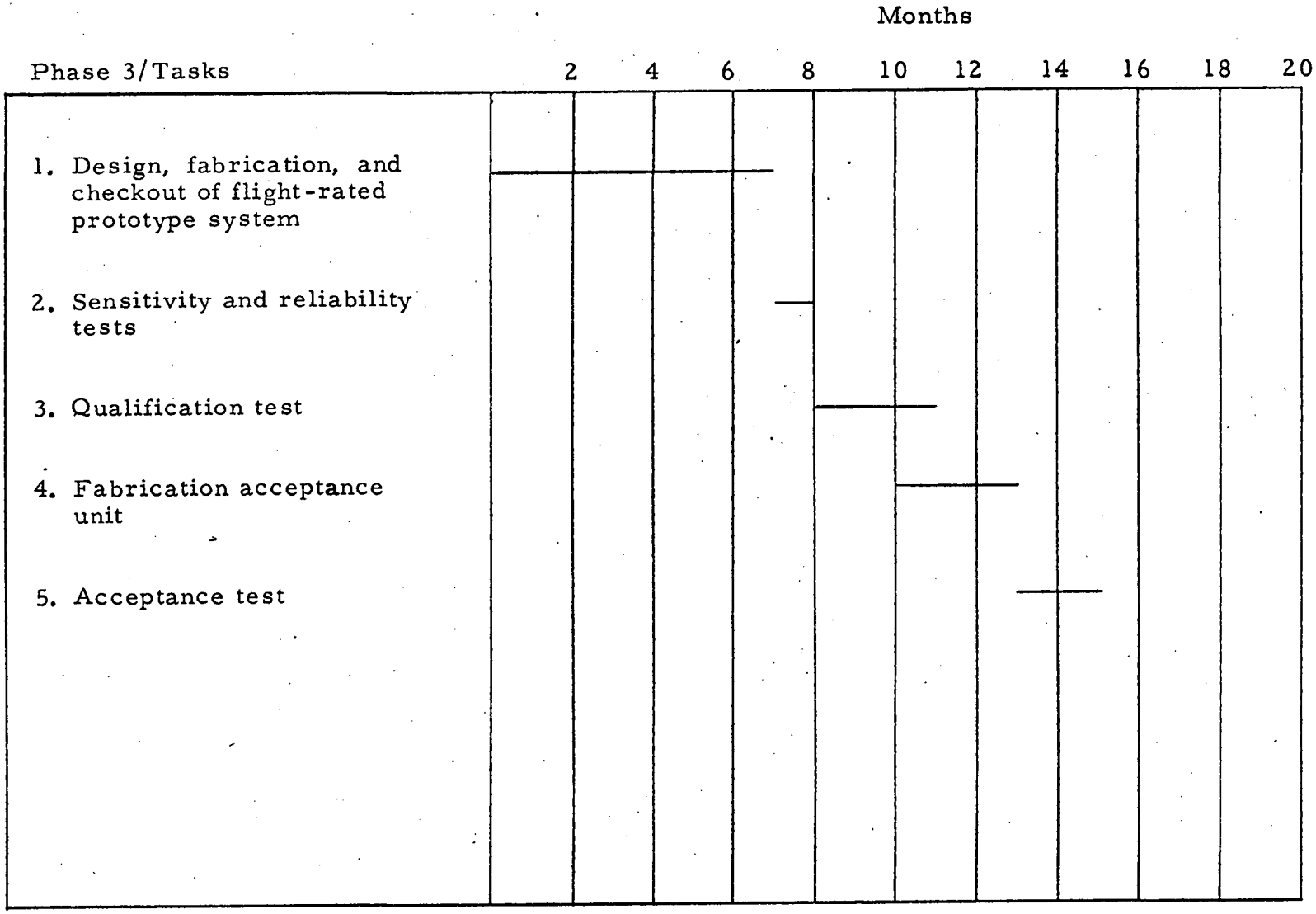


Figure 55

Program Schedule
Carbon Sensor



Cassette Chemiluminescence Bacterial Sensor -

Phase 1 - Present Program (Contract NAS 9-12548) - 12 Months (Fig. 56)

Objective: To modify the reagent subsystem of the sensor developed on Contract NAS 9-12548, for Zero-g compatibility. Also, to redesign the capsule conveyor and perform additional sensitivity testing.

Phase 2 - 13 Months (Figure 57)

Objective: Design, fabrication and checkout of a miniaturized and modularized flight-rated prototype. Tasks include:

1. Design, fabrication and checkout of a miniaturized and modularized flight-rated prototype.
2. Sensitivity and reliability testing.
3. Reagent and component replacement package design and fabrication. Reagent life studies.
4. Field testing of sensor interfaced with water regeneration system.

Phase 3 - 16 Months (Figure 58)

Objective: Testing of flight-rated units. Tasks include:

1. Design, fabrication and checkout of a flight-rated prototype.
2. Sensitivity and reliability tests.
3. Qualification tests; shock, vibration and other tests to achieve flight-rated status.
4. Fabrication of flight-rated units for acceptance testing.
5. Acceptance testing.

Figure 56

Program Schedule
Cassette Chemiluminescence Bacterial Sensor

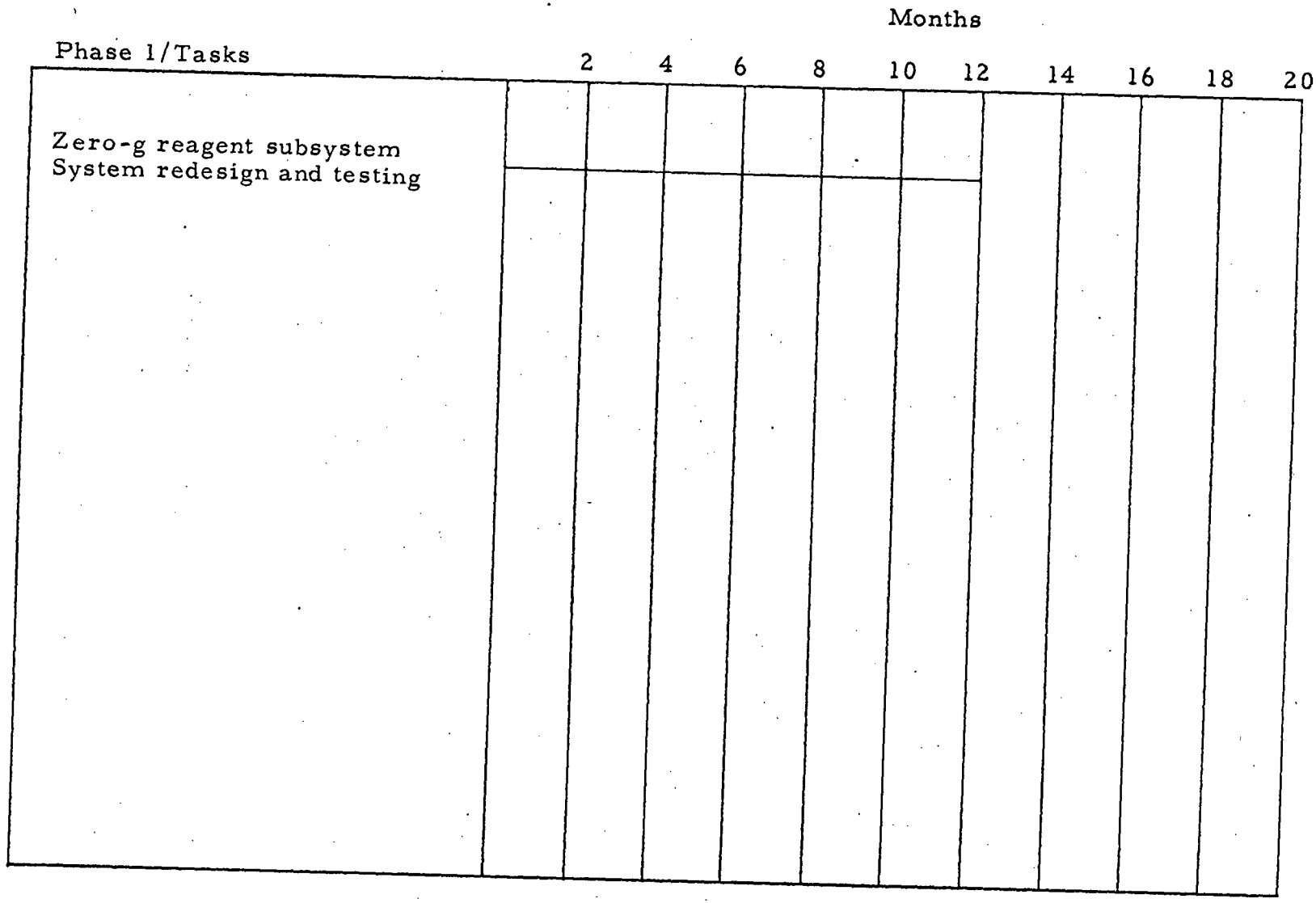


Figure 57

Program Schedule
Cassette Chemiluminescence Bacterial Sensor

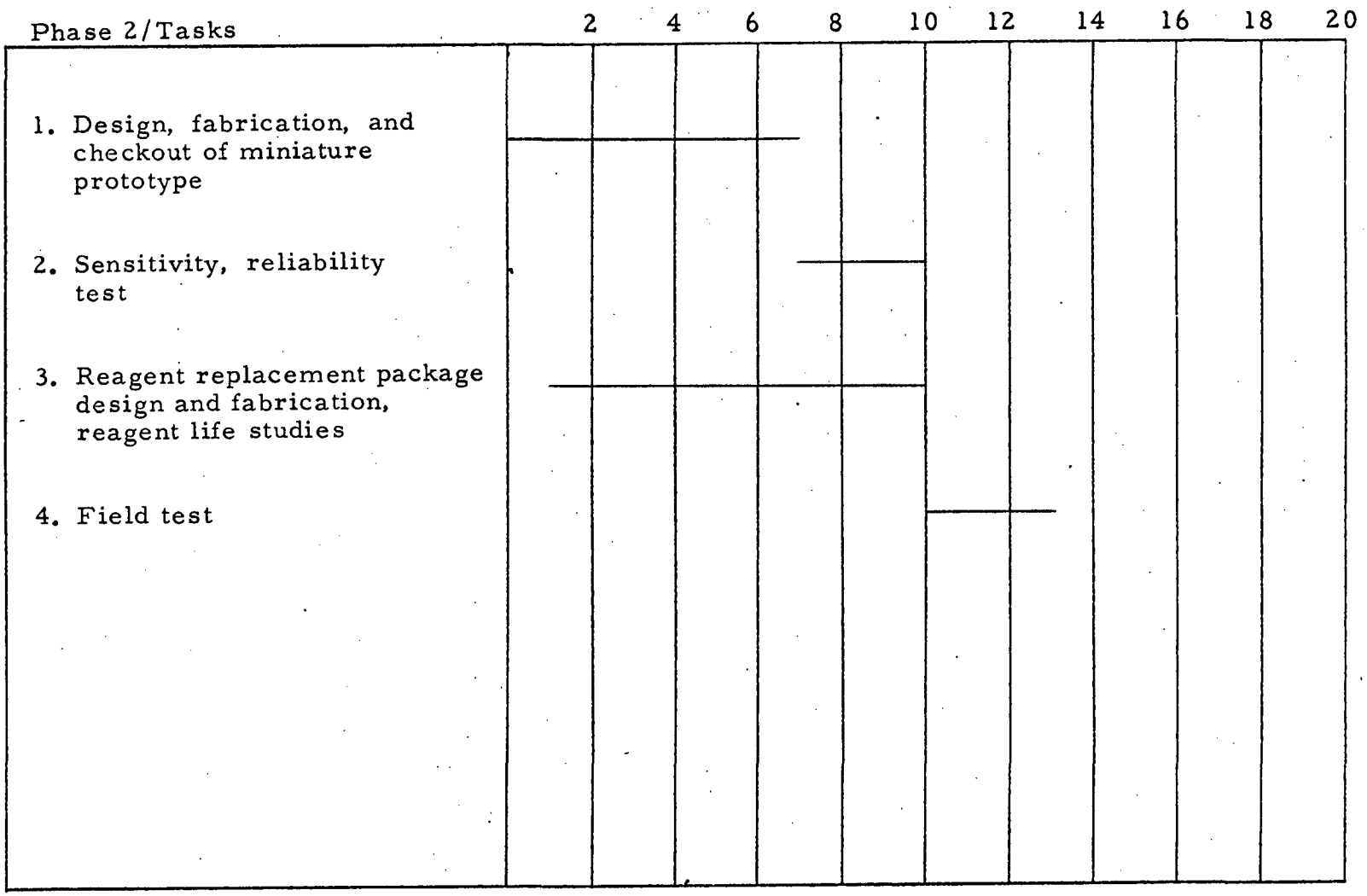
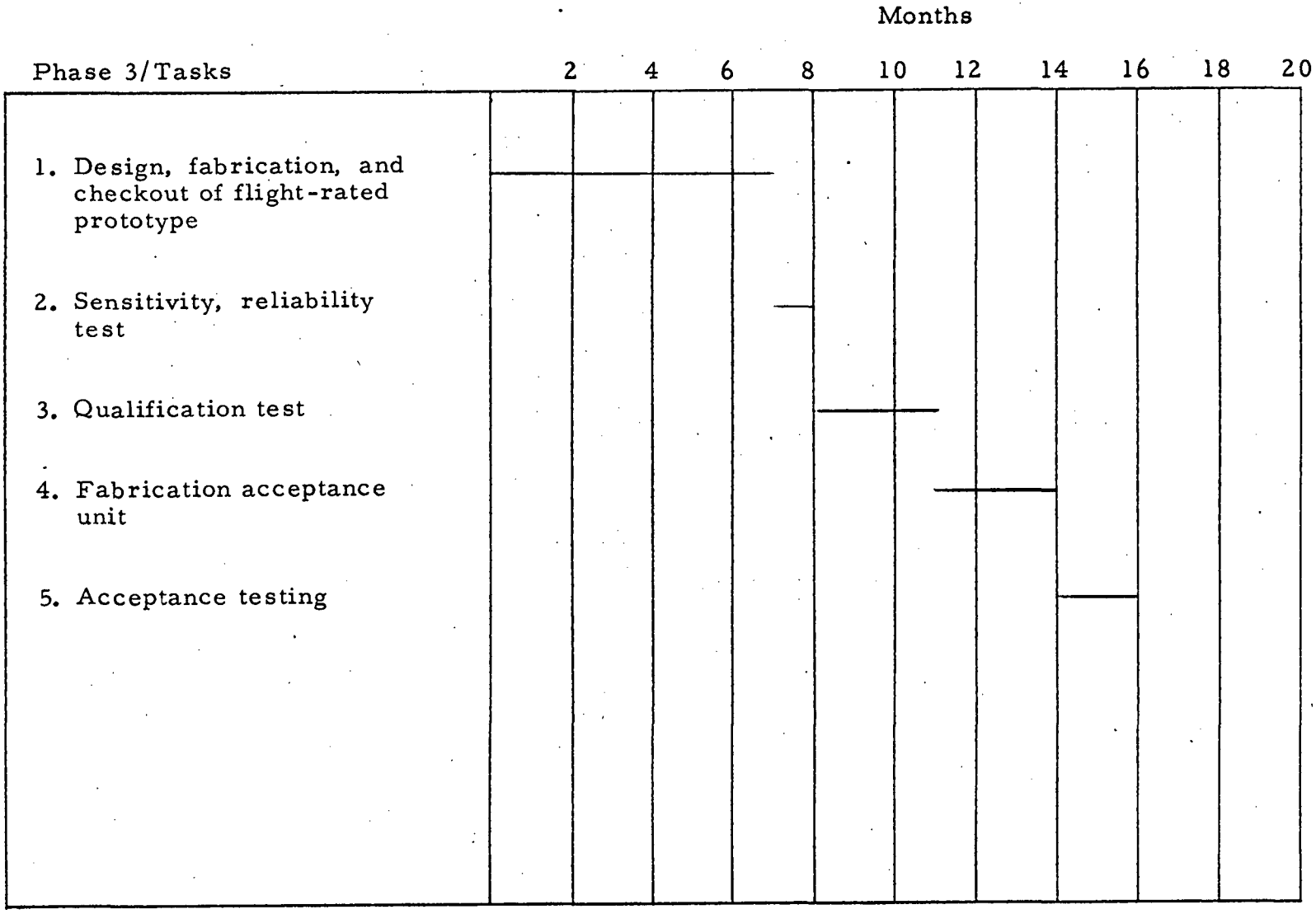


Figure 58

Program Schedule
Cassette Chemiluminescence Bacterial Sensor



APPENDIX

Biosensor Test Data Calculation of Average Value and Standard Deviation

BIOSENSOR SIGNAL RESPONSE TO E. coli

CONDITIONS:

Sample Size: 10 ml

Sample Flowrate: 17 ml/min.

Run No.	Date	Challenge Level (Cells/ml)	Total Challenge (Cells)	Net Chemiluminescense Signal (volts)*
3	4-29-71	1×10^5	1×10^6	24.5
3	"	1×10^5	1×10^6	25.5
4	"	1×10^5	1×10^6	24.5
4	"	1×10^5	1×10^6	25.5
				$\bar{X} = 25.0$
				$S = \pm .6$

*Values corrected for water blanks (rounded to nearest 1/2 volt).

BIOSENSOR SIGNAL RESPONSE TO E. coli

CONDITIONS:

Sample Size: 10 ml

Sample Flowrate: 17 ml/min.

Run No.	Date	Challenge Level (Cells/ml)	Total Challenge (Cells)	Net Chemiluminescense Signal (volts)*
7	4-30-71	1×10^4	1×10^5	11.5
7	"	1×10^4	1×10^5	15.0
8	"	1×10^4	1×10^5	11.5
8	"	1×10^4	1×10^5	12.5
11	5-1-71	1×10^4	1×10^5	15.5
11	"	1×10^4	1×10^5	19.0
12	"	1×10^4	1×10^5	16.5
12	"	1×10^4	1×10^5	19.5
				$\bar{X} = 15.1$
				$S = \pm 3.2$

*Values corrected for water blanks (rounded to nearest 1/2 volt).

BIOSENSOR SIGNAL RESPONSE TO E. coli

CONDITIONS:

Sample Size: 100 ml

Sample Flowrate: 17 ml/min.

Run No.	Date	Challenge Level (Cells/ml)	Total Challenge (Cells)	Net Chemiluminescense Signal (volts)*
15	5-1-71	1×10^3	1×10^5	17.0
15	"	1×10^3	1×10^5	18.0
				$\bar{X} =$ 17.5
				$S = \pm$ .7

*Values corrected for water blanks (rounded to nearest 1/2 volt).

BIOSENSOR SIGNAL RESPONSE TO E. coli

CONDITIONS:

Sample Size: 400 ml

Sample Flowrate: 17 ml/min.

Run No.	Date	Challenge Level (Cells/ml)	Total Challenge (Cells)	Net Chemiluminescense Signal (volts)*
17	5-1-71	2.5×10^2	1×10^5	15.5
17	"	2.5×10^2	1×10^5	18.0
				$\bar{X}$ = 16.8
				S = ± 1.8

*Values corrected for water blanks (rounded to nearest 1/2 volt).

BIOSENSOR SIGNAL RESPONSE TO E. coli

CONDITIONS:

Sample Size: 400 ml

Sample Flowrate: 10 ml/min.

Run No.	Date	Challenge Level (Cells/ml)	Total Challenge (Cells)	Net Chemiluminescense Signal (volts)*
19	5-4-71	2.5×10^2	1×10^5	17.5
19	"	2.5×10^2	1×10^5	18.0
				$\bar{X}$ = 17.8
				S = ± .4

*Values corrected for water blanks (rounded to nearest 1/2 volt).

BIOSENSOR SIGNAL RESPONSE TO E. coli

CONDITIONS:

Sample Size: 400 ml

Sample Flowrate: 17 ml/min.

Run No.	Date	Challenge Level (Cells/ml)	Total Challenge (Cells)	Net Chemiluminescense Signal (volts)*
59	2-25-72	75	3×10^4	16.8
59	"	75	3×10^4	15.8
				$\bar{X} = 16.1$
				$S = \pm .4$

*Values corrected for water blanks (rounded to nearest 1/2 volt).

BIOSENSOR SIGNAL RESPONSE TO E. coli

CONDITIONS:

Sample Size: 400 ml

Sample Flowrate: 17 ml/min.

Run No.	Date	Challenge Level (Cells/ml)	Total Challenge (Cells)	Net Chemiluminescense Signal (volts)*
23	5-5-71	50	2×10^4	10.5
23	"	50	2×10^4	9.0
25	"	50	2×10^4	11.0
25	"	50	2×10^4	13.0
35	5-19-71	50	2×10^4	7.5
35	"	50	2×10^4	8.0
				$\bar{X} = 9.8$
				$S = \pm 2.1$

*Values corrected for water blanks (rounded to nearest 1/2 volt).

BIOSENSOR SIGNAL RESPONSE TO E. coli

CONDITIONS:

	6-3-71	5-5-71
Sample Size:	364 ml	350 ml

Sample Flowrate: 15.5 and 14.6 ml/min.

Run No.	Date	Challenge Level (Cells/ml)	Total Challenge (Cells)	Net Chemiluminescense Signal (volts)*
37	6-3-71	50	1.8×10^4	10.0
37	"	50	1.8×10^4	8.0
21	5-5-71	50	1.75×10^4	4.5
21	"	50	1.75×10^4	5.0
				$\bar{X}$ = 6.9
				S = ± 2.6

*Values corrected for water blanks (rounded to nearest 1/2 volt).

BIOSENSOR SIGNAL RESPONSE TO E. coli

CONDITIONS:

Sample Size: 400 ml

Sample Flowrate: 17 ml/min.

Run No.	Date	Challenge Level (Cells/ml)	Total Challenge (Cells)	Net Chemiluminescense Signal (volts)*
47	6-17-71	20	8×10^3	1.5
47	"	20	8×10^3	2.0
49	6-18-71	20	7.7×10^3	6.5
49	"	20	7.7×10^3	4.5
50	"	20	7.7×10^3	5.5
50	"	20	7.7×10^3	5.5
39	"	20	8×10^3	2.0
39	"	20	8×10^3	3.5
40	6-4-71	20	8×10^3	2.0
40	"	20	8×10^3	3.0
41	"	20	8×10^3	2.5
41	"	20	8×10^3	2.5
				$\bar{X} = 3.4$
				$S = \pm 1.7$

*Values corrected for water blanks (rounded to nearest 1/2 volt).

BIOSENSOR SIGNAL RESPONSE TO E. coli

CONDITIONS:

Sample Size: 400 ml

Sample Flowrate: 17 ml/min.

Run No.	Date	Challenge Level (Cells/ml)	Total Challenge (Cells)	Net Chemiluminescense Signal (volts)*
43	6-10-71	10	3.7×10^3	1.5
43	"	10	3.7×10^3	1.0
52	6-18-71	10	3.8×10^3	2.5
52	"	10	3.8×10^3	1.5
54	"	10	3.8×10^3	2.5
54	"	10	3.8×10^3	2.0
55	6-21-71	10	3.8×10^3	2.5
55	"	10	3.8×10^3	1.5
57	"	10	3.8×10^3	1.5
57	"	10	3.8×10^3	2.0
				$\bar{X} =$ 1.8
				$S = \pm$ .6

*Values corrected for water blanks (rounded to nearest 1/2 volt).

BIOSENSOR SIGNAL RESPONSE TO E. coli

CONDITIONS:

Sample Size: 400 ml

Sample Flowrate: 17 ml/min.

Run No.	Date	Challenge Level (Cells/ml)	Total Challenge (Cells)	Net Chemiluminescense Signal (volts)*
62	3-1-72	10	4×10^3	4.5
62	"	10	4×10^3	3.5
73	3-6-72	10	4×10^3	5.0
75	"	10	4×10^3	4.0
84	3-16-72	10	4×10^3	5.5
84	"	10	4×10^3	5.5
84	"	10	4×10^3	2.0
85	"	10	4×10^3	6.5
85	"	10	4×10^3	6.0
85	"	10	4×10^3	2.5
94	3-24-72	10	4×10^3	7.5
94	"	10	4×10^3	1.5
100	3-30-72	10	4×10^3	7.5
100	"	10	4×10^3	2.5
101	"	10	4×10^3	7.5
101	"	10	4×10^3	2.0
102	"	10	4×10^3	5.5
102	"	10	4×10^3	1.0
105	4-11-72	10	3.7×10^3	7.0
105	"	10	3.7×10^3	8.0
107	4-12-72	10	3.7×10^3	4.0
106	"	10	3.5×10^3	2.5
			$\bar{X}$ =	4.6
			S = $\pm$	2.1

*Values corrected for water blanks (rounded to nearest 1/2 volt).

BIOSENSOR SIGNAL RESPONSE TO E. coli

CONDITIONS:

Sample Size: 400 ml
Sample Flowrate: 17 ml/min.
Sample Incubated: 120 min.

Run No.	Date	Challenge Level (Cells/ml)	Total Challenge (Cells)		Net Chemiluminescense Signal (volts)*
84	3-16-72	10	4×10^3	Tube inc.	11.5
85	"	10	4×10^3	" "	9.5
107	4-12-72	10	4×10^3	Coil inc.	16.0
				$\bar{X}$ =	12.3
				S = ±	3.3

*Values corrected for water blanks (rounded to nearest 1/2 volt).