U.S. Department of Commerce
National Technical Information Service

N74 29769

PRELIMINARY FLIGHT PROTOTYPE SILVER ION MONITORING SYSTEM

BECKMAN INSTRUMENTS, INC.
ANAHEIM, CA

JUN 74

2(mix)

FR-2656-101

DRL No. T868
Line Item No. 4
DRD MA-183T
Contract No. NAS9-1338
NASA CR-13436

FINAL REPORT

PRELIMINARY FLIGHT PROTOTYPE SILVER ION MONITORING SYSTEM

(NASA-CR-134361) PRELIMINARY FLIGHT PROTOTYPE SILVER ION MONITORING SYSTEM Final Report (Beckman Instruments, Inc., Anaheim, Calif.) 214 p HC $13.75
N74-29769
CSCL 14B G3/14
Unclas
44761

June, 1974

Prepared for:

National Aeronautics and Space Administration
Johnson Spacecraft Center
Houston, Texas 77058

Beckman® INSTRUMENTS, INC.
ADVANCED TECHNOLOGY OPERATIONS
ANAHEIM, CALIFORNIA 92806

1

FR-2656-101

DRL No. T868
Line Item No. 4
DRD MA-183T
Contract No. NAS9-13387

FINAL REPORT

PRELIMINARY FLIGHT PROTOTYPE SILVER ION MONITORING SYSTEM

June, 1974

Prepared by: J. Brady 6-28-74
Program Engineer Date

Approved by: J M Welch 6-28-74
Program Manager Date

Approved by: J Morgan 6-28-74
Contracts Administration Date

Approved by: ______ ______
Date

Approved by: ______ ______
Date

1a

ABSTRACT

This report describes the design, fabrication, and testing of a preliminary flight prototype silver ion monitoring system developed under Contract NAS9-13387. The monitoring system is based on potentiometric principles and utilizes a solid-state silver sulfide electrode paired with a pressurized double-junction reference electrode housing a replaceable electrolyte reservoir. The design provides automatic electronic calibration utilizing saturated silver bromide solution as a silver ion standard.

This report describes the design and fabrication of the system, the problem of loss of silver ion from recirculating fluid, its cause, and corrective procedures. The instability of the silver sulfide electrode is discussed as well as difficulties met in implementing the autocalibration procedure.

CONTENTS

PARAGRAPH PAGE

CONTENTS (Continued)

PARAGRAPH PAGE

CONTENTS (Continued)

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (Continued)

LIST OF TABLES

1.0 SUMMARY

Under contract NAS9-13387 Beckman Instruments was to design, fabricate and perform verification tests on a Preliminary Flight Prototype Silver Ion Monitoring system with zero-gravity capability.

The program was divided into five tasks:

- Preliminary Flight Prototype Design
- Fabrication of Preliminary Flight Prototype
- Design Verification Testing
- Delivery of Preliminary Flight Prototype
- Data and Program Management.

For the purpose of efficiency, the design and fabrication efforts were divided between a fluid handling unit and an electronics unit. The fluid handling unit contained the sensor chamber and electrodes, pump/motor, components of the calibration loop such as ion exchange and silver bromide columns as well as solenoid valves and necessary connecting tubing and miscellaneous hardware.

The electronics unit consisted of the preamplifiers, amplifiers, readout circuit and meter, timing circuit and digital calibration loop for automatic calibration as well as thermocompensating circuits plus power supply and actuators for the solenoid valves.

The design of the fluid handling unit provided for two operating modes:

1. A monitoring mode in which a portion of the water in the potable water system, upstream of the heaters and chillers, would be routed into the silver ion monitor and pumped through a sensor chamber, at a constant rate, where a pair of potentiometric electrodes would contact the solution and measure the concentration of the silver

ion. The measuring electrode was a silver sulfide ion-selective electrode while the reference was a very low flowing pressurized double-junction reference having a replaceable rolling diaphragm electrolyte reservoir. The signal generated by the electrode pair would be processed and the silver ion concentration presented on a two-inch diameter meter. Temperature compensation for electrode thermal characteristics would be provided.

2. A calibration mode was provided in which a pair of solenoid valves actuated by the electronics closed and formed a closed "calibration" loop consisting of the sensor chamber, pump/motor, solenoid valves, ion exchange column and silver bromide column. The basis for the calibration was that water would be pumped through the ion exchange column where all anions and cations would be removed. The water would then pass through the silver bromide column where it would become saturated with silver ions and bromide ions. Since the saturation of the water with silver bromide is a function of the temperature, a "known" concentration would be produced which would be pumped through the sensor chamber where the concentration would be sensed by the electrode pair.

   The electronics unit would process the signal(s) from the electrodes and during the calibration mode would compare the electrode signal with a known signal and automatically adjust the readout accordingly.

   The electronics unit would contain the timer and sequencer as well as solenoid valve drivers which would automatically put the system in the calibration mode once every twenty-four hours. The electronics would also contain the power supply for the monitoring system.

The detailed design phase also included a Failure Mode and Effect Analysis (FMEA).

In general, the design and fabrication of the Preliminary Flight Prototype Silver Ion Monitor System followed the Instrument Package Definition of the previous contract, NAS9-12733. However, several changes were made to reduce significantly size and/or weight and increase reliability. Readily available off-the-shelf hardware was used for the fluid handling unit, with the exception of the sensor chamber and columns, for the purpose of cost reduction.

Also, the electronic unit utilized off-the-shelf components and circuit boards so that the program was not burdened with flight configuration electronic packaging.

The total Preliminary Flight Prototype Silver Ion Monitor System with a preliminary case measures 35.56 centimeters (14 in.) wide, 40.6 centimetrs (16 in.) high, and 22.2 centimeters (8.75 in.) deep and weighs 8.734 kilograms (19.2 lbs).

Preliminary testing of the fluid handling unit revealed a very rapid loss of silver ion during recirculation of 50 and 500 ppb silver ion solutions. The loss of silver ions was not observed with a single pass of silver ion solution.

Radioisotope tests revealed that the silver was being adsorbed on the surfaces of the system, in particular, the surface of the 316 stainless steel. A subsequent radioisotope test showed that the lower the fluid to metal surface ratio the faster the silver was adsorbed. Also, static vs. agitated tests showed that agitated or stirred tests revealed more rapid adsorption than static tests.

Replacement of as much stainless steel as feasible with non-metallics, e.g., Teflon, nylon, produced a reduction in the rate of depletion and an improvement of 12.5 to 1 in the rate of depletion.

Concurrently with the loss of silver ion from solution, loss of sensitivity or degradation of the silver sulfide electrode was observed during recirculation tests, but not when the silver ion solutions were pumped through in a single pass. A cause and effect relationship of this phenomenon is not being postulated although there may be a relationship.

Numerous attempts were made to rejuvenate the degraded electrodes, but none of the methods produced 100 percent rejuvenation. Polishing the exposed surface as one might polish a lens was the most satisfactory, indicating that the degradation was probably a surface phenomenon.

At one point in the study of the loss of silver ion from solution, an attempt was made to use the silver bromide column as a constant source of silver ions. However, after checking the silver bromide column with a single pass of water and realizing theoretical saturation or silver ion content from the column effluent, recirculation of the fluid produced a lower than theoretical concentration of silver ion--50 instead of 73 ppb at 24°C (75°F). The concentration, measured by system electrodes as well as an independent electrode system, exhibited a random up-down variation of about 10 to 15 ppb. Extensive flushing of the silver bromide column with distilled water would rejuvenate it, but the cause of the lowering and variation of the output has not been resolved.

The silver ion monitoring system was modified to substitute non-metallic materials to as great an extent as possible for 316 stainless steel material. This included all fluid lines and most surfaces within the sensor chamber. Following this, the system was integrated with the electronics and system tests begun. Testing proceeded in a stepwise fashion to insure that all subsystems were functioning properly before final system integration and test. The first of these tests confirmed that the materials substitution had achieved their intended purpose in that significant depletion rates were not occurring. These tests were conducted in a flow-through mode. Following this, recirculation tests were accomplished for relatively short time intervals (less than one day). The electronic integration was next accomplished, exclusive of the calibration loop, and finally, attempts were made to integrate the calibration loop into the system.

While completely trouble-free operation was not achieved, positive indications of concept validity were obtained.

Thus, it appears that silver ion can be measured in a flowing or recirculating system employing specific ion electrodes. It also appears that satisfactory accuracy and precision is achievable. However, all program objectives have not been achieved in two major areas.

a. We have not identified factors which equate to stable, long-term, electrode performance. Using identical fabrication techniques and homogenous material, inter- and intra-lot success is completely unpredictable.

b. Another area deals with the reliability of operation. A flight prototype system should be at the stage of foolproof operation. The system as it currently exists requires too much attention to be considered operational. Many of the more troublesome artifacts can be associated with the test system, e.g., excessive bubble formation, noise pickup, flow irregularities, etc. Nevertheless, it is only proper that a continuous monitoring system should function in such an environment for such will be the real world. Other artifacts result from long-term quality of the electrode itself. While good runs have been obtained, they have been too infrequent to be encouraging. Even these have not been long enough in duration to satisfy minimum mission requirements.

2.0 INTRODUCTION

Actual experience and tests have proven that spacecraft potable water systems require sterilization to ensure crew safety and mission success. Although the potable water may be pure when delivered, it may become contaminated at use points. Consequently, a bactericide must be added to the water, and continuous monitoring of the bactericide concentration is advisable to ensure effectiveness of the microbial control.

One approach to the problem has been the use of silver ions as the bactericide. During NASA MSC Contract NAS9-12733, the feasibility of using an ion selective electrode technique for monitoring the concentration of the silver ion in the potable water system was demonstrated. Under that contract, an Instrument Package Definition was derived for a preliminary flight prototype Silver Ion Monitor System with zero-gravity capability.

The effort under Contract NAS9-12733 was continued under Contract NAS9-13387, during which a preliminary flight prototype Silver Ion Monitoring System was designed, fabricated, and subjected to preliminary testing.

The design, fabrication, and testing of the preliminary flight prototype unit was intended to provide data to contribute to the design and fabrication of a qualifiable flight unit. This final report summarizes the results of this program.

3.0 CONCLUSIONS

1. It has been demonstrated that silver ions rapidly deplete from aqueous solution. The rate of depletion is strongly influenced by the materials to which it is exposed and the relative ratio of volume to surface area. Rapid depletion was observed in stainless steel systems and the depletion rate was increased when the fluids were circulating. Less depletion was observed when stainless steel components of the system were replaced with selected non-metallics. Depletion rates of 25×10^{-6} grams/liter/hour (0.40×10^{-6} oz/lb/hr) of silver were observed when circulating in stainless steel systems as opposed to 2×10^{-6} grams/liter/hour (0.03×10^{-6} oz/lb/hr) when the stainless steel was largely substituted with Teflon and nylon.

2. Silver sulfide sensing electrodes, as fabricated under this program, have proved to be unreliable and do not meet minimum mission requirements.

3. The double junction reference electrode has been successfully operated for 40 days.

4. While the feasibility of performing automatic calibration has been demonstrated, the use of a silver bromide column to provide standard solutions has yet to be demonstrated. Further design optimization is required in this area.

While the design of the individual components of the silver ion monitoring system have been validated, reliable operation has not been achieved. Major effort will be required in the optimization of sensing electrode design and minor engineering optimization in the electronics and calibration loop to provide long-term, stable, trouble-free operation.

4.0 RECOMMENDATIONS

In view of the stand-by nature of the silver ion monitor at the present time, it is not recommended that NASA invest substantially more funds in the optimization of prototype hardware at this point in time. However, in order to carry this program through to a logical stopping point, it is recommended that consideration be given to the sensor development program to determine the characteristics of materials and methods that will produce an electrode meeting at least minimum mission requirements. Several questions that must be addressed in such a program would be:

Failure Mode

- Why do electrodes fail?
- What conditions accelerate failure?
- What conditions are stabilizing?

Fabrication

- What are the key determinants in the manufacturing process?
- What produces a good electrode?
- Are other materials more satisfactory?

This program should be a low-level effort until it is certain that these parameters are completely understood and an adequate test history, considering the design constraints uncovered during this program, are obtained.

If these questions are resolved, a reasonable holding position would result. Further development efforts could take place or, alternatively, the technology could be set aside to await a demand for this measurement.

5.0 TECHNICAL DISCUSSION

5.1 Review of Preliminary Testing Data

Solid-state silver sulfide electrodes were developed by Beckman under NASA Contract NAS9-12733. The solid-state configurations were developed because of the requirement for zero gravity (g) and ±6 g exposure. Preliminary evaluation by both laboratory and test fixture tests to simulate spacecraft use conditions demonstrated the suitability of such electrodes for use in zero g, and analysis indicates the feasibility of use in a ±6 g exposure.

5.1.1 Sensitivity

The sensitivity of the solid-state silver sulfide electrode was measured in dilutions of an atomic absorption standard ($AgNO_3$) at concentrations between 10 and 10,000 ppb silver ion and found to conform to the theoretical Nernstian response. When plotted on semilog paper with the concentration on the log axis and response in millivolts on the linear numerical axis, a straight line resulted. Test fixture tests at 10, 25, and 45°C (50, 77, and 113°F) resulted in a straight-line plot over the concentration range of 25 to 100 ppb of silver ion.

5.1.2 Precision (Coefficient of Variation)

During the technique-selection phase of Contract NAS9-12733, both commercial silver sulfide and solid-state silver sulfide electrodes were evaluated. The precision for the solid-state electrode for various silver ion concentrations varied between 0.23 and 0.97 at silver ion concentrations of 500 and 50 ppb, respectively, and in all cases was better than any of the commercial electrodes tested.

5.1.3 Stability

The stability of the solid-state silver sulfide was determined in the test fixture at 25°C (77°F). The electronics and recorder were first evaluated and found to have drifted less than the equivalent of 1 ppb over an 18-hour period. The stability of the electrode was then measured and found to drift less than ±0.6 ppb silver ion over a one-hour period using a 50 ppb silver ion solution. The poor stability of the silver ion solution prevented longer stability time evaluation. The use of a column of silver bromide/glass beads would provide a suitable, stable, silver ion solution for long-term stability evaluation of the Preliminary Flight Prototype Silver Ion Monitoring System.

5.1.4 Behavior in Response to Pressure Changes

The solid-state silver sulfide electrode is not generally sensitive to such physical changes as pressure and flow because of the electrochemical mechanism by which it develops a millivolt output in response to changes in silver ion concentration. The reference electrode, however, due to its sensitive liquid-liquid junction with the sample, is sensitive to pressure and flow changes. Proper design of the reference and measuring cell for a particular application can minimize the effects of both pressure and flow.

The solid-state silver sulfide in combination with the quartz fiber junction pressure-equalizing reference was tested in a test fixture at temperatures of 10, 25, and 45°C (50, 77, and 113°F). The flow was held constant at 100 ml/min. (13 lb/hr) and the pressure varied between 6.89×10^4 and 3.10×10^5 N/m^2 (10 and 45 psig). The maximum apparent offset observed was 12 percent of the true silver ion concentration. The offset was attributed primarily to the response of the reference electrode and small artifacts introduced by the pressure equalizing loop. This apparent offset can undoubtedly be minimized through optimized pressure equalization design.

5.1.5 Behavior in Response to Flow Changes

Sudden or large changes in the flow rate of liquid passing the liquid junction of the reference electrode will disturb the junction and result in a change in the millivolt output of the electrode pair. The solid-state silver sulfide electrode in combination with the quartz fiber junction pressure-equalizing reference was evaluated in the test fixture at 10, 25, and 45°C (50, 77, and 113°F). The effects of flow were determined by holding the pressure constant at 1.72×10^5 N/m^2 (25 psig) while varying the flow between 150 and 450 ml per minute (19.8 and 59.5 lb/hr). The maximum apparent offset due to flow changes was found to be 12 percent of the true silver ion concentration at 10 and 45°C. The maximum offset at 25°C (77°F) was 8 percent, or approximately 2 ppb.

5.1.6 Behavior in Response to Temperature Changes

The electrode pair, consisting of a solid-state silver sulfide electrode and quartz fiber junction pressure-equalizing reference electrode, was tested at 10, 25, 45, and 65°C (50, 77 113, and 149°F) in a test fixture with silver ion concentrations between 25 and 125 ppb. With the exception of the 65°C (149°F) test, the response was linear. The poor response at 65°C was found to be the result of a failure of the adhesive/sealant used to hold the silver sensitive silver sulfide pellet in the electrode body.

6.0 MONITORING SYSTEM DESIGN AND FABRICATION

6.1 General

The detailed design of the Preliminary Flight Prototype Silver Ion Monitoring System generally followed the Instrument Package Definition Report* derived under the previous contract, NAS9-12733. However, several changes were made to reduce significantly size and/or weight and increase reliability. In addition, a substitution was made for the qualifiable fluid pump/motor for cost reduction.

6.2 System Design Philosophy

The basic philosophy of the approach to the instrument design was to approximate as close as practical a flight configuration using off-the-shelf components where possible. The individual components chosen were as close as practical to available space-qualified component fit and function, yet did not burden the development program with the high cost of the qualified components. The constraints of low weight and volume were given prime consideration during the design stage.

6.3 Monitoring System General Description

6.3.1 General

The monitoring system consists of two inter-related subsystems--a silver ion monitoring subsystem and an automatic calibration subsystem. A number of components such as the electronics package, pump and sensor chamber, and solenoid valves are necessarily common to both subsystems. Figure 6-1 shows a flow diagram of the silver ion monitoring system. The two modes of operation can be followed by means of the arrows.

---

*Beckman Report COR-2639-1 dated 23 March 1972

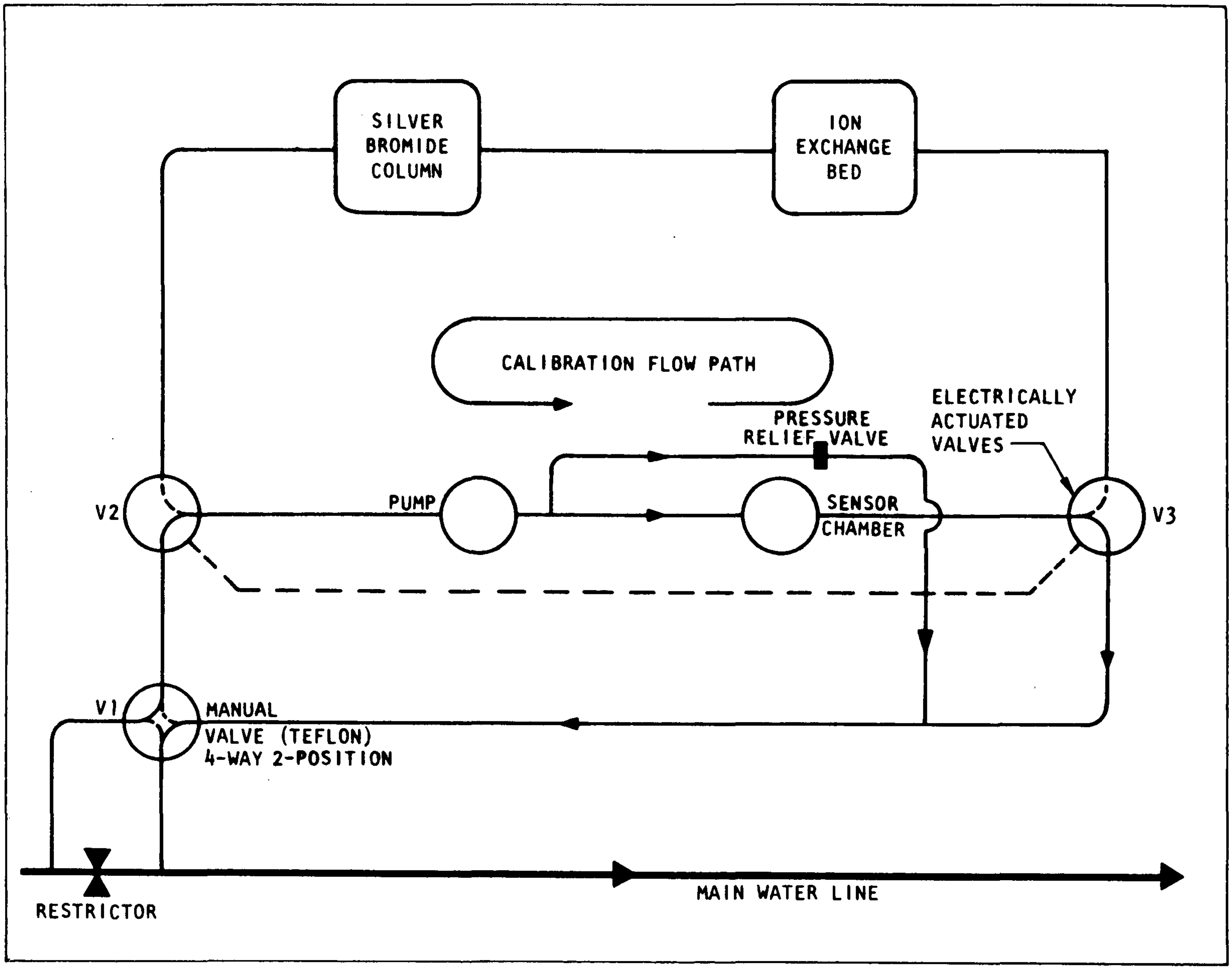


Figure 6-1. Flow Diagram--Prototype Silver Ion Monitoring System

In the monitoring mode, the sample flows from the potable water system of the Shuttle through the system isolating valve V1, through valve V2, then through the pump and sensor chamber. The pump provides a constant flow 100 ml/min. (13.2 lb/hr) of sample to the sensor chamber. The effluent from the sensor chamber returns to the water system through valves V3 and V1. As the water sample passes through the sensor chamber, the concentration of the silver ion in the water is detected by the potentiometric electrodes. The system design provides for the processing of the signal from the electrodes by the electronics package and the concentration of the silver ion in the water to be indicated on the front panel meter. During periods in which water in the main water line would not be flowing, the pump would circulate the water through the monitoring system and through a portion of the main water line, thus providing a continuous indication of the silver ion content of the water in that section of the main water line connected to and/or adjacent to the monitoring system. A pressure relief valve is included in the system to protect the components of the sensor chamber from excessive pressure which could develop as a result of solenoid valve malfunction.

The design of the silver ion monitoring system includes automatic calibration. In the automatic calibration mode, a timer circuit in the electronics package initiates the calibration sequence approximately once every 24 hours. Solenoid valves V2 and V3 are activated, placing the pump and sensor chamber in a closed loop with the two columns, thus forming the calibration loop. The pump circulates the water in the line through valve V3 and into the deionizer column where the ion exchange resins remove all of the silver and bromide ions. The deionized water is then routed to the silver bromide column. The silver bromide column is filled with a mixture of glass beads and granular silver bromide, AgBr. Water passing through the silver bromide column becomes saturated with silver bromide at a concentration defined by the solubility coefficient of the AgBr at the ambient temperature of the system. This is the calibration fluid which is passed through valve V2 and pumped to the sensor chamber where the concentration of the silver ions would be detected. The automatic calibration electronics compare the output of the electrodes with a known value and adjust the readout accordingly.

6.3.2 System Size and Weight

Physically, the silver ion monitoring system consists of two sub-units, a fluid handling unit, and an electronic unit. These are mounted in a single package measuring 35.56 centimeters (14 in.) wide, 40.6 centimeters (16 in.) high, and 22.2 centimeters (8.75 in.) deep. The system is shown in Figure 6-2.

The packaging of the monitoring system as shown in Figure 6-2 was intended only to serve as a temporary housing to permit early integration of fluid handling components with the electronic unit and to provide spatial relationship data for a final packaging design.

The total weight of the monitoring system is 8.734 kilograms (19.2 lb). The fluid handling unit weighs 5.110 kilograms (11.24 lb) while the electronics and preliminary case weigh 3.624 kilograms (8.0 lb).

Table 6-1 lists the weights of the individual components of the fluid handling unit and the weight of the total electronics unit.

The preliminary packaging attempt of placing both the fluid handling components and the electronic components in one package is a departure from the Instrument Package Definition concept and was intended to reduce the overall size and weight of the monitor and to aid in the integration of the electronic and fluid components.

6.4 The Fluid Handling Unit

The fluid handling unit is shown in Figure 6-3. The major components of this unit are the sensor chamber which houses the electrodes, the pump which circulates the water sample calibrating fluid, the two column assemblies which would contain the ion exchange resins and the silver bromide, and the valves. The components are mounted as shown on a supporting frame. All components are mounted to the frame directly or by brackets. Ample space is provided to service the sensors and replaceable electrolyte cartridge. Replacement of the cartridge does not require any other mechanical or electrical disassembly.

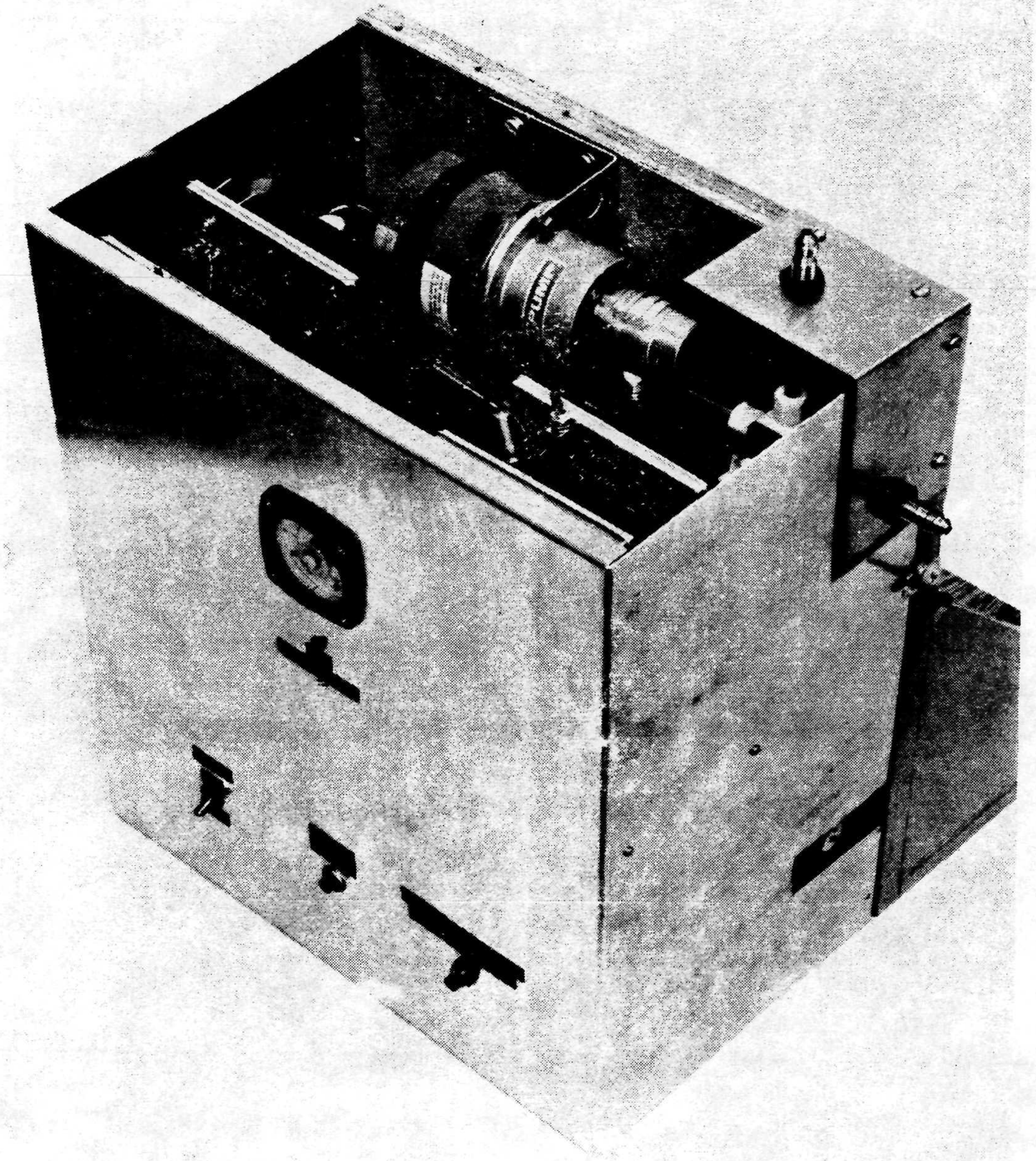


Figure 6-2. Preliminary Prototype Silver Ion Monitor--Test Packaging

Table 6-1. System Weight and Weight of Individual Components

Component	Weight grams	oz.
Fluid Handling Unit		
Ion Exchange Column	165	5.82
Silver Bromide Column	182	6.42
Calibration Loop Tubing & Fittings	323	11.39
Pump-motor Combination with Bracket	1472	51.9
Solenoid Valve + AN Fittings (2)	940	33.16
Sensing Electrode	65	2.29
Primary Reference	43	1.52
Teflon Isolation Valve, V1 + Bracket	114	4.0
Measuring Loop Tubing & Fittings	467	16.47
Pressure Relief Valve	66	2.33
Sensor Chamber	898	31.67
Support (estimated)	375	13.23
Electronics Unit		
Electronics + Preliminary Case 35.56 x 40.6 x 22.2 cm (14 x 16 x 8.7 in.)	3624	128.0
TOTAL SYSTEM WEIGHT	8.734 kg	19.2 lb

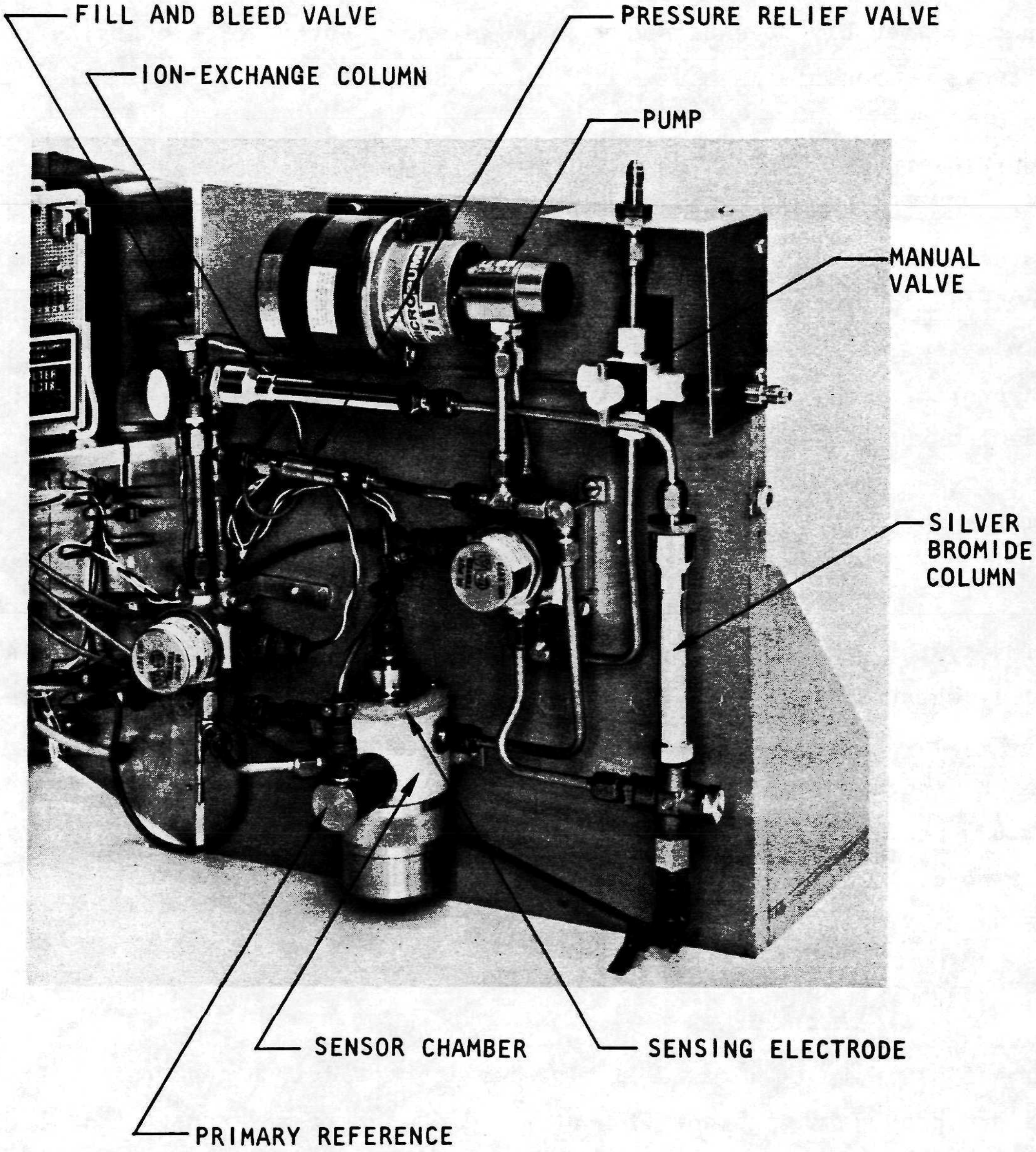


Figure 6-3. Fluid Handling Unit of Silver Ion Monitor

The two-column assemblies are replaced by loosening the appropriate AN nuts on the column connecting fitting then unscrewing the columns from the system. After replacement of the columns, the water would have to be replenished and all the air introduced during replacement would have to be removed from the calibration loop. A fill-and-bleed valve is provided for this purpose. The entire assembly is enclosed with an aluminum cover which contains the electronic components.

Within the fluid handling unit the water sample is exposed to a variety of components and material surfaces. Table 6-2 lists the materials and surface area of each component exposed to the water sample. The surface areas were calculated from shop drawing dimensions or dimensions taken from components. In a few cases where actual dimensions could not be readily obtained, approximations were used. Errors due to approximations are expected to be less than 10 percent.

6.4.1 Components

6.4.1.1 Manual Valve

The system uses a Teflon, manual, 4-way, 2-position valve that would be used only when the sensor chamber, silver bromide column, or deionizer is to be serviced. The valve chosen for this purpose is 5.4 centimeters (2-1/8 in.) high, and the body is a 2.54-centimeter (1-in.) cube, plus fittings for the 0.635-centimeter (1/4-in.) diameter, stainless steel tubing. This is a commercial valve manufactured by Fluorocarbon Company of Anaheim, California, P/N SC P2-24-4C.

6.4.1.2 Fluid Pump

The fluid pump is a fixed-displacement, motor-driven gear pump. Its purpose is to provide a constant flow of sample water to the sensor cell during sensing and calibration. The gear pump is a magnetically coupled gear pump with a 316 stainless steel housing and Teflon gears on 316 stainess steel shafts.

Table 6-2. Surface Areas of Materials Exposed to Water Sample

		Exposed Surface	
Component	Material	cm^2	in^2
System Isolation Valve	Teflon		
Recirculating		3.27	0.5
Normal use		6.54	1.0
Solenoid Valves (2)	Anodized Aluminum	3.9 ea	0.6 ea
Tubing, 1/4" OD	316 Stainless Steel(SS)		
Monitoring loop		157.0	24.0
Calibration loop		107.9	16.5
Common to both loops		53.6	8.2
Tubing Fittings	316 Stainless Steel		
Monitoring loop		62.8	9.6
Calibration loop		82.4	12.6
Common to both loops		49.0	7.5
Pump	Teflon	52.3	8.0
	316 Stainless Steel	30.0	4.6
Electrode Cell	Rubber	21.6	3.3
	316 Stainless Steel	94.9	14.5
	KEL-F	170.1	26.0
	Epoxy	1.96	0.3
	Polypropylene	5.9	0.9
Columns			
Ion Exchange	316 Stainless Steel	78.5	12.0
Silver Bromide	316 Stainless Steel	78.5	12.0
TOTALS	316 Stainless Steel	589.4	90.9
	Rubber	21.6	3.3
	KEL-F	170.1	26.0
	Epoxy	19.6	3.0
	Anodized Aluminum	7.8	1.2
	Teflon	58.9	9.0

The internal bypass is set to 25 psid. The model 12-50-316 gear pump is a motor-pump combination weighing approximately 1.587 kilograms (3.5 lb). The motor that drives the pump is a shaded pale induction motor, 115 Vac, 50/60 cycle, 350.7 rad/sec (3350 rpm), 0.98 amp, with a thermal protector. The pump-motor is 9.36 centimeters (3.69 in.) high, 8.58 centimeters (3.38 in.) wide, and 19.3 centimeters (7.59 in.) long, and is manufactured by Micropump Corp. of Concord, California.

The above pump was substituted for the high cost, qualified, flight-approved Hydro-Aire component defined in the Instrument Package Definition, and was purchased at approximately one-tenth the cost of the Hydro-Aire component.

6.4.1.3 Sensor Chamber

The sensor chamber provides a flow path by which the active parts of the sensing electrodes are brought in contact with the water sample (Figure 6-4 and Table 6-3, and Figure 6-4A and Table 6-4).

The sensor chamber has been designed to be cylindrical in shape and contains the silver ion sensing electrode, the reference electrode, the electrolyte chamber, quartz fiber junction, and the replaceable electrolyte cartridge. A thermocompensator is also mounted in the chamber.

Within the sensor chamber there are two flow paths:

- Water Sample. As the sample flows through the chamber, it passes between the sensing electrode and the quartz junction of the reference, then past the thermocompensator. The water sample then flows through the cavity occupied by the rolling diaphragm and to the chamber exit port, thus applying system pressure via the diaphragm on the electrolyte reservoir in addition to the spring pressure. Equalizing the pressure on both sides of the quartz junction with system pressure is required to minimize sensitivity of the reference to pressure changes (Figure 6-4 and Table 6-3).

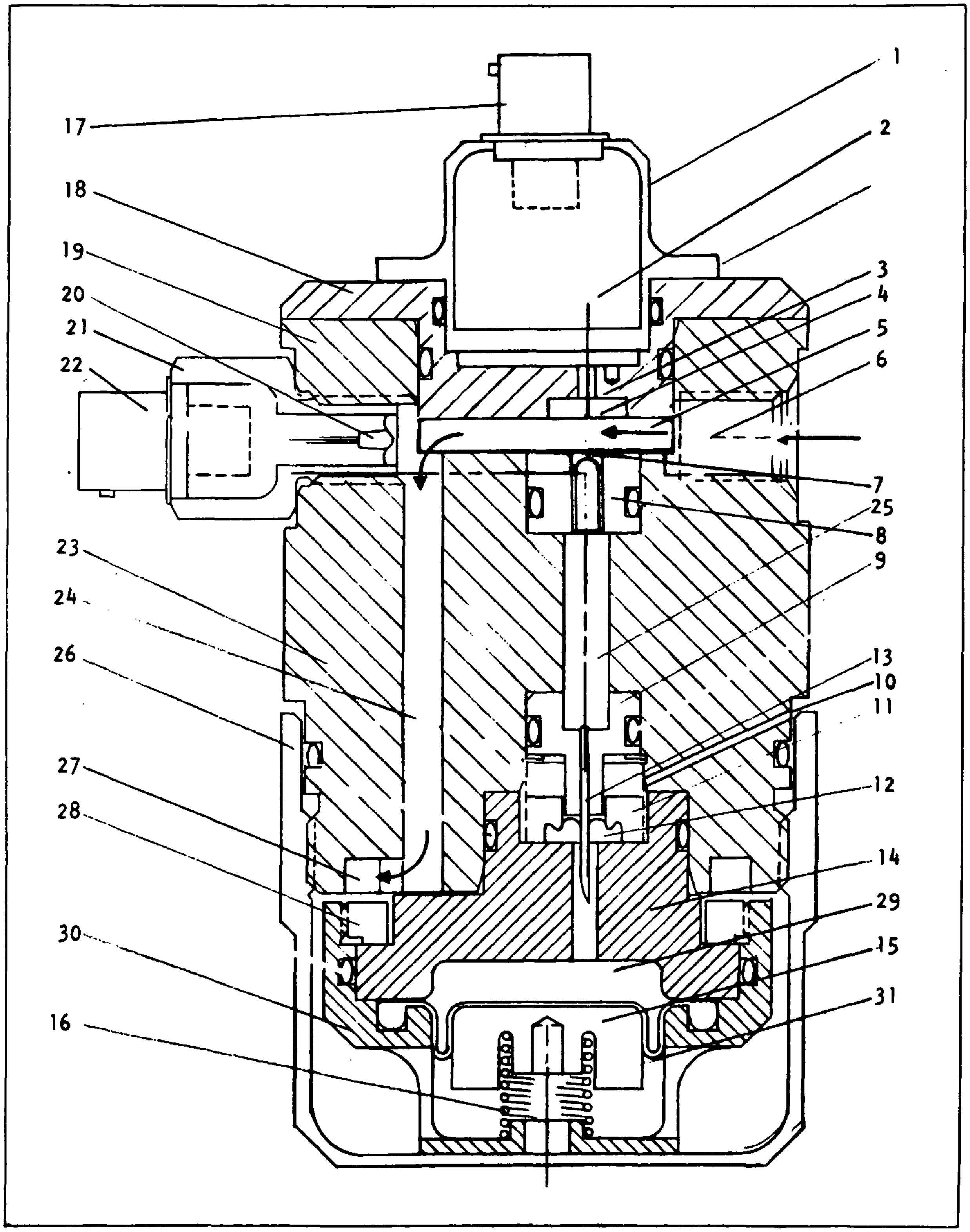


Figure 6-4. Sensor Chamber--Cross Section (Exit Port not Shown)

Table 6-3. Components--Sensor Chamber Cross Section (Figure 6-4)

1. Cap, Preamplifier, Sensing Electrode
2. Silver Wire to Preamplifier
3. Silver Sulfide Pellet
4. Sensor/Liquid Interface
5. Water Flow Path
6. Water Entrance Port
7. Quartz Fiber Junction
8. Quartz Fiber Junction Mount
9. Needle Mount
10. Vent
11. Nut, Septum Retainer
12. Septum, Silicone Rubber
13. Needle, Huber Bevel
14. Top, Electrode Reservoir
15. Piston, Diaphragm
16. Spring, Rolling Diaphragm
17. Electrical Connector, Sensing Electrode
18. Housing, Sensing Electrode
19. Chamber Body - Top
20. Thermocompensator (Thermistor)
21. Thermocompensator Housing
22. Electrical Connector Reference Electrode
23. Chamber Body
24. Water Flow Path, Downward
25. Electrolyte Chamber
26. Cap, Chamber, Lower
27. Water Flow Path - Lower
28. Nut, Retaining, Reservoir Top
29. 1M Potassium Nitrate
30. Bottom, Electrolyte Reservoir
31. Rolling Diaphragm

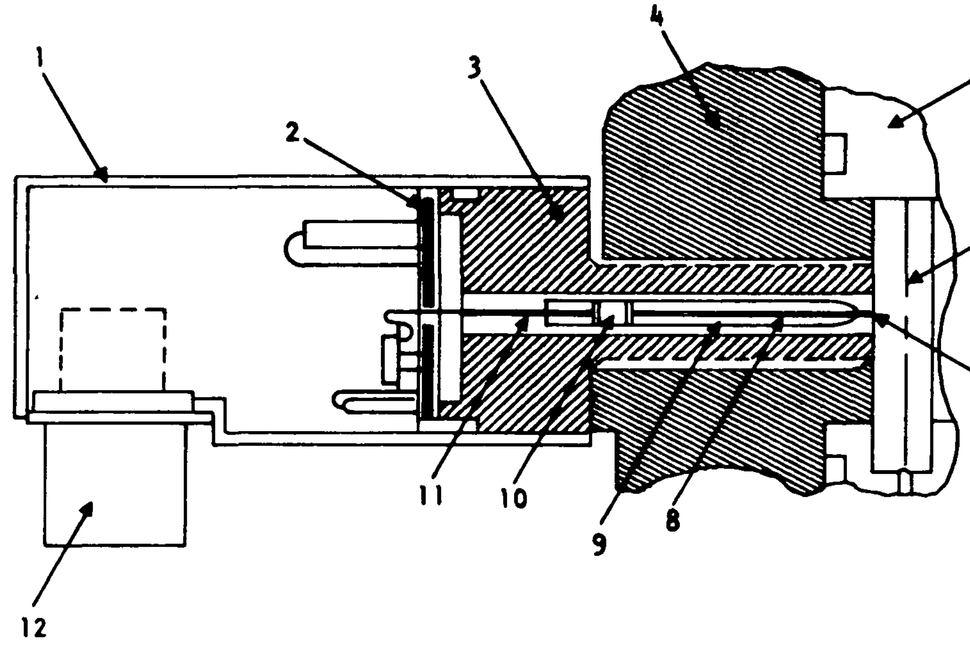


Figure 6-4A. Sensor Chamber Cross Section Through Reference Electrode

View A-A

Table 6-4. Components--Sensor Chamber Cross Section Through Reference Electrode. View A-A (Figure 6-4A)

No.	Part	Drawing or P/N	Material
1	Cover, Preamplifier Reference Electrode	AG0044	Aluminum, nickel plated
2	Preamplifier	AG0043	Mixed-Ag0044
3	Housing, Reference Electrode	Ag0045	Polypropylene (PP)
4	Sensor Chamber Body	--	KEL-F
5	Quartz Fiber Junction Mount	--	Polypropylene
6	Electrolyte Chamber	--	Contains electrolyte 1M Potassium Nitrate
7	Diffusion Junction	--	Ceramic thread in glass tube
8	Electrolyte Gel	--	0.1M Potassium Chloride (KCl) 1.0M Potassium Nitrate (KNO_3) 3% Carboxy Methyl Cellulose (CMC)
9	Silver Wire Coated with Silver Chloride	--	Silver wire-silver chloride
10	Cap, Sealing	--	Silicone rubber
11	Silver Wire Direct from Electrode to Preamplifier	--	Silver wire
12	Electrical Connector, Bendix	PT1H-8-4-PW	Ceramic and nickel plated copper

- Electrolyte. The 1M KNO_3 electrolyte which is stored in the rolling diaphragm reservoir flows through the interconnecting needle into the electrolyte chamber, then through the quartz fiber junction into the sample flow path. The flow is estimated to be about 50 microliters (1.69 x 10^{-3} fl. oz) per day. The concept of a replaceable rolling diaphragm reservoir is proposed to simplify maintenance and increase reliability. The replaceable reservoir is described in paragraph 6.4.1.5.4.

The sensor chamber differs from the chamber described in the Instrument Package Definition in that the flow path of the water sample and the pressure-equalizing sample paths have been combined to eliminate a blind path which could present filling problems, and electrode noise due to air pockets oscillating against the rolling diaphragm. The site of the thermocompensator has been changed and the top of the chamber modified to accept a larger modified sensing electrode (described in paragraph 6.4.1.4).

The sensor chamber is connected to the monitoring system as shown in Figures 6-1 and 6-3. All tubing parts are AN 10050-4. The electrical connections between the sensor chamber and electronics subassembly utilize Bendix or other approved electrical disconnects. The component parts of the sensor chamber are shown in Figure 6-5, with materials and weights given in Table 6-5.

The sensor chamber measures 5 centimeters (2 in.) in diameter and 12.7 centimeters (5 in.) in length. Its weight is 907.5 grams (1.99 lb).

6.4.1.3.1 Sensor Chamber Interface

The sensor chamber is connected to the water system via V1 and to the calibration loop when the two electrically-operated solenoid valves, V2 and V3, are activated (Figure 6-1). These valves will be activated automatically during the short calibration sequence which will be controlled by the calibration electronics.

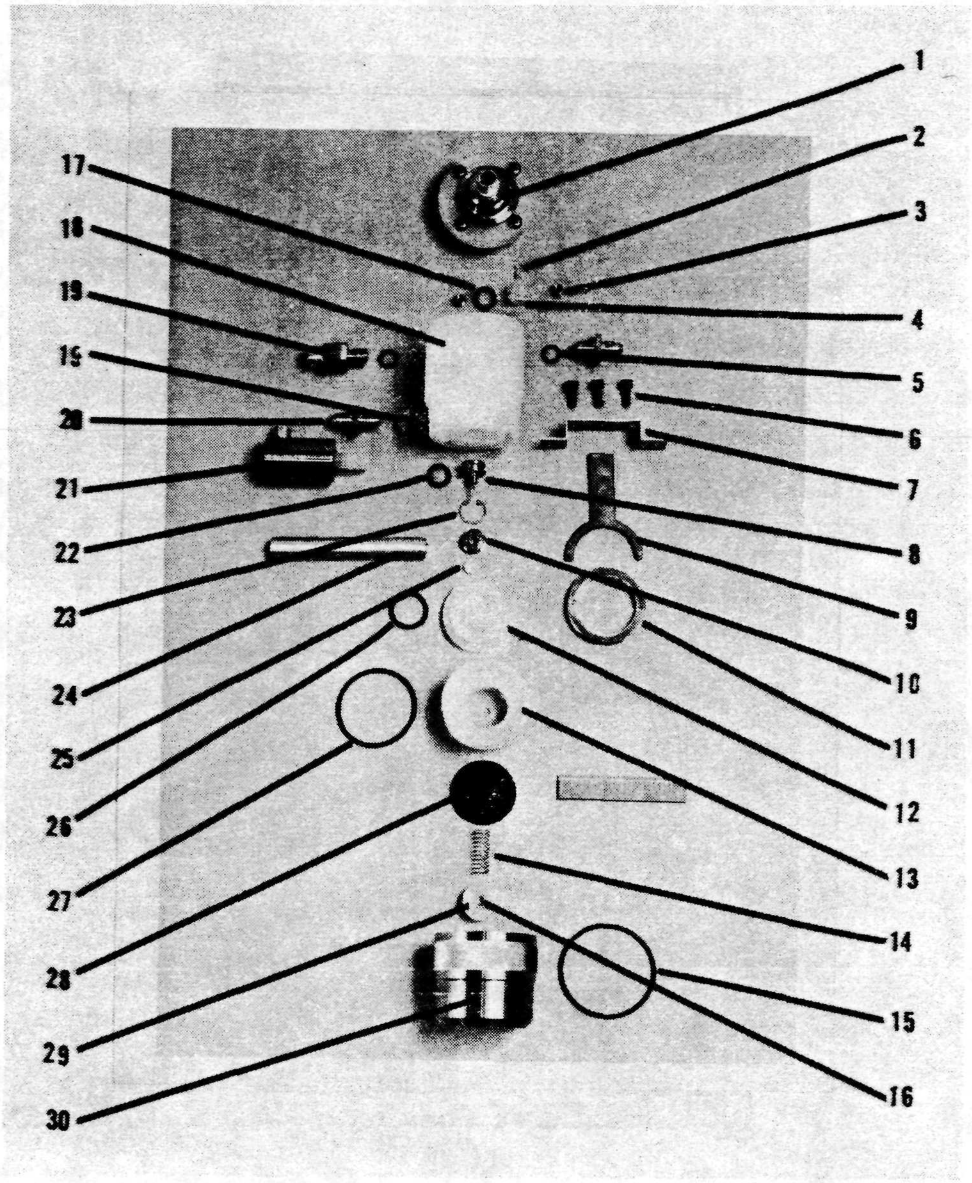


Figure 6-5. Sensor Chamber Component Parts and Tools

Table 6-5 (Sheet 1 of 2). Component Parts and Tools—Sensor Chamber (Figure 6-5)

No.	Part	Drawing or P/N	Material	Weight Grams	oz.
1	Sensing Electrode Ass'y	AG00	See Table 6-2	65.5	2.3
2	Quartz Fiber Junction	AG0041	Lead Glass Quartz Fiber	0.5	0.02
3	Speedserts, Tridair Industries	SPB-1032S (4)	Stainless Steel	2.8	0.1
4	Quartz Fiber Junction Mount	AG0030	Polypropylene	1.3	0.05
5	O-Ring, Parker	3-904	N674-7 Nitrile	0.1 ea	
6	Mounting Screws Pan Head	10-32X.37 (3)	Steel	7.8	0.28
7	Bracket, Cell Mount	AG0056		12.5	0.44
8	Needle Ass'y	AG0022	316 SS	9.3	0.33
9	Spanner Wrench (required for assembly)	AG0032	SS	----	----
10	Nut, Septum Retaining	AG0021	316 SS	6.1	0.22
11	Nut, Retaining Upper Diaphragm Support	AG0024	316 SS	33.9	1.2
12	Top, Electrolyte Reservoir	AG0025	KEL-F	47.4	1.67
13	Bottom, Electrolyte Reservoir	AG0026	KEL-F	49.9	1.76
14	Spring, Rolling Diaphragm	AG0035	302 CRES Cond 13	2.0	0.07
15	O-Ring, Parker	2-111	N674-7 Nitrile	1.2	0.04
16	Speedsert	SPB-1032-S	SS	1.0	0.04
17	O-Ring, Parker	2-111	N674-7 Nitrile	0.9	0.04
18	Chamber Body	AG0027	KEL-F	378.0	13.33
19	Thermocompensator Ass'y	AG0023	316 SS Epoxy	20.2	0.71
19A	O-Ring, Parker	3-904	N674-7 Nitrile	0.1	----
20	Union	AN815-4K (2)	316 SS	38.8	1.37

Table 6-5 (Sheet 2 of 2). Component Parts and Tools--Sensor Chamber (Figure 6-5)

No.	Part	Drawing or P/N	Material	Weight Grams	oz.
21	Reference Electrode Ass'y (Primary)		Mixed	43.0	1.52
22	O-Ring, Parker	2-111	N674-7 Nitrile	0.8	0.04
23	Retainer Ring	N-5000-62-H	316 SS	0.5	0.02
24	Wrench, Septum Retainer (req'd for assembly)	AG0033	SS	----	----
25	Septum, Hamilton		Silicone Rubber	1.0	0.04
26	O-Ring, Parker	2-117	N674-7 Nitrile	0.45	0.02
27	O-Ring, Parker	2-134	N674-7 Nitrile	1.0	0.04
28	Diaphragm, Rolling (Bellophram)	3-112-94-CBJ	BUNA-N	2.6	0.09
29	Piston, Diaphragm	AG0020	KEL-F	4.7	0.17
30	Cap, Chamber, Lower	AG0029	316 SS	174.0	6.17
			TOTAL	907.5	(1.99 lb)

6.4.1.3.2 Materials and Subsystem Compatibility

All items in contact with the potable water are 316 stainless steel, KEL-F, Teflon, or epoxy with the exception of the sensors and solenoid valves. Materials in contact with the potable water (see paragraph 6.3.3 and Table 6-2) were not expected to affect or be affected by the system water. However, during testing, a rapid depletion of silver ion from the water was observed and was traced to adsorption of silver on the surfaces of the system, especially the 316 stainless steel. This adsorption is described in paragraphs 8.4 through 8.7.

6.4.1.4 Prototype Silver Ion Sensing Electrode

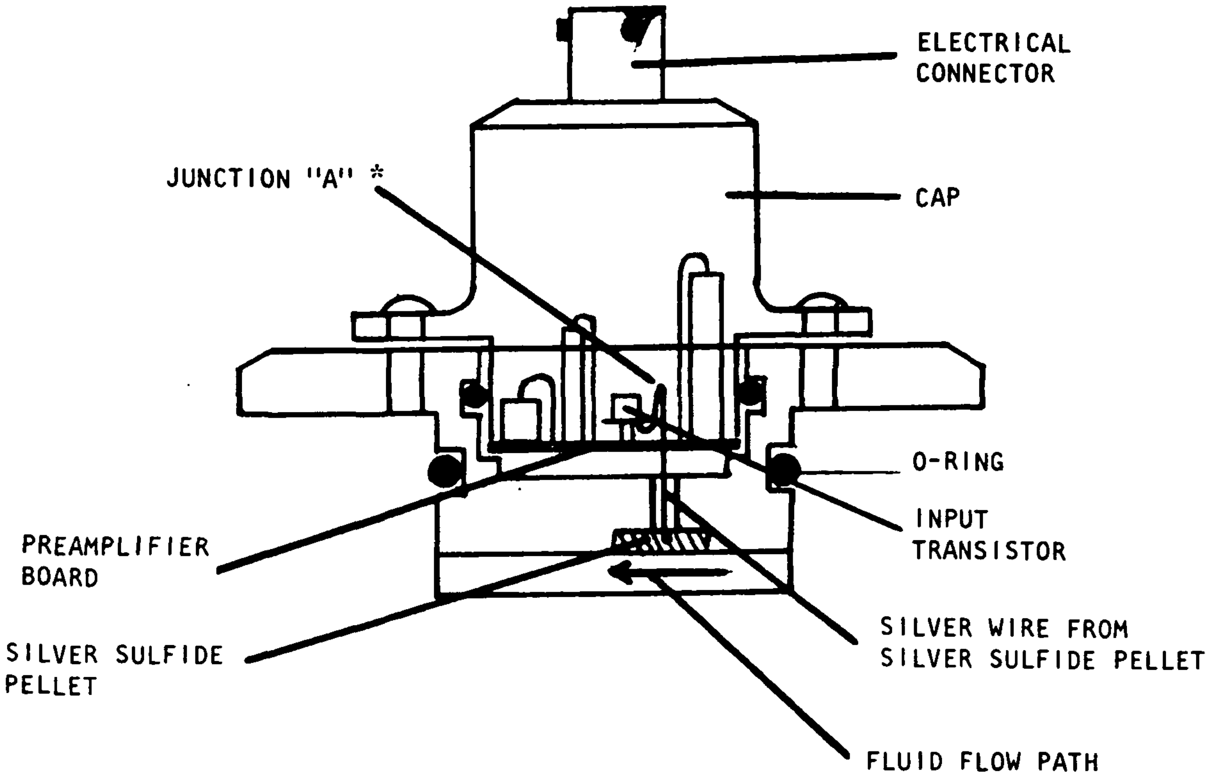
The prototype silver ion sensor is a solid-state silver sulfide electrode which was shown to exhibit Nernstian response to lower than 10 ppb of silver ion. The active element of the electrode consists of a dense silver sulfide pellet or membrane fabricated with a silver wire as an integral part of the pellet.

The silver sulfide pellet and integral silver wire were cemented in a polypropylene housing which also contained a preamplifier located as close as possible to the sensing element and connected to the element by the silver wire. The electrode develops a millivolt (potential) output as a result of exchange or transport of silver ions from a sample solution through the pellet or membrane. The electrode exhibits Nernstian response to changes in silver ion activity, that is, 59 millivolts per decade change in silver ion activity at 25°C (77°F).

The inclusion of the preamplifier in the electrode housing was recommended by the design review board to reduce interference and background noise. The configuration of the prototype silver ion sensing electrode is shown in Figure 6-6 and the component parts in Figure 6-7 and Table 6-6.

6.4.1.4.1 Adhesives and Fabrication Techniques for Wide Temperature Use Sensing Electrodes

In parallel with the prototype electrode design effort, several epoxies and RTVs and varied fabrication techniques were investigated for sealing the silver sulfide pellets in the polypropylene bodies to produce a sensing (silver sulfide) electrode with wide temperature use--in particular, use at 65°C (149°F).



*Junction "A"--Junction of silver wire from silver sulfide pellet with transistor input--also preamplifier bypass test connection.

Figure 6-6. Configuration of Prototype Silver Sulfide Electrode with Preamplifier and Cap

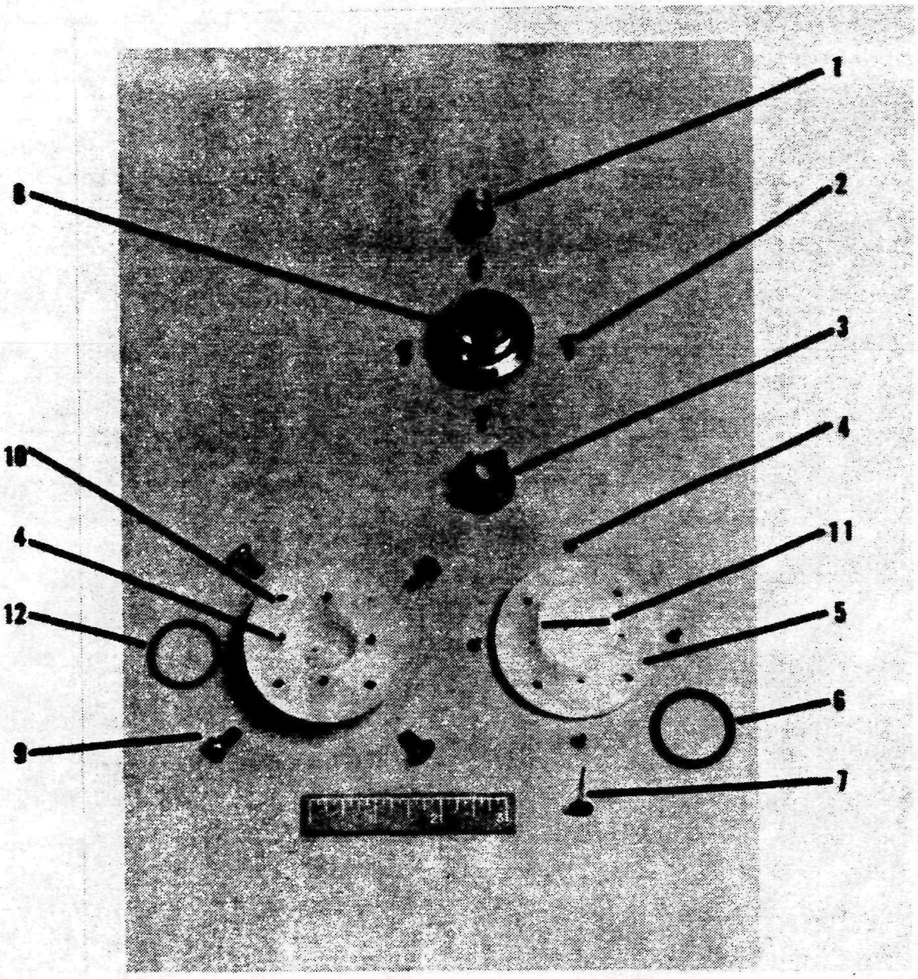


Figure 6-7. Prototype Sensing (Silver Sulfide) Electrode--Component Parts

Table 6-6. Component Parts - Prototype Sensing (Silver Sulfide) Electrode (see Figures 6-6 and 6-7)

No.	Part	Drawing or P/N	Material	Weight (Grams)	Weight (oz.)
1	Connector, Electrical Bendix	PT1H-8-4PW	Brass-Nickel Plated	5.8	0.2
2	Screws, Cap Retaining	4-40X.31 (4)	SS	1.95	0.7
3	Preamplifier	AG0038	Mixed, see AG0039	6.7	0.24
4	Speedserts, Tridair Industries	SPA-0440-S (4)	SS	0.5	0.02
5	Electrode Body, Bottom View		Polypropylene	24.1	0.84
6	O-Ring, Outside, Parker	2-121	N674-7 Nitrile	0.6	0.02
7	Silver Sulfide Pellet with Silver Wire		Ag_2S/Ag	0.5	0.02
8	Cap, Sensing Electrode	AG0034	Aluminum Nickel Plated	15.8	0.56
9	Screws, Electrode Retaining	10-32X.63 (4) Pan Head	SS	9.4	0.33
10	Electrode Body, Top View		--	---	--
11	Water Flow Path		--	---	--
12	O-Ring, Inside, Parker	2-022	N674-7 Nitrile	0.25	0.01
			TOTAL WEIGHT	65.5	2.3

A wide temperature range sensing electrode was needed since the silver ion monitors were originally intended to be placed downstream of the water heaters and chillers in the water system. This presented numerous other problems in addition to those associated with the electrodes; therefore, the location of the silver ion monitor(s) was changed to upstream of the heaters and chillers. Consequently, all effort was terminated toward developing a higher use temperature electrode. Since the test data is no longer relevant to the present program, it is presented in condensed form in Appendix A.

6.4.1.5 Reference Electrode

A variety of reference electrode designs were evaluated during the technique testing phase of the previous contract. The final configuration that was used to obtain concept verification data was based on an earlier Beckman effort for NASA in the preliminary design of a water pH monitoring system for Apollo. This design appeared to meet all the system requirements. The prototype design is shown as part of Figures 6-4 and 6-4A, and is described in the following paragraphs. Figure 6-8 and Table 6-7 show the component parts of the primary reference.

The reference electrode subsystem consists of the following components, all contained within or attached to the sensor chamber.

- A silver-silver chloride primary reference containing a diffusion junction and a saturated solution of potassium chloride as the electrolyte;
- A bridging or secondary electrolyte chamber containing one molar potassium nitrate;
- A quartz fiber junction having a flow of approximately 50 microliters (1.69×10^{-3} fl oz) per day of electrolyte;
- A replaceable electrolyte cartridge;
- A needle to connect the secondary electrolyte chamber with the reservoir.

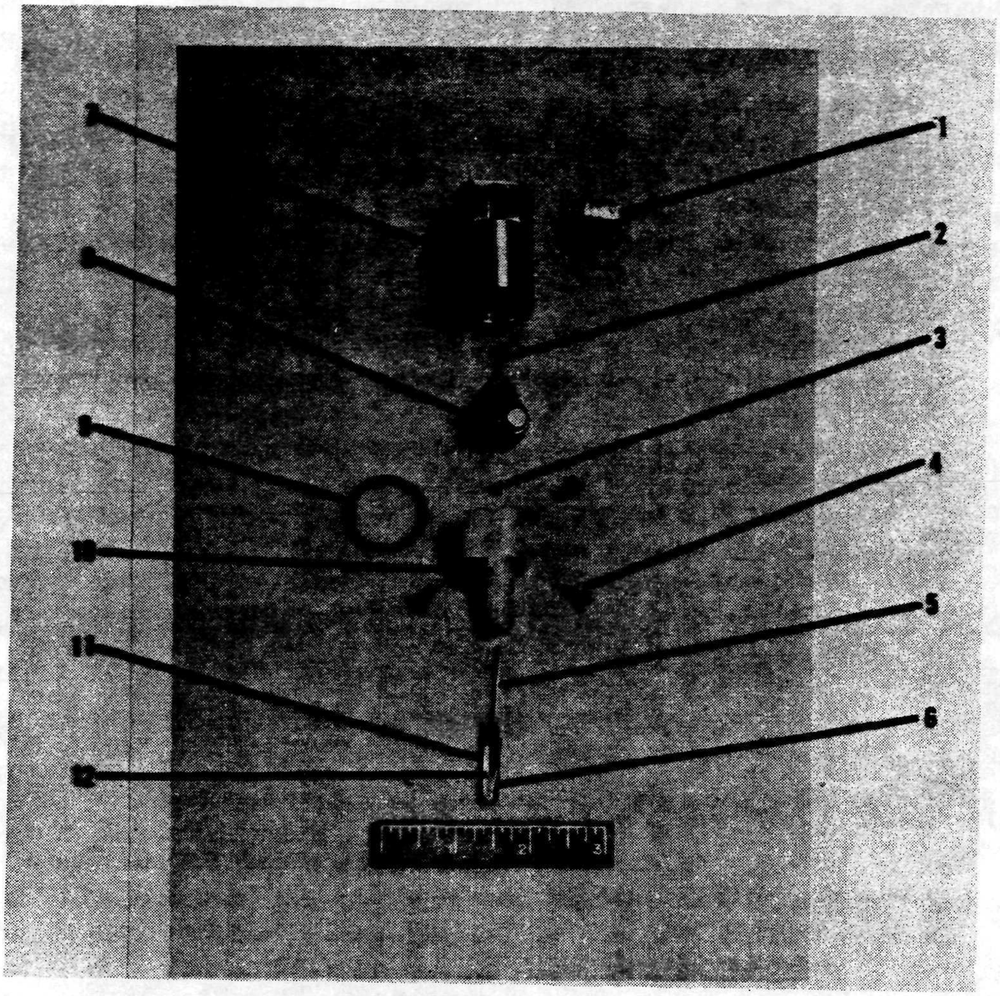


Figure 6-8. Reference Electrode (Primary)--Component Parts

Table 6-7. Component Parts - Reference Electrode (Primary) Figure 6-8

No.	Part	Drawing or P/N	Material	Weight (Grams)	Weight (oz.)
1	Connector, Electrical Bendix	PT1H-8-4PW	Brass-Nickel Plated	5.8	0.2
2	Screw, Preamplifier Retainer	2-56 x .31	SS	0.5	0.02
3	Speedserts, Tridair Industries	SP-0256-S	SS	0.1	0.004
4	Screws, Cap Mounting	4-40 x .31 Pan Head(3)	SS	1.45	0.05
5	Wire, Silver	0.025 dia	Ag	0.15	0.004
6	Ceramic Thread (Diffusion Junction)	0.040 dia		<0.1	<0.004
7	Cap, Preamplifier Reference Electrode	AG0044	Aluminum Nickel Plated	15.2	0.54
8	Preamplifier, Reference Electrode	AG0043	Mixed See AG0044	6.5	0.23
9	O-Ring, Cap Sealing, Parker	2-020	N674-7 Nitrile	0.2	0.007
10	Housing, Reference Electrode	AG0045	Polypropylene	6.9	0.24
11	Electrode, Glass Body		Glass	4.2	0.15
12	Electrolyte Gel		0.01M KCl 1.0M KNO_3 3% CMC Water	2.0	0.07
			TOTAL WEIGHT	43.0	1.5

6.4.1.5.1 Silver-Silver Chloride Electrode

The silver-silver chloride primary reference has an inner glass body mounted in a plastic housing, the top of which also contains a preamplifier connected directly to the internal silver wire. The internal silver wire is coated with silver chloride and surrounded by a gel containing 0.01 molar potassium chloride and 1 molar potassium nitrate. A porous ceramic rod provides a diffusing liquid junction with the 1M KNO_3 electrolyte in the electrolyte chamber.

6.4.1.5.2 Quartz Fiber Junction

The quartz fiber junction consists of quartz fiber(s) heat sealed in the end of a glass tube which is cemented in a polypropylene disc. The disc is held in place opposite the active element of the sensing electrode (silver sulfide pellet) by a portion of the lower section of the sensing electrode housing. The periphery is sealed by means of an O-ring. The quartz fiber junction may be replaced after removal of the sensing electrode from the sensor chamber.

6.4.1.5.3 Secondary Electrolyte Chamber

The secondary (1M KNO_3) electrolyte chamber forms a part of the sensor chamber body. The body of the silver-silver chloride reference electrode extends into the electrolyte chamber. The 1M KNO_3 electrolyte connects the quartz fiber junction to the diffusion junction of the silver-silver chloride electrode, thus establishing a double-junction reference.

6.4.1.5.4 Electrolyte Cartridge

The replaceable electrolyte cartridge contains approximately 5 ml of 1M KNO_3, which would be expended in approximately 100 days when installed in the sensing unit. The cartridge body is KEL-F and contains a rolling rubber diaphragm. A spring is provided to press on the diaphragm and produce a constant electrolyte pressure on the quartz fiber junction. The water from the sample stream is routed to the outside of the rolling diaphragm to balance the sample pressure seen by the quartz fiber junction. Thus, the actual pressure differential across the quartz fiber junction is that supplied by the spring. The cartridge would be prefilled, and have an estimated shelf life of greater than 2 years.

The cartridge has been designed to be sealed by a silicon rubber septum. When installed in the sensor chamber, a hypodermic-type needle pierces the septum, allowing the electrolyte to enter the secondary electrolyte chamber. The electrolyte cartridge is not intended for in-flight replacement but for ground replacement.

6.4.1.5.5 Electrolyte Needle

The hypodermic-type needle which connects the electrolyte reservoir with the secondary electrolyte chamber is stainless steel and is soldered to a 316 stainless steel mount. The periphery of the needle mount, when in place, is sealed with an O-ring. A retaining ring holds the needle mount in place in the body of the sensor chamber.

6.4.1.6 Chamber Cap

The lower section of the sensor chamber which contains the electrolyte cartridge is covered with a 316 stainless steel screw-on cap. The cap provides a chamber in which the water sample applies system pressure to the rolling diaphragm of the electrolyte cartridge. An O-ring provides a seal between the cap and sensor chamber body.

6.4.1.7 Thermocompensator

The thermocompensator consists of a specially chosen thermistor pair having electrical characteristics that vary with temperature in such a manner as to compensate electrically for response changes of the sensing electrode temperature variation. The thermocompensator is located in the main flow path of the water sample within the sensor chamber (see Figure 6-4).

The thermocompensator is mounted in the sensor chamber via a threaded connection and is readily replaceable.

6.4.2 Calibration System

6.4.2.1 Theoretical Design

The approach for accurate calibration is based on the principle of obtaining a known concentration of silver ions by saturating deionized water with silver bromide. At a given temperature, the concentration of the silver ions in the saturated solution would be accurately known. A closed-loop calibration system circulates water through an ion exchange column where all silver ions are removed, then through a silver bromide/glass bead column where the water becomes saturated with silver ions. The saturated solution passes through the pump, then through the sensor chamber where the silver ions are detected by the electrodes. The automatic calibration electronics compares the output of the electrodes with the known value and performs an electronic compensation accordingly. Since the solubility of the silver bromide in water varies significantly with small changes in temperature, a means of compensating for the change in solubility is required. A thermocompensator, located at the silver bromide column exit and connected to the calibrating electronic circuitry, should provide the necessary correction. However, such correction has not been demonstrated due to malfunction of the thermocompensator. In addition, the water recirculating through the calibration loop has not become saturated to the correct level of silver ion as it passes through the silver bromide column. The cause of this has not yet been determined. The calibration loop is shown as part of Figure 6-1 and in Figure 6-3.

6.4.2.2 Mechanical Design

During the calibration mode, both 3-way, 2-position solenoid valves are energized, providing a closed loop of fluid for circulation through the silver ion sensor chamber. The water first goes through an ion exchange column where the anions and cations are removed. The fluid then enters the silver bromide column where the silver bromide saturates the fluid with 70-80 ppb [Ag^+] at 25°C (77°F).

The use of individual columns for the ion exchange resin mix and the silver bromide is a departure from the Instrument Package Definition. The estimated weight of the dual-column assembly is 1360 grams (3 lb), while the actual weight of the two packed columns with fittings and thermocompensator is 398 grams (14 oz)--a savings of almost 1000 grams (2.2 lb). In addition, the use of two columns in place of the originally proposed dual-column assembly provides for easier replacement, and facilitates smaller packaging of the mounting system. The configuration of both columns is identical, while the packing of each is

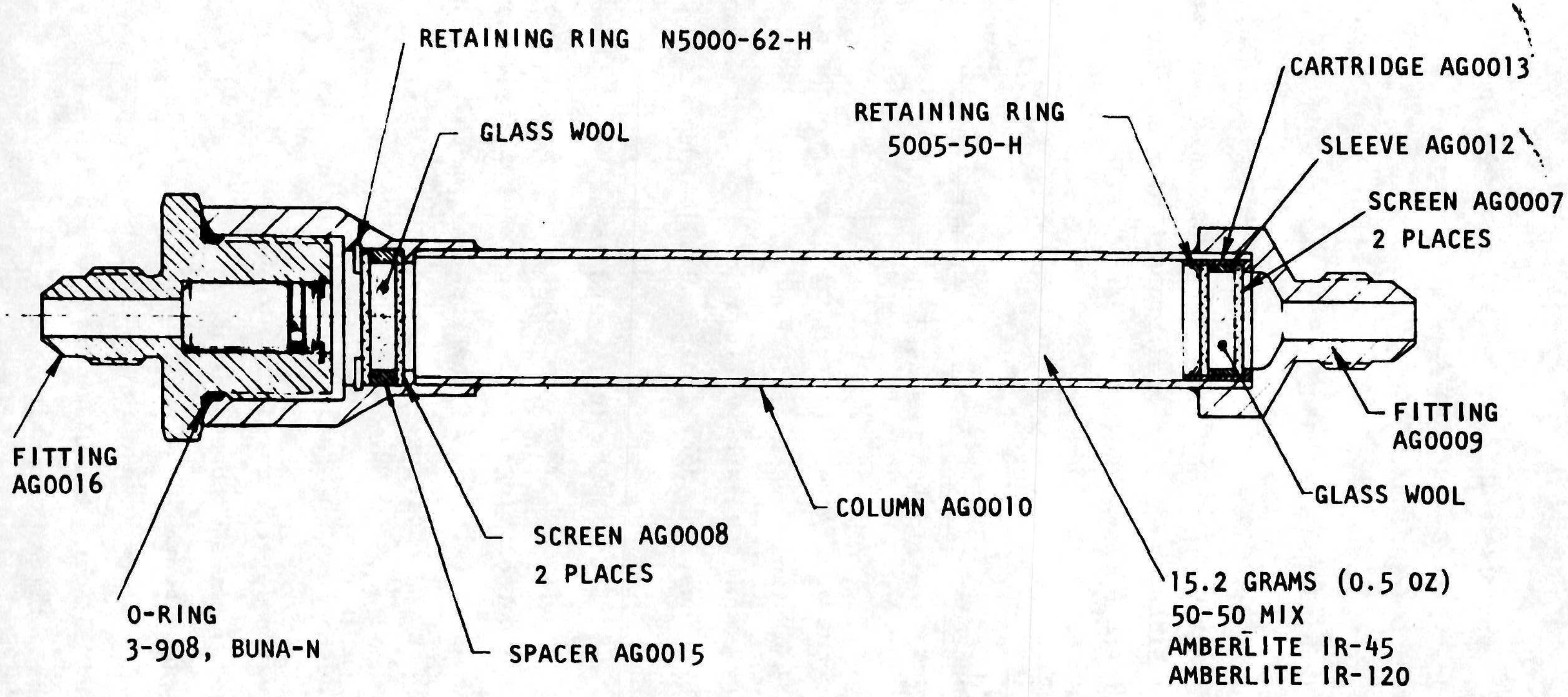


Figure 6-9. Ion Exchange Column

different. Figure 6-9 shows the configuration of the ion exchange column. The overall dimensions of the column are 2.54 centimeters (1.0 in.) diameter by 14.2 centimeters (5.6 in.) long.

6.4.2.3 Ion Exchange Column

The column contains 15.2 grams (0.5 oz) of a 50-50 mixture of Amberlite anionic type IR-45 and cationic type IR-120 ion exchange resins. These resins remove silver and bromide ions as well as other ions from the calibration fluid. The deionized water is then routed to the silver bromide column.

6.4.2.3.1 Preparation Procedure

The preparation procedure described in the Chemtric Inc. Final Report 3097, dated July 1972 (NASA CR 115595) was used as a guide.

Resin IRA-402 was not available either locally or from the manufacturer, Rohn & Haas. Since it is a strong basic resin used only to control pH, a substitute was not used because our test system fluids did not contain any strong acids such as HCl and HF--thus, did not require pH adjustment.

Analytical grade amberlite resins IR-120 and IR-45 were washed separately by placing a 50 cm^3 quantity in a 2.54-cm diameter by 38 cm Pyrex glass chromatography column and percolating 6 to 7 liters of boiling deionized water through the column over a period of one hour, at which time the effluent of the column was clear and odorless.

The stainless steel column (or canister) and fittings were prepared as follows:

1. Hot water detergent solution wash
2. Rinsed 5 times with deionized water
3. Soaked 18 hours in 30% nitric acid
4. Rinsed 5 times with deionized water
5. Soaked 18 hours in 20% ammonium hydroxide
6. Rinsed 5 times with deionized water
7. Rinsed 5 times with distilled water
8. Dried at 75°C (167°F) in oven for 18 hours

The resins were mixed 50-50 by volume and the column packed as described in the Chemtric report. As a departure from the recommended procedure, however, the packed column was not sterilized for the following reasons:

1. Cleaning and baking of the stainless steel ports should have effected sterilization of these ports.
2. Washing of the analytical grade resins with boiling water should have sterilized the resins.
3. Input to the column was to be distilled water containing 50 ppb or greater of silver ion which should not contain any live organisms.
4. Circulation or recirculation through the system of distilled water containing a bactericidal level of silver ion should keep the other non-sterilized components of the system free of live organisms.

The departures from recommended procedures may have resulted in the inability to obtain theoretical responses when the calibration loop was placed into the system. The relationship of the departures to the observed effects, however, are not readily apparent.

6.4.2.4 Silver Bromide Column

The silver bromide column contains 35.5 grams (1.25 oz) of a silver bromide/glass beads mixture. As the calibration water passes through the bed of silver bromide/glass beads, it becomes saturated with silver bromide.* The 50-micron glass beads are mixed with the silver bromide to increase the surface area of the silver bromide. The ratio by weight of the glass beads to silver bromide is 1/0.8. There are suitable screens and filtration material at the inlet and outlet to prevent loss of the glass beads/silver bromide granules.

The glass beads/silver bromide mixture used was that supplied by Chemtric, Inc.

---

*Demonstrated to be true for flow-through tests (see Section 7.2.4.4), but fluid recirculating in calibration loop failed to reach theoretical level of 78 ppb at 25°C.

The stainless steel column and fittings were prepared the same as the ion exchange column and fittings described in Section 6.4.2.3.

6.4.2.5 Fill and Bleed Valve

Provision to add water and bleed any trapped air when the deionizer column or silver bromide column is replaced is provided by the fill and bleed valve located in the AN938 TEE which connects the deionizer column to the output of of solenoid valve V3.

6.4.2.6 Interface Design

During the calibration mode, the point of interface is at the solenoid valves. The normally closed solenoids open when energized, isolating the calibration loop. Energizing the two solenoids requires approximately 55 watts.

6.4.2.7 Solenoid Valves

The selected solenoid valves are 3-way, 2-position, normally closed valves that are flight-qualified, off-the-shelf components.* The power required is 18 to 28 Vdc. The coil has a resistance of 39 ±2 ohms at 21°C (70°F). The body is fabricated from 2014-T6 aluminum with a stainless steel spindle. All parts are AND10050-4. The valve has passed a 250,000-cycle endurance test conducted by the manufacturer.

6.4.3 Pressure Relief Valve

A small relief valve is included to reduce the pressure from the fluid pump to the sensor chamber. If the relief valve opens, the excessive flow would be routed to the main flow line. The valve is an in-line relief valve with 316 stainless steel body and fittings, 302 stainless steel spring, Buna "N" O-ring, and Teflon gasket--model SS-4CA-3 manufactured by Nupro Company, Cleveland, Ohio.

---

*Manufactured by Futurecraft, P/N 20950, and qualified by North American Rockwell Corporation.

6.5 Monitor Electronics

6.5.1 General

The monitor electronics were designed to perform the following basic functions:

a. Amplify and condition the signal from the electrode system to give a readout in parts per billion of silver ion:

b. Compensate automatically for temperature variations in the solution and system;

c. Generate an automatic timing sequence that would periodically calibrate the unit;

d. Allow a calibration sequence to be manually initiated at any time, but without affecting the automatic sequencer;

e. Give an indication if calibration is not achieved by the end of the calibration period; indicator would be automatically reset at the start of each calibration sequence;

f. Store the last output just prior to a calibration interval so that it could be manually recalled during a calibration period.

Although the original design concept was modifed somewhat later in the program, the original rationale will be discussed first. The modifications are described in Section 9.0.

Figure 6-10 shows the indicators and controls that are required for the sensor electronics. The original general block diagram for the electronics is shown in Figure 6-11.

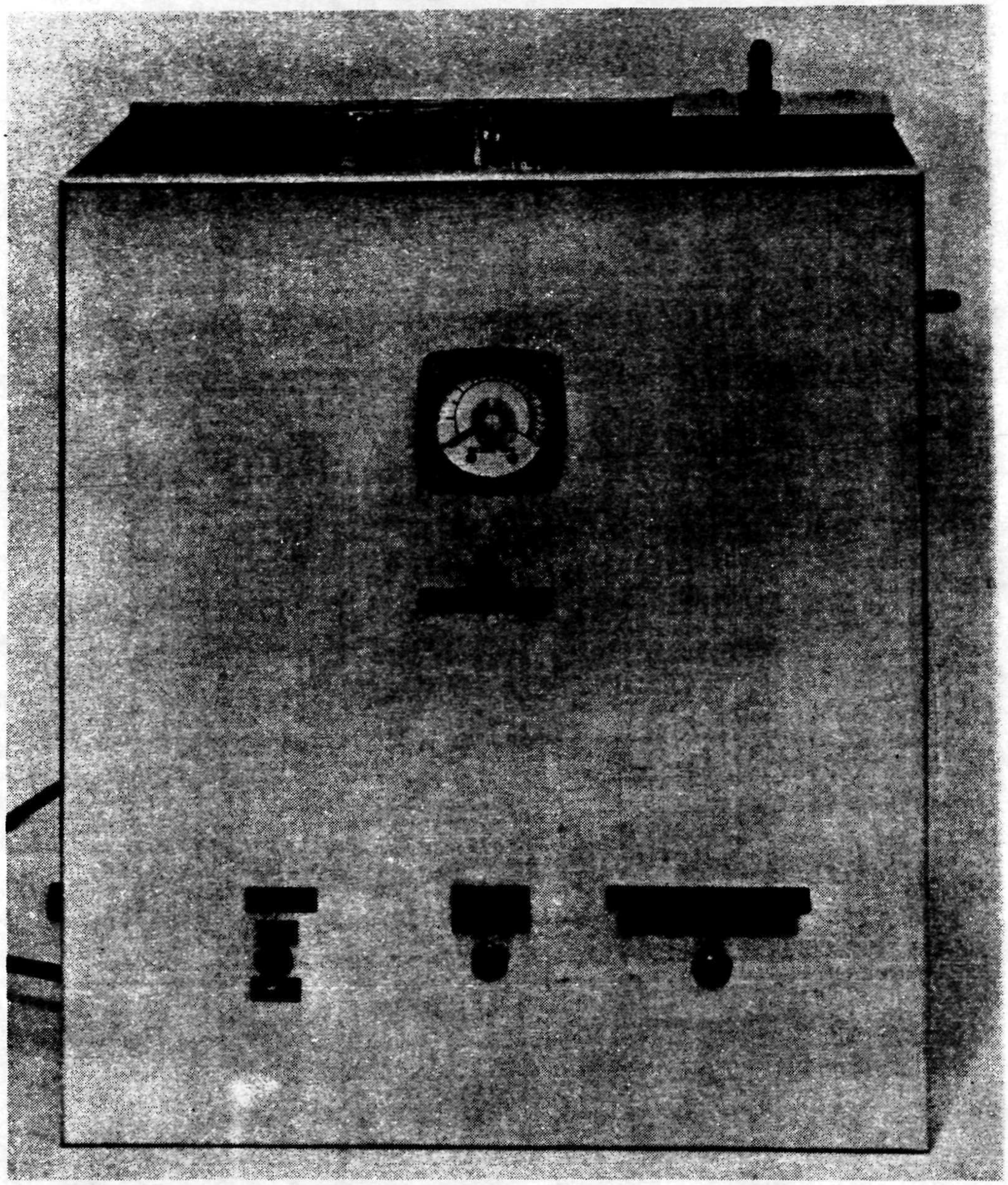


Figure 6-10. Electronic Controls and Indicators

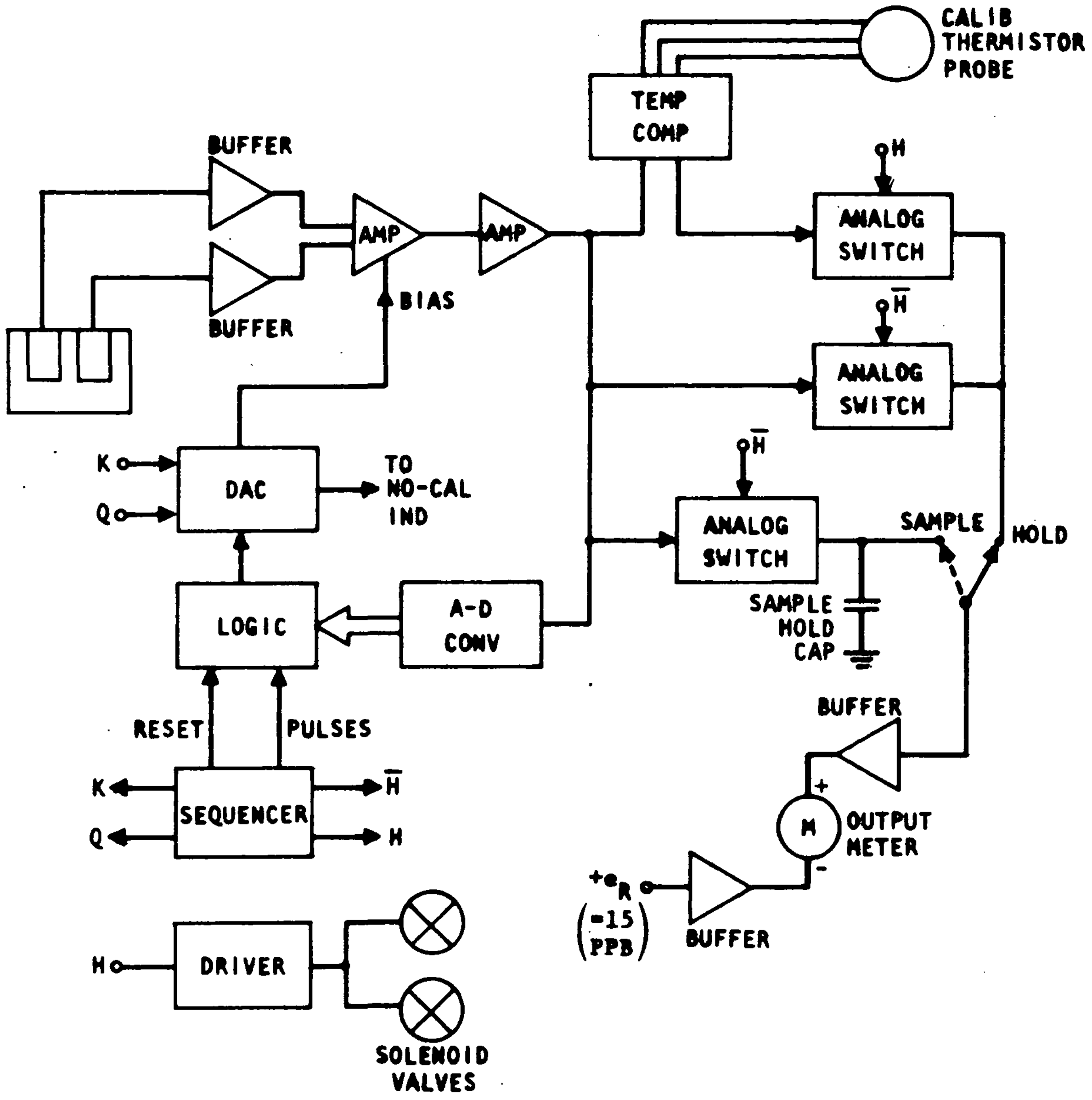


Figure 6-11. Monitor Electronics Block Diagram

6.5.2 Electrical Design

The electronics may be broken down into the following basic functions:

- Logic and Valve Actuation
    - a. Sequencer
    - b. Logic
    - c. Valve driver
    - d. Valves
- Calibration Electronics
    - a. Comparators
    - b. Analog-to-digital and digital-to-analog converters
    - c. Counter logic
- Signal Processing and Readout
    - a. Electrode preamplifiers
    - b. Buffers
    - c. Instrumentation amplifier
    - d. Thermocompensation circuits
    - e. Sample-and-hold circuit
    - f. Readout meter
- Electronic Integration Components
    - a. Power conditioning
    - b. Wiring harness
    - c. Front panel

6.5.2.1 Logic and Valve Actuation

A detailed block diagram of the logic and sequencer system is shown in Figure 6-12. The unit consists of a clock oscillator, base divider, divider chain, logic, and drivers. The logic is positive.

The clock oscillator consists of a pair of operational amplifiers (741s) connected as discriminator and integrator circuits in a loop. The output of the

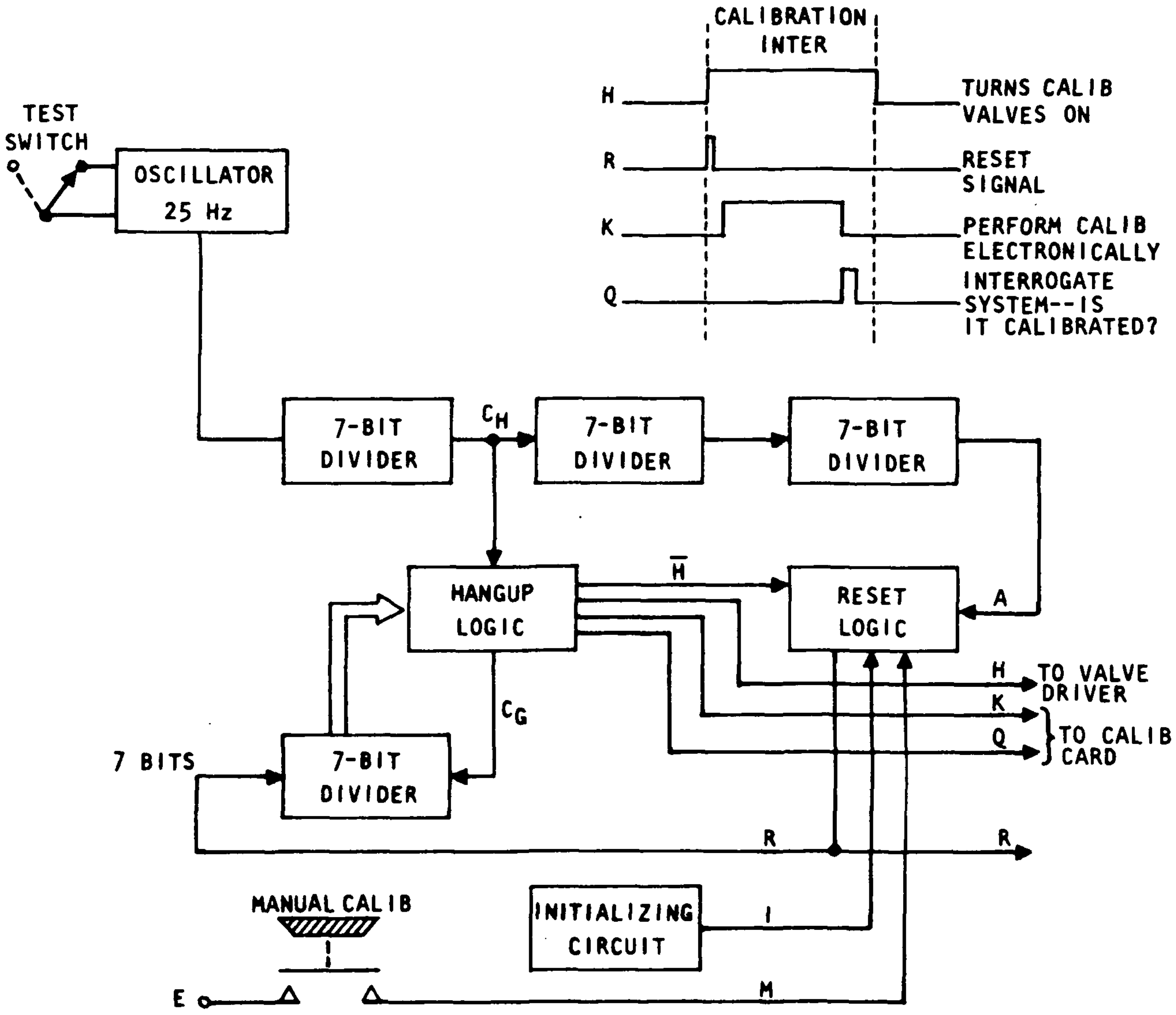


Figure 6-12. Sequencer Logic--Block Diagram

oscillator loop is a 25 Hz square wave. After level buffering, the 25 Hz square wave is divided down by means of three CD4024AK's (each is a 7 flip/flop divider chain). Several of these divider outputs are used to operate additional logic which generates the signals to operate valves and places the unit in calibration.

Approximately every 24 hours, a reset signal, which acts as a "hang-up" counter, is generated by the sequencer and divider. The "hang-up" counter counts up to seven, which takes about 10 minutes. When it reaches seven, it "hangs-up", and stays in this state until 24 hours later, when the next reset pulse arrives.

The outputs of the "hang-up" counter generate all calibration signals. The 10 minute period in which the "hang-up" counter operates coincides with the calibration interval.

A reset signal (and hence an additional calibration interval) may also be initiated manually at any non-calibration time by the manual initiation of a calibration switch.

6.5.2.2 Automatic Calibration Electronics

The calibration electronics responds to the signal from the logic every 24 hours, or whenever the calibration sequence is manually initiated. The "stabilize system" signal is on for seven count periods. This amounts to about 10 minutes.

In the Instrument Package Definition (Report COR-2639-1, 23 March 1972), the calibration electronics contain a motor-driven potentiometer to adjust or calibrate the system. The prototype monitor, however, utilizes analog and digital logic circuits to accomplish calibration. This change was recommended as part of the findings of the preliminary Failure Mode and Effects Analysis (FMEA) to reduce weight, size, and power requirements and to increase reliability.

Figure 6-13 shows a block diagram of the calibration electronics.

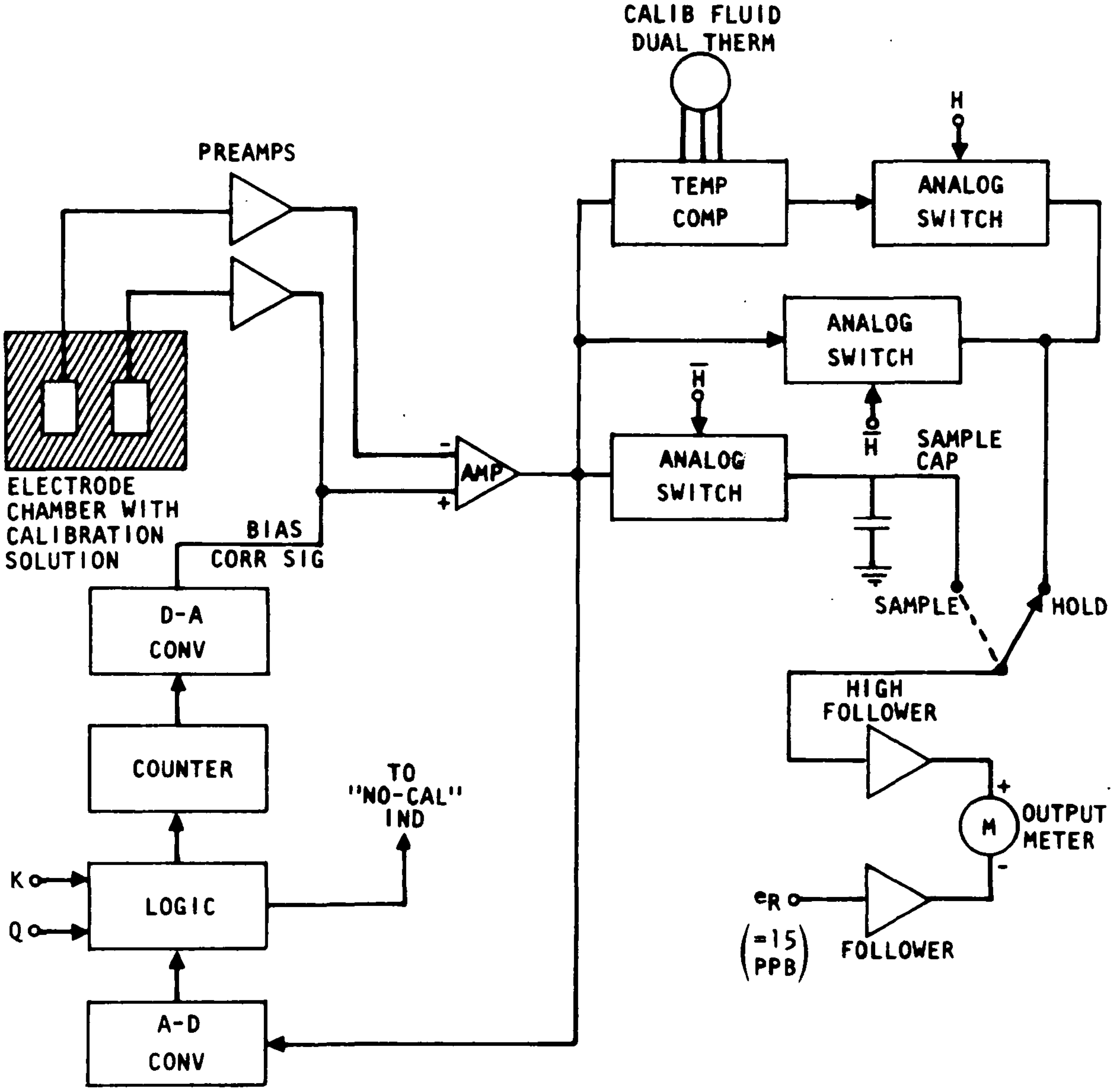


Figure 6-13. Calibration Electronics--Block Diagram

During the calibration period, the sequencer actuates the solenoid valves and places the fluid system in a calibration configuration. Also, the amplifier output is fed to an analog-to-digital converter. The digital output is logically examined to see if it is in a desired "dead zone." If it is, nothing happens. If not, pulses (derived from the sequencer) are allowed to operate a counter and digital-to-analog converter. As the counter counts up, the digital output is converted to a bias correction voltage which is fed back to the amplifier. The dead zone corresponds to the correct output for the calibration silver concentration. When the dead zone is reached, no more pulses are allowed to pass. The counter/digital-to-analog converter (DAC) stays in that state, generating that bias correction voltage until the next calibration interval.

During the start of calibration, the dead zone may be below the voltage at which the calibration system starts. If so, the counter gets up to its maximum count and resets, then continues counting up to where it finds the dead zero zone (Figure 6-14).

After the calibration is supposedly finished (but before the end of the calibration interval), the logic checks to see if the amplifier is in the dead zone. If it isn't, the NO-CALIBRATION light comes on (and stays on until the next calibration interval) to alert the operator that the system is not in calibration.

6.5.2.3 Signal Processing and Readout

Figure 6-15 is a block diagram of the original signal processing and readout system. Each system electrode has a preamplifier within the electrode body. These preamplifiers are FET-input types with an input impedance of 10^{15} ohms.

The difference between the two electrode preamplifier outputs is further amplified by two differential amplifiers whose outputs are referenced to solution ground. The first differential amplifier has an input for the calibration bias signal and has its feedback resistor value modified appropriately by the electrode chamber's dual thermocompensator, so that the temperature effect on electrode characteristics are cancelled out. The thermocompensator also responds to temperature changes more quickly than the system temperature will ever change.

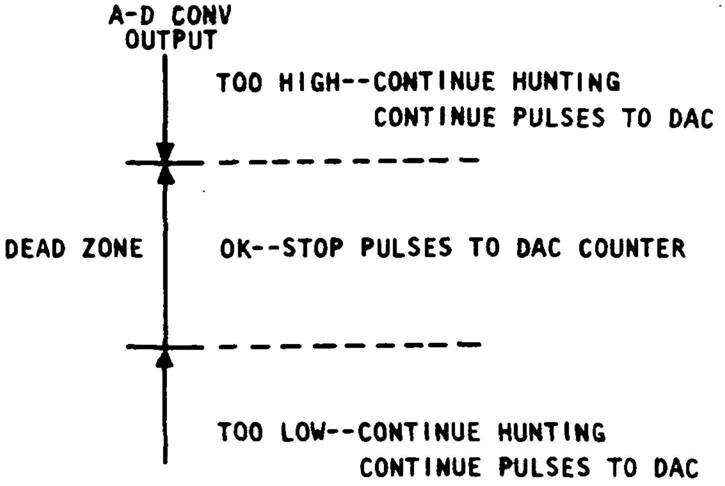


Figure 6-14. Calibration Comparator Characteristics

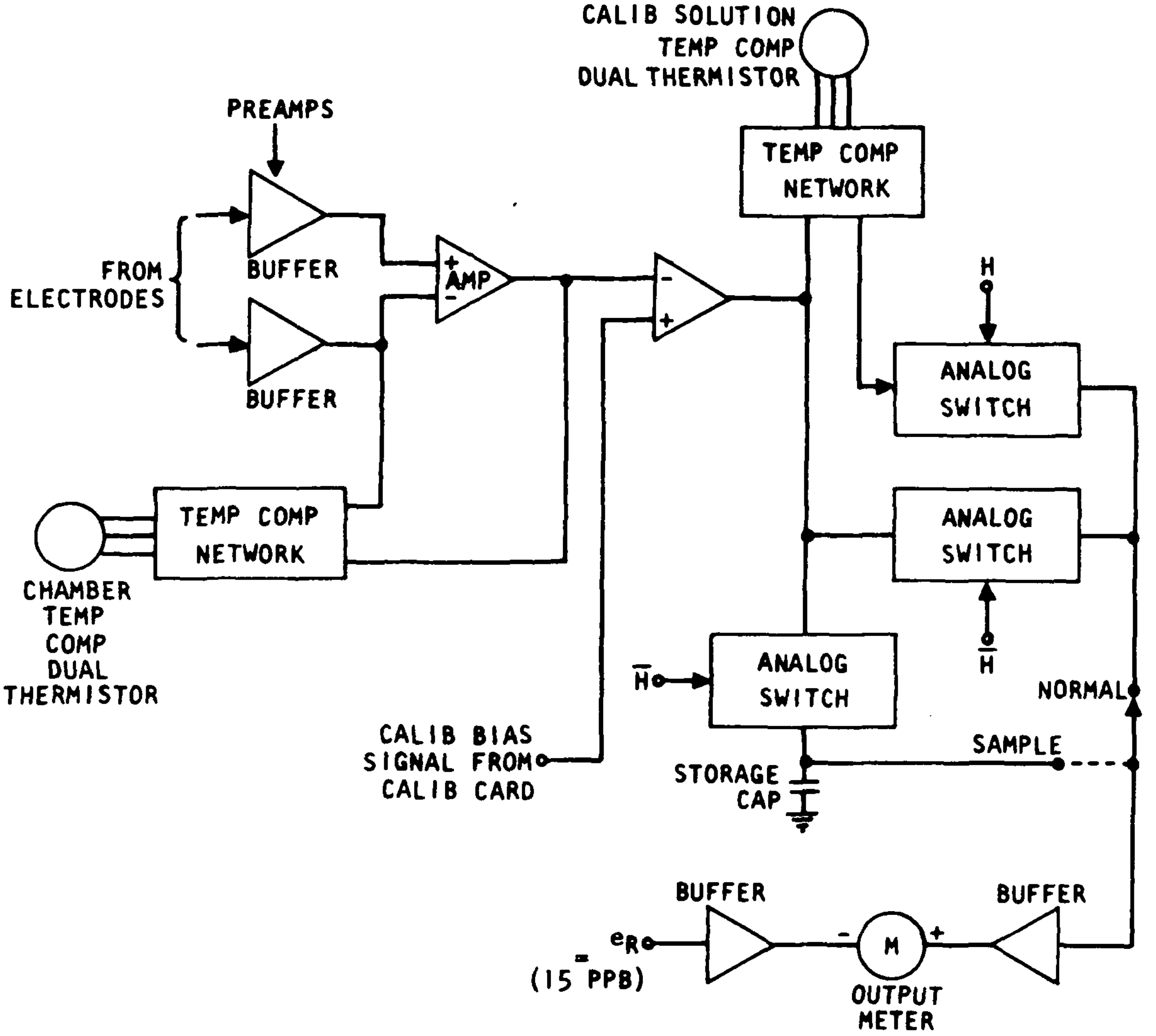


Figure 6-15. Signal Processing and Readout--Block Diagram

The second differential amplifier feeds a temperature correcting network (used only in calibration) and two analog switches, controlled by analog switch $\bar{H}$. During normal operation, both analog switches are shorted out, so the signal is fed to the meter, which is referenced to a voltage equivalent to 15 ppb of silver.

A thermocompensator in the silver bromide bed compensates for variations in the degree of saturation solubility with temperature. If this compensator has incorrect characteristics, the system calibrates with an error that is dependent on temperature. This compensator has a temperature response that is much shorter than the initial stabilization period that occurs at the start of the calibration cycle.

During calibration, the two analog switches from the second amplifier are open and a third analog switch closes to connect the calibration temperature compensation network.

The signal is now corrected for any temperature variations in the calibration fluid concentration.

If the sample/hold switch is pressed, the meter should read out the value of the last reading prior to calibration (stored in the storage capacitor).

6.5.2.4 Electronic Integration

- Power Conditioning. The following voltages are required to operate the electronics:

  110 Vac, 50/60 Hz - Pump
  +28 Vdc - Valves
  +15 Vdc - Preamp, Amplifier, and Sequencer
  + 5 Vdc - Logic
  -15 Vdc - Preamp, Amplifier, and Sequencer

  Power at 110 Vac, 50/60 Hz would be obtained from the spacecraft supply, as would +28 Vdc from which the remaining dc voltages would be derived. Figure 6-16 shows the power distribution and conditioning system.

EMI/RFI filters, protective zeners, resistors, and circuit breakers were not used on the prototype.

- Packaging and Interconnections. The preamp buffers are in a shielded section of each electrode housing. The balance of the electronics, less the pump-motor and valves, is on printed circuit boards. Shielded wires are used to interconnect the following items:

  Indicators and controls on panel
  Electronics PC Board
  Vlaves
  Pump-motor
  Input power lines
  Electrodes
  Thermistors in system

6.6 Material

In addition to the materials used in the sensor chamber, the following materials were originally used in the system:

- Supporting frame and cover--aluminum
- Tubing--0.64 cm (1/4 in.) 316 stainless steel
- Solenoid valves--aluminum
- Manual valve--Teflon
- Electronic housing--aluminum
- All MS fittings--316 stainless steel
- Two-column assemblies--316 stainless steel

6.7 Finishes

All aluminum parts in contact with the water have been anodized per MIL-A-3625, and all stainless steel parts passivated per MIL-S-5002 or electropolished.

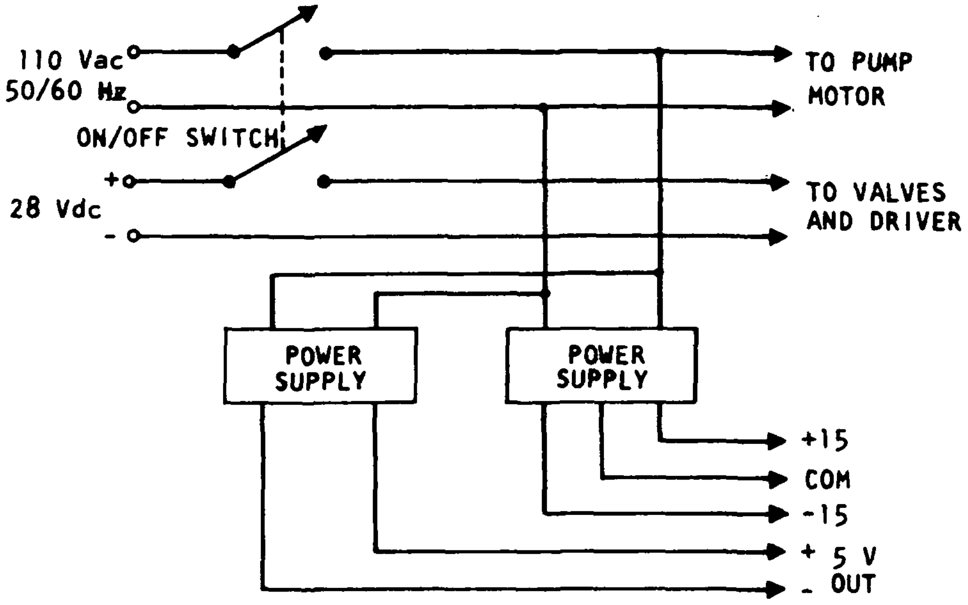


Figure 6-16. Power Distribution and Conditioning System

6.8 Interface Requirements

The silver ion monitoring system requires the following interface requirements with the Space Shuttle vehicle:

- An electrical connection is required for 28 Vdc and 110 Vac, 50/60 Hz, spacecraft power. The power requirements are estimated to be approximately 30 watts during the silver ion concentration monitoring mode, and approximately 85 watts during the calibration mode.
- Two liquid connections at each monitoring site are required. The interface connections would be made to the main water line via two stainless steel, double-ended, shutoff, quick disconnects. The use of double-ended shutoffs would eliminate leakage whenever the silver ion detector assembly is removed from the main line. The suggested quick disconnect is a commercial component--Swagelok P/N 400QC-6.

6.9 Preliminary FMEA

The detailed design phase included a preliminary Failure Mode and Effect Analysis (FMEA). Each system component (electrical and mechanical) was studied for possible failure modes. Each failure mode was considered as to its effect on system performance. Any nonfail-safe situation was rectified by design or component changes. Quality assurance, reliability, and safety were included in the preliminary FMEA (Appendix B).

7.0 PRELIMINARY TESTING

7.1 General

The preliminary testing program was designed to test independently each major component under as many simulated use conditions as practical to determine performance characteristics, i.e., response of sensing electrode, to determine mechanical stability with particular attention to pressure, flow, and temperature effects, and to determine if the purchased or fabricated parts met design specifications and were suitable for the intended application.

The preliminary testing program was intended to encompass all testing, including integration and troubleshooting, prior to verification testing. However, during the early stages of testing the fluid handling unit and the potentiometric electrodes, a rapid loss of silver ion was observed from the recirculating water. In addition, a degradation of the silver sulfide electrode was noted. Following the modifications described in Section 9.0, the electronics were integrated with the remainder of the system. This is described in Section 10.3.5.

The rationale used for choosing the test conditions was based on the characteristics of the Space Shuttle Potable Water System. However, since the silver ion monitor will be upstream of both the water chiller and heater, the proposed test temperature range was limited to ambient--23.9 ±8.3°C (75 ±15°F).

Prior to assembly, each component was separately tested under simulated use conditions. However, since the function(s) and performance(s) of the components or subsystems vary widely, they were divided into two subsections. Paragraph 7.2 describes the Criteria and Preliminary Testing of Components—Fluid Handling Unit, which includes the following components:

- Sensing electrode
- Reference electrode

- Ion exchange column
- Silver bromide column
- Solenoid valves
- Motor-pump combination
- Sensor chamber
- Manual valve
- Pressure relief valve

Paragraph 7.3 describes the Criteria and Preliminary Testing of Components--Electronic Section. The preliminary testing was such that unacceptable performance characteristics, design weaknesses, or other problems could be detected and corrected prior to final assembly or verification testing.

7.2 Criteria and Preliminary Testing of Components--Fluid Handling Unit

7.2.1 Sensing Electrode (Solid State, Silver Sulfide)

7.2.1.1 Criteria--Design Goals

- The sensing electrode must exhibit typical Nernstian response--59 mV/decade ±2 mV--at 25°C (77°F) from 15 ppb to 150 ppb silver ion concentration;
- The sensing electrode must not exhibit a noise factor in excess of 10 percent full-scale of meter reading, or 1.5 ppb, whichever is greater;
- The sensing electrode must be physically stable and show less than 15 percent apparent offset from known concentrations of silver ion due to pressure and flow changes, as defined for the system;
- The sensing electrode must not exhibit a thermal degradation due to exposure over the temperature range of 15.6 to 32.2°C (60 to 90°F). Instability, excess noise, or change in Nernstian response outside the range of 59 mV/decade ±2 mV with temperature compensation will be cause for rejection;
- The sensing electrode must have a temperature coefficient that can be readily compensated for electronically (thermocompensator, i.e., resistor or thermistor in the measuring circuit).

7.2.1.2 Test Procedure

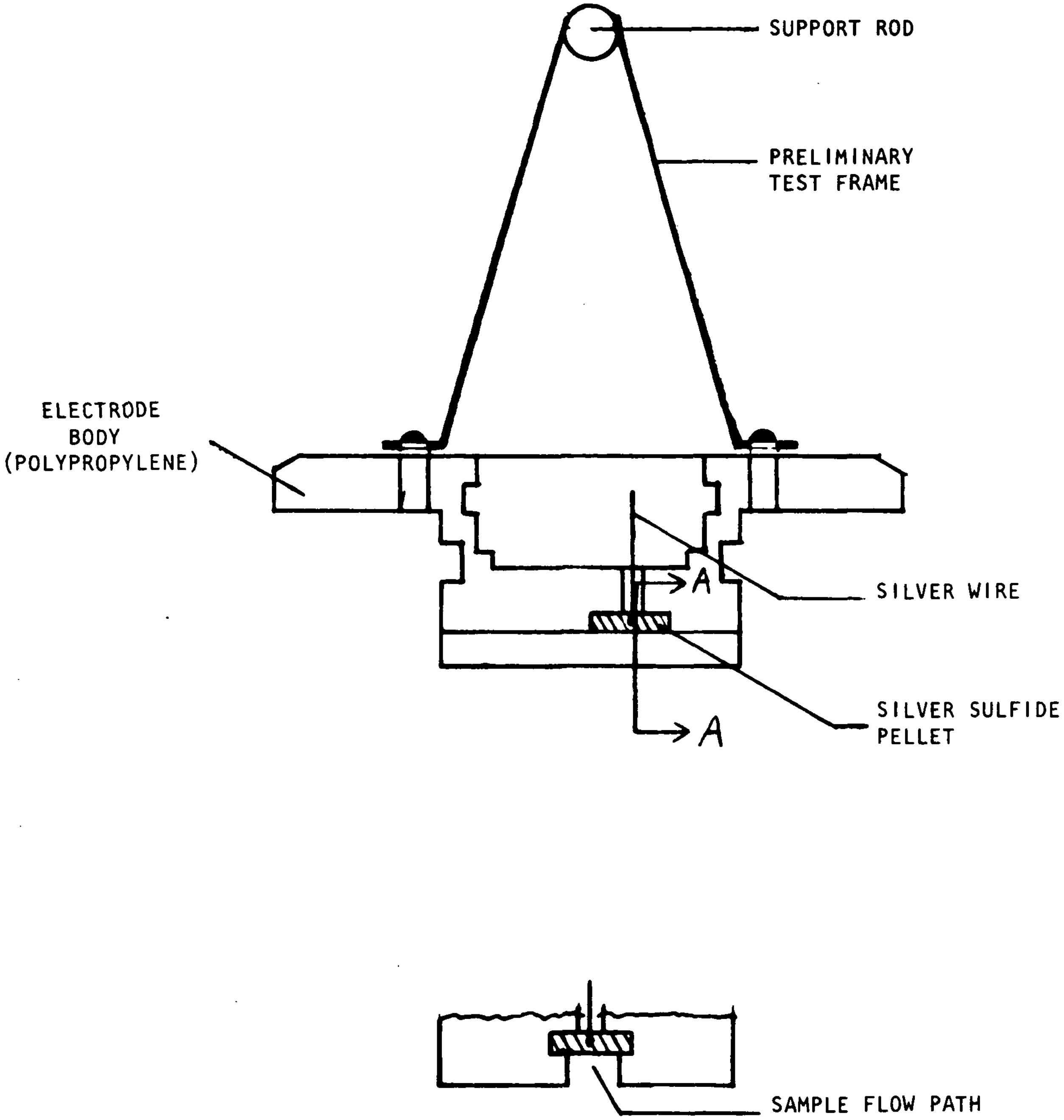
Due to the inclusion of a preamplifier in the sensing electrode housing, the configuration of the electrode was such that pressure, flow, and thermal characteristic tests required the use of the sensor chamber. These tests, however, were never performed since they were precluded by the effort expended toward the problem of loss of silver ion from solution.

The response tests were made following conditioning in 10 ppm silver ion solution at 40°C (104°F) for 72 hours. The tests were made prior to installing the preamplifier and shielding cap as shown in Figure 7-1.

The tests were performed at ambient temperature--25°C (77°F)--utilizing the beaker test setup shown in Figure 7-2. The components are identified in Table 7-1. The electrode was supported by a test frame and support bar as shown in Figure 7-1. Only that portion of the electrode containing the silver sulfide pellet or membrane was immersed in the test solution. Test solutions of 50 and 500 ppb silver ion were used. Between changing of test solutions, the beaker and electrodes were dip-rinsed in a portion of the new test solution which was discarded. The millivolt response readings were taken after the strip chart recording indicated a stable reading.

7.2.1.3 Test Results

The prototype silver ion sensing electrodes were identified with the letters PR plus a number. Table 7-2 gives the preliminary test data on the first batch of seven electrodes. Of the seven electrodes, two exhibited theoretical Nernstian response with low noise and no drift, while two exhibited borderline response but were usable. Later, two other batches were made of a modified sensor configuration. Data on these are given in Section 10.



SECTION THROUGH A-A

Figure 7-1. Prototype Sensing Electrode (Silver Sulfide) Configuration (Series PR) without Cap and Preamplifier

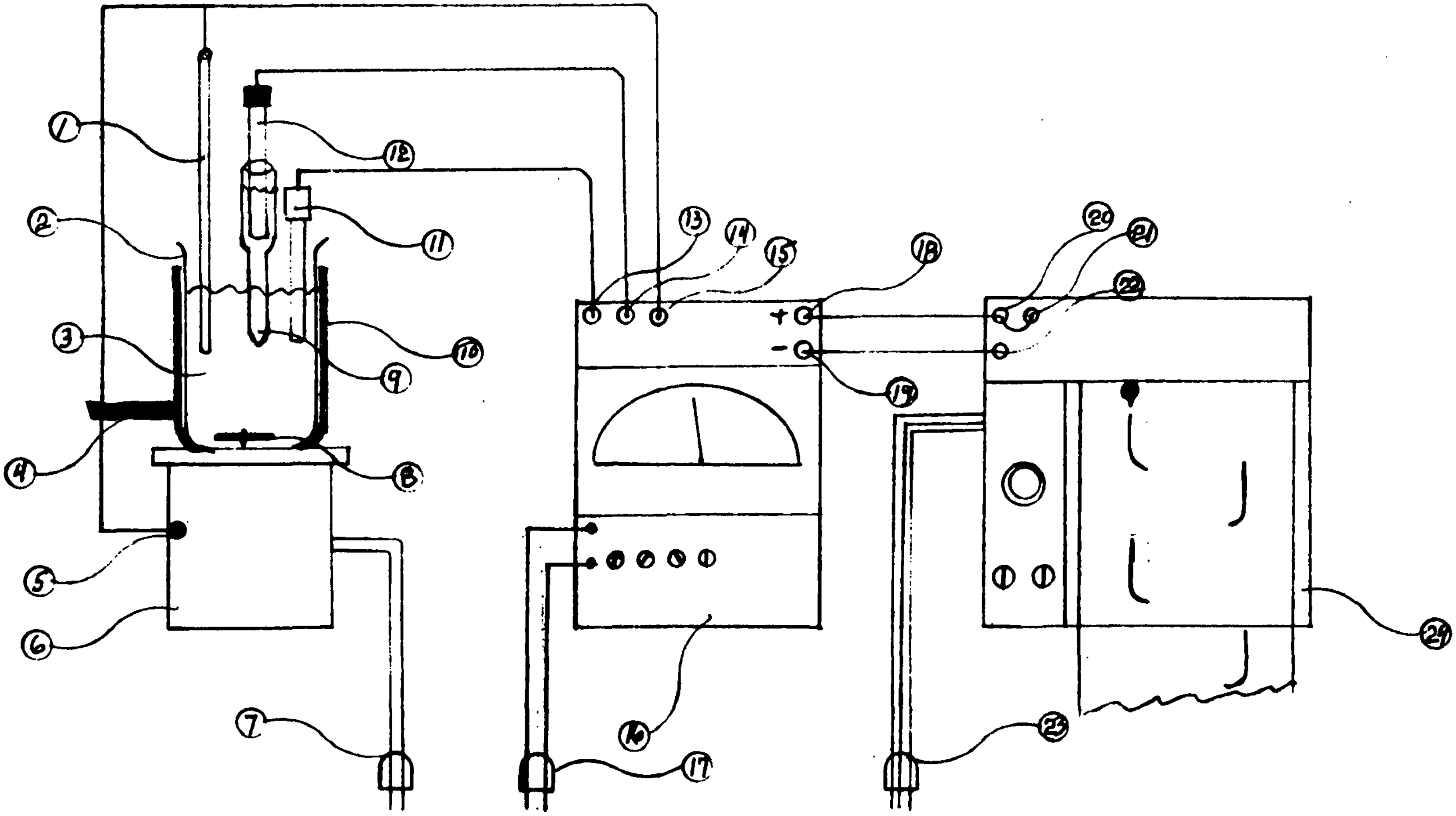


Figure 7-2. Beaker Test Setup

Table 7-1. Component Identification--Beaker Test Setup

1. 316 Stainless-steel rod or tube for solution ground
2. Glass beaker, 100 or 600 ml, shielded with item 4
3. Liquid sample, 80 or 500 ml
4. Aluminum foil shield connection to solution ground
5. Ground or frame connection on stirrer
6. Magnetic stirrer
7. Magnetic stirrer power connection - no ground
8. Teflon coated stirring bar
9. Salt bridge with ceramic junction containing 1M KNO_3 solution
10. Aluminum foil shield on beaker
11. Silver sulfide electrode, any configuration
12. Reference electrode - Beckman Perma Probe No. 39407
13. Glass electrode connection
14. Reference electrode connection
15. Solution ground
16. pH meter, Beckman Century SS-1 No. 76009 or Beckman 940 pH Analyzer
17. pH meter power connection - no ground connection
18. Positive output from pH meter
19. Negative output from pH meter
20. Positive input to strip chart recorder
21. Guard connection with jumper to positive input
22. Negative input to strip chart recorder
23. Recorder power connection - with ground connection
24. 10-inch strip chart recorder, Beckman 100 mV range, No. 100500

Table 7-2. Preliminary Test Data--Sensing Electrodes

Identification	Response at 25°C (77°F) mV/decade	Noise mV	Drift
PR-1	59	±1	None
PR-2	<20	±1.75	Continuous Upward
after 2nd conditioning	44		
PR-3	60	±2	None
PR-4 after 2nd conditioning	60	±1.75	Slow Downward
PR-5 after 2nd conditioning	56	±1	None
PR-6	42	±1	None
PR-7	64	±2	None

NOTE: Electrodes PR-1 and -3 Nernstian response, acceptable

Electrodes PR-5 and -7 borderline but usable

7.2.2 Reference Electrode

7.2.2.1 General

The reference electrode is composed of more than fifteen components, most of which have no active function other than support, sealing, etc.; therefore, there are no meaningful tests for most of these parts. Since such components account for about 80 percent of the sensor chamber, the reference electrode could only be tested when the sensor chamber was completely assembled, containing a sensing electrode. Two components, however, did lend themselves to preliminary screening tests--the primary silver-silver chloride reference, and the quartz fiber junction.

7.2.2.2 Quartz Fiber Junction

The quartz fiber junction must provide a liquid-liquid junction with the sample and must have the following characteristics:

- Flow rate of electrolyte, one molar potassium nitrate (1M KNO_3), through the junction must be very low--between 50 to 150 µl per day under a force of $6.89 \times 10^3 \pm 1.72 \times 10^3$ N/m^2 (1 psig ±0.25 psig);
- The electrical resistance across the junction must be less than 40 kilohms when measured in 1M KNO_3 at ambient temperature.

7.2.2.2.1 Test Procedure

The quartz fiber junction is formed at the end of a 15-cm (6-inch) length of glass tubing and is tested in this configuration prior to final assembly. The quartz fiber junction was connected to a 0.1 ml glass pipette (graduated in 0.01 ml) with an adapter. The pipette and junction were filled with 1M KNO_3 solution. The pipette and junction were held vertically and air pressure at 6.89×10^3 N/m^2 (1 psig) applied to the top of the pipette. The movement of the meniscus past the graduations was observed over a period of hours. The 24-hour flow was then calculated.

The electrical resistance of the junction was measured by filling it with 1M KNO_3 solution, immersing the tip in the same solution; then a pair of silver wires placed in the fluids on both sides of the junction and connected to a conductivity meter. The resistance across the junction was measured at 1000 Hz to prevent polarization.

7.2.2.2.2 Test Results

Since the fabrication of a quartz fiber junction having the required characteristics is not an exact science, a large number of junctions were made and tested. The data on those few which were acceptable are shown in Table 7-3.

Table 7-3. Quartz Fiber Junction Test Results

No.	Flow μl/day at 6.89×10^3 N/m^2 (1 psig)	Resistance K ohms at 1000 Hz
13	100	5.55
25	200	5.0
28	250	7.9
8	350	6.5
NOTE: Nos. 25 and 28 are usable if spring pressure reduced to 227 grams (0.5 lb).		

7.2.2.3 Primary Silver-Silver Chloride Reference

- The primary reference must not exhibit noise in excess of 1.5 mV, or drift in excess of ±1.5 mV in 20 hours;
- The primary reference should exhibit theoretical output of -173 mV ±20 at 25°C (77°F) against a silver-silver chloride electrode with saturated KCl electrolyte;
- The electrical resistance must not be greater than 20K ohms;
- When paired with a sensing electrode (Paragraph 2.2.1), the response shall be 59 ±2 mV/decade at 25°C (77°F).

7.2.2.3.1 Test Procedure

The noise, drift, and response were determined by connecting the test reference and a known stable silver-silver chloride reference to a pH meter which was connected to a 10-inch recorder. Both electrodes were placed in a constantly stirred 1M KNO_3 solution. The pH meter was operated in the expanded millivolt mode and the recorder adjusted for one chart division to equal 1 mV. The test was performed for 20 hours continously, and the output of the pH meter recorded.

The 20-hour response of the reference paired with a silver ion sensing electrode was not performed due to the rapid loss of silver ion from solution during recirculation.

7.2.2.3.2 Test Results

The prototype primary reference is a silver-silver chloride electrode with 0.01 molar potassium chloride electrolyte. The PERMA-PROBE is a silver-silver chloride electrode with saturated potassium chloride electrolyte. Theoretical difference then, when tested as a pair, should be -173 mV at 25°C (77°F).* Plus or minus 20 mV from theoretical is acceptable since adequate system calibration is provided and absolute mV are not measured or required. The results are given in Table 7-4.

---

*Potassium chloride solubility 1 gm in 2.8 ml H_2O at 25°C (77°F) (Merck Manual, Eighth Ed., 1968)

Molar concentration (or moles per liter) of saturated potassium chloride solution at 25°C (77°F)

$$\text{then} \quad \frac{\frac{1000 \text{ ml}}{2.8 \text{ ml}}}{74.55 \text{ gm/mole}} = 4.79 \text{ molar}$$

The PERMA-PROBE and prototype reference form a concentration cell of potassium chloride. Therefore, the Nernst equation can be used to calculate the theoretical potential difference between the two electrodes.

$$\Delta E = 2.3 \frac{RT}{F} \log \frac{[\text{KCl } 0.01 \text{ M}]}{[\text{KCl sat}]}$$

(footnote continued on page 7-11)

Table 7-4. Prototype Reference Electrode Characteristics
(Tested Without Preamplifier)

Reference	Vs. Perma Probe Reference			Vs. Silver Sulfide Electrode mV/decade at 25°C (77°F) 50 to 500 ppb $[Ag^+]$
	Response mV	Noise mV	20 Hr Drift mV	
R-1	-136	----	----	Rejected
R-2	-155	<0.2	+1.5, -0.5	58 ±1
R-3	-156	<0.2	+0.5, -1	59 ±1
R-4	-152	<0.2	+1, -0.5	59 ±1

7.2.3 Ion Exchange Column

7.2.3.1 General

The ion exchange column is located upstream of the silver bromide column in the calibrating loop. It is packed with a mixture of anion and cation exchange resins, and its purpose is to remove the anions and cations from the circulating liquid prior to passage of that liquid into the silver bromide column. The

---

at 25°C (77°F) becomes

$$\Delta E = 0.059 \log \frac{[\text{KCl } 0.01 \text{ M}]}{[\text{KCl } 4.79 \text{ M}]}$$

$$\Delta E = 0.059 \log \frac{\bar{2}.000}{0.68034}$$

$$= 0.059 \times 2.9397 = 0.173 \text{ V}$$

$$= 173 \text{ mV}$$

The sign is dependent upon which electrode is made the reference with respect to the pH meter.

anticipated maximum concentration of silver ion in the calibrating loop will be 115 ppb silver, and will only reach that level when the ambient temperature to which the silver bromide column is exposed reaches 32.2°C (90°F).

7.2.3.2 Criteria

- The ion exchange column must reduce the concentration of silver and bromide ions and other interfering ions to below 10 ppb;
- The column must effect the removal of the ions in one pass through at flow rates up to 150 ml/min (20 lb/hr) at 25°C (77°F);
- The column must operate at pressures up to $1.65 \times 10^5 \pm 6.89 \times 10^4$ N/m^2 (24 ±10 psig), and pass a test pressure of double the possible maximum 3.31×10^5 N/m^2 (48 psig);
- The ion exchange resin mixture must have a sufficient ion removal capacity for a 30-day mission during which the automatic calibration cycle is one 10-minute calibration every 24 hours.

7.2.3.3 Test Procedure and Results

1. The following components were connected in series: sample reservoir, pump, ion exchange column, pressure gage, and flowmeter. A silver ion solution of 300 ppb was pumped through the system at 150 ml/min (20 lb/hr), 1.72×10^5 N/m^2 (25 psig) at ambient temperature. The effluent from the system was collected and measured for silver ion content and found to be below 2 ppb.
2. The ion exchange column was pressure-tested for double the operating pressure by plugging one end of the column and pressurizing the column with nitrogen gas up to 3.44×10^5 N/m^2 (50 psig). No leaks were observed.
3. The capacity of the ion exchange resins was tested by pumping through the column the equivalent of 0.0174 gram of silver bromide, AgBr, which would be three times the calculated maximum amount of AgBr dissolved in the calibrating fluid for a mission duration of 30 days. A solution containing 115 ppb silver ion was then pumped through the

column at 150 ml/min (20 lb/hr) and the effluent of the column measured for silver ion content, using a silver sulfide sensing electrode. An indication of below 10 ppb silver ion was found, indicating acceptable capacity.

7.2.4 Silver Bromide Column

7.2.4.1 General

The silver bromide column contains 35.5 grams of a 0.8 to 1 mixture of silver bromide powder and very small (about 500-micron-diameter) glass beads. The column is located downstream from the ion exchange column and receives the deionized water from that column. Its purpose is to saturate the water flowing through it with silver bromide; more specifically, silver ions [Ag^+] and bromide ions [Br^-]. The level of saturation is temperature dependent. The quantity of silver bromide is much greater than the calculated requirement, but the excess is needed to effect saturation at a fast flow-through rate.

7.2.4.2 Criteria

- The silver bromide column must saturate the deionized water passing through it in one pass at flow rates up to 150 ml/min (20 lb/hr) at 25°C (77°F). The silver ion concentration must be within ±5 ppb of published data--75 ppb at 25°C (77°F).
- The column must operate at pressures up to 1.72×10^5 N/m^2 (25 ±10 psig) and pass a test pressure of double the possible maximum, or 3.44×10^5 N/m^2 (50 psig).
- The silver bromide column must have a sufficient capacity to saturate the deionized water of the calibration loop for a 30-day mission during which the automatic calibration cycle is one 10-minute calibration every 24 hours.

7.2.4.3 Test Procedure and Results

1. The saturation capability of the silver bromide column was tested using the components described in Paragraph 7.2.3.3. The silver

bromide column was placed downstream of the ion exchange column. A silver ion solution having a concentration of 300 ppb silver ion was pumped from the reservoir through the test setup to waste at 150 ml/min (20 lb/hr) at 1.72 x 10^5 N/m^2 (25 psig) and ambient temperature. The effluent from the system was collected and measured for silver ion concentration and found to be 73 ppb which is in good agreement with handbook data of 75 ppb at the test temperature. Preliminary testing of the silver bromide column did not include recirculating through the test setup.

2. The silver bromide column was pressure tested for double the operating pressure by plugging one end of the column, filling with water, and then pressurizing to 3.44 x 10^5 N/m^2 (50 psig) with nitrogen gas. No leaks were observed.

3. The capacity of the silver bromide column to saturate the deionized water was tested by pumping through the column sufficient deionized water at 65°C (150°F) to remove approximately 0.0174 gram (6.1 x 10^{-4} oz) of silver bromide, which is the maximum calculated amount of AgBr required for a 30-day mission, plus a safety factor of 2X, during which the automatic calibration cycle is one 10-minute calibration every 24 hours. Following this procedure, the column was cooled to ambient and deionized water passed through the column at 150 ml/min (20 lb/hr). The effluent of the column was collected and measured for silver ion using a silver sulfide sensing electrode. Silver ion concentration was within ±5 ppb of published saturation values of 75 ppb and was considered acceptable.

7.2.4.4 Silver Bromide/Ion Exchange Columns Combined

The ion exchange column and silver bromide column are used in combination to supply a stable calibrating fluid, containing 75 ppb ±3 ppb of silver ion. After testing each of the individual columns separately they were combined and tested again.

The ion exchange column was placed upstream of the silver bromide column and the combination subjected to the various tests as given in Table 7-5. The test fluids were pumped through to waste or collected for analysis.

Table 7-5. Combined Ion Exchange/Silver Bromide Columns Tests

Test Fluid[1]	Flow ml/min (lb/hr)	Effluent Concentration ppb $[Ag^+]$ [2]
Distilled Water	100 (13.23)	75
Distilled Water	450 (59.5)	73
Deionized Water	100 (13.23)	75
Deionized Water	450 (59.5)	74
50 ppb $[Ag^+]$	100 (13.23)	75
50 ppb $[Ag^+]$	450 (59.5)	74
150 ppb $[Ag^+]$	450 (59.5)	73
300 ppb $[Ag^+]$	100 (13.23)	74

[1] Pumped through to waste

[2] Determined in beaker test setup

7.2.5 Solenoid Valves

7.2.5.1 General

The solenoid valves are flight-qualified standard components manufactured by Futurecraft of California. They are 3-way, 2-position, normally closed valves which operate on 18 to 28 Vdc. Both valves in the system operate together when the calibration system is in operation. The valves are designed for 4.13×10^6 N/m^2 (0 to 6000 psig) operation pressure and have been cycled over 250,000 times without failure by the vendor, prior to shipment.

7.2.5.2 Criteria

The following are the required parameters to be tested:

- Operation at low voltage (18 Vdc)
- Operation at low and high pressure 6894 to 6.89×10^5 N/m^2 (1 to 100 psig)

- Proof pressure test of 13.79×10^5 N/m^2 (200 psig)
- Dielectric test of 100 Vac (rms) for 5 minutes
- Leakage--zero external, 1 drop per minute internal.

7.3.5.3 Acceptance Tests

The following tests were conducted by the manufacturer prior to acceptance of the valve:

1. Proof pressure test of 13.79×10^5 N/m^2 (200 psig) for 5 minutes.
2. Dielectric test of the solenoid. The solenoid shall withstand 100 Vac (rms) for one minute. Leakage current shall not exceed 2 milliamps.
3. Leakage shall not exceed one drop per minute after current is removed with 3.44×10^5 N/m^2 (50 psig) water applied to the inlet.
4. Standard pressure and dielectric test procedures shall be used.

In addition to the above tests, the hysteresis characteristics of the valve were determined. This information was compared to the valve driver parameters to make certain that:

a. Minimum current supplied by driver is greater than minimum current required to actuate the valve.

b. Maximum leakage current from the driver in the normally open position of the valve is far below minimum current required to actuate the valve.

7.2.5.4 Test Results

Futurecraft, the manufacturer of the valves, performed the acceptance tests and provided a certified test data sheet. The valves were found to meet or exceed the specifications.

The valves were operated with the valve drivers of the electronic section and found compatible.

Due to the heat generated by the solenoids when operated at 28 volts dc, it was found necessary to operate the valves at 18 volts dc to prevent unnecessary heating of the ion exchange and silver bromide column since each column is in close proximity to one of the valves. At 18 volts the heating effect of the columns is minimized. In the low or no convection of zero g, the heating effects would be less, but flight hardware design might require thermal shielding of the columns.

7.2.6 Motor/Pump Combination

7.2.6.1 General

A motor/pump is used to drive the water at a constant flow rate through the silver ion monitor. The motor/pump is intended for continuous operation including calibration. The motor operates on 115 Vac.

7.2.6.2 Criteria

The following were the required parameters to be tested:

- Operation at various inlet pressures--6894 to 3.10×10^5 N/m^2 (1 to 45 psig)
- Leakage--zero external
- Flow rate test--100 ±20 ml/min. (13.5 lb/hr)

7.2.6.3 Acceptance Test Procedure and Results

The following tests were conducted prior to acceptance of the motor/pump;

1. The motor/pump operated satisfactorily with the inlet pressures varied between 6894 to 3.10×10^5 N/m^2 (1 to 45 psig).

2. The pump was tested for external leakage up to maximum operating pressure of 3.10×10^5 N/m^2 (45 psig). No leakage was observed.

3. The motor/pump was tested and found to provide a flow rate of 100 ±20 ml/min. (13.5 lb/hr) with a minimum output pressure of 1.39×10^5 N/m^2 (20 psig).

Note:

1) It was found necessary to fill the system with water using gravity flow or gas pressure to initiate pumping action.

2) The output pressure of the pump varied ±3447 N/m^2 from 3.45×10^4 N/m^2 (±0.5 psig from 5 to 45 psig).

3) The output volume varied ±25 ml/min. in a random manner.

7.2.7 Sensor Chamber

7.2.7.1 General

The sensor chamber provides a flow path by which the active parts of the sensing electrodes are brought in contact with the water sample.

The sensor chamber was designed to be cylindrical in shape and contain the silver ion sensing electrode, reference electrode, electrolyte chamber, quartz fiber junction, and replaceable electrolyte cartridge. A thermocompensator is mounted in the chamber. In order to perform a preliminary test of the sensor chamber, the assembly of the chamber must be complete with the exception of the thermocompensator.

One of the most significant changes in the observed response characteristics of an electrode pair (sensing and reference) when placed in a housing for continuous contact with a flowing sample is the increase in noise and an offset or error due to pressure and flow. The design of the flow path and placement of electrodes is a critical factor. The evaluation and testing of the sensor chamber, then, considered the effect(s) of the cell on the electrode response as well as operating and proof-pressure tests.

The effect of pressure on an electrode pair, especially the reference electrode, can only be evaluated when the electrodes are mounted in a cell. However, the observed sensitivity to pressure changes is generally a characteristic of the electrodes and not due to cell configuration.

The reference electrode, with the exception of the primary silver-silver chloride reference, is an integral part of the sensor chamber and could not be tested unless completely assembled and tested as part of the sensor chamber. The following criteria and test procedures are based on these characteristics. Also, the primary reference and sensing electrode were previously tested and this test data used as a basis for the evaluation of the sensor chamber tests.

7.2.7.2 Criteria

- The effect(s) of the flow within the test chamber upon the response of the electrode pair shall not cause an increase in noise or drift in excess of that originally observed for that electrode pair.
- The expected flow rate through the sensor cell of 100 ml/min. ±20 ml (13.5 lb/hr) shall not cause an offset of greater than 10 percent from the known concentration of the test solution.
- The sensor chamber must show no leakage at double the expected maximum pressure or 3.45×10^5 N/m^2 (50 psig).

7.2.7.3 Test Procedure and Results

1. The sensor chamber was connected in series with a 1 liter reservoir, pump, flowmeter, and pressure gage and fitted with stable sensing (PR-11) and reference (R4) electrodes. The preamplifiers were bypassed and the electrodes connected directly to a Beckman Century SS pH meter and the response recorded on a Beckman 10-inch Recorder. The sample fluid was pumped through to waste at approximately 120 ml/min. Typical response showed no noise and a 99 percent response time of 3.25 minutes from 500 to 50 ppb and 4 minutes from 50 to 500 ppb, which included flushing of the reservoir with the new solution. Drift at 50 ppb silver ion concentration for 60 minutes was less than ±3 ppb or within instrument error.

2. Sensing electrode PR-16 and reference electrode R4 were installed in the sensor chamber and connected directly to a Beckman Century SS pH Meter, bypassing the preamplifier. A 500 ppb silver ion solution was pumped through the system at approximately 120 ml/minute from reservoir to waste--the recorded output was 325 millivolts. Sensing electrode PR-16 was removed from the sensor chamber and tested in a beaker setup with PERMA-PROBE reference and the same 500 ppb solution--the output was 476 millivolts or a differential of 151 millivolts. Since the testing of the prototype reference R4 against the PERMA-PROBE reference was shown to be 152 millivolts (Paragraph 7.2.2.3.2), this demonstrated that a flow rate of approximately 120 ml/minute through the sensor chamber caused an offset of the indicated silver ion concentration of 1 mV or 20 ppb at 500 ppb or 2 ppb at 50 ppb, which is 4 percent and well within the instrumental error.

3. The sensor chamber was filled with water and the exit port closed with an AN 929 cap. The sample entrance port was connected to a nitrogen gas source and pressurized 3.45 x 10^5 N/m^2 (50 psig). No leakage was observed.

7.2.8 Manual Valve

The manual valve is a 4-way, 2-position Teflon valve. It is a standard purchased item with one function--to isolate the preliminary flight prototype silver ion monitor from the main water system. It is expected that the valve will be used only during routine maintenance. The valve was checked for ease of manual operation, and pressure checked for leaks at double the maximum operating pressure, or 3.45 x 10^5 N/m^2 (50 psig). The valve is of sufficient size that any flow restriction will be insignificant.

7.2.9 Pressure Relief Valve

7.2.9.1 General

The relief valve protects the system from excessive pressure only during the closed loop calibration mode.

7.2.9.2 Criteria

The following are the required parameters to be tested:

- Crack pressure: 9.65×10^4 to 1.93×10^5 N/m^2 (14 to 28 psig), inlet-zero outlet.
- Flow at 2.07×10^5 N/m^2 (30 psig) or less: 100 ml/min. minimum.
- Proof pressure of 2.45×10^5 N/m^2 (50 psig).

7.2.9.3 Test Procedure and Results

1. The relief valve was subjected to an increasing pressure. The valve cracked (began to flow) at 1.93×10^5 N/m^2 (28 psig). Crack flow is defined as 1 drop per second.

2. The flow was measured at 21°C (70°F) with 2.07×10^5 N/m^2 (30 psig) applied to the inlet. The flow was greater than 100 ml per minute.

3. The relief valve was pressurized to 6.98×10^5 N/m^2 (100 psig) with the outlet plugged. The valve did not leak externally.

7.3 Criteria and Preliminary Testing of Components--Electronic Section

7.3.1 Introduction

The prototype testing program was broken down into several broad categories:

1. Tests on characteristics of unique components in the system;

2. Troubleshooting and functional testing of subsections following prototype fabrication;

3. Functional testing of entire system as a working unit.

(Categories 1 and 2 are explained in the following sections. Category 3 was performed as part of design verification testing.)

7.3.2 Unique Component Tests

7.3.2.1 Thermocompensators

The thermocompensators were tested with the remainder of the system as part of the integration of the electronics.

7.3.2.2 Power Supply Modules

These are purchased items, and were given simple functional tests, under rated load, to verify that the manufacturer's specifications were met on the following parameters:

a. Input regulation:	0.5% or better
b. Load regulation:	0.5% or better
c. Percent ripple:	0.5% Vrms or better
d. Efficiency:	40% or better at full load
e. Temperature rise:	42.2°C (108°F) maximum at full load
f. Current limiting:	150% maximum load.

The specifications were met or exceeded by the power supply modules.

7.3.2.3 Preamplifier Test

The preamplifiers were designed to be mounted in a shielded section of each electrode housing. The shielded section or cap of each electrode contained the cable connector for amplifier/power connections and a solution ground connection.

After fabrication, a set of preamplifiers (one reference electrode preamplifier AG0044 and one sensing or silver sulfide electrode preamplifier AG0038) were tested as a pair as follows:

The inputs to the preamplifiers were connected to an electrode simulator box, Figure 7-3. The outputs were connected to the input of the breakout box of the test setup of Figure 7-4. Operating power for the preamplifiers was also obtained from the breakout box. The simulator was adjusted to simulate typical outputs of an electrode pair in silver ion solutions between 15 and 150 ppb

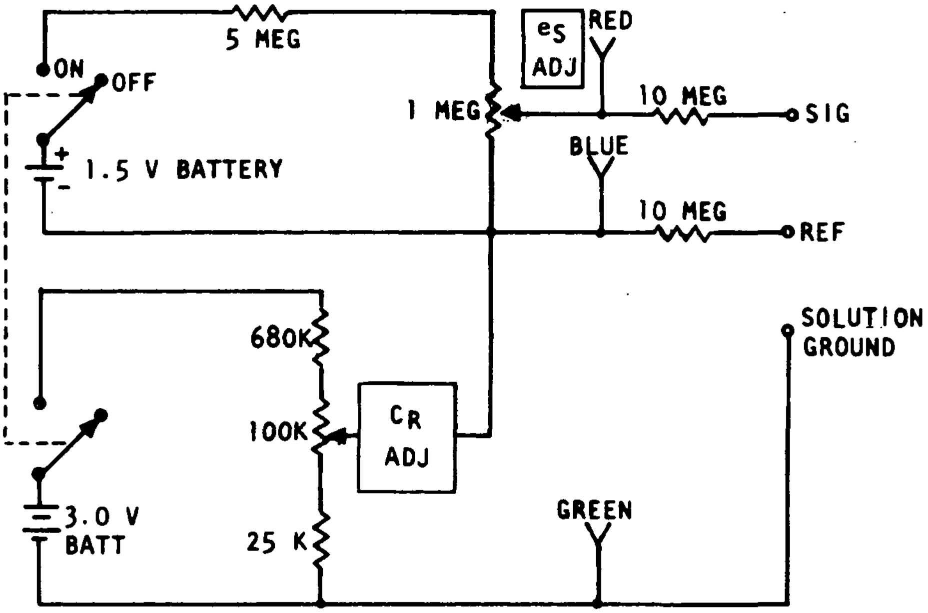


Figure 7-3. Electrode Simulator Box Circuit

silver ion while system output was monitored with a digital volt meter (DVM). When simulated Nernstian electrode response into the preamplifiers resulted in Nernstian output as monitored by the DVM, the preamplifiers were considered acceptable. All four sets of preamplifiers fabricated tested satisfactorily.

Care was taken in the grounding of the digital voltmeter, the preamplifier, and solution ground. Solution ground, power supply chassis, and DVM chassis all went to a common point, which was also connected to the preamplifier's shield.

After this test, the preamplifiers were installed in the electrode assemblies. Testing of each of the electrode assemblies was not accomplished due to redesign of the electronics and sensing electrodes. A functional test of the fluid handling unit was performed with the preamplifiers bypassed and the output of the electrodes connected to a pH meter.

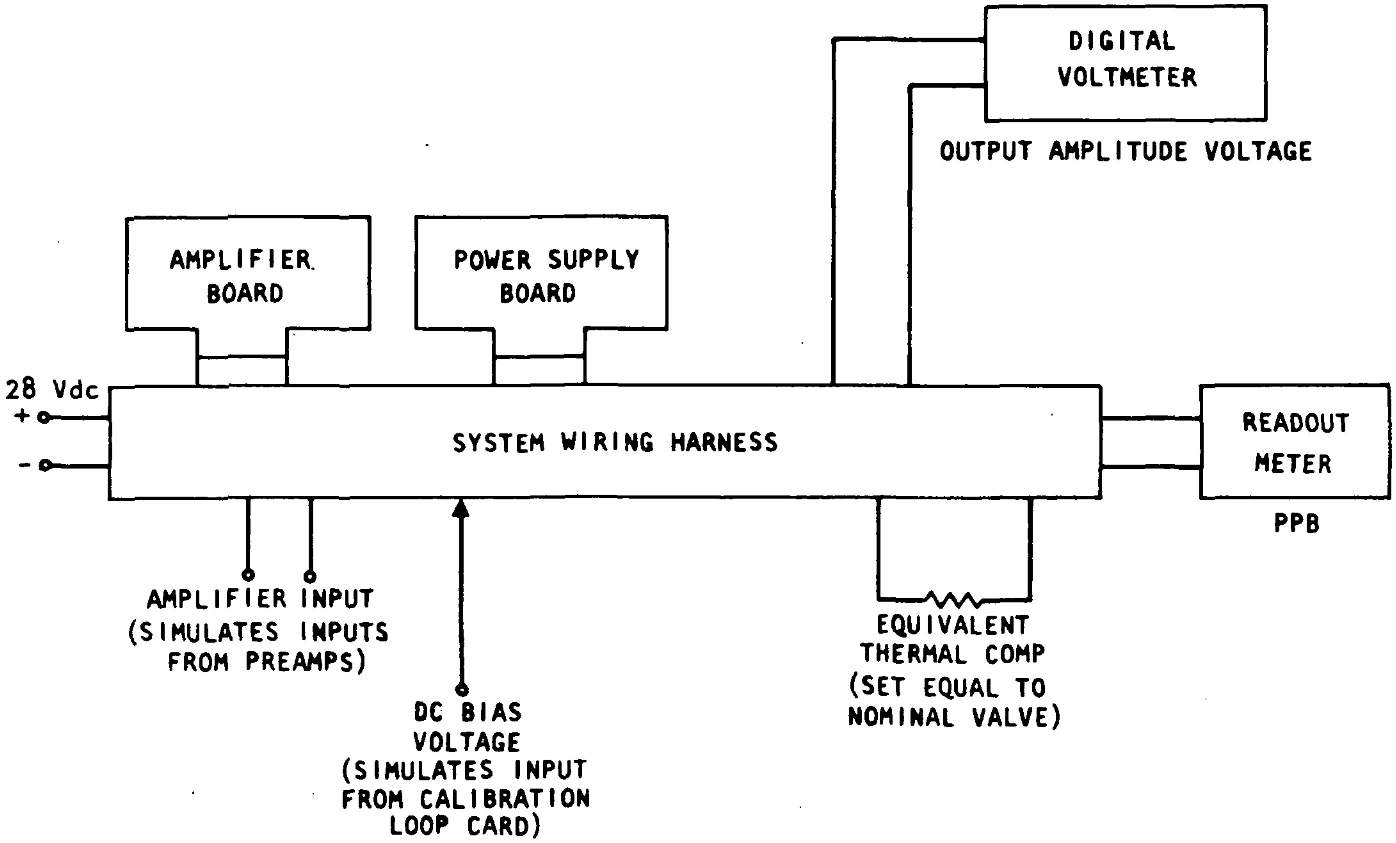


Figure 7-4. Amplifier and Readout Test Setup

7.3.3 Troubleshooting and Functional Testing of Subsection

7.3.3.1 General

The majority of the electronics were located on four large circuit boards. The electronics were tested by plugging into breakout boxes during tests of individual boards. For larger scale tests, the boards were actually plugged into the system wiring harness.

7.3.3.2 Amplifier and Readout

This subsystem consisted of the amplifier, sample/hold circuit, meter scale controls, and the readout meter--all operating independently of any actual control or calibration circuitry, except by simulation. The test procedures and results are shown below:

d. The amplifiers and readout worked correctly, giving the correct meter readout in ppb corresponding to the equivalent voltage inputs.

e. The sample and hold circuits worked correctly in both modes.

f. A "decay" test was run on the sample and hold circuit. A reading (full scale) was stored for ten minutes and then read. It was supposed to drop less than 1 percent in the ten minute period. In the test, the actual decay was so much smaller than 1 percent as to be negligible (see Figure 7-5).

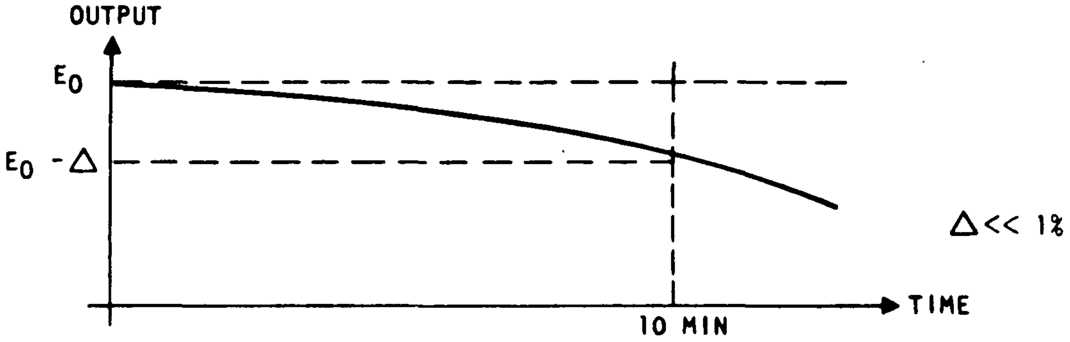


Figure 7-5. Sample/Hold Circuit Output vs. Time

7.3.3.3 Electrode Assembly, Preamplifier, Amplifier, and Readout

This test was to ensure that the entire data chain (electrodes, preamplifiers, amplifier, and readout) operated together. The test procedures and results are shown below:

a. Setup (see Figure 7-6).

b. The bias was left at the same setting as in the previous section.

c. Tests were run with various concentrations of silver ion (i.e., 50, 100, and 150 ppb) at room temperature.

d. Two difficulties were noted:

    1. While the meter gave the correct reading, the reading also fluctuated randomly about the correct value. This occurred whether or not the solution was being stirred. The rate of this variation

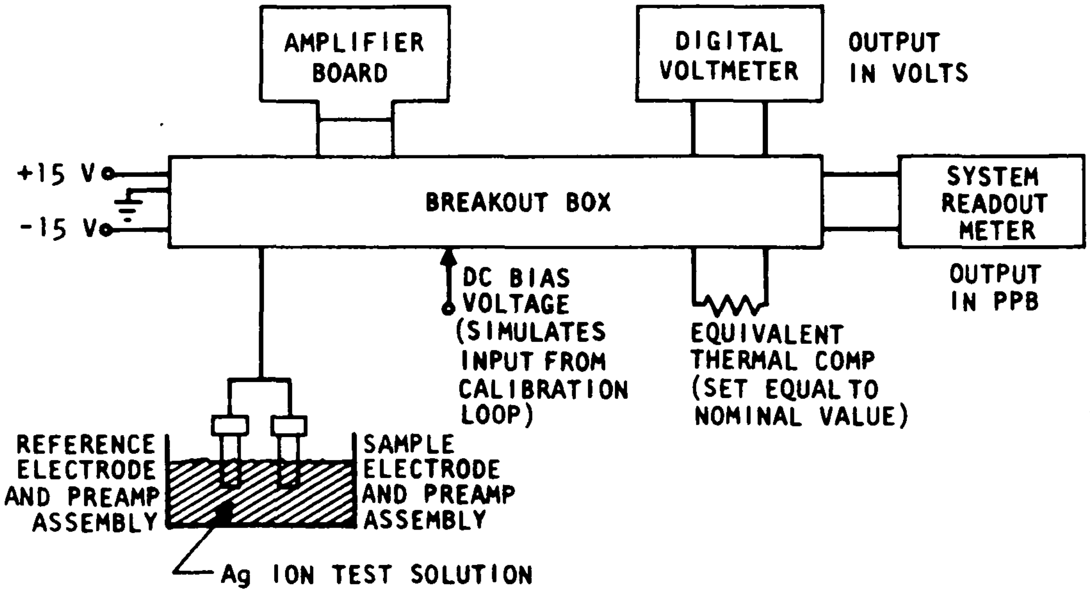


Figure 7-6. Electrode Assembly, Preamplifier, Amplifier, and Readout Test Setup

was very low, on the order of 0.1 to 1.0 Hz. Such a variation was not observed when the electrodes were replaced by simulated inputs (from batteries), so it was concluded that the cause was related to the solution and/or the electrodes, rather than the electronics. The variation could be reduced by adding rolloff capacitors (approximately 100 microfarads) across the feedback resistors in the two amplifier stages.

2. Any concentration of silver solution rapidly dropped off. A decay of 50 percent in 20 to 30 minutes was usually noted.

7.3.3.4 Sequencer

The sequencer is essentially a timer that produces the sequence shown in Figure 7-7. During the calibration time, the system is switched into the calibration mode, and automatic calibration effected.

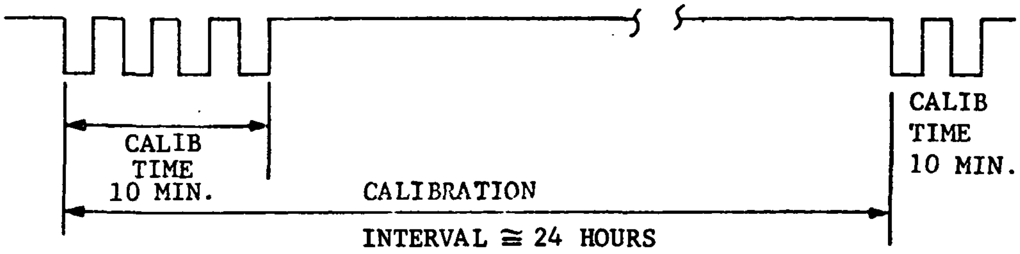


Figure 7-7. Timing Sequence

The sequencer, located in the main circuit board, is capable of being tested independently of the rest of the system.

Due to the long duration between calibration sequences, the sequencer tends to be time-consuming to test. This was easily overcome, however, by speeding up the rate at which the sequencer operates. Sequencer speed is controlled by a master clock pulse whose rate is determined by a resistor and capacitor on the main circuit board. By bridging this time constant resistor with a 50th of its value (through a switch), the entire cycle of the sequencer can be speeded up about 50 times. The calibration interval becomes about 29 minutes, and the calibration time 12 seconds. The sequencer functions may now be checked in a reasonable time. The test procedure and results are shown below:

a. Test Setup (see Figure 7-8).

b. The sequencer was checked for correct operation by monitoring the points of interest with a recorder. The accuracy of the timing intervals was not critical, so it was required to fall only within ±20 percent. The following parameters were measured:

   1. Calibration interval--29 minutes
   2. Calibration time--12 seconds.
   3. Clock interval--1.7 seconds.
   4. Stabilize signal--12 seconds.
   5. Verify calibration signal--1.7 seconds.

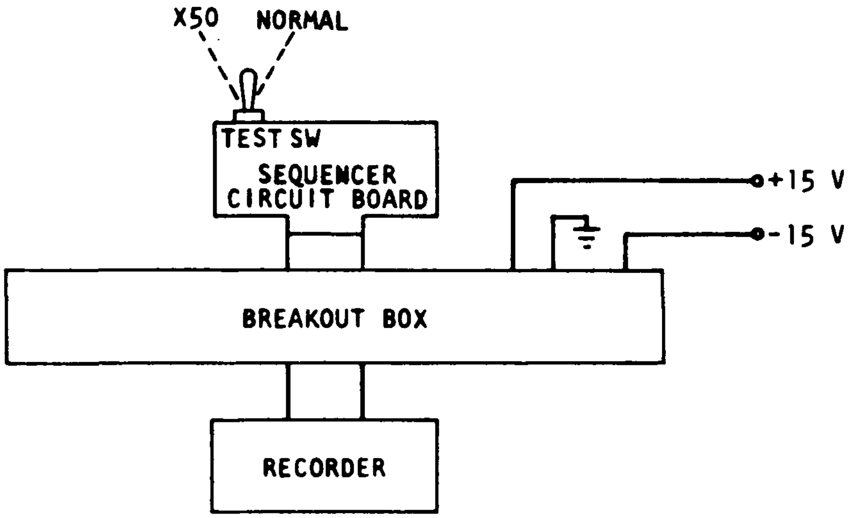


Figure 7-8. Sequencer Test Setup

c. Final verification was conducted at true sequencer rates. After the operation of the sequencer was verified, the speed was switched back to normal. The unit was allowed to run overnight, while being monitored by a recorder. The time intervals obtained were 50 times those obtained in the above section. All sequencer intervals fell well within ±20 percent of values required.

7.3.3.5 Driver

The driver turns on the solenoid valves. The test procedure and results are shown below:

a. Test setup (see Figure 7-9).

b. Worst case conditions were simulated: maximum load (1.5X the current for 2 valves), minimum driver input signal 3 Vdc at minimum supply voltage (24 Vdc) and maximum supply voltage (32 Vdc).

c. The driver was tested for the following:

  1. Complete turn-on. Verify that output transistor did indeed turn on fully.

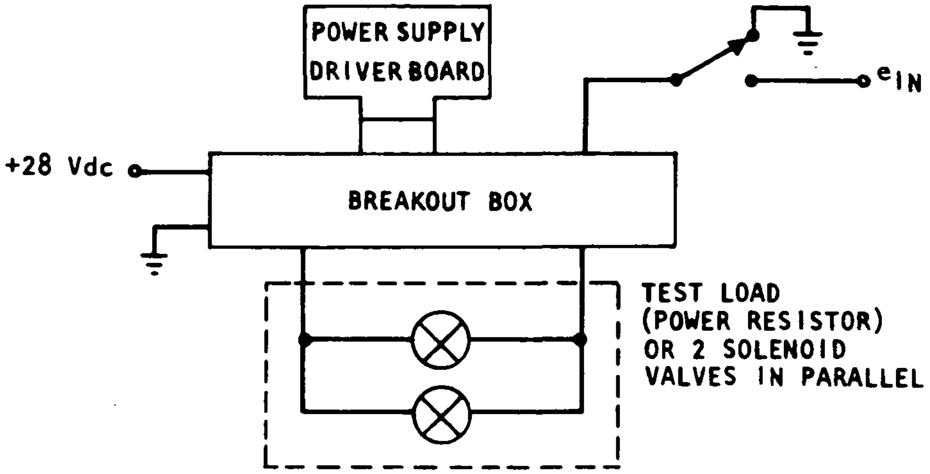


Figure 7-9. Driver Test Setup

2. Leakage current in OFF mode was much smaller than valve's minimum turn-on current.

3. Driver transistor power dissipation--unit was left on for much longer than the 10-minute actuation period in system (30 min.). The temperature of the case on the last driver transistor still stayed well within its safe limit of 55°C (131°F).

7.3.3.6 Calibration System

The system consists of an analog-to-digital (A-D) converter, a counter, digital-to-analog converter (D-A), and logic.

During the calibration time, power is applied to the solenoid valves, which energize and cause a known concentration of silver ion to pass through the system. The calibration A-D converter changes the amplifier output to a digital code and examines it with logic to determine if it falls within the dead zone (allowable amplifier output during calibration). If not, the logic allows a counter to count. The counter's outputs go to a D-A converter, which generates a bias correction signal for the amplifier. This causes the amplifier output to change. When the amplifier output reaches the dead zone, the logic shuts off the counter, and the bias correction signal stays at that value. At the end of the calibration sequence, the system checks itself to verify that the amplifier output is in the dead zone. If not, a NO-CAL light is turned on until the next calibration sequence.

In this test, the calibration fluid was simulated by inputting an equivalent voltage into the amplifier input. Power was applied externally to simulate its application by the sequencer during a calibration time. The test procedures and results are shown below:

a. Test setup (see Figure 7-10).

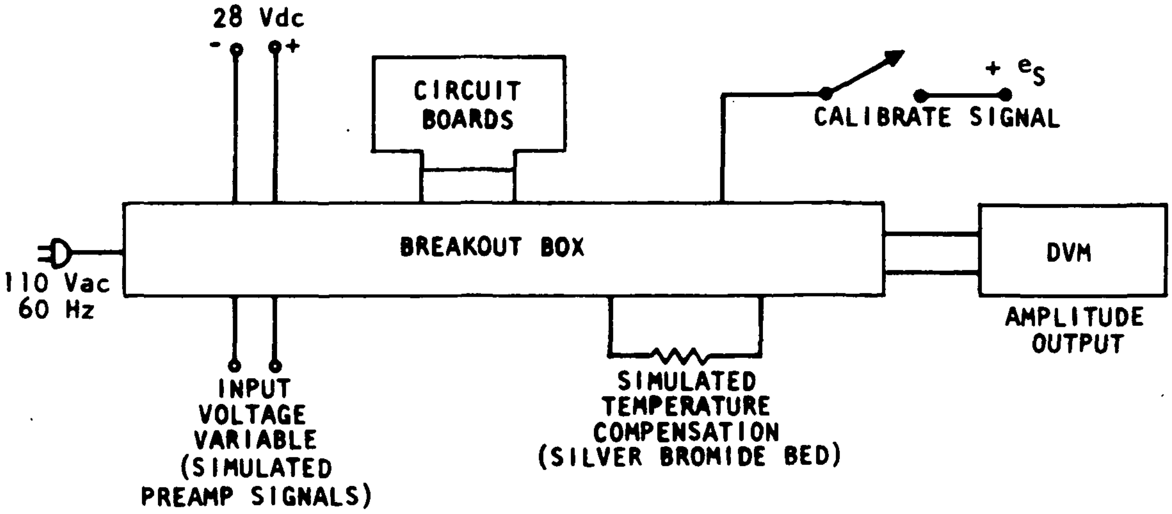


Figure 7-10. Calibration Test Setup

b. The calibration system's bias line was connected to the amplifier.

c. Upon application of the calibration signal, the calibration D-A started counting (the amplifier output was set out of the calibration deadband). This test was repeated a number of times, with the input voltage (simulated signal) started out at various values (in band, out of band high, out of band low, etc.) to verify correct operation.

d. Although the system did operate correctly, some problems were noted. These are listed below:

1. During calibration, the meter would go through a wide range, "pegging" at both extremes before coming up to the calibration value. This was due to setting the system to give too wide a range of correction. Having the meter "pegged" during calibration is probably not desirable (even though it does come back to the correct value). A suggested solution would be to drastically reduce the automatic correction range. Gross correction required (when changing electrodes) could be achieved with a trimpot. Fine correction to offset effects of aging in electrodes, etc., could then be done by the automatic calibration, which would cover no more than perhaps ±20 ppb of the calibration value.

2. Unless the solution fluctuation problem (reported in Section 7.3.3.3) is corrected, the present calibration system will not work. As soon as the dead zone (Figure 7-11) is acquired, a fluctuation in the solution would cause the system to leave the dead zone and start "hunting" again. Either the fluctuations must be eliminated or a "catch" circuit must be added to the calibration loop. A "catch" circuit would "lock" the system into the dead zone once it was acquired. Subsequent solution fluctuations would have no effect. A "lock" circuit would be relatively simple to implement--an additional flip/flop and a few logic changes. Even if the fluctuation problem is solved, a "lock" circuit would be highly desirable, as it would make calibration more certain.

The problems noted in d., above, were corrected by redesign of the electronics (see Section 9.0).

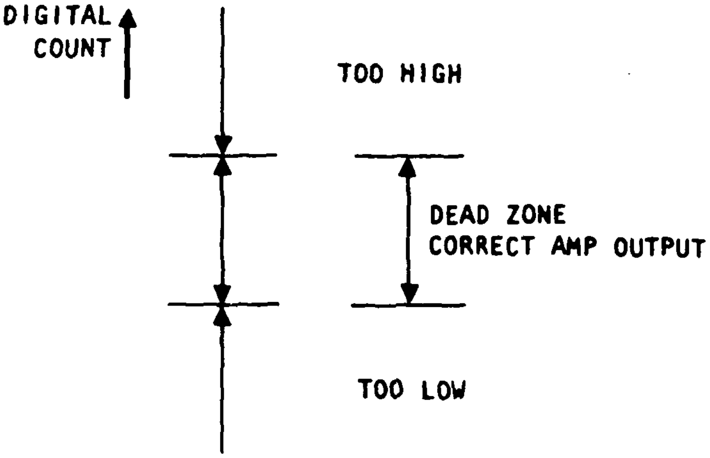


Figure 7-11. Calibration Dead Band

7.3.3.7 Thermocompensator for Silver Bromide Column

The system was run in the calibration mode, with a simulated electrode signal fed to the amplifier. The thermal compensator was simulated by means of an external resistor, and correct gain adjustment of the amplifier over the simulated temperature range was verified. It was found that a thermal compensator with a somewhat wider range of change should be used instead of the one specified.

7.3.3.8 NO CALIBRATE Lamp Driver and Latch Circuit Test

This circuit is actuated by a signal from the logic toward the end of the calibration time. If the calibration has been completed successfully prior to this signal, the system will be in the dead zone and the latch circuit will not be actuated. If, however, proper calibration has not taken place and the DAC is outside the dead zone, the logic will trigger the latch circuit which will operate the driver and hold the NO CALIBRATE (see Figure 6-10) lamp on until the next calibration time (24 hours later, or until a manual calibration occurs). At the next calibration time, the circuit will be unlatched and calibration will again be attempted. Test procedures and results are shown below:

a. Test setup (see Figure 7-12).

b. The simulated bias was set to an extreme, out of the calibration dead zone.

c. The STABILIZE signal was applied.

d. The CHECK signal was applied. The NO CALIBRATE indicator should have come on, but did not.

The above problem was corrected as part of the electronics redesign (see Section 9.0).

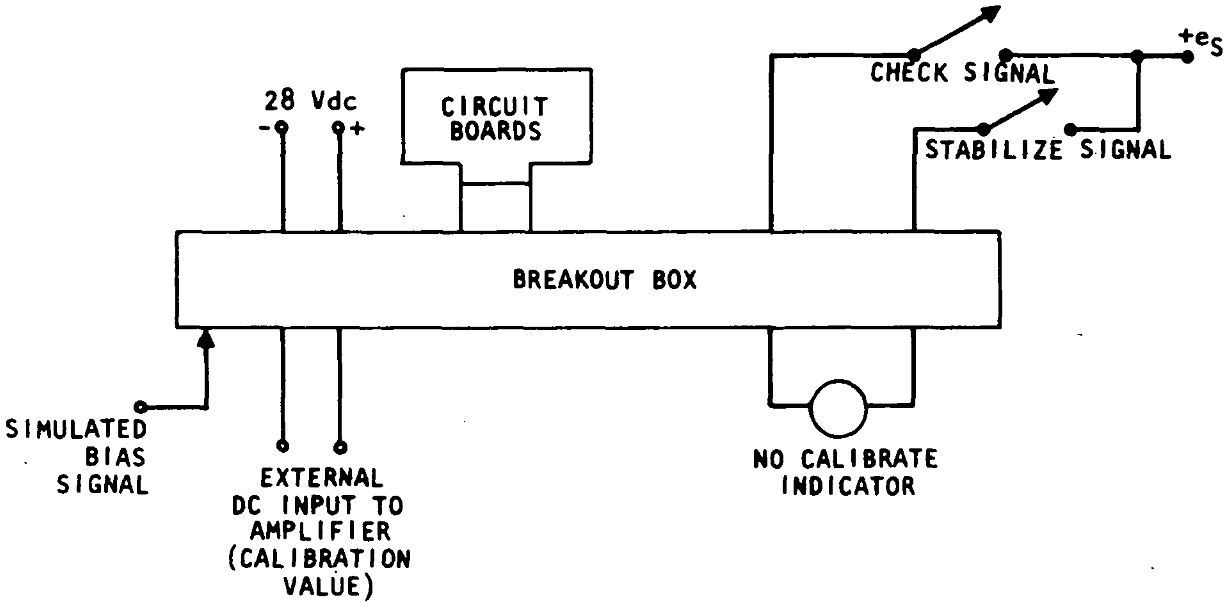


Figure 7-12. Test Setup for NO CALIBRATE Lamp Driver and Latch Circuit Test

8.0 FUNCTIONAL TESTING OF THE FLUID HANDLING UNIT AND LOSS OF SILVER ION

8.1 Preliminary Functional Testing

A pressure gage and flowmeter were temporarily installed downstream of the sensor chamber and the fluid handling system filled with water. The system was pressurized to 3.45×10^5 N/m^2 (50 psig) with nitrogen, and no leaks were observed in the measuring loop. The two solenoids were opened using a separate power supply and the calibration loop was observed for leaks--none was found. The pump/motor was energized and found to give approximately 100 ±20 ml/min. (13.5 lb/hr) at external pressures from 0 to 3.45×10^5 N/m^2 (0 to 50 psig).

The prototype fluid handling unit was connected to the environmental test fixture as shown in Figure 9-1 and the water in the test fixture pumped through at rates from 0 to 150 ml/min. (0 to 19.8 lb/hr) at 1.72×10^5 N/m^2 (25 psig). The pump/motor unit in the fluid handling unit maintained the 100 ±20 ml/min. (13.5 lb/hr) flow through the sensing chamber.

8.2 Monitoring Mode Tests

The reference and silver sulfide prototype (PR) electrodes, having been previously tested using a beaker test setup and pH meter, were installed in the sensor chamber. Calibrating solutions of 50 and 500 ppb silver ion were pumped through to waste to calibrate the system. The PR-1 electrode exhibited a response of 59 mV/decade (50 to 500 ppb) as it did in the previous beaker test.

These tests utilized a Beckman 940 pH Analyzer instead of the prototype electronics and readout, since the intention was to check each section of the prototype with a known working system. Later, a Beckman Century SS pH Meter was substituted for the 940 Analyzer to provide greater range and range switching convenience, and direct millivolt readout.

Initial recirculation tests in prototype systems in the monitoring mode showed abnormal response of silver sulfide electrode PR-1 such as wave-like, up-down drift of ±15 mV (35 ppb) and being very noisy. Also, recirculating a 75 ppb silver ion solution showed an immediate drop in indicated silver ion concentration of 26 mV or 47 ppb in 10 minutes.

The electrode was then allowed to remain in contact with a 50 ppb silver ion solution (approximately 50 ml) in the prototype system over the weekend. After 72 hours, the response was checked by pumping through the system to waste 50 and 500 ppb silver ion solutions. The response was 52 mV/decade--a drop of 7 mV/decade or slight loss of sensitivity.

Recycling an initially 50 ppb silver ion solution through the prototype system with continuous monitoring showed a complete loss of silver ion in 2 hours. Retesting the electrode with fresh 50 and 500 ppb silver ion solutions indicated a loss of sensitivity estimated to be greater than 15 mV/decade, but this could not be measured because of the erratic response of the electrode.

Short time exposure of other silver sulfide electrodes of the PR configuration to recirculating 50 ppb solution showed a loss of sensitivity of 50 to 54 mV/decade, and recycling always indicated an immediate lowering of the silver ion concentration.

Removal of these PR electrodes from the prototype system and testing in a beaker set up with a pH meter always showed 54 mV/decade or less.

The above described problems caused the monitoring mode tests to be discontinued in favor of tests designed to determine the cause of the loss of silver ion from solution and the degradation or loss of sensitivity of the silver sulfide sensing electrode.

8.3 Degradation or Loss of Sensitivity of Sensing Electrodes and Loss of Silver Ion from Solution

Silver sulfide electrodes may undergo degradation for a number of reasons, such as, poisoning or surface contamination, aging, thermal degradation, or by a change in composition of the silver sulfide.

The rapid degradation or partial loss of sensitivity described in Paragraph 8.2 was unexpected.

Since the PR electrode tested in the prototype system had previously exhibited a 57 to 60 mV/decade sensitivity in a beaker test(s), it was thought that the lower sensitivity exhibited by these electrodes after a short time (up to 2 hours) testing in the prototype system was due to (1) contamination of distilled water used to dilute the Atomic Absorption Standard (A.A. Std), (2) contamination of the glassware, (3) degradation of the A.A. Std., (4) inadequate conditioning of the electrode resulting in poor stability. Tests showed that these suppositions were not correct.

It was also postulated that an exposure of the silver sulfide electrode to low (50 ppb) concentrations of silver ion degraded the electrode, causing a loss of sensitivity.

Static exposure tests of silver sulfide electrodes, both PR configuration and on older electrodes, to 50 and 500 ppb silver ion solutions for 48 to 72 hours were inconclusive since some electrodes showed a loss of sensitivity in the 500 ppb concentration while others showed no loss when exposed to 50 ppb silver ion solutions for the same period.

A number of exposure tests of the electrodes to both recirculating fluid and fluid that was pumped through to waste (single pass) were performed. These are described below.

Fifty ml of a 500 ppb silver ion solution was recirculated in the prototype system for 48 minutes, at which time the indicated concentration was less than 2 ppb silver ion. The sensitivity of the electrode had changed from 56 to 37 mV/decade.

The test was repeated, but recording the output of the pH meter using silver sulfide electrode PR-16.

Time Minutes	$[Ag^+]$ Conc ppb	
0	500	
25	72	
44	18	
100	5.2	Noisy and up-down drift
256	less than 2	

The electrode was removed from the prototype system and retested in a beaker setup. It gave 56 mV/decade or no change.

To determine if simple exposure to silver ion solution was responsible for the occasionally observed loss of sensitivity of the electrodes, the following test was performed. The PR-16 electrode and another silver sulfide electrode were exposed to 50 and 500 ppb silver ion solutions for 91 hours. There was no electrical connection made to the solutions or the electrodes. Following exposure, the electrodes were tested for response. Results were as follows:

	Solution Conc. ppb $[Ag^+]$		Electrode Response mV/decade	
Electrode	Before	After*	Before	After*
PR-16	50	<1	56 ±1	58 ±1
EP-2	500	420	58	46

These results indicate that <u>some</u> silver sulfide electrodes are more resistant to degradation in low silver ion concentrations while others exhibit lowering of sensitivity when exposed to low ppb silver ion solutions.

Since there were a number of electrical components in the fluid handling unit other than the electrodes it was thought that parasitic currents in the system could be responsible for the degradation of the electrodes. This postulate was tested as follows:

---

*91 hours at room temperature--static beaker test--no electrical connections

Silver sulfide electrode PR-16, which had previously shown no loss of sensitivity when exposed to 50 ppb silver ion solutions, was installed in the prototype system. 500 ppb silver ion solution was recirculated for 90 minutes. The electrode was connected to the pH meter <u>only</u> during the periodic measurements. The silver ion loss was as follows:

Time (min)	Indicated $[Ag^+]$ Conc (ppb)
0	500
2	500
12	210
22	110

The solution was removed from the system and the silver ion concentration measured in an independent beaker test showed less than 5 ppb silver.

PR-16 electrode was removed from the system and tested for response. It showed a loss of sensitivity during the test of from 53 mV/decade at start to 39 mV/decade at completion of test.

The recirculation test was repeated with another silver sulfide electrode PR-12. However, this time <u>all</u> electrodes (sensing [PR-12], reference, and solution ground) were only connected to the pH meter during periodic measurements. Data are as follows:

Time (minutes)	Indicated $[Ag^+]$ Conc (ppb)
0	500
10	500
20	28
30	28
40	12
50	21
60	20

Actual analysis of the fluid in a separate beaker test showed 170 ppb at the end of 60 minutes. Electrode PR-12 was in error by 150 ppb due to loss of sensitivity, At the time it was thought that the limiting of the time the electrodes were connected to the pH meter (about 8 minutes out of 60) resulted in a reduced loss of silver from the recirculating fluid, indicating that a parasitic current might be flowing in the system.

If the adsorption and a chemical reactivity process were in competition with the electrolysis process, the electrolysis process could be more rapid. If this is the case, then the removal of silver from 50 ml of a 500 ppb silver ion solution in 30 minutes would require a leakage current of 12.4 microamps.

Probable electrical causes of loss of silver ion from the solution recirculating in the Silver Ion Monitoring System were investigated. The following is the result of that study.

The prototype of the silver ion instrument for the Space Shuttle is experiencing a decay in silver ion concentration which may be associated with the electronics. If this is the case, a reduction of $[Ag^+]$ ion to Ag must be occurring due to a parasitic current flow. The reaction taking place may be characterized as:

$$[Ag^+] + e \longrightarrow Ag$$

To assess the parasitic current(s) involved, one may determine the magnitude of charge transfer involved as follows:

Silver's molecular weight--107.87 g/mole
6.02×10^{23} mole^{-1}
6.24×10^{18} electroncs/ampere-second
Weight of solution in the loop--50 g
Weight of silver to produce 1 ppb change--5×10^{-8}g

$$\frac{5 \times 10^{-8}\text{g Ag} \times 6.02 \times 10^{23}[Ag^+]/\text{mole Ag}}{107.87 \text{ g Ag/mole Ag} \times 6.24 \times 10^{18}[Ag^+]/\text{amp-sec}} = 4.46 \times 10^{-5} \text{ amp-sec/1 ppb change}$$

Since changes of approximately 500 ppb have been observed in 30 minutes time, a value of

$$\frac{4.46 \times 10^{-5} \text{ amp-sec}}{1800 \text{ sec}} \times 500 \text{ ppb change} = 1.24 \times 10^{-5} \text{ A}$$

$$= 12.4 \ \mu\text{A leakage current}$$

may be assumed. This is approximately 10^6 times the value of the bias current

To establish the source of the fault, the following procedures were performed:

1. With 500 ppb solution circulating in the loop, the pH meter was connected to the solution ground, reference electrode, and signal electrode with a microammeter in each lead. If currents sufficient to produce the observed effects were present, they would be readily observed. If currents greater than 1 μA were observed, corrective action would have to be taken to restore the electronics to specification. However, no measurable currents were detected in the reference, sensing, or solution ground lines when connected to a Beckman Century SS pH Meter.
2. Since no significant currents were observed in step 1, the loop was run to see if the silver ion concentration decayed. A 500 ppb silver ion solution was recirculated for 60 minutes at which time the silver ion concentration was 44 ppb. All three electrodes were connected to the pH meter. Since no electrical paths were found, the loss of silver ion must be a chemical phenomenon.
3. With the system configured as in Figure 8-1, and with the solution ground, reference electrode, and signal electrode open circuited, solution decay in the loop could only be the result of galvanic effects due to dissimilar metals or chemical phenomenon. Leaving solution in the loop with the pump running and not running should distinguish between the differences of loss of silver concentration that has not been determined by steps 1 or 2.
4. A 500 ppb silver ion solution was recirculated for 60 minutes. All three electrodes were open circuited (not connected to pH meter). The same results as in 2, above, were observed.

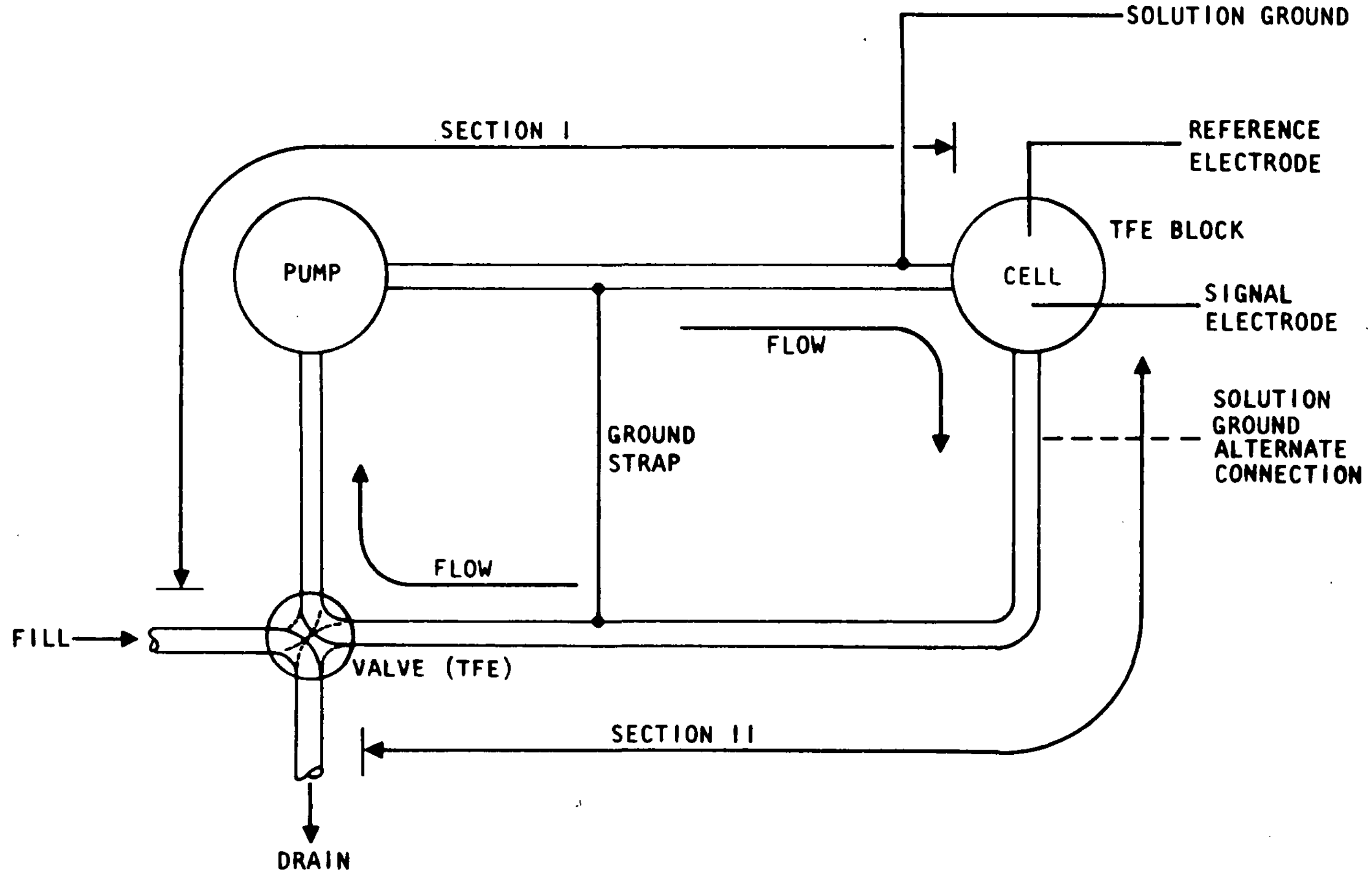


Figure 8-1. Silver Ion Monitor Simplified Flow Diagram

5. The system was flushed with a 500 ppb silver ion solution and then filled with fresh solution and the pump turned off. After 60 minutes, the fluid in the system was removed by pressurizing with nitrogen and then analyzed for silver:

   Start: 500 ppb [Ag^+]
   Finish: 270 ppb [Ag^+]

Conclusions from above tests:

1. Loss of silver is not due to parasitic currents.
2. Loss of silver probably is due to adsorption of chemical reaction of silver ion solution with surface(s) of exposed materials forming non-ionizable compounds.
3. Galvanic action due to dissimilar metals is not likely since the only known metal is 316 stainless steel.

To duplicate our findings of the previous contract, the Teflon cell and original electrodes of the breadboard system were substituted for the new prototype electrodes and the KEL-F electrode cell. After recirculating a 500 ppb silver ion solution for 60 minutes, the silver ion concentration had dropped to 80 ppb [Ag^+].

The prototype cell and electrodes were replaced in the system and a series of tests was performed in which a 500 ppb silver ion solution was pumped from a reservoir through the system and then to waste. The system consisted of the pump, Teflon valve, 316 SS tubing, prototype KEL-F electrode cell and electrodes, and a 316 SS glass flowmeter. The flow was 125 ml/minute for 60 and 120 minutes. In one series the electrodes were connected to a pH meter, while in the second series the electrodes were open circuited. In all tests the silver sulfide electrodes showed very little change in sensitivity.

The results of one flow-through test using a 500 ppb silver ion solution at 24°C (75°F) (thermostated) 125 ml/min. at 1.93×10^5 N/m^2 (28 psig) showed a loss of only 20 ppb silver ion after 30 minutes flow-through, but surprisingly showed a loss of 100 ppb silver ion after 60 and 120 minutes with no essential change in electrode sensitivity.

The test was repeated and after two hours of passing a 500 ppb silver ion solution through the system to waste, the effluent from the system was still at the 500 ppb level.

The flow-through test was repeated using a 50 ppb silver ion solution and the same conditions as the 500 ppb test. The following results were observed:

- Initial concentration - 50 ppb [Ag^+]
- System effluent after 20 minutes - 35 ppb [Ag^+]
- System effluent after 120 minutes - 44 ppb [Ag^+]

The silver sulfide electrode exhibited no significant change in sensitivity.

The above test was repeated but the flow was reduced to 80 ml/minute. The initial concentration of silver ion in the effluent from the system was down from 50 ppb to 40 ppb with an up-down response, but after 60 minutes and through to 120 minutes the effluent level was steady at 50 ppb.

A total of 22 recirculation tests and 18 flow-through tests was performed. Of these, all recirculation tests showed a rapid loss of silver ion while only one of the flow-through tests showed any significant (greater than 5 percent) loss of silver ion. Also, in these same tests only two out of 18 different silver sulfide electrodes showed any significant loss of sensitivity when exposed to the flow-through liquid, but 20 out of 22 different electrodes showed a loss of sensitivity of from 5 to 20 mV/decade over the 50 to 500 ppb silver ion range when exposed to the recirculating fluid.

The static exposure tests of the electrodes to 50 and 500 ppb silver ion solutions showed that a few electrodes were more resistant to degradation than others.

The significance of the above is that it appears to show a connection between the degradation of the silver sulfide electrodes and the recirculated fluid which has been shown to lose silver ion rapidly.

Several methods were investigated to rejuvenate those electrodes which had exhibited a loss of sensitivity. The methods were: (1) cleaning the surface of the silver sulfide with 600 grit carbide paper, (2) chemically cleaning the surface with nitric acid followed by ammonium hydroxide, (3) removal of 7.6×10^{-3} cm (0.003 in.) or 2.5×10^{-2} cm (0.010 in.) from the silver sulfide surface, (4) electrolysis. These rejuvenation methods were either less than 25 percent successful and/or resulted in unstable response. Polishing the surface of the pellet, as one would an optical lens, was the most successful. However, the majority of the new configuration silver sulfide electrodes used in the recirculating tests could not be rejuvenated by any procedure.

It has been postulated that the degradation of the silver sulfide electrodes in the recirculating fluid, which was losing silver ions rapidly, was due to an attempt by the system to attain an equilibrium condition by some process(es) which caused the transfer of silver ions from the silver sulfide pellet into the solution. Since the movement of silver ions in the solid pellet would, according to the theory of solid state physics, move slower than in the recirculating fluid, the surface of the pellet would become depleted or partially depleted of silver ions, thus resulting in a partial loss of sensitivity or degradation.

The above postulate does not appear to be true because of the following facts:

- Removal of three to ten-thousandths of an inch from the exposed surface of the silver sulfide pellet was only successful in rejuvenating a small percentage of the electrodes so treated.
- Polishing the exposed surface of the silver sulfide pellet of a degraded electrode was successful in about 60 percent of the attempts to rejuvenate such electrodes.
- The radioisotope test showed that silver was being deposited or exchanged on the surface of the silver sulfide pellet from the silver ion (silver nitrate) solution.

The conclusion from the above tests to determine the cause and/or manner in which the silver ion is lost from the recirculating solutions and the studies on the degradation of the silver sulfide electrode can be simply stated as--

the loss of silver ion from the solution and the degradation of the electrodes are a result of the instability of the silver ion and some of its compounds.

The instability of the silver ion in the presence of light is well known since it forms the basis for photography. Silver is very readily reduced from its ionic form to metallic form by many substances. Indeed, the handbook oxidation potential for silver gives the following half-reaction:

$$Ag + \chi H_2O \rightleftharpoons [Ag^+]\ (Ag) + e^- \quad - \quad 0.7995$$

The large negative potential indicates that the simple silver ion is capable of oxidizing not only many common anions but water as well and is, therefore, very unstable and prefers the lower free energy state of metallic silver.

It is not surprising, therefore, to find numerous journal articles dealing with the adsorption of trace silver ion on a variety of surfaces and/or materials by such recognized experts as R. A. Durst and associates of the National Bureau of Standards* and others.

Durst et al claims that the use of a silver ion selective electrode for monitoring silver ion losses in investigations of trace silver adsorption on container surfaces offers the advantage of less complex and costly equipment, simplified procedure, and improved precision over the radiometric method. For a 0.2 ppm silver solution the adsorption levels at the end of 30 days increased in the order: Vycor < polyethylene ≈ Teflon < Desiccated Pyrex < Pyrex. Metal surfaces were not tested.

In support of the use of silver ion as a bactericide, NASA and contractors have also made studies on the depletion of silver ion from solution under various conditions.

It was not surprising, therefore, to observe a loss of silver ion from solution during the monitoring test (paragraph 8.2). What was difficult to comprehend was the rate and quantity of silver lost or adsorbed by the system.

---

* R. A. Durst and B. T. Duhart, Anal. Chem., 42, No. 9 (1970).

The next step in determining the rapid loss of silver ion from the solution was the effect of materials in the prototype system.

The static, recirculating and flow-through tests did not help to account for the rapid loss of silver ion from the recirculating silver ion solutions in the prototype system. Material incompatibility was suspected, thus the following tests were performed.

1. Test of individual components exposed to 500 ppb silver ion solution.
   Exposure conditions: Static - at room temperature - in dark
   Storage - four days duration - in glass beakers.

Component	Fluid Volume ml	$[Ag^+]$ Concentration ppb Before	After
None (control)	500	500	500
SS-316 Cap (bottom of cell)	500	500	240
KEL-F (cell body)	500	500	<1
Electrolyte Reservoir Assy (KEL-F, 316-SS, Buna N rubber, silicone rubber)	500	500	70
Thermistor Sensor Assy (316-SS, epoxy, thermistor)	100	500	3.5

   The small area of the epoxy, approximately 0.1 square inch, should not affect the loss of silver ion from the solution in the amount indicated. Therefore, a second test was performed.

2. A modified prototype system consisting of pump (SS-316), SS-316 tubing and fittings and a 1-liter glass beaker containing 800 ml of 500 ppb silver ion solution was tested. The solution was continuously recirculated and at 10-minute intervals a 50 ml sample was removed for silver ion measurement, then returned to the system. Periodically, different materials were added to or removed from the beaker. A summary of the results is given on the following page:

Material or Component	Exposure Time (min.)	Change in [Ag^+] Conc. ppb
None (system only)	30	-90
Epoxy, Kenics 78-05-083, 25 grams (2.45" dia. x 0.5")	30	-60
Electrode Body, 23.7 grams (Polypropylene)	30	-40
KEL-F 2" dia. x 4.2" long (unused)	30	-40

The above losses in silver ion were not significant when compared to previous recirculating tests showing 500 ppb loss in 25 minutes, and therefore the tests were inconclusive.

The conclusions which may be made from the above data and previous test data are as follows:

1. Material(s) within the system reacts with the silver ion of the recirculating 50 to 500 ppb Ag NO_3 solution in such a manner as to either complex the silver ion or take the ion out of the solution.
2. There may be only an apparent loss of silver since the silver sulfide sensing electrodes detect only silver ions.
3. The loss of sensitivity of the silver sulfide electrode may be, in some manner, directly related to the apparent loss of silver ion from the recirculating solution.
4. The reaction or mechanism which is responsible for the loss of the silver ion appears to be time dependent since pumping the silver ion fluid through the system to waste does not show much loss of silver ion but, while recirculating the fluid in the system, a rapid and continuous loss of silver ion is observed.

5. Under the present conditions the recirculating of a small quantity of Space Shuttle potable water through the Silver Ion Monitoring System and through a short link of the water system during periods of non-use would result in rapid loss of silver ion from the water and a loss of sensitivity of the silver ion sensing electrode.

In view of the above conclusions, Beckman suggested that a possible solution to the problem would be a minor modification of the originally conceived placement of the monitor in the potable water system. The proposed modified system is shown in the block diagram, Figure 8-2. Theoretically, recirculating of the water through the silver ion source should continuously replenish any silver ions lost from the water due to adsorption or chemical reaction(s). Thus, based on the results of the previously described tests, the silver sulfide electrode should continuously monitor the level of silver ion in the major portion of the water system without being subjected to those conditions which are suspected to cause loss of sensitivity.

In order to determine characteristics and stability of such a proposed system, the original test breadboard and prototype system were modified to simulate a system such as that shown in Figure 8-2. A block diagram of the test setup is shown in Figure 8-3. All components with the exception of the electrodes and electrode cell, the glass tube of the flowmeter, and the Teflon valve and pump gear were of 316 stainless steel.

The silver bromide, AgBr, column used was the canister prepared for the previous contract which had yielded theoretical saturation of AgBr or 73 ppb silver ion at flow rates up to 450 ml/minute.

Four liters of water were recirculated through the system at 150 ml/min. at 1.93×10^5 N/m^2 (28 psig) and at 23.9°C (75°F). The fluid in the system was sampled periodically for 28 hours and the silver ion concentration determined in an independent electrode system. The silver ion level remained below 50 ppb the entire time.

The silver bromide column was removed from the system and flushed with 20 ml distilled water by gravity flow. The output of the column was still below 50 ppb silver ion.

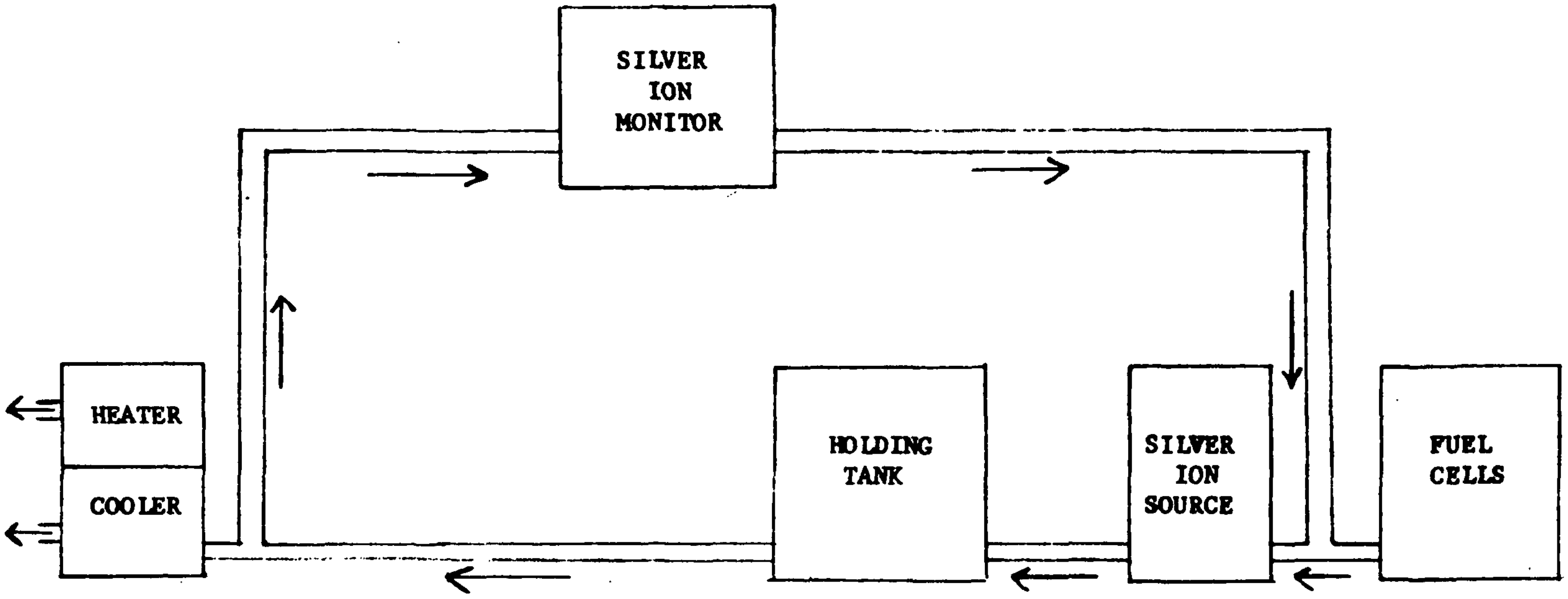
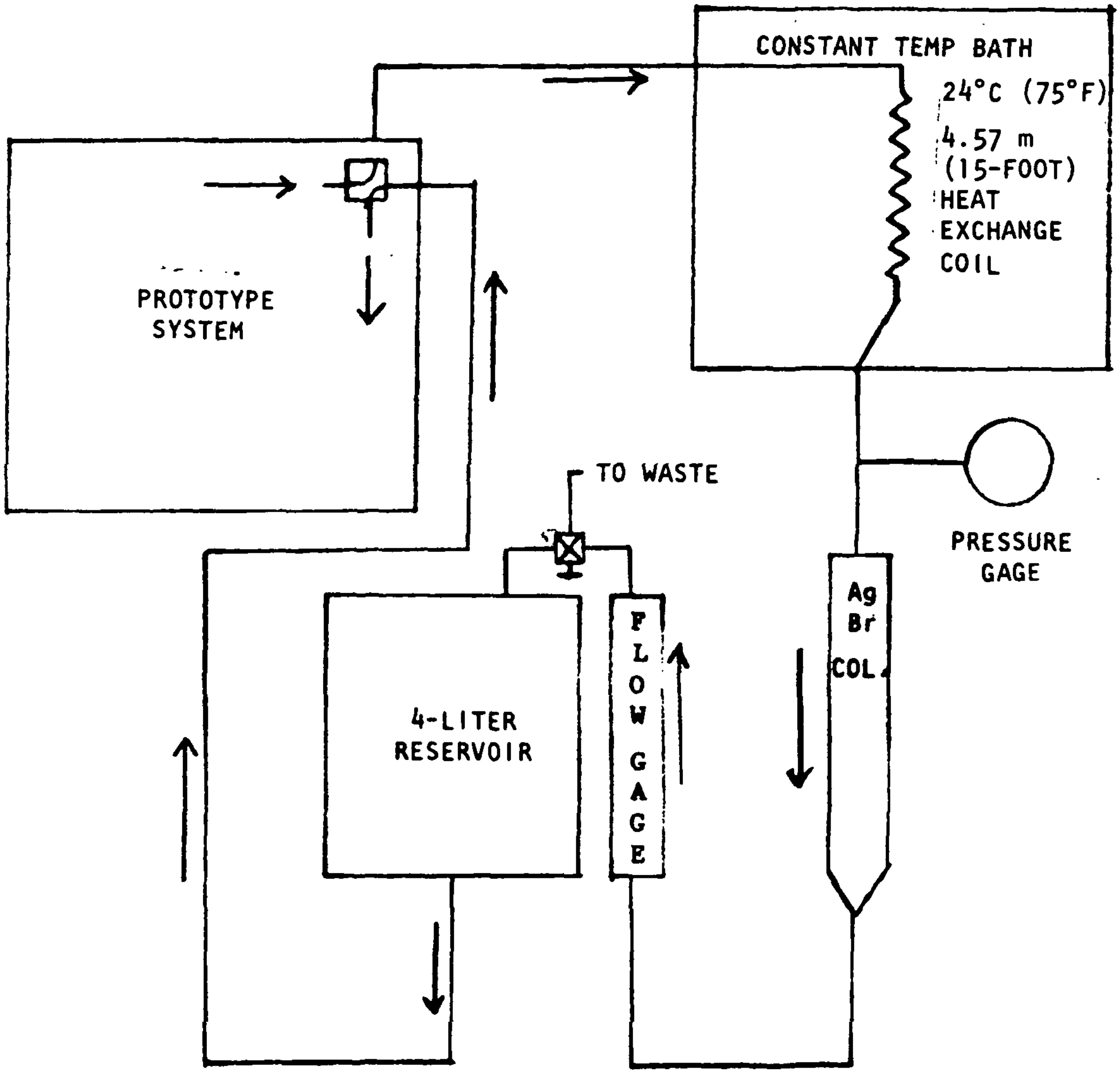


Figure 8-2. Proposed Modified Water System



Flow 150 ml/min. at 1.93×10^5 N/m^2 (28 psig)

Figure 8-3. Breadboard and Prototype Modification

The test setup including the prototype system with electrode cell and electrodes was cleaned as follows:

The system was flushed with 1.89×10^{-2} m^3 (5 gallons) of distilled water, and the last 100 ml was sampled at the waste connection (see Figure 8-3). Silver ion level in effluent from the system was 63 ppb. This test was repeated with an additional 1.89×10^{-2} m^3 (5 gallons) of water, and the effluent still remained at the 63 ppb level.

Four liters of water were recirculated in the system for 19 hours, at which time the silver ion level was found to be 25 ppb. The system was emptied and cleaned as follows:

1. Recirculated a one-liter dilute ammonium hydroxide solution for one hour.
2. Flushed 30 minutes with deionized water.
3. Recirculated a one-liter dilute nitric acid solution for one hour.
4. Flushed one hour with deionized water, followed by eight liters distilled water.
5. Removed the electrode cell from the system and checked the sensing and reference electrodes for proper response. Flushed the electrolyte reservoir and filled with fresh electrolyte and checked the quartz fiber junction for proper electrical resistance.

An additional 150 grams of silver bromide and 260 grams of glass beads were added to the silver bromide column which was then flushed with deionized water and distilled water until the theoretical 73 ppb level of silver ion was found in the column effluent. The electrode cell, electrodes, and silver bromide column were connected into the system, and 50 and 500 ppb silver ion solutions were pumped through the system. Unstable up-down response was observed, but no loss of sensitivity of the silver sulfide electrode was seen.

Four liters of water were then recirculated through the system for 19 hours at 25°C (77°F), 75 ml/min. at 1.93×10^5 N/m^2 (28 psig). The indicated silver ion level at the end of the period was 22 ppb. The silver bromide column was removed from the system and flushed 1.5 hours with deionized water at approximately 100 ml per minute, followed by 12 liters of distilled water which finally produced a column effluent of 66 ppb silver ion at 22°C (71.6°F)--almost theoretical.

The system was further modified as of October 17, 1973, by adding an ion exchange column immediately upstream of the silver bromide column (Figure 8-4) to determine if the interfering materials were ionic in nature. The ion exchange column contained approximately 130 grams of a 50/50 mixture of Amberlite IR-120 and Amberlite IR-45. Four liters of water were recirculated through the system for 19 hours at 75 ml/min. and 1.99×10^5 N/m^2 (29 psig) at 25°C (77°F) and the fluid in the system at the output of the silver bromide column (V2 in Figure 8-4) was sampled at various times. The silver ion level was as follows:

Time	Silver Ion Level (ppb)
20 min.	42
90 min.	42
19 hours	58
25 hours	50
44 hours	45

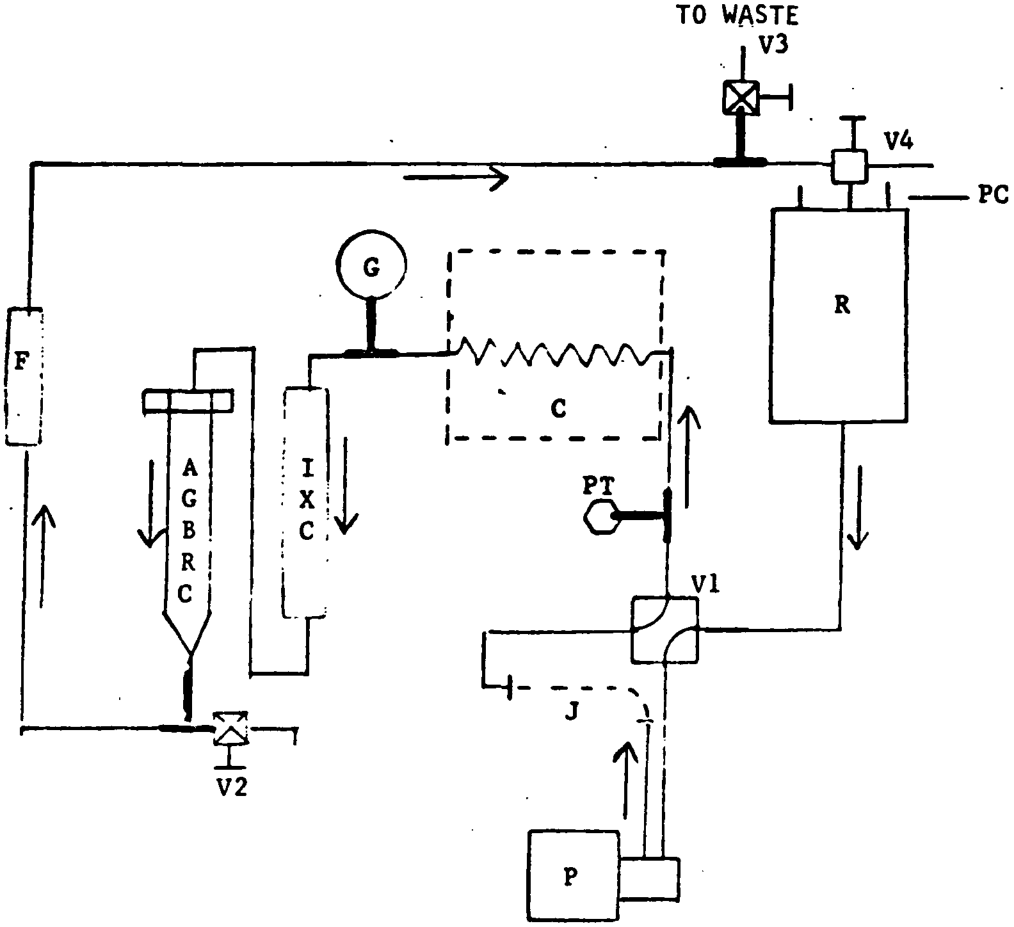
The pump was removed from the system and 4 liters of distilled water were passed through the system 3 times by pressurizing the reservoir with 3.45×10^4 N/m^2 (5 psig) nitrogen, collecting the effluent at the output of the silver bromide column (V2 of Figure 8-4), and returning some to the reservoir.

After three passes through the system at approximately 75 ml per minute at 25°C (77°F), the silver ion level was found to be 60 ppb.

The conclusions from these last tests are as follows:

1. The 316 stainless steel pump with Teflon gears appears to contribute to the loss of silver ion but is not the sole cause of the loss.

2. Some material(s) within the system may react with the silver ions of the circulating liquid to form a non-ionized compound since the silver ions are observed to decrease during recirculation and the addition of an ion exchange column upstream of the silver bromide column does not



R	4-Liter Reservoir, 316 SS
P	Pump, 316 SS and Teflon
C	4.57 m x 6 m OD (15 ft x 1/4 in.) 316 SS Coil in Constant Temp Bath
G	Pressure Gage, 316 SS Tube
IXC	Ion Exchange Column, 381 m x 25.4 m ID (15 x 1 in.), 130 gms mix, IR120-IR45
AGBR	Silver Bromide/Glass Bead Column (∼300 g AgBr)
F	Flowmeter, 316 SS and Glass
PT	Pressure Transducer Connection
PC	Reservoir Vent and Filling Connection
J	Jumper Tube in place of Electrode Cell
V1	System Isolation Valve - Teflon
V2	Sampling Valve #1 - 316 SS
V3	Sample Waste - 316 SS
V4	Sampling Valve #2 - 316 SS

Tubing and Fittings 316 SS

Figure 8-4. Modified System as of 17 October 1973 result in a theoretical silver ion level in the effluent of the silver bromide column.

3. The central issue was still unresolved. Independent reference checks showed that the electrodes were indeed measuring silver loss but it could not be resolved from these data whether the loss was real or only apparent, i.e., whether the silver was actually leaving the solution or being converted to a form that could not be measured by potentiometric methods.

   An attempt was made to resolve this issue by comparing total silver concentration as determined by atomic absorption spectroscopy to ionic activity as measured by electrode but the results were inconclusive at these low levels.

   It was considered essential to resolve this issue. If the silver was being converted to a non-ionized form, it might still be bacteriostatic, but it would mean that another monitoring technique would have to be employed. If on the other hand, the silver was leaving solution, the problem became one of material compatibility, not only in the monitor but elsewhere in the system, since silver depletion would compromise the bacteriostatic effectivity of the approach.

   To arrive at this answer, it was decided to employ a radioactive tracer technique in conjunction with electrode analyses as described in the following section.

8.4 Radioisotope Tracer Test to Determine Areas of Adsorption of Silver Ion

8.4.1 Purpose

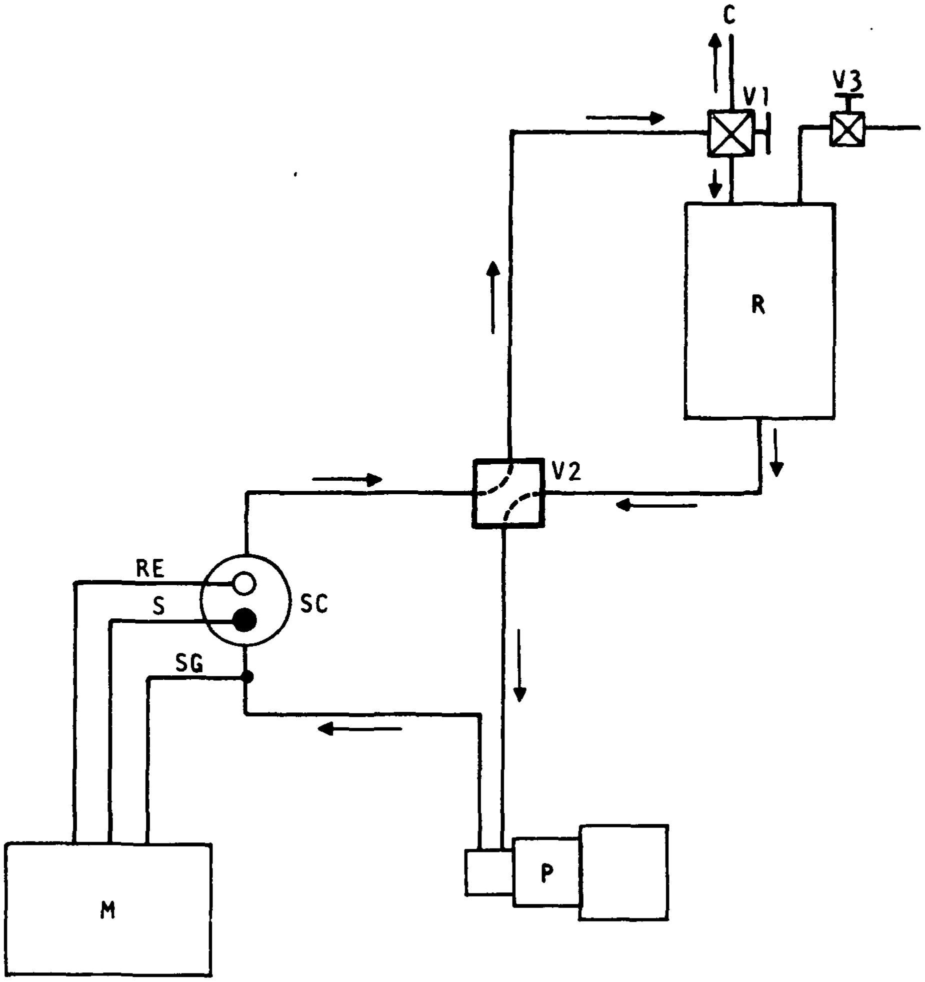
In an attempt to obtain a very sensitive reference method for measuring total silver, a radioactivity approach was selected. A given level of radioactive silver will provide the same level of activity whether it is present in ionic form or in a complex form. Thus, observing the behavior of the radioactivity level of a circulating silver solution over time and comparing that level to a measured ionic silver activity would yield information on the chemical state of the silver. That is, if the radioactivity level of the circulating solution remains constant while the ionic activity falls, it can be inferred that the silver remains in solution but in a form unavailable for measurement by the electrode. If, on the other hand, the radioactivity of the solution falls in conjunction with the ionic activity, it can be inferred that silver is leaving solution and that the electrode is actually measuring all of the silver in that solution. If silver was being depleted from the solution, it would have to be deposited on some surface(s) of the system and it should be possible to determine relative deposition by scanning component parts for radioactivity. A tracer level of Ag-110m was used for this study.

8.4.2 Method

A 500 ml (16.9 fl oz) solution of 500 ppb silver ion [Ag^+] containing 250 micrograms of silver was prepared with approximately 29 μCi (microcuries) of Ag-110m added as a radioactive tracer. The quantity of silver added to the 500 ppb solution by the addition of the tracer was 3.189×10^{-11} mole/ml or 0.689 percent, which was insignificant when the overall error was determined. The tracer was introduced into the system as shown in Figure 8-5 and recirculated for two hours.

Prior to introduction of the fluid into the system, a one ml sample was taken as a control sample. Also, the fluid was measured for silver ion concentration with a silver sulfide electrode test setup.

During the recirculation period, fluid samples were taken every 10 minutes. These samples, consisting of a one-ml aliquot, were measured for radioisotope activity by "counting" the disintegrations per minute (dpm) in a Beckman Biogamma well counter. Simultaneously, a measurement of silver ion concentration in the recirculating fluid was made with the system's electrodes. At thirty-minute intervals, a 50 ml sample of the fluid was removed and analyzed for silver ion concentration with an external electrode system. The 50 ml sample was returned to the system within five minutes.



M - Beckman Century-SS pH Meter
V1 - Selection valve, sample-waste or reservoir return
R - 4-liter 316 stainless-steel reservoir
V2 - Teflon valve-system isolation
P - Gear Pump, 316 stainless steel with Teflon gears
SC - Electrode cell--Kel-F, polypropylene, Buna N, stainless-steel and epoxy
S - Sensing electrode
RE - Reference electrode
SG - Solution ground connection
C - Collection point for liquid passed through system
V3 - Vent and filling connection and valve

Figure 8-5. Prototype System Setup for Radioisotope Silver Tracer Test

At the end of the two-hour recirculation test, the system was dismantled and each of the parts rinsed well with distilled water. The parts were then soaked (silver extracted) in a solution of approximately 25-percent nitric acid for one hour to remove any silver that had been adsorbed or deposited on the part. A one-ml aliquot of each solution was then counted to determine the quantity of silver that had been removed from the part. At that time, the total recovery of silver was approximately 42.9 percent. The remaining silver that was not recovered was not removed from the parts in this first wash.

A second soaking of the parts in nitric acid recovered more silver. The total silver recovered from the parts was 163.6×10^{-6} grams (5.8×10^{-6} oz) and that remaining in the solution (as determined by the radioisotope activity) was 53.5×10^{-6} grams (1.89×10^{-6} oz) or a total of 217.1×10^{-6} grams (7.65×10^{-6} oz) accounted for out of 250×10^{-6} grams (8.8×10^{-6} oz) of starting silver or 86.8 percent recovery.

8.4.3 Results

Table 8-1 gives the decrease of silver with time as measured by the three separate methods.

Figure 8-6 is a plot of the decrease of silver with time.

Table 8-2 gives the data on the part and material, and the amount of silver recovered from each part.

8.4.4 Conclusions

The conclusion of this experiment is that the silver ion that was circulating in the system was adsorbed onto the parts of the system, in particular the stainless steel parts (tubing, fittings, and internal parts of the pump). The sources of error in the measurement of the radioactive material are estimated to be less than 0.2 percent. The other errors that may enter into the final determinations are those that normally occur in pipetting techniques and those associated with the electronic systems.

Table 8-1. Decrease of Silver Ion with Time

Time (min)	[Ag$^+$] ppb System Electrodes	Reference Electrodes	Ag-110M Tracer
0	500	500	500
10	400		349
20	340		263
30	290	250	249
40	250		218
50	230		196
60	190	210	179
70	180		159
80	150		148
90	150	185	136
100	150		
110	125		114
120	135	170	107

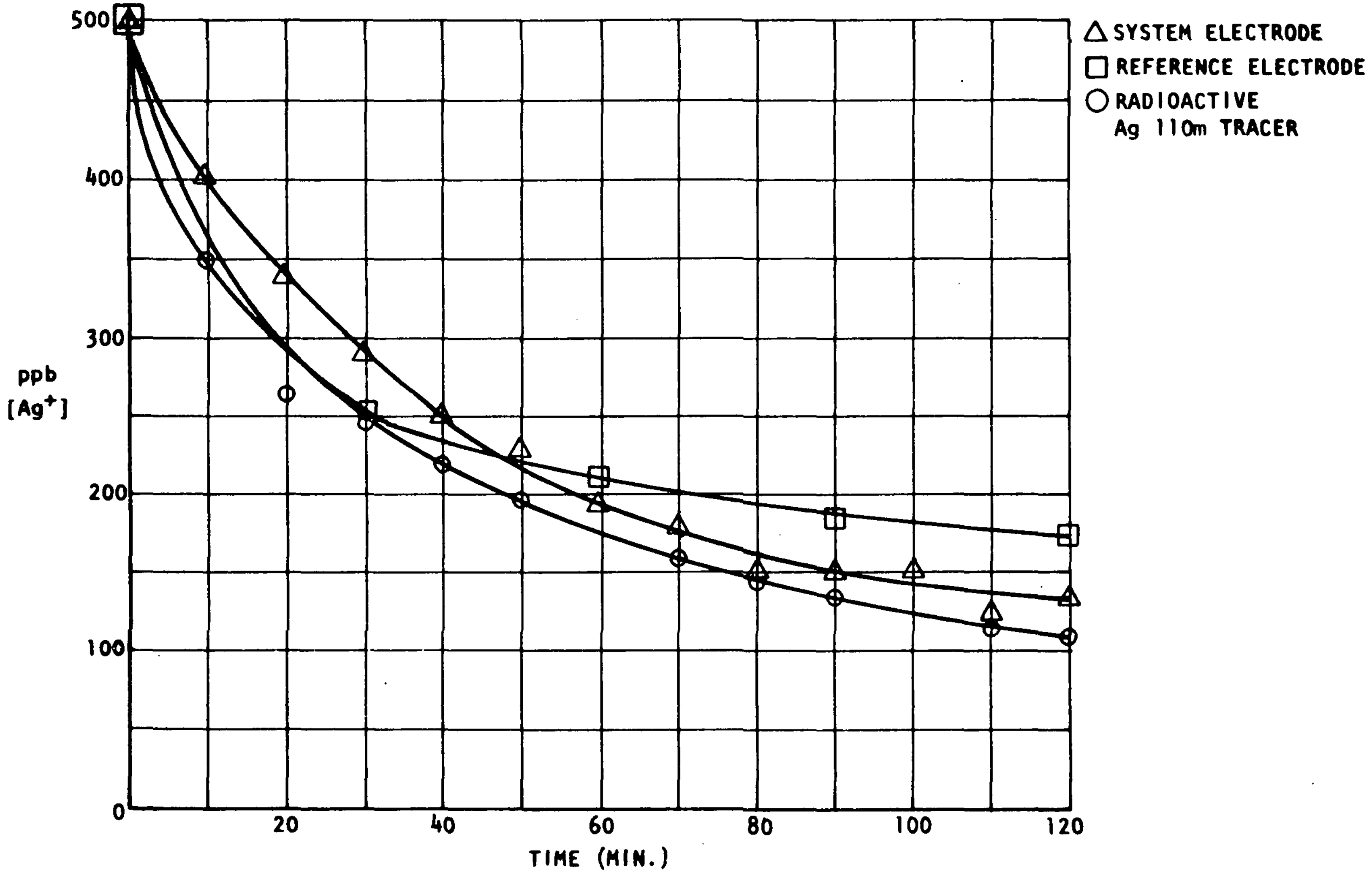


Figure 8-6. Decrease of Ag Ion Concentration with Time

Table 8-2. Amount of Silver Removed from the System Parts by Nitric Acid

		Area Exposed to Solution		Silver Removed[1] g x 10^{-6}		
Part Description	Material	in.^{2}	cm^2	A	B	Total
Electrolyte Reservoir	316 SS	1.5	9.63	2.6	3.9	6.5
	Rubber	0.63	4.04			
	Kel-F	17.49	112.3			
Pump	Teflon	8.0	51.4	1.12	1.89	3.01
	316 SS	4.6	29.5	15.57	26.28	41.85
Isolation Valve (V2)	Teflon	0.98	6.29	1.3	5.96	7.26
Selector Valve V1	316 SS	0.98	6.29	1.0	1.03	2.03
Sensor Chamber	Kel-F	8.8	56.5	3.2	2.34	5.54
Sensor Cap	316 SS	4.15	26.6	2.4	3.9	6.3
Fittings & Tubing	316 SS	33.6	215.8	22.1	53.7	75.8
Sensor Electrode	Silver Sulfide	0.09	0.58	-	4.3	4.3
4 liter Reservoir	316 SS	19.6	125.9	5.5	5.5	11.0
TOTAL		101	648.6			163.6

Summary

	Ag Recovered			Surface Area		
Material	g x 10^{-6}	oz x 10^{-6}	% Recovered	cm^2	in.^{2}	%
Stainless Steel	137.52	4.85	55.0	64.4	398.6	63.7
Non-metals	26.08	0.919	10.4	36.6	250	36.3
Remaining in Solution	53.5	1.886	21.4	--	---	--
Sub Total	217.1	7.657	86.8	101	648.6	100
Silver in Starting Solution	250	8.8	100			

[1] Removal of silver by soaking parts in dilute (approximately 30%) nitric acid. Concentration of silver determined by counting dpm's of a one-mil aliquot of the acid.

A - First silver recovery effort

B - Second silver recovery effort

This conclusion was in conflict with earlier studies showing minimal depletion of silver on stainless steel surfaces over extended periods of time. Accordingly, the conditions of these earlier experiments were studied to determine which, if any, were sufficiently different to account for the results of this study. Two conditions were determined as potential variables that could have accounted for the discrepancy. These were the exposed volume/surface area relationship and the condition of the water during the test. The earlier studies had employed a stagnant system in a tank providing a volume ratio/stainless steel of approximately 6 cc/cm^2 while the test system we employed had a ratio of approximately 1 cc/cm^2 which was effectively increased by circulation of the test solution.

The effect of these variables on the rate of silver depletion was examined as described in the following section.

8.5 Radioisotope Test to Determine Rate of Adsorption of Silver on Stainless Steel and the Effect of Agitation

8.5.1 Purpose

The purpose of the second radioisotope test was to determine the rate at which silver was adsorbed on 316 stainless steel in comparison to the ratio of the metal surface to the silver ion solution in stirred and non-stirred samples.

8.5.2 Method

Five identical sets of 2 beakers each were set up with each beaker containing 500 ml (16.9 fl oz) of a 500 ppb silver ion solution to which had been added 29 μCi of Ag-110m as in the previous test (Paragraph 8.5).

Into each set of beakers were placed different quantities of 316 stainless steel test coupons to achieve different ratios of liquid-to-metal surface. The liquid-to-metal surface ratios are given in Table 8-3.

One series of beakers was a static test while in the other series the test coupons were hung from a support and rotated at approximately 12.56 rad/s (120 rpm).

Table 8-3. Liquid-to-Metal Surface Ratio for the Second Radioisotope Test

Beaker	Ratio ml fluid/cm^2 Metal Surface Control
1	0
2	0.701
3	1.449
4	2.87
5	5.757

In each set of test coupons, a small coupon was selected which was removed periodically for determination of the deposited silver by measuring the activity of the isotope on its surface.

At specific intervals, a 0.5 ml aliquot was removed from each beaker for "counting". At other intervals, a 50 ml sample from each beaker was removed for silver ion determination by an electrode test setup, then returned to the beaker.

The sampling schedule is given in Table 8-4.

The test was run for 10 days with additional measurements made on the 24th day.

Series A was stirred while series B was static. Thus, Beaker 1A was stirred with no metal exposed to the fluid.

Table 8-4. Radioisotope Test Sampling Schedule

Day	Time	Liquid Counting Sample	50 ml $[Ag^+]$ Measuring Sample	Metal Coupon Count
1	0	X	X	X
	15 min	X		
	30 min	X		
	60 min	X	X	
	2 hr	X		
	4 hr	X	X	
	8 hr	X	X	X
2	24 hr	X	X	X
3		X	X	X
4		X	X	X
		X	X	X
7		X	X	X
8		X	X	X
9		X	X	X
10		X	X	X
24		X	X	X

During the test, a black substance had fallen into three of the test solutions, 1A, 4A and 5A, from the Delrin bearings of the stirring mechanism. This caused a very rapid loss of silver ion from the solutions and such beaker tests were then discontinued.

The test data is presented in Tables 8-5 through 8-9 and shown graphically in Figures 8-7.

Table 8-5. Silver 110m--Liquid Volume/Metal Surface Adsorption Study (Control) (Glass Slides in Place of Metal Coupons)

Time	Stirred Ag-110m		[Ag+]	Unstirred Ag-110m		[Ag+]
Min/Days	cpm	% Orig. Act.	ppb	cpm	% Orig. Act.	ppb
0 m	67227	100.0	500	71407	100.0	500
15 m	66994	99.6	440	71063	99.5	
30 m	65813	97.9		70830	99.2	
60 m	66008	98.2		69407	97.2	440
120 m	67593	100.5		71864	100.6	
240 m	66438	98.8	420	72236	101.1	420
360 m	64089	95.3		70324	98.5	
480 m	60586	90.1	420	68622	96.1	420
	57270	85.2	420	65649	91.9	422
1 day	60997	90.6	400	69679	97.6	400
2 days	57121	85.0	390	63480	88.9	400
3 days	34904	51.9	12	64809	90.1	385
4 days	Contaminated from stirrer			65056	91.1	390
5 days	Contaminated from stirrer			60244	84.4	370
6 days	Contaminated from stirrer			61419		400

Table 8-6. Silver 110m--Liquid Volume/Metal Surface Adsorption Study (Liquid Volume/Metal Surface Ratio--0.701 ml/cm^2)

	Stirred			Unstirred		
Time Min/Days	Ag-110m cpm	% Orig. Act.	[Ag+] ppb	Ag-110m cpm	% Orig. Act.	[Ag+] ppb
0 m	71404	100.0	500	72402	100.0	500
15 m	55927	78.3		69219	95.5	
30 m	48442	67.8		63741	88.0	
60 m	24336	34.1	140	62053	85.6	340
120 m	2924	4.1		54067	74.6	
240 m	911	1.3	225	47704	65.8	260
360 m	760	1.1		41171	56.8	
480 m	616	.1	15	35087	48.4	200
1 day	406	0.1	8	19930	27.5	120
2 days	Discontinued			10730	14.8	62
3 days				4253	5.9	26
6 days				687	0.1	7.8
7 days				994	1.3	9.8
8 days				782	1.0	9.6
9 days				Discontinued		

Table 8-7. Silver 110m--Liquid Volume/Metal Surface Adsorption Study (Liquid Volume/Metal Surface Ratio--1.449 ml/cm^2)

	Stirred			Unstirred		
	Ag-110m		[Ag+]	Ag-110m		[Ag+]
Time Min/Days	cpm	% Orig. Act.	ppb	cpm	% Orig. Act.	ppb
0 m	67267	100.0	500	68744	100.0	500
15 m	63338	94.4		65798	95.4	
30 m	68257	101.7		65419	94.9	
60 m	61740	92.0	385	65382	94.8	400
120 m	56619	84.4		63529	92.1	
240 m	49308	73.5	270	61855	89.9	355
360 m	41137	61.3		56888	82.5	
480 m	30785	45.9	190	52033	75.4	325
1 day	9213	13.7	58	43400	62.9	270
2 days	3279	4.9	17	38415	55.9	220
3 days	929	1.4	9.2	29811	43.4	185
6 days	959	1.4	3.3	14229	20.6	79
7 days	Discontinued due to low activity			11911	17.3	68
8 days				8892	12.9	56
9 days				5943	8.6	50

Table 8-8. Silver 110m--Liquid Volume/Metal Surface Adsorption Study (Liquid Volume/Metal Surface Ratio--2.87 ml/cm^2)

Time	Stirred			Unstirred		
	Ag-110m		[Ag+]	Ag-110m		[Ag+]
Min/Days	cpm	% Orig. Act.	ppb	cpm	% Orig. Act.	ppb
0 m	75964	100	500	76695	100	500
15 m	74802	98.1		74453	96.8	
30 m	74234	98.0		72643	94.4	
60 m	71412	94.3	400	71724	93.2	440
120 m	68826	90.9		70305	91.4	
240 m	63747	84.2	355	68606	89.2	370
360 m	62428	82.4		63797	82.9	
480 m	56593	74.7	325	59041	76.8	350
1 day	44676	60.0	270	53979	70.1	320
2 days	39952	52.6	220	51987	67.8	315
3 days	24348	3.2	185	45007	58.7	270
6 days	14545	19.1	76	35318	40.0	210
7 days	8981	11.8	40	34627	45.1	195
8 days	1521	2.0	8.8	29505	38.5	175
9 days	Discontinued			27328	35.6	170

Table 8-9. Silver 110m--Liquid Volume/Metal Surface Adsorption Study (Liquid Volume/Metal Surface Ratio--5.747 ml/cm^2)

Time	Stirred Ag-110m		[Ag+]	Unstirred Ag-110m		[Ag+]
Min/Days	cpm	% Orig. Act.	ppb	cpm	% Orig. Act.	ppb
0 m	72930	100.0	500	74216	100.0	500
15 m	72247	99.0		74834	101	
30 m	72378	99.2		72835	98.3	
60 m	70750	96.9	440	73312	99.0	440
120 m	71737	98.3		73117	98.7	
240 m	69177	94.8	420	73102	98.7	400
360 m	68848	94.3		71137	96.0	
480 m	63153	86.5	400	66294	89.5	400
1 day	17882	24.5	9.5	63955	86.3	385

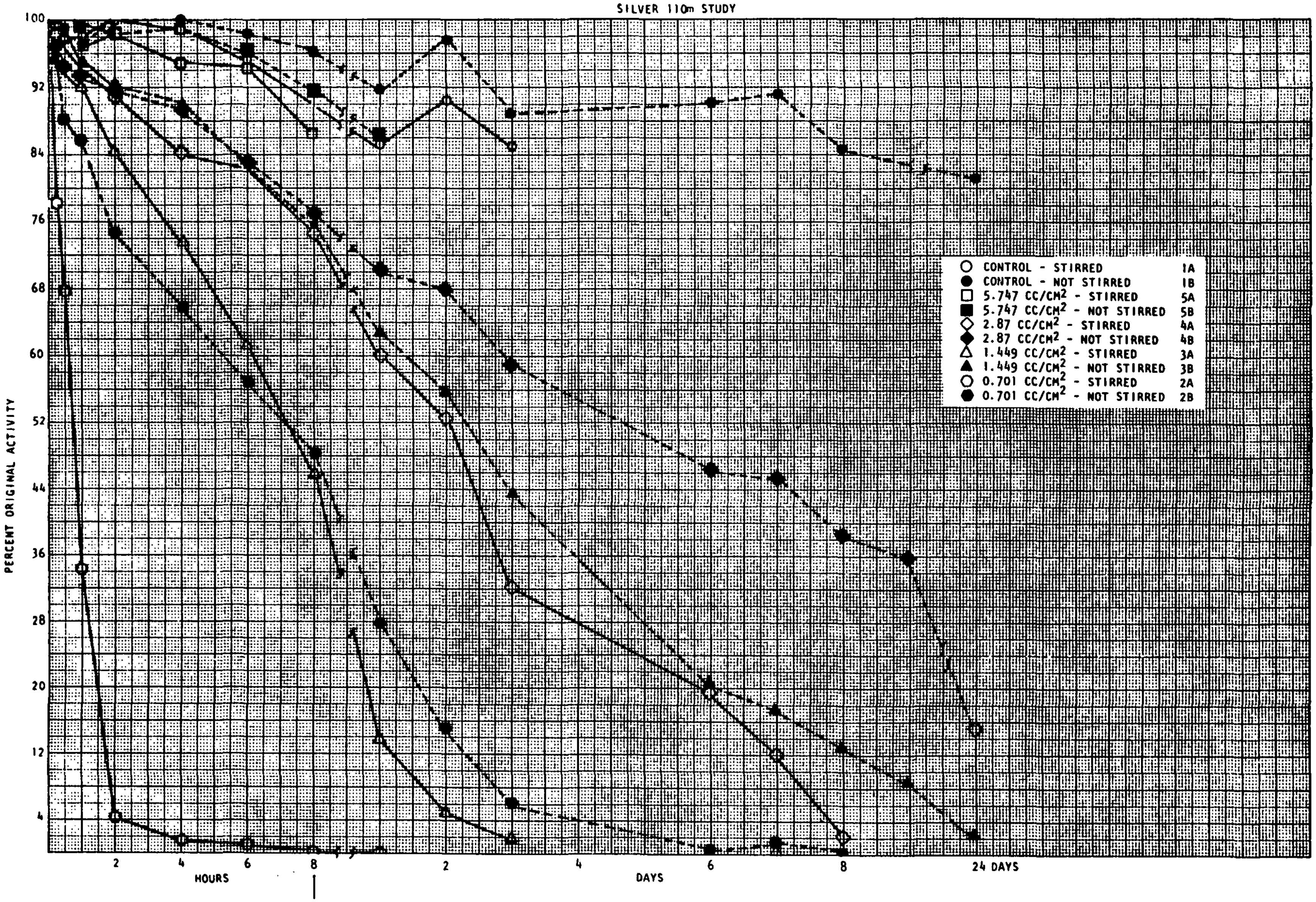


Figure 8-7. Isotope Depletion Vs. Stainless Steel Surface Area and Agitation

8.5.3 Conclusions

- The lower the ratio of liquid-to-metal surface, the faster the adsorption of silver on the metal surface.
- Agitation or stirring more than doubles the rate of adsorption of silver on the metal surface.
- After approximately two days, loss of silver ion in beakers containing only glass decreases at a very slow rate.
- It appears feasible to minimize silver loss to the system by minimizing exposure of the fluid to stainless steel surfaces. The closer one can approach the 6 cc/cm^2 level, the less will be the effect. Similar studies should be conducted, however, on materials considered substitutes for the stainless steel.

8.6 Radioisotope Test to Determine Rate of Adsorption of Silver on Teflon and the Effect of Agitation

8.6.1 Purpose

The purpose of the third radioisotope test was to determine the rate at which silver was adsorbed on Teflon for comparison with the rate of adsorption on 316 stainless steel in stirred and non-stirred samples.

8.6.2 Method

Four identical sets of 2 beakers each were set up with each beaker containing 500 ml (16.9 fl oz) of a 500 ppb silver ion solution to which had been added 29 μCi of Ag-110m as in the previous test (Paragraph 8.5.2).

Into each of the beakers were placed different quantities of Teflon test coupons to achieve different ratios of liquid-to-Teflon surface.

One series of beakers was a static test, whil in the other series the test coupons were hung from a support and rotated at approximately 12.56 rad/s (120 rpm).

At specific intervals a 0.5-ml aliquot was removed from each beaker for counting. At the same time, a 50-ml sample was removed from each beaker for silver ion determination by an electrode test setup. The 50-ml samples were returned to the beakers after the determination. The sampling schedule is given in Table 8-10.

Table 8-10. Radioisotope Test Sampling Schedule (Teflon)

Day	Time	Liquid Counting Sample	50-ml [Ag^+] Measuring Sample
1	0	X	X
	1 hr	X	X
	2 hrs	X	X
	4 hrs	X	X
	8 hrs	X	X
2	24 hrs	X	X
3		X	X
4			
4		X	X
6		X	X

The test was run for 6 days with a repeat of the stirred control (1C) and the stirred 5.747 cc/cm^2 sample (4C) for 19 hours because of contamination encountered during initial testing.

Series C was stirred while series D was static. Beakers 1C and 1D (controls) contained glass slides in place of the Teflon coupons.

The test data are presented in Table 8-11 and shown graphically in Figure 8-8.

Table 8-11. Silver 110m--Liquid Volume/Teflon Surface Adsorption Study (Liquid Volume/Teflon Surface Ratio [L/T])

	HOURS										DAYS							
	0		1		2		4		8		1		2		4		5	
	%	cpm	%	cpm	%	cpm	%	cpm	%	cpm	%	cpm	%	cpm	%	cpm	%	cpm
Beaker 1C (stirred) Ag 110m cpm/0.5 ml fluid (Control)	100	66 641	100	67 447	100	68 113	100	67 182	100	68 306	100	68 588	100	67 271	100	68 185	100	70 071
L/T Ratio = "0"																		
Repeat Test	100	66 374	99	65 899	99	66 096	95	63 342	-	-	95	63 495	(19 hrs)	-	-	-	-	-
[Ag$^+$] ppb 50 ml sample (Control)	100	500	96	480	96	480	96	480	92	460	84	420	84	420	88	440	84	420
L/T Ratio = "0"																		
Repeat Test	100	500	96	480	96	480	96	480	-	-	92	460	(19 hrs)		-	-	-	-
Beaker 1D (static) Ag 110m cpm/0.5 ml fluid (Control)	100	70 971	95	67 327	94	66 994	94	66 786	95	67 534	90	63 959	92	65 035	89	63 281	96	68 501
L/T Ratio = "0"																		
[Ag$^+$] ppb 50 ml sample	100	500	96	480	96	480	96	480	88	440	84	420	88	440	92	460	88	440
Beaker 2C (stirred) Ag 110m cpm/0.5 ml fluid	100	62 737	90	57 021	83	51 773	63	39 405	42	26 376	6	3 611	2.3	1 450	1	688	-	-
L/T Ratio = 0.701 cc/cm^2																		
[Ag$^+$] ppb 50 ml sample	100	500	80	400	70	350	54	270	32	160	3.2	16	1.6	8	1.2	6	-	-
Beaker 2D (static) Ag 110m cpm/0.5 ml fluid	100	66 211	92	61 136	96	63 485	95	63 192	97	64 434	90	60 204	91	60 313	96	63 683	93	61 307
L/T Ratio = 0.701 cc/cm^2																		
[Ag$^+$] ppb	100	500	92	460	94	470	88	440	84	420	76	380	82	410	82	410	78	390
Beaker 3C (stirred) Ag 110m cpm/0.5 ml fluid	100	65 231	100	65 987	95	61 806	98	64 170	97	63 274	90	58 871	90	58 563	84	55 078	83	54 287
L/T Ratio = 1.449 cc/cm^2																		
[Ag$^+$] ppb 50 ml sample	100	500	92	460	92	460	88	440	86	430	76	380	78	390	80	400	72	360
Beaker 3D (static) Ag 110m cpm/0.5 ml fluid	100	66 019	98	64 410	96	63 545	97	64 023	97	64 117	100	68 814	93	61 405	93	61 226	92	61 025
L/T Ratio = 1.449 cc/cm^2																		
[Ag$^+$] ppb	100	500	96	480	96	480	92	460	88	440	76	380	82	410	84	420	78	390
Beaker 4C (stirred) Ag 110m cpm/0.5 ml fluid	100	67 103	100	66 874	98	66 024	90	60 528	85	57 312	62	42 144	37	24 962	20	13 314	Discontinued	
L/T Ratio = 5.747 cc/cm^2																		
Repeat Test	100	66 360	98	64 838	97	64 466	94	62 047	-	-	96	63 559	(19 hrs)		-	-	-	-
[Ag$^+$] ppb	100	500	96	480	92	460	84	420	75	375	52	260	30	150	0.6	53	Discontinued	
Repeat Test	100	500	96	480	96	480	96	480	-	-	91	455	(19 hrs)		-	-	-	-
Beaker 4D (static) Ag 110m cpm/0.5 ml fluid	100	67 096	98	65 851	94	63 186	99	66 424	94	62 963	90	60 371	97	65 197	92	61 832	92	61 929
L/T Ratio = 5.747 cc/cm^2																		
[Ag$^+$] ppb 50 ml sample	100	500	92	460	92	460	92	460	84	420	80	400	80	400	84	420	80	400

---

cpm = counts per minute

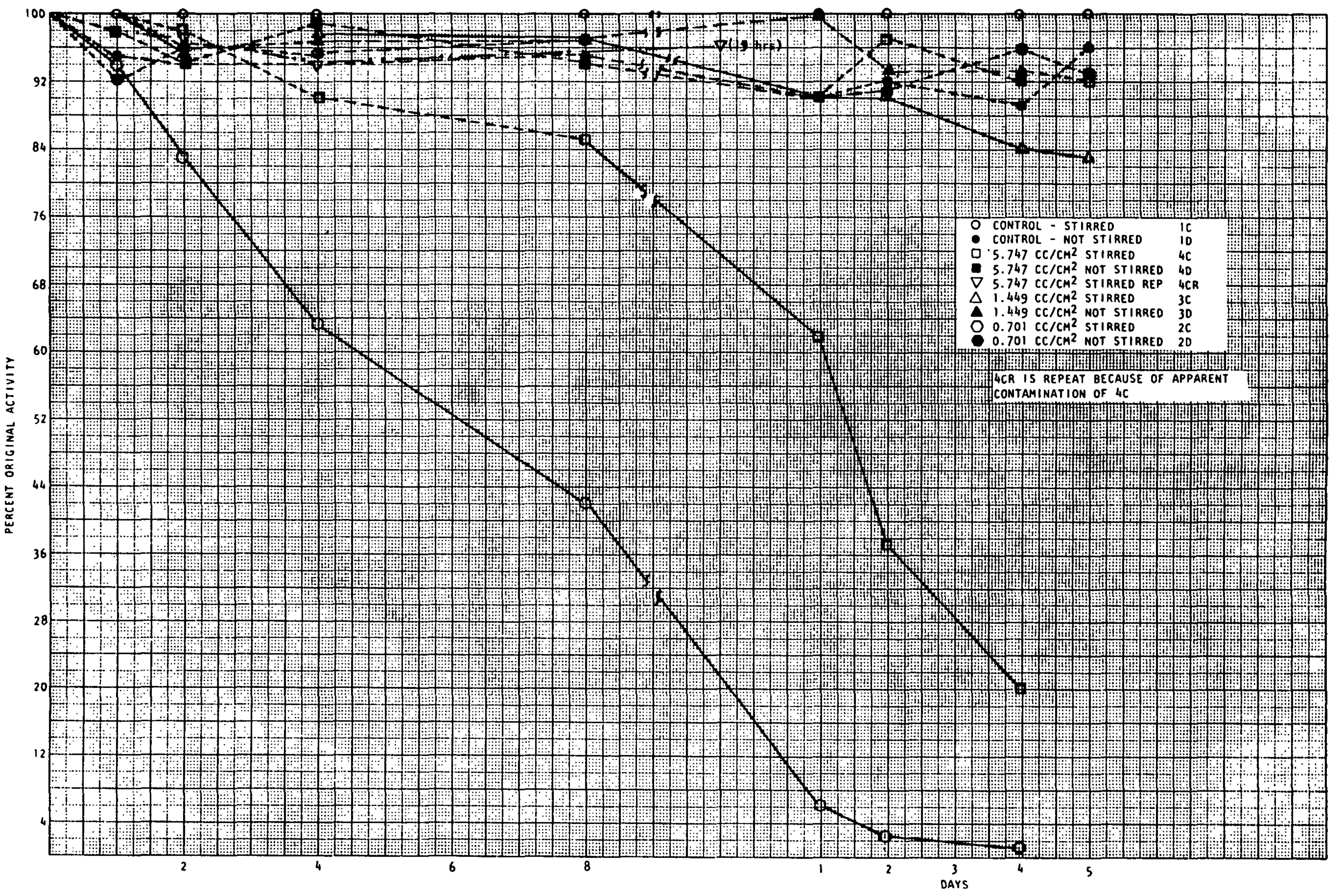


Figure 8-8. Isotope Depletion Vs. Teflon Surface Area and Agitation

8.6.3 Conclusions

- No significant depletion rates were observed with Teflon except at low volume/area ratios and even then, only when the fluid was agitated.
- The worst case condition, i.e., stirred at .701 cc/cm^2, exhibited only a 17-percent loss of silver in two hours, compared with a 96-percent loss with stainless steel under identical conditions.

It is important to note that the 1.449 cc/cm^2 stirred test with Teflon, which was approximately the liquid-to-surface ratio of the silver ion monitor test setup, showed essentially the same adsorption characteristics of silver as the control.

9.0 SYSTEM MODIFICATIONS

9.1 General

The fluid handling unit of the monitoring system was modified to reduce the rate of depletion of silver ion from the recirculating solution. This was accomplished by substituting, where possible, Teflon or nylon components for the stainless steel components.

The silver sulfide sensing electrode was modified to provide a configuration that facilitated easier handling and testing. In addition, the modification eliminated the need for a separate preamplifier for each electrode.

An overall redesign of the electronics was performed to correct several circuit design deficiencies and reduce complexity as well as size and weight.

9.2 Modifications

9.2.1 Fluid Handling Unit

Modifications to the fluid handling unit were made as follows:

- The stainless steel tubing and fittings were changed to Teflon tubing and nylon fittings.
- The stainless steel pressure relief valve was removed from the system.
- The lower chamber cap (Figure 6-5, No. 30) was refabricated from KEL-F.
- The stainless steel pump head was replaced by a Teflon head.

It was observed that the pump did not develop a sufficiently high pressure to damage the sensor chamber components. Therefore, no substitution was made for the pressure relief valve since a suitable plastic valve was not readily available. A flow diagram of the modified system is shown in Figure 9-1.

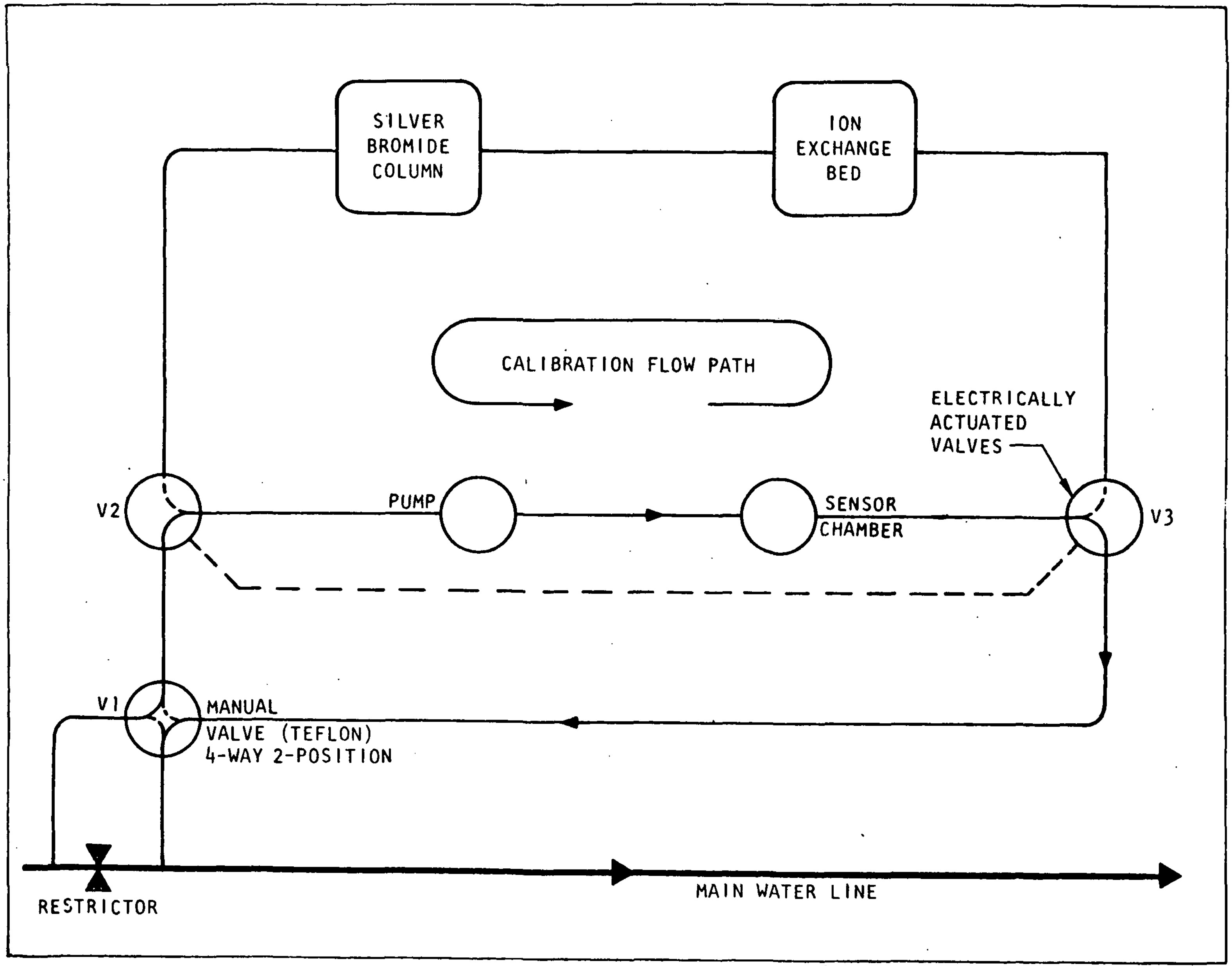


Figure 9-1. Flow Diagram--Modified Prototype Silver Ion Monitoring System

Checkout tests showed that the system, as assembled, was prone to pick up electrostatic interference from the external environment including body capacitance. Such interference was not observed with the all stainless steel system, because the stainless steel provided the shielding. The external interference was reduced to an insignificant level by encasing the plastic fluid lines in metallic shielding braid which was connected to the solution ground.

Figure 9-2 shows the modified fluid handling unit.

The two Teflon pump heads functioned properly for less than one week, at which time their output pressure and flow fell to less than 6.89×10^4 N/m^2 (10 psig) and 40 ml/min. (5.4 lb/hr) resulting in erratic, noisy, and non-reproducible electrode response with continual drift. The cause of failure of the Teflon pump heads was probably due to cold flow or wear. The original stainless steel pump head was reinstalled in the system.

The modification of the fluid system by substituting Teflon and nylon for stainless steel has significantly changed the surface areas of materials exposed to the water sample.

Table 9-1 gives the various surface areas exposed to the water sample.

9.2.2 Sensing Electrode Modifications

During earlier phases of the current effort, difficulty was experienced with the PR-type sensing electrodes in that irreversible deterioration occurred following recirculation of silver solutions. A particular problem arose since the electrode pellets were cemented into an electrode housing which was also the top of the sensor chamber (see Figures 6-4, 6-5, and 6-6). As a result, failure of an electrode dictated discarding this relatively expensive part. While the deterioration problem has never been resolved, it was noted that a few electrodes of an earlier configuration were still useable (see Figure A-1). Thus the prototype sensing electrode housing was modified to permit the use of these electrodes (see Figure 9-3), and the designation changed to Sensor Chamber Cap.

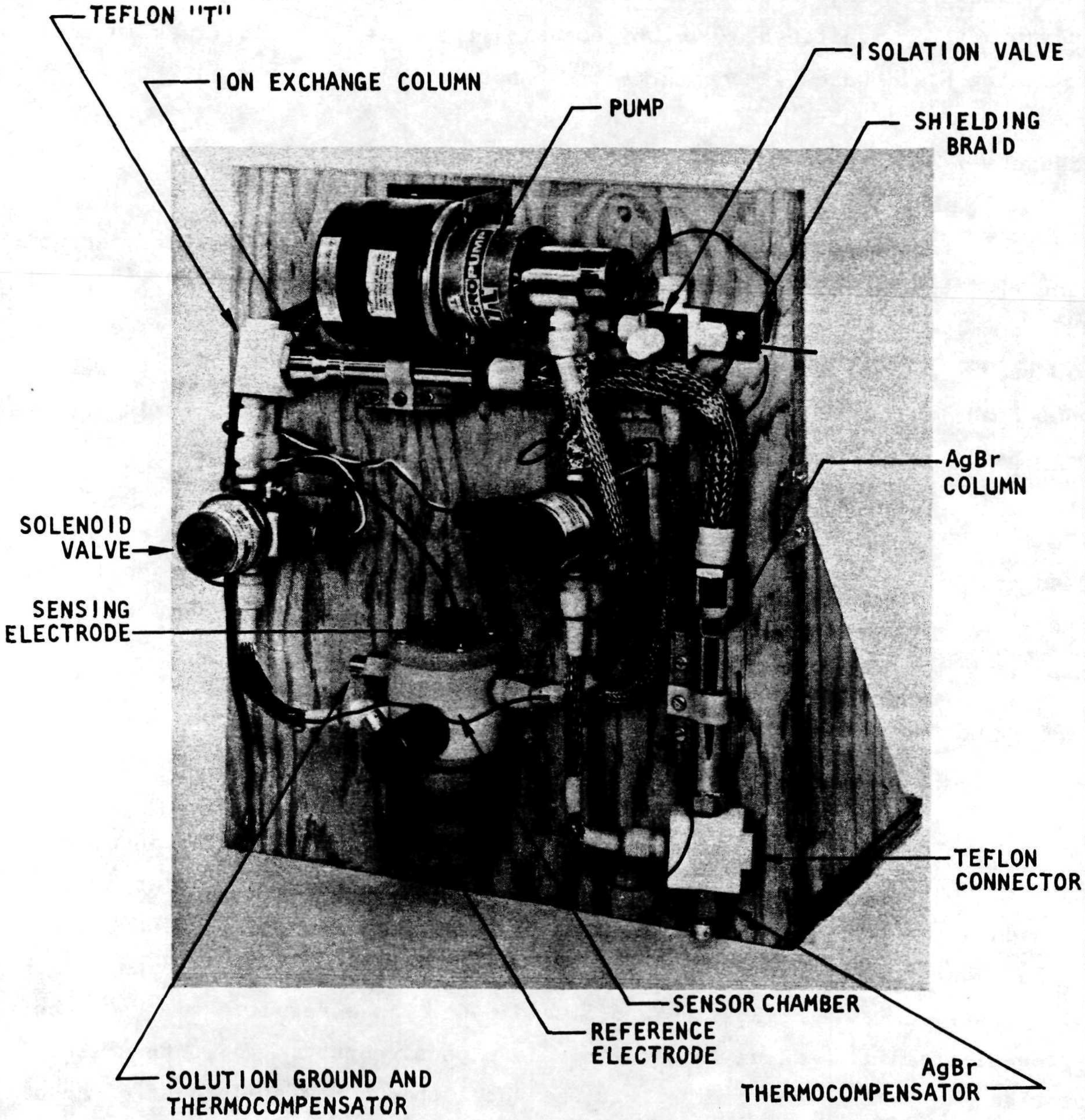


Figure 9-2. Modified Fluid Handling Unit--Silver Ion Monitor

Table 9-1. Surface Areas of Materials Exposed to Water Sample for Modified System

Component	Material	Exposed Surface	
		cm^2	in.^{2}
System Isolation Valve	Teflon		
Recirculating		3.27	0.5
Normal Use		6.54	1.0
Solenoid Valves (2)	Anodized Aluminum	3.9 ea	0.6 ea
Tubing, 1/4" OD	Teflon		
Monitoring Loop		157.0	24.0
Calibration Loop		107.9	16.5
Common to Both Loops		53.6	8.2
Tubing Fittings	Nylon		
Monitoring Loops		62.8	9.6
Calibration Loop		82.4	12.6
Common to Both Loops		49.0	7.5
Pump	Teflon	52.3	8.0
	316 Stainless Steel	30.0	4.6
Electrode Cell	Rubber	21.6	3.3
	316 Stainless Steel	4.9	0.76
	KEL-F	260.0	40.3
	Epoxy	1.96	0.3
	Polypropylene	5.9	0.9
Columns			
Ion Exchange	316 Stainless Steel	78.5	12.0
Silver Bromide	316 Stainless Steel	78.5	12.0
TOTALS	316 Stainless Steel	187.0	28.9
	Rubber	21.6	3.3
	KEL-F	260.0	40.3
	Epoxy	19.6	3.0
	Anodized Aluminum	7.8	1.2
	Teflon	323.7	50.2
	Nylon	145.2	22.5

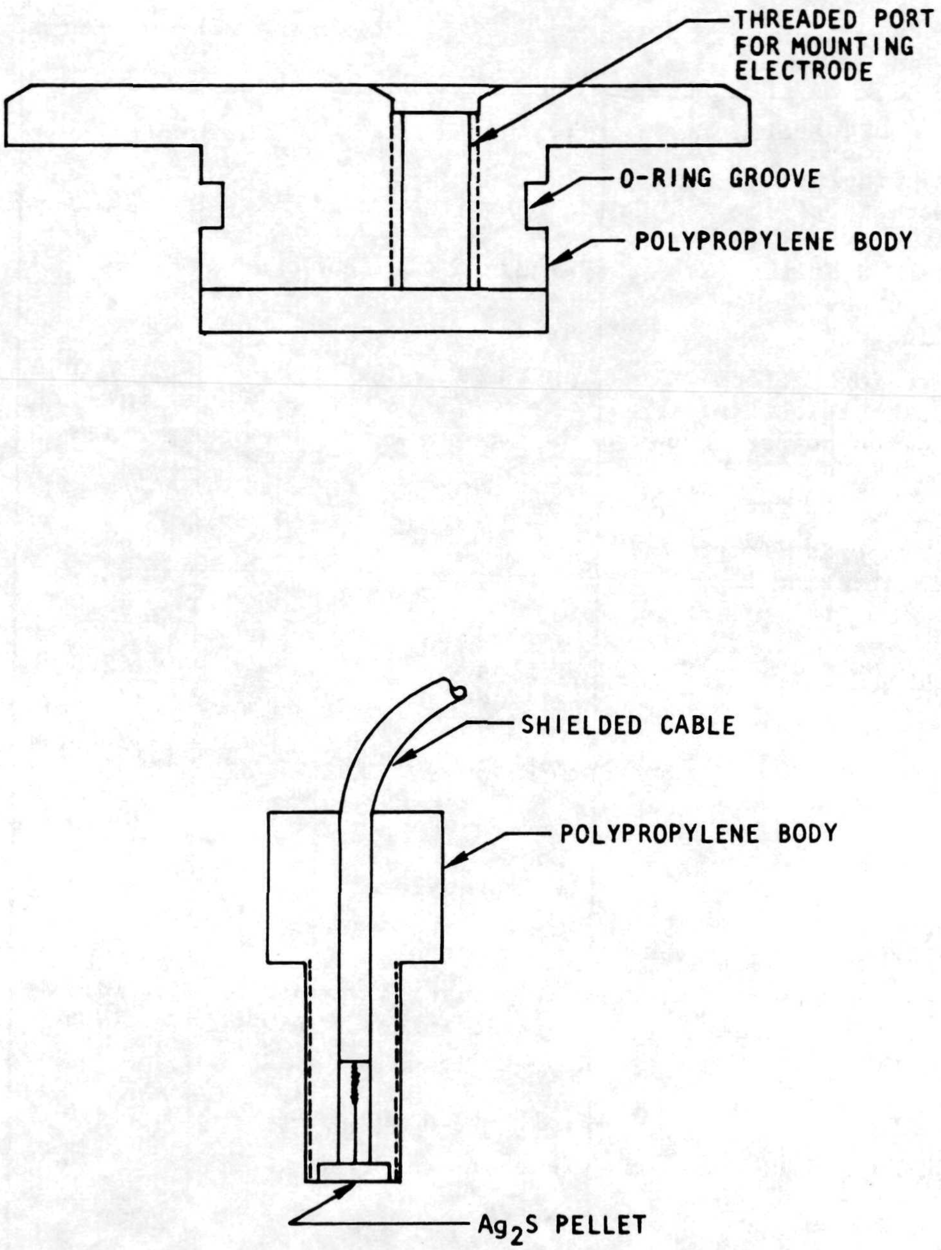


Figure 9-3. Sensor Chamber Cap--Cross Section (Modified Sensing Electrode Housing)

The modified housing does not contain a preamplifier, cap, or electrical connector. These are mounted in the electronics assembly and connected to the electrode via a shielded cable. Therefore, one preamplifier can be matched with the input circuits and used with many sensing electrodes.

A new electrode configuration suitable for use with the new chamber cap was designed. This configuration employs the same silver sulfide pellet diameter, 0.546 cm (0.215 in.) as was used in the sensing electrode for the flow cell setup of the initial development program, NAS9-12733. The integral PR-type sensing electrodes used a silver sulfide pellet of 0.86 cm (0.34 in.) diameter. Since the function of the silver sulfide pellet is not area dependent, the change in size of the pellet of the sensing electrode did not compromise any functional characteristic. The size change was required for the new electrode configuration.

The new configuration is threaded to permit it to be readily mounted in the Sensor Chamber Cap. In addition, the new configuration permits unrestricted access to the exposed surface of the silver sulfide pellet for cleaning and polishing. Testing and calibration of the electrode in a beaker is facilitated by its smaller size. The new electrode configuration is shown in Figure 9-4. Twelve of these electrodes have been fabricated and tested. The electrode data are reported in Section 10.3.4.

9.2.3 Sensor Chamber

As a result of the modification of the sensing electrode and substitution of plastic parts for stainless steel parts, the sensor chamber was modified.

The modified sensor chamber component parts are shown in Figure 9-5, and listed in Table 9-2.

9.2.4 Electronics

Previous testing indicated that there were several deficiencies in the silver ion monitor electronic design. It was determined that substantial reduction in complexity could be achieved by overall design.

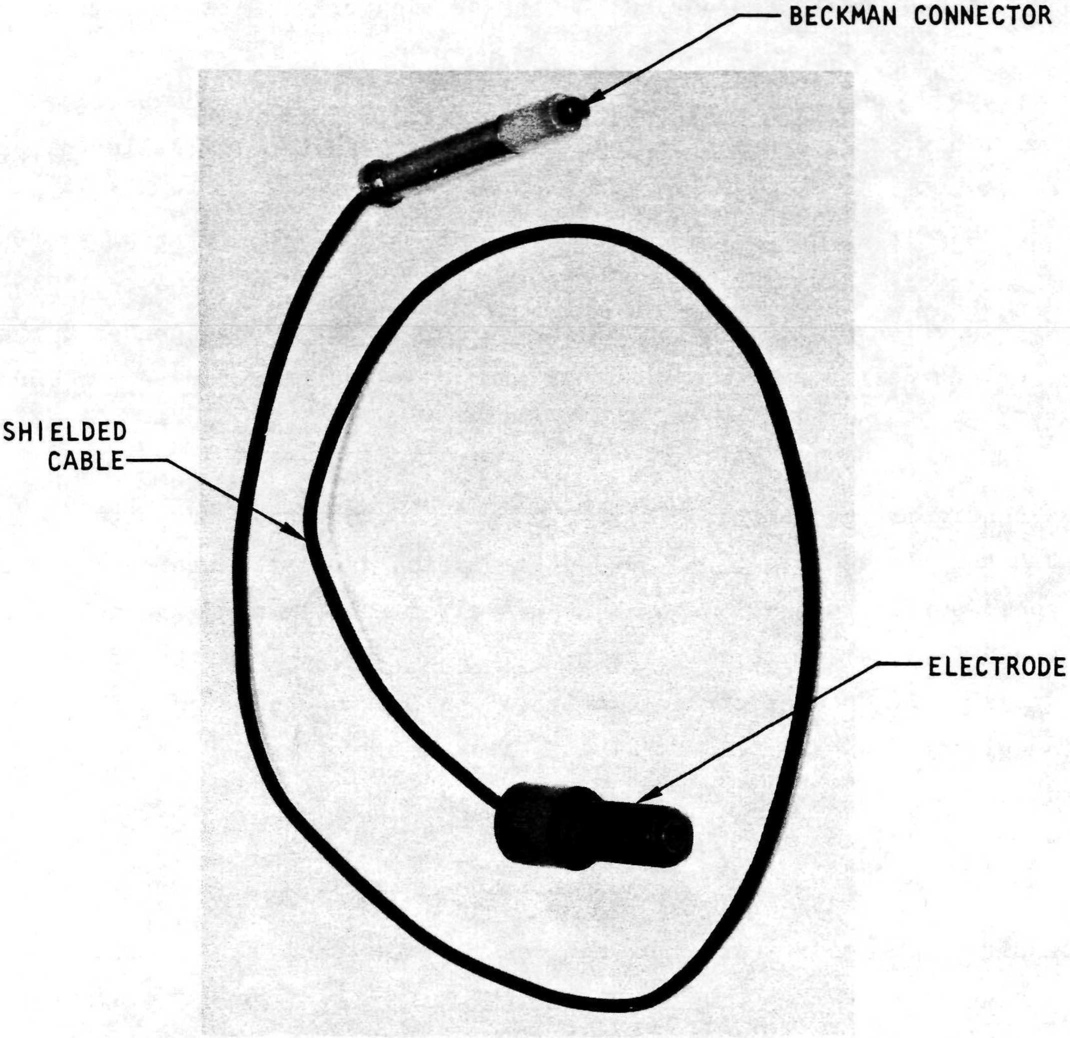


Figure 9-4. New PR Sensing Electrode Configuration

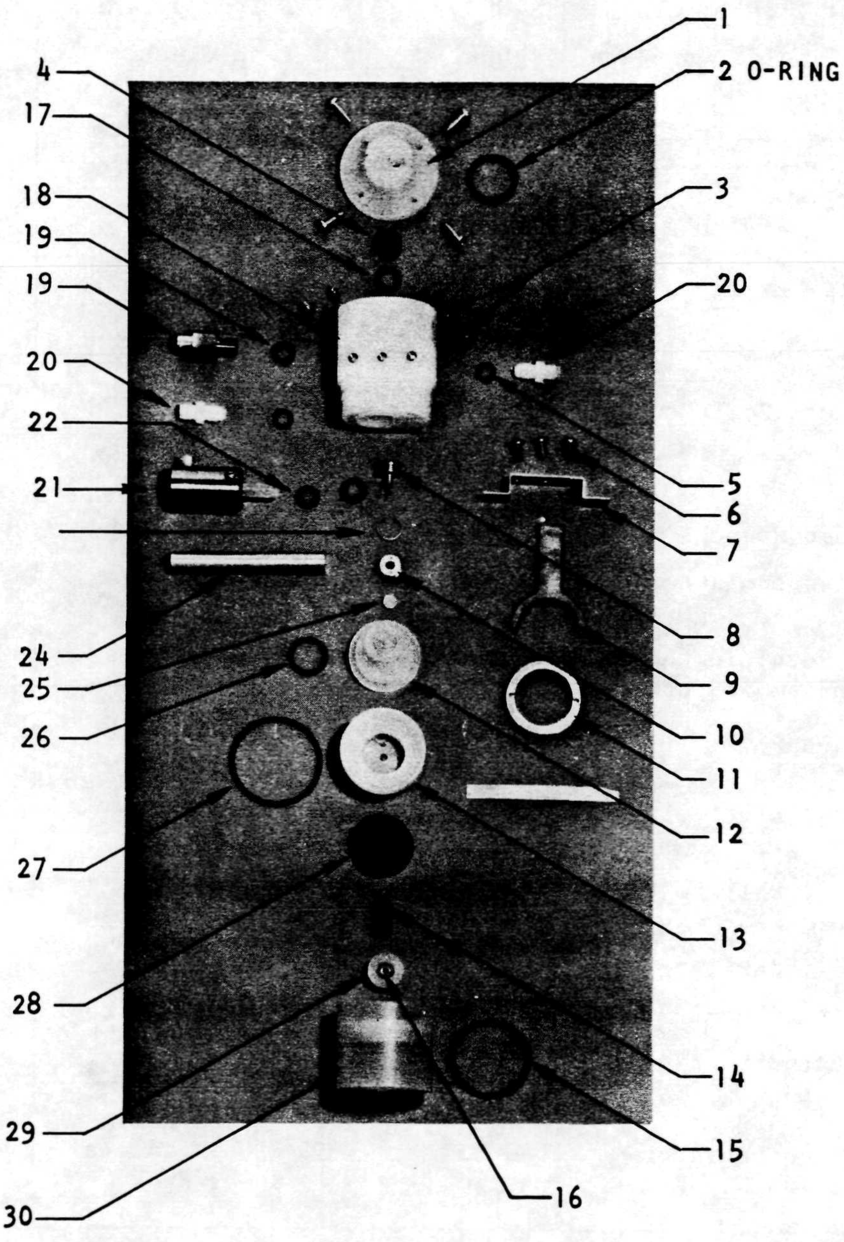


Figure 9-5. Modified Sensor Chamber Component Parts

Table 9-2 (Sheet 1 of 2). Component Parts--Modified Sensor Chamber (Figure 9-5)

No.		Drawing	Material	Weight	
				Grams	Oz
1	Sensor Chamber Cap*	Ag0070	Polypropylene	35.0	1.2
2	Quartz Fiber Junction	Ag0041	Lead Glass Quartz Fiber	0.5	0.02
3	Speedserts, Tridair Industries	SPB-10328 (4)	Stainless Steel	2.8	0.1
4	Quartz Fiber Junction Mount	Ag0030	Polypropylene	1.3	0.05
5	O-Ring, Parker	3-904	N674-7 Nitrile	0.1 ea	
6	Mounting Screws Pan Head	10-32X.37 (3)	Steel	7.8	0.28
7	Bracket, Cell Mount	AG0056		12.5	0.44
8	Needle Assembly	AG0022	316 Stainless Steel	9.3	0.33
9	Spanner Wrench	AG0032	Stainless Steel	-	-
10	Nut, Septum Retaining	AG0021	316 Stainless Steel	6.1	0.22
11	Nut, Retaining Upper Diaphragm Support	AG0024	316 Stainless Steel	33.9	1.2
12	Top, Electrolyte Reservoir	AG0025	KEL-F	47.4	1.67
13	Bottom, Electrolyte Reservoir	AG0026	KEL-F	49.9	1.76
14	Spring, Rolling Diaphragm	AG0048	302 CRES Cond 13	2.0	0.07
15	O-Ring, Parker	2-111	N674-7 Nitrile	1.2	0.04
16	Speedsert	SPB-1032-S	Stainless Steel	1.0	0.04
17	O-Ring, Parker	2-111	N674-7 Nitrile	0.9	0.04
18	Chamber Body	AG0027	KEL-F	378.0	13.33
19	Thermocompensator Assembly	AG0037	316 Stainless Steel Epoxy	20.2	0.71

*Modified Components

Table 9-2 (Sheet 2 of 2). Component Parts--Modified Sensor Chamber (Figure 9-5)

No.	Part	Drawing	Material	Weight Grams	Oz
19A	O-Ring, Parker	3-904	N674-7 Nitrile	0.1	-
20	Union--Swagelok to AN*	NY400-6-4AN (2)	Nylon	4.5	0.16
21	Reference Electrode Assembly (Primary)		Mixed	43.0	1.52
22	O-Ring, Parker	2-111	N674-7 Nitrile	0.8	0.04
23	Retainer Ring	N-5000-62-H	316 Stainless Steel	0.5	0.02
24	Wrench, Septum Retainer Nut	AG0033	Stainless Steel	-	-
25	Septum, Hamilton		Silicone Rubber		
26	O-Ring, Parker	2-117	N674-7 Nitrile	0.45	0.02
27	O-Ring, Parker	2-134	N674-7 Nitrile	1.0	0.04
28	Diaphragm, Rolling (Bellophram)	3-112-94-CBJ	BUNA-N	2.6	0.09
29	Piston, Diaphragm	AG0020	KEL-F	4.7	0.17
30	Cap, Chamber, Lower*	AG0029	KEL-F	25.9	0.9
			TOTAL:	694.6	(1.53 lb)

*Modified Components

Figure 9-6 is a schematic of the redesigned silver ion monitor electronics. The following features are incorporated to improve performance and reduce complexity.

9.2.4.1 Common Mode Range Increased

Tests using the original silver ion electronics indicated that large common mode potentials (~200 mV) were occurring between the solution ground and the sensing and reference electrodes. This resulted in substantial drift as the common mode rejection of the original electronics was very low. Also, the high gain of the original preamplifiers resulted in saturation of the preamplifiers at high common mode conditions.

A fully differential amplifier consisting of Z1 and the associated resistors was added in the redesigned electronics package. The preamplifier gain was also reduced to 4X from 40X. This change has resulted in greatly reduced electronic drift.

9.2.4.1.1 Common Mode Rejection Ratio

Differential amplifiers with a single output, such as used in pH meters and also in the silver ion monitor, have two inputs which share a common ground. Ideally, no signal that is common to both inputs should appear in the output. That is, if the same signal were applied to both inputs, there should be no output signal. The ability of an amplifier to achieve this is called its "common-mode-rejection-ratio." This is defined as:

$$\text{CMRR} = \frac{\text{Gain of Amplifier to Difference Signal}}{\text{Gain of Amplifier to Common Signal}}$$

In the silver ion monitor the two inputs are the reference electrode input and the sensing electrode input which share the solution ground connection at a common ground.

9.2.4.2 Calibration Accuracy

The original digital-to-analog converter circuit (DAC) which was implemented with a discrete resistor adder network was found to lack monotonicity. This

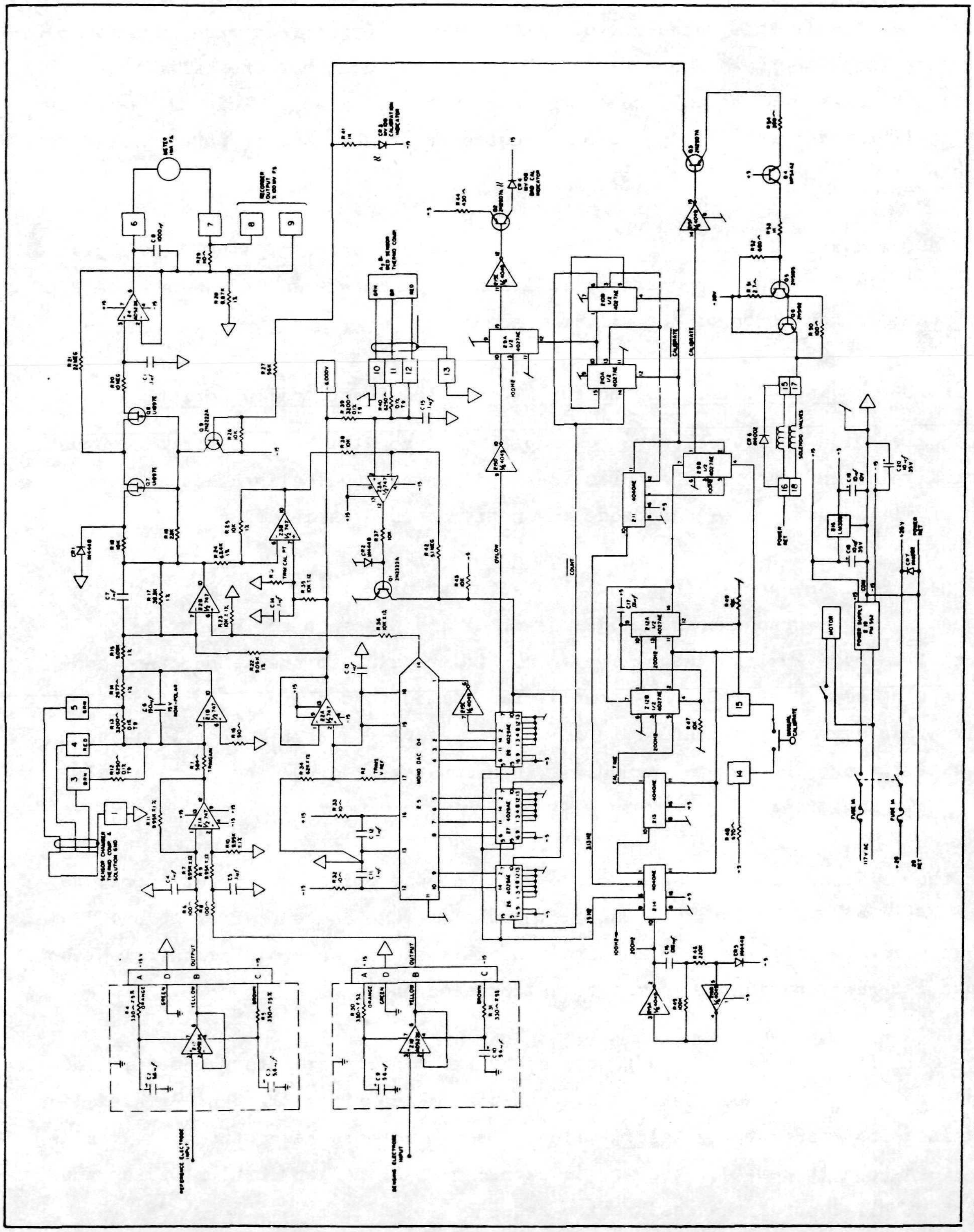


Figure 9-6. Redesigned Silver Ion Monitor Electronics--Schematics

resulted in the system occasionally "over-running" a calibration point. A fully monotonic 10-bit integrated circuit DAC was used in the redesigned monitor electronics (Z5). Up/down counters (Z6, Z7, Z8) were used for the calibration register instead of up only counters used in the original. This scheme allows the calibration bias voltage to be adjusted up or down and is particularly insensitive to electrode noise.

The ADC and associated logic used to sense the calibration point were replaced by a single hysteresis comparator (Z3A and Q1). This greatly reduced the size and power consumption of the silver ion monitor.

9.2.4.3 Revised Silver Ion Monitor Electronics Functional Description

The silver ion monitor electronics amplify and condition the electrode output for display on meter or chart recorder and control the calibration sequence and interval, adjusting for electrode asymmetry at each calibration.

Signals from the preamplifier modules enter at pins 1 and 2. Amplifier Z1A rejects the electrode common mode potential and presents the electrode differential voltage, multiplied by the preamplifier gain, to the temperature compensation amplifier Z1B. Resistor R1 is trimmed to set overall system gain. Electrode asymmetry potential is adjusted by amplifier Z2B. The signal then passes through the sample and hold switch consisting of Q7 and Q8 to sample and hold amplifier Z4.

In the calibrate mode, Q7 and Q8 are off and Z4 provides an output signal to the meter and chart recorder indicating the voltage concentration of the fluid just prior to calibration. The droop of this sample and hold circuit is less than 1 percent during an 11-minute calibration period.

The calibration time base is generated by the clock oscillator consisting of inverters Z15Z, b, and counters Z14 and Z13. Flip-flops Z12a and b initialize calibration whenever the Caltime line (Z13 pin 1) goes high, the manual calibrate button is pushed, or power is turned on. Flip-flops Z9b, Z10a, a, and counter Z11 control the calibration sequence.

The calibrate line (Z9b pin 1) defines the calibration period of approximately 11 minutes. When calibrate goes high, Z15a turns on Q3, Q4, Q5, and Q6, activating solenoid valves connected at pins 15, 16, 17, and 18. These valves direct flow through the AgBr column providing known [Ag^+] concentration for calibration.

Simultaneously, the sample and hold switch driver Q9 is turned on, turning Q7 and Q8 off, thus locking the output at the precalibration value. The calibration indicator LED is also turned on.

After 2 to 3 minutes of the calibration sequence have passed, flip-flop Z10b is clocked by counter Z11 giving an output, pulse (Z10b pin 1). This output resets the bad cal flip-flop (Z9a). After five minutes of the calibration sequence have passed, counter Z11 clocks flip-flop Z10a forcing signal count low.

When the count is low, the calibration register, consisting of counters Z6, 7, and 8, is enabled and counts up or down under control of the hysteresis comparator, consisting of Z3A and Q1. The output of the calibration register controls DAC Z5, adjusting electrode asymmetry through amplifier Z2B. Amplifier Z3B offsets the output signal of Z2B so that it may be compared with the AgBr reference column temperature by the hysteresis comparator consisting of Z3A and Q1.

A bad calibration is signaled by a calibration register overflow or underflow condition that occurs when the adjustment range is exceeded (Z8 pin 2 goes low). Should a bad calibration occur, flip-flop Z9 is set and Z15e and Q2 turn on the bad cal indicator.

At the end of the calibration period flip-flop Z9b is set by an output from counter Z11 (Z11 pin 1), thus terminating the calibration period and doing the following: turn off Q3, Q4, Q5, Q6; release solenoid valves; turn off Q9; turn on Q7, Q8; turn off calibrate indicator; reset flip-flops Z10a, b.

The original four component boards and supporting bracket, which occupied a volume of 10 x 11 x 35.5 cm (3.9 x 4.3 x 13.9 in.) were replaced by one electronic package, measuring 3.8 x 12.7 x 26.7 cm (1.5 x 5.0 x 10.5 in.). The weight of the electronics plus the preliminary case was reduced from 3624 grams (218 oz or 8 lb) to 3288 grams (116 oz or 7.25 lb).

This weight includes all the connecting cables and connectors, readout meter and switches.

Figure 9-7 shows the redesigned silver ion monitor electronics.

9.2.5 Size and Weight of Modified System

The weight of the system was reduced by material substitutions, electronics redesign, and elimination of the pressure relief valve and fittings. Concurrently, weight was added by the necessary use of metal shielding braid. The weight of the modified system and of individual components is given in Table 9-3.

The actual size of the electronics was reduced as described in Section 9.2.3; however, no reduction in the outside package of the system was attempted since weight and size reduction were not included in the modification goals.

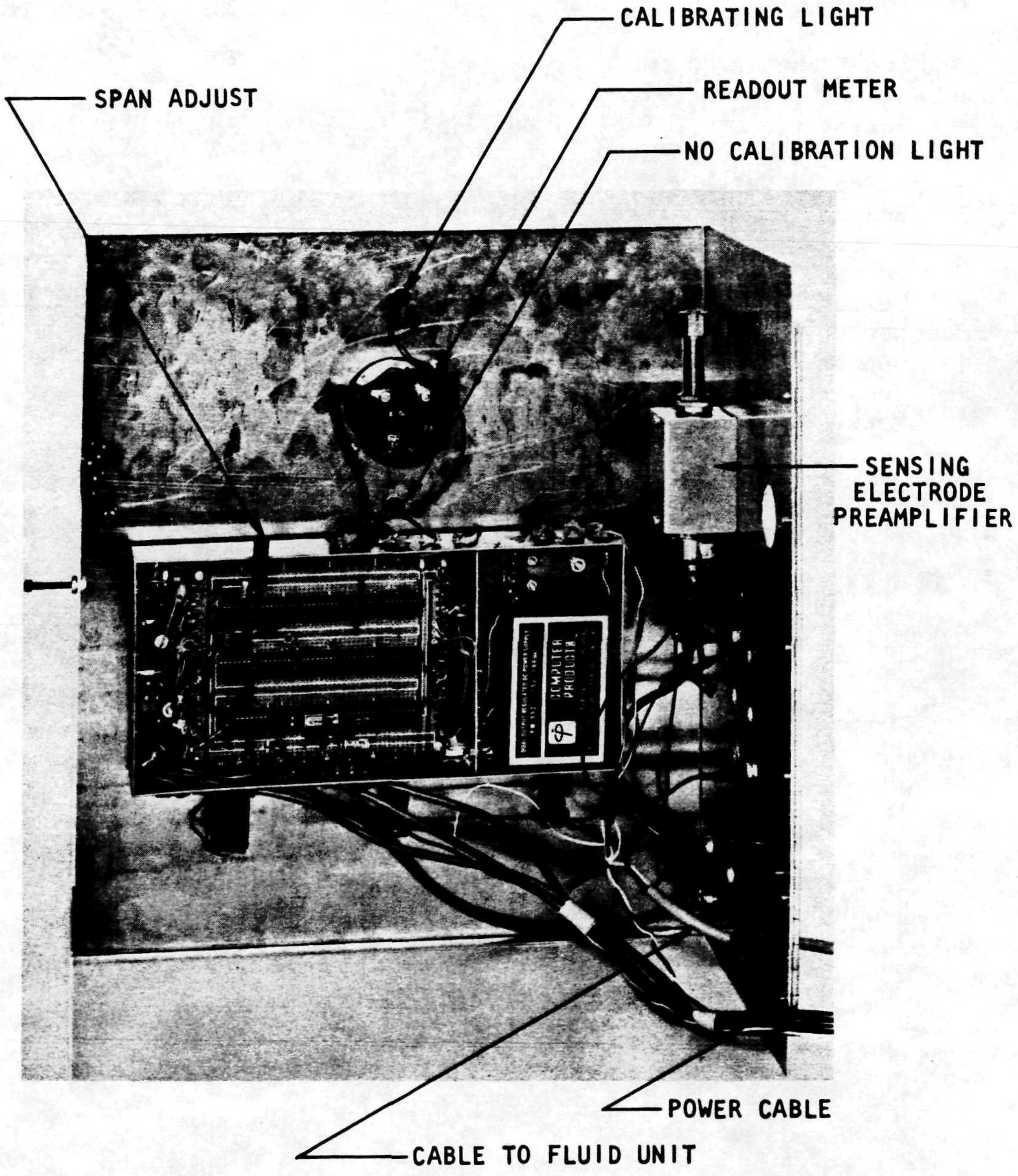


Figure 9-7. Redesigned Silver Ion Monitor Electronics--Packaging

Table 9-3. Modified System Weight and Weight of Individual Components

Component	Weight Grams	Oz
Fluid Handling Unit		
Ion-Exchange Column	165	5.82
Silver Bromide Column	182	6.42
Calibration Loop Tubing and Fittings	115	4.1
Pump-Motor Combination with Bracket	1472	51.9
Solenoid Valve + Nylon Fittings (2)	836	29.5
Sensing Electrode with Cable and Connector	23.8	0.8
Primary Reference	43	1.52
Teflon Isolation Valve, V1 + Bracket	114	4.0
Measuring Loop Tubing and Fittings	43	1.52
Sensor Chamber	694.6	24.5
Support (estimated)	375	13.23
Metal Shielding Braid	127	4.5
Redesigned Electronics Unit		
Electronics + Preliminary Case (35.56 x 40.6 x 22.2 cm)	3288.0	116.0
TOTAL SYSTEM WEIGHT REVISED:	7.478 kg	
	16.5 lb	

10.0 DESIGN VERIFICATION TESTING

10.1 Purpose

It was originally intended that after the preliminary testing of individual components and subsystems, the preliminary flight prototype silver ion monitor would be assembled, functionally tested, and adjusted for optimum response. The totally integrated system would then be subjected to testing to verify its capability to operate under anticipated use conditions. These tests were to consider flow, pressure, temperature effects, silver ion concentration, and zero gravity compatibility. Calibration requirements were to be established as part of the verification testing.

The verification testing phase of the program was originally divided into six subtasks:

a. Design test fixture modification
b. Modify test fixture
c. Perform environmental testing
d. Establish zero gravity compatibility
e. Establish calibration requirements
f. Perform life testing

Subtasks a. and b. were performed in parallel with the final fabrication of the fluid handling unit. The problem of the loss of silver ion from solution during recirculation was identified soon after assembly of the fluid handling unit and subsequent radioisotope tests revealed that the silver was depositing on the stainless steel surfaces. Modification of the fluid handling unit by substituting Teflon and nylon for stainless steel was implemented to reduce the loss of silver ion from the solution recirculating in the system.

The modifications to the system required that additional subtasks be included in the testing phase of the program and that they be performed prior to subtasks c. through f. These subtasks were as follows:

- Determine effectiveness of Teflon substitution.
- Determine response and degradation characteristics of new sensing electrodes.
- Integrate fluid unit with redesigned electronics.
- Determine system operating characteristics with automatic calibration.

The effort expended toward the above subtasks precluded the remainder of the verification tests subtasks c. through f. However, portions of subtasks e. and f. were performed as part of the four additional subtasks.

During the performance of the various tests necessary under the current effort, the test fixture was modified several times and/or parts used in temporary test setups.

10.2 Test Fixture Design Modification

The test fixture fabricated and used under the Residual Water Bactericide Monitor Development Program, Contract NAS9-12733, was modified to facilitate the various tests of the prototype flight monitor subsystems. As originally modified, it was intended to be used to simulate a main water line of the Space Shuttle's potable water system and was to provide variations in pressure, flow, silver ion concentration, temperature, as well as a stable source of silver ion concentration for the life testing. Consequently, a number of modifications to the original design were required. The modifications were as follows:

- Replacement of the Micro Pump #12-41-316-759
- The flow cell was replaced by two "Ts" and a flow restrictor across which the flight prototype monitor will be connected
- The cover of the fluid reservoir, which was previously clamped on, was welded on to permit pressurizing the system to 4.8×10^5 N/m^2 (70 psig) with nitrogen gas

- The thermocouple was relocated to a "T" just upstream of the connection to the flight prototype monitor.
- A needle valve and bypass was added in parallel with the silver bromide canister to permit variation of silver ion concentration at a constant temperature.

Figure 10-1 shows a block diagram of the modified environmental test fixture and connection to the preliminary flight prototype monitor.

10.3 Testing

10.3.1 General

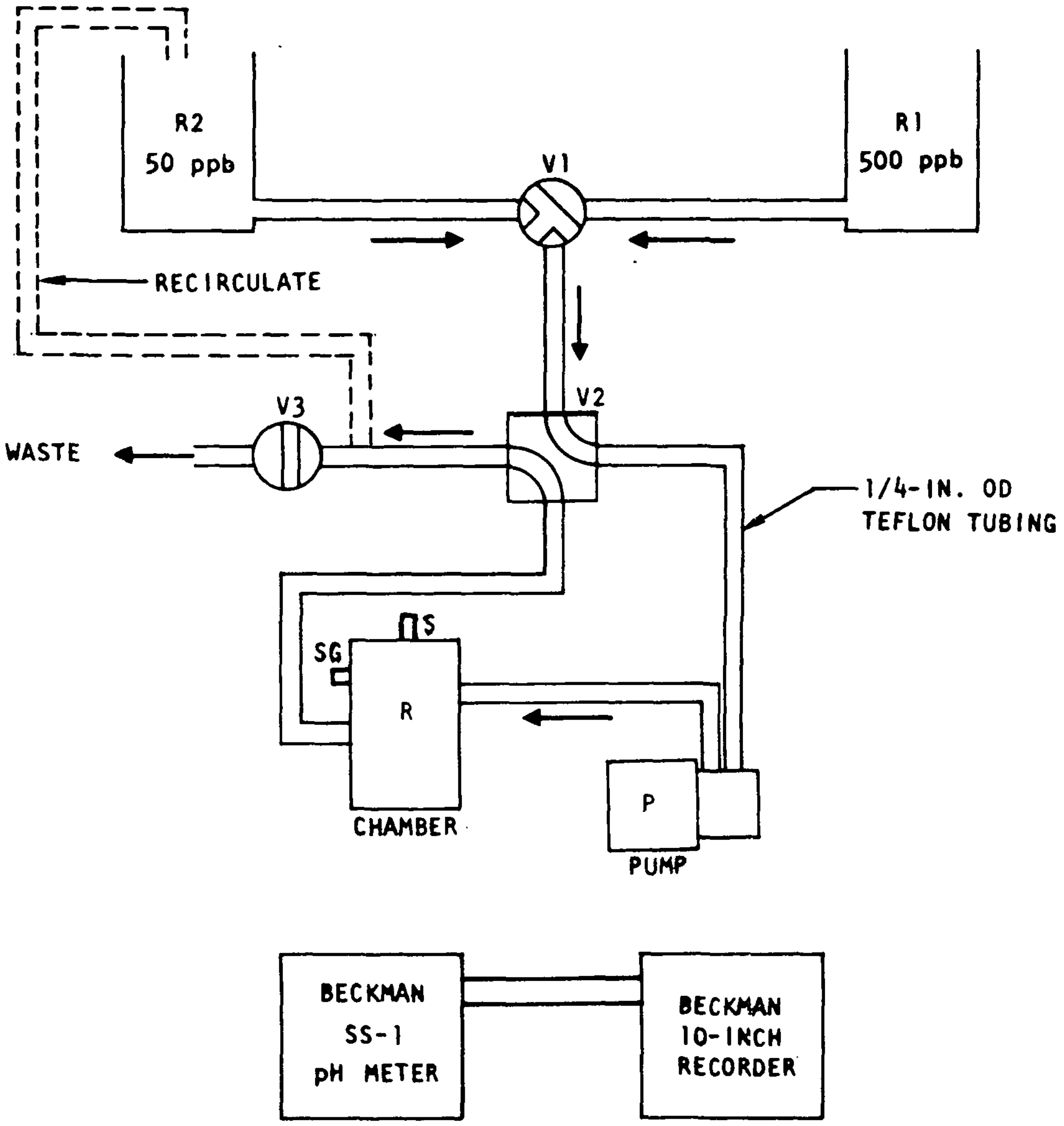
Following completion of mechanical modifications, the system was assembled for testing without the solenoid valves and calibrating loop (see Figure 10-2). The test design was to progress in a stepwise fashion to demonstrate that the reduction in stainless steel areas had lowered the rate of silver ion depletion. Testing began with a simple flow-through system and progressed to the complete recirculating system. A Beckman Century SS pH Meter was employed.

10.3.2 Flow-Through Testing

Flow-through testing of silver solutions at the 50- and 500-ppb level was conducted. These solutions were pumped through the sensing cell to waste while sensor output was constantly being monitored. Tests were conducted with a 50-ppb solution for up to two hours with satisfactory performance, i.e., less than 1.4 mV drift and no silver depletion observed. No electrode deterioration occurred.

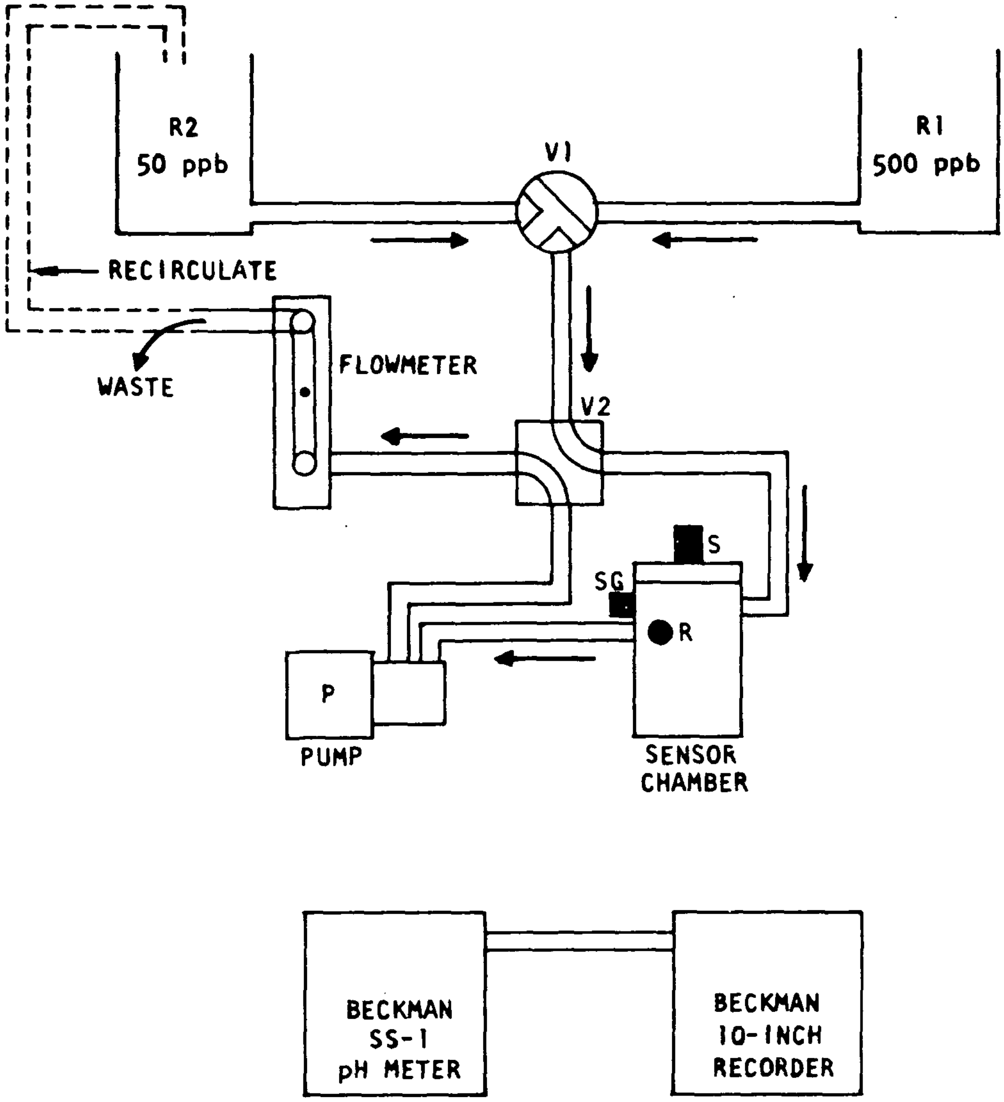
10.3.3 Recirculation Testing

Following the successful completion of the flow-through tests, 50-ppb silver solutions were recirculated, utilizing a reservoir volume of 1000 ml. During an overnight run of eighteen hours, a gradual decline in silver level occurred, followed by a gradual increase to an apparent level of approximately 60 ppb (based on recalibration). Independent beaker tests following the completion of the overnight run showed a silver level of 22 ppb--a significant improvement over the stainless steel system (see Figure 10-3). The apparent increase in



R1,R2 - 1-Liter Reservoirs, Glass
V1 - Selection Valve, Glass
V2 - Isolation Valve, Teflon
S - Sensing Electrode
SG - Solution Ground
R - Reference Electrode

Figure 10-1. Test System as of 6 March 1974



IDENTIFICATION OF COMPONENT PARTS FOR TEST SYSTEM

R1, R2 - 1-Liter Reservoirs, Glass
V1 - Selection Valve, Glass
V2 - Isolation Valve, Teflon
S - Sensing Electrode
SG - Solution Ground
R - Reference Electrode
FM - Flowmeter with Needle Valve Regulator

Figure 10-2. Test System as of 15 March 1974

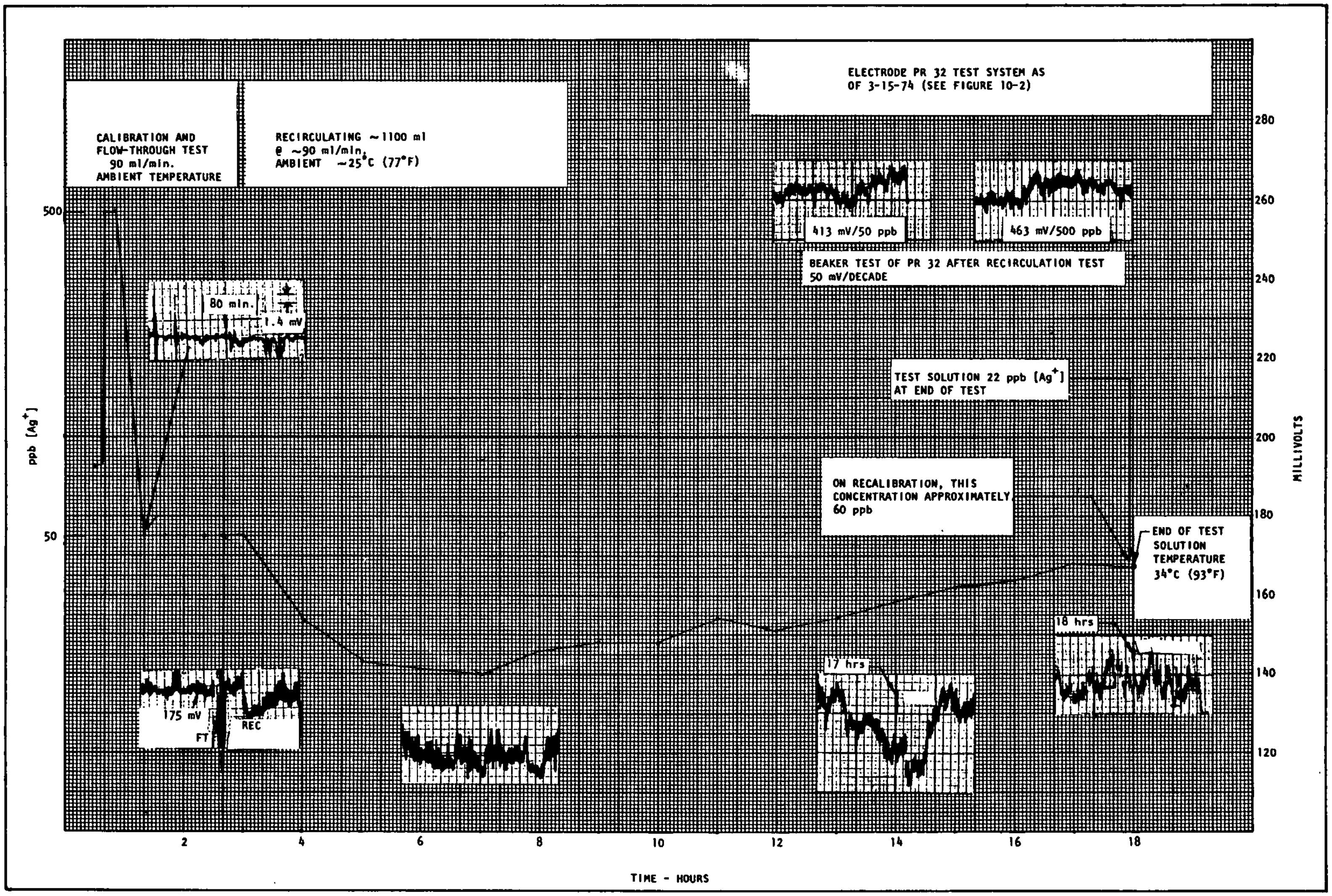


Figure 10-3. Flow-Through and Recirculation Test Data

silver level in the recirculating system has been attributed to a temperature increase of the circulating solution to 34°C (93°F) contributed by the pump. This was the first time the silver level remained high enough to warrant that length of test, and thus the first time that the heat rise was observed. Although the monitoring system electronics has temperature compensation capability, such was not the case with the pH meter setup.

To eliminate this heat buildup, the recirculating fluid was passed through a coil which was immersed in a constant temperature bath at 25°C (77°F). The coil was initially fabricated of glass tubing to provide reasonably efficient heat transfer, but either the coil was continually breaking or connections were leaking, thereby effectively ruining the experiment due to loss of fluid. Eventually, the coil was constructed of Teflon which appeared to afford adequate heat transfer; however, insertion of this Teflon cooling loop caused an increase in system noise.

The flow of the low conductivity fluid through the 15 feet of Teflon tubing apparently forms an electrostatic generator which was thought to be the source of the noise. Later it was found that by some undetermined mechanism the Teflon tubing loop was picking up noise from the electrical components of the constant temperature bath. Removal of the Teflon loop from the constant temperature bath reduced the noise significantly.

The overnight recirculation test was repeated three times. At the end of about 16 hours the silver ion concentration of the recirculating fluids showed 26, 18, and 16 ppb, down from a starting level of 50 ppb. The differences between the silver ion concentration at the end of the four tests was probably due to temperature differences (no thermostatic control of the recirculating fluid), flow rate changes, and ±2 ppb measurement errors.

A previous recirculation test with a stainless steel fluid system and a one-liter reservoir exhibited a loss of silver ion of from 50 ppb to less than 1 ppb in two hours (see paragraph 8.2).

The recirculation tests clearly demonstrate the effectiveness of the substitution of Teflon for stainless steel in the reduction of the loss rate of the silver ion.

During the recirculation tests with the stainless steel, during which silver ion was lost rapidly and the silver ion concentration dropped to below 2 ppb, the silver sulfide electrode in the system always degraded rapidly--sometimes irreversibly. The degradation was noted as a loss in sensitivity from the original Nernstian response of 59 mV/decade to below 54 mV/decade. Noise and drift usually accompanied the loss in sensitivity.

During the recirculation tests with the Teflon system in which the silver ion level never fell below 16 ppb, some of the silver sulfide electrodes were observed to be very stable while others slowly became unstable with or without a loss of sensitivity. Rapid degradation during recirculation was not observed.

10.3.4 Electrode Response and Degradation

10.3.4.1 Sensing Electrode

Twelve of the new configuration electrodes (see Figure 9-4) were fabricated in two batches of six each. Five of the electrodes of the first batch, which originally exhibited satisfactory responses, degraded following combined exposure to the recirculating silver solutions in the Teflon fluid system and solutions in beaker tests. Their history prior to failure was reviewed in an attempt to discover a failure mode.

All electrodes were conditioned in a 10 ppm silver ion solution and treated the same except for exposure time. None was exposed to silver ion solutions lower than 16 ppb, and all were stored dry when not being tested

Table 10-1 shows the responses of the five electrodes before and after degradation. The history and data on these electrodes contained nothing that would indicate a definite failure mode.

Table 10-1. Electrode Response Before and After Degradation (First Batch)

	INITIAL RESPONSE[1]		FINAL RESPONSE			Exposure Time[3] To Degradation
Electrode No.	Span mV/Decade	Noise[2] mV	Span mV/Decade	Noise[2] mV	Drift	(Hrs)
PR 32	63	±1.4	118	±2.5	Continuous	17
PR 33	57	±1.4	44	±4	"	28
PR 34	60	±0.7	69	±3.5	"	2.2
PR 35	59	±0.5	69	±5	"	38
PR 36	58	±2	40	±5	"	18

[1] After conditioning.

[2] 1-mV noise approximately equivalent to 2 ppb $[Ag^+]$ at 50 ppb level.

[3] Exposure time includes both beaker and system tests.

Although only conjecture, the possibility exists that the silver sulfide pellets were formed with inadequate pressure due to a faulty hydraulic press. The hydraulic press used to form the pellets was later found to be functioning improperly when a second batch of electrodes was attempted.

It was thought that one possible mode of electrode failure was the diffusion of the silver ion solutions through the epoxy seal between the pellet and electrode body. One technique of attaining a good seal that is used commercially is to wax impregnate the lower portion of the electrode.

An attempt was made to utilize wax impregnation as a means of sealing the electrode to effect electrode stabilization. The electrode so treated degraded in the same manner as the other electrodes.

One electrode of an earlier configuration (see Figure A-1), RSB-2, fabricated in July, 1973, was found to have exceptional stability. This electrode had always been stored dry when not in use. However, to determine the stability of this electrode with a continuous exposure to silver ion solutions, it was stored in a stirred 50 ppb silver ion solution when not in use. The electrode remained stable for 80 days then developed a slight drift, but the noise remained less than ±0.7 mV.

It was observed that the electrodes developed a "memory response" after exposure to the same silver ion concentration for greater than 6 hours. "Memory response" is a typical membrane electrode response occurring after a prolonged exposure to a single ion concentration. The acceptable current mechanism for such a response is that the membrane (the silver sulfide pellet in the sensing electrode) becomes saturated with a given ion concentration. After saturation the electrode is slow to respond to other ion concentrations because the membrane must be desaturated and a new equilibrium established between the membrane and the fluid to which it is exposed. Desaturation of the membrane (the silver sulfide pellet) is most efficiently accomplished by recycling between a high and low ion concentration until repeatability without drift at both levels is attained. Electrode RSB-2 has been responding readily to the desaturation procedure.

A second batch of the new configuration electrodes was fabricated using a hydraulic press of tested performance. The electrodes were conditioned in 10 ppm of silver ion at 40°C (104°F) for 72 hours. Three of the electrodes were found to have acceptable response characteristics. One electrode, PR 46, was observed to have very good stability and was used in the monitoring system prior to and after integration of the fluid unit with the electronics. This electrode was exposed intermittently to silver ion fluids in beaker tests and in the monitoring system for 334 hours before degradation was observed. During this period the electrode exhibited "memory response" but responded to the desaturation procedure readily.

Degradation of PR 46 was observed after prolonged (greater than 4 hours) exposure to the effluent of the calibration loop (ion exchange resin column and silver bromide column). Initially, following the first exposure to the calibration loop, the electrode showed a loss of sensitivity of 6 mV per decade with increase of noise and drift. Cleaning the surface of the silver sulfide pellet with 600 grit carbide paper and buffing on a soft cloth rejuvenated the electrode (59 mV decade with ±0.7 mV noise). Final degradation was observed as an increase in noise to ±3.5 mV and continuous drift. Rapid cycling between 50 and 500 ppb silver ion solutions showed that the response had not changed significantly (less than ±2 mV decade).

Following exposure to the effluent of the calibration loop, electrode RSB-2, which was used in the beaker test setup, also showed signs of degradation about the same as PR 46. This electrode, however, was successfully rejuvenated by buffing with a soft cloth and cycling between 50 and 500 ppb silver ion solution.

At the present time there is no evidence that the effluent from the calibration loop is a cause of electrode degradation other than the coincidence of both electrodes (PR 46 and RSB-2) showing signs of degradation at about the same time.

The second good electrode degraded, i.e., exhibited noise and continuous drift, during storage. Rejuvenation methods were not effective.

The third electrode was not used or tested after initial evaluation.

10.3.4.2 Reference Electrode and Electrolyte Reservoir

A study of the stability of the reference electrode was made by making periodic checks of a primary reference electrode, R4, which was in constant use in the sensor chamber for a period of 40 days. The electrode did not change its characteristics throughout the period nor did it become noisy.

The electrolyte reservoir was cleaned and refilled on April 9, 1974, with one molar potassium nitrate solution (1M KNO_3) to which was added one percent carboxymethylcellulose as a thickening agent. After 40 days the reservoir still contained sufficient electrolyte to provide correct operation of the reference electrode.

10.3.5 Integration of Electronics with Fluid Handling Unit

Just prior to integrating the electronics with the remainder of the monitoring system, the stability of the system was checked by a flow-through test for a period of 7 hours with calibration only at the start. Fifty and 150 ppb solutions were pumped through to waste and millivolt readings were taken by a pH meter at least 5 minutes after a stable response was indicated. The data are shown in Figure 10-4. At the 150 ppb level the average deviation was ±3.5 mV or ±8 ppb (5%) and at the 50 ppb level the average deviation was ±2 mV or 2 ppb (4%). The recorded output from the pH meter showed approximately ±0.7 mV noise with an occasional 14 mV spike. A slight up/down drift was also observed.

The output of the ion exchange/silver bromide columns was also checked prior to connecting into the integrated system. De-ionized water was flowed through the ion exchange and silver bromide columns at 80 ml/minute at 25°C and the silver ion concentration of the effluent determined in a beaker test setup. The concentration was 76 ppb silver ion, which is in good agreement with a theoretical of 78 ppb.

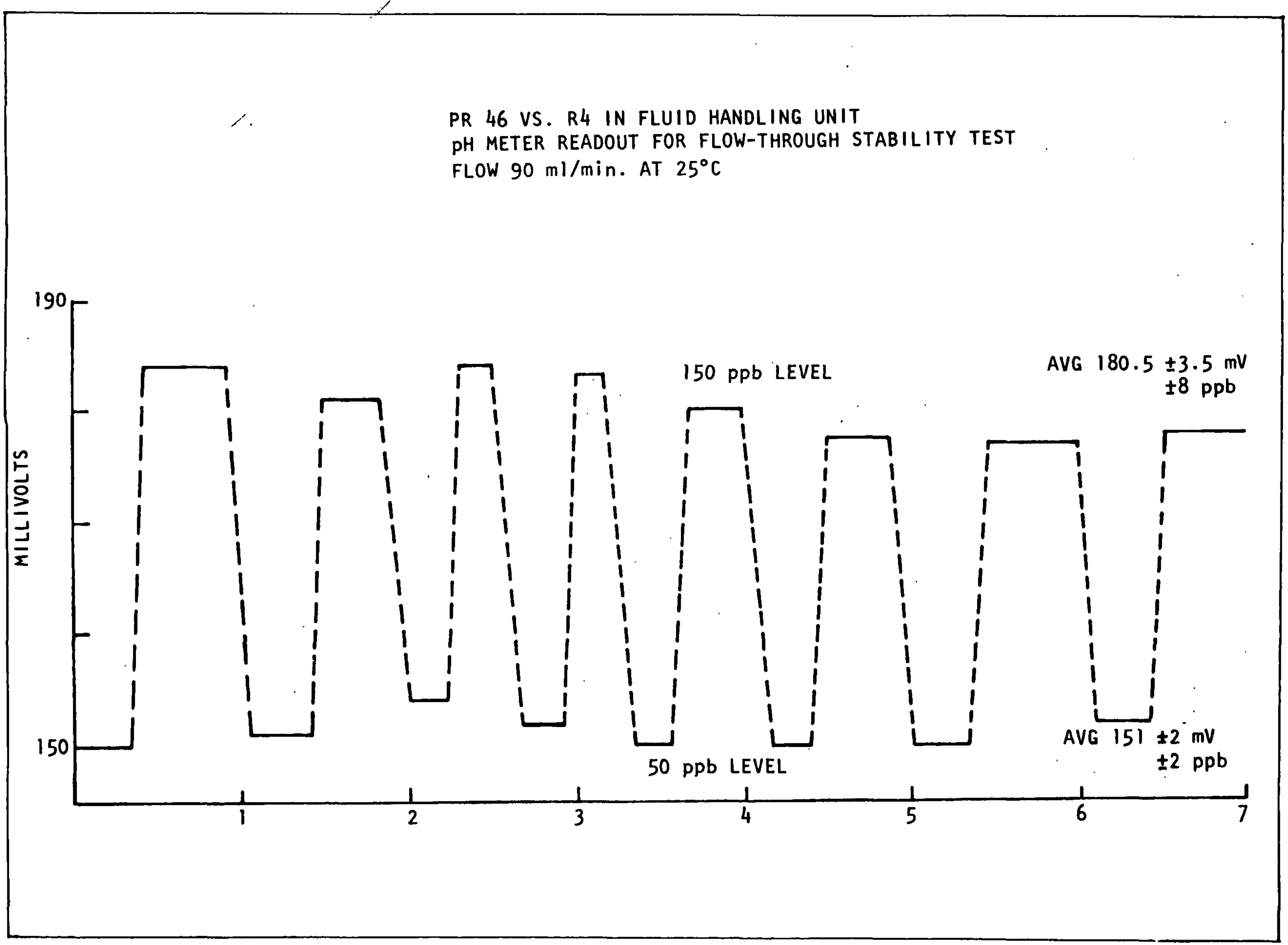


Figure 10-4. Flow-Through Stability Test Data

The electronics were connected to the other components of the system and 50 and 150 ppb silver ion solutions pumped through the system. Much noise was observed with a continuous drift. Shielding the fluid unit with metallic shielding braid and connecting it to the solution ground was found to be necessary. Also, adequate grounding of all metal components of the system was found to be very critical. Grounding of the pump motor frame to the solution ground was found necessary to prevent pickup of ac interference voltages from the motor via capacitive coupling.

Noise and drift were still observed. The 4.57 meter (15-foot) Teflon heat transfer loop was found to be picking up noise from the constant temperature bath components. The Teflon loop was removed from the constant temperature bath resulting in a significant reduction in system noise.

The apparent reason for the increased noise with the re-designed electronics over that observed with the pH meter was that the pH meter had a much higher common mode rejection ratio than the system electronics. The preamplifiers were modified to increasd the common mode rejection ratio and resulted in a reduction of the noise.

During preliminary recirculation tests in the measuring mode bubbles were observed to form slowly in the system about the same time that the recorded response started to show drift and an increase in noise. It was postulated that perhaps the bubbles were forming in the pump then moved downstream to the sensor chamber causing, at least in part, the observed noise and drift. However, placing the pump downstream of the sensor chamber did not reduce the noise or drift or bubble formation. It was noted that the slower flow rates favored bubble accumulation in various locations of the monitoring system.

With the exception of the bubble formation, the short recirculation tests indicated that the system in general was functioning properly.

A temporary modification of the test setup permitted flow-through calibration with 50 and 150 ppb silver ion solutions. The system's meter did not indicate the concentration correctly since the automatic calibration had not been permitted to function yet. The output of the electronics was monitored with a pH meter in place of the system's meter.

The system responded to the 50 ppb solution with a 153 mV output and to the 150 ppb solution with a 183 mV response. Thus a sensitivity of 63 mV/decade was demonstrated. The system was immediately switched to the automatic calibration mode with fluid recirculating through the calibration loop (pump, ion exchange column, silver bromide column, and sensor chamber).

After about 10 minutes, or sufficient time for the system to effect calibration, the system output was 53 mV. This indicated a concentration of silver ion in the effluent of the silver bromide column to be below 2 ppb while the actual concentration was approximately 60 ppb.

In an attempt to ascertain the source of error or problem, the preamplifiers were bypassed and the output of the electrodes connected directly to a pH meter. The recirculation of the fluid in the calibration loop was continued. A continuous downward drift was observed. The output of the silver bromide column was found to have degraded to 60 ppb or 28 ppb below theoretical.

The test setup was modified to that shown in Figure 10-5 and Table 10-2. This modification retained automatic calibration but used a 75 ppb silver ion solution from the reservoir R3. It also made possible continuous flow-through testing with two different silver ion concentrations, usually 50 and 150 ppb. Recirculation using either a 1 or 18 liter reservoir was also provided.

A 12-hour flow-through test was conducted using the test setup. The needle value on the flow gauge was used to adjust the flow to 90 to 95 ml/minute at 25°C.

Automatic calibration, about every 3 hours, was employed. The three reservoirs were kept filled with freshly analyzed silver ion solution. The results of the test are shown in Figure 10-6. The graph shows the meter readings while the corresponding data below the reading show the actual silver ion concentration of the fluid and the error in ppb of silver ion. Between the third and fifth

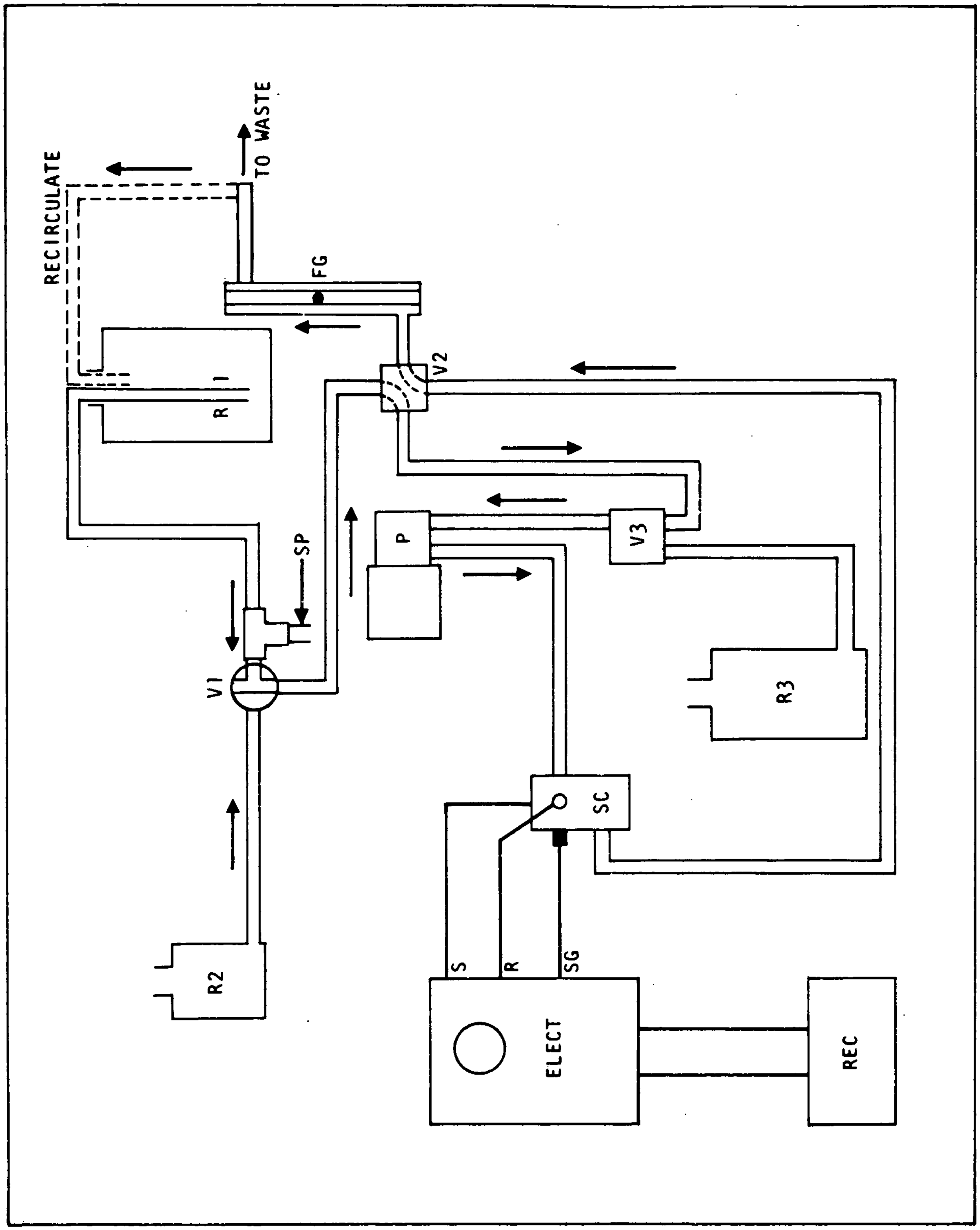


Figure 10-5. System Test Setup as of 11 April 1974

Table 10-2. Component Identification for System as of 4-11-74

R3	- 3-liter calibration fluid reservoir--75 ppb [Ag^+]
R1	- 18-liter reservoir--approximately 50 ppb [Ag^+]
R2	- 1-liter reservoir--150 ppb [Ag^+]
V1	- Selection valve--glass
SP	- Sampling point for 5-gallon reservoir
V2	- Isolation valve
V3	- Solenoid valve--calibrating or test fluid
P	- Pump--316 stainless steel
SC	- Sensor chamber
S	- Sensing electrode connection
R	- Reference electrode connection
SG	- Solution ground connection
ELECT	- System electronics
REC	- 10-inch Beckman recorder
FG	- Flow gage
Tubing between V1 and R1,R2--Tygon	

hour, electronic adjustments were necessary otherwise the response was very good. The average error over the 10 operating hours was 2 ppb with 5 ppb being the largest.

The data show a system operating reasonably well but with an error of 10 percent while the goal for the system was 5 percent.

Since the system, exclusive of the calibration column, appeared to be functional, attention was again focused on the calibration loop. The silver bromide column was repacked with the silver bromide/glass bead mixture from the large column which had been filled by Chemtric, Inc. The effluent from the column was 72 ppb which was 6 ppb below theoretical. Even though the column output was slightly lower than ideal, a 2-hour flow-through test was performed using automatic calibration but initiated manually instead of by the electronics.

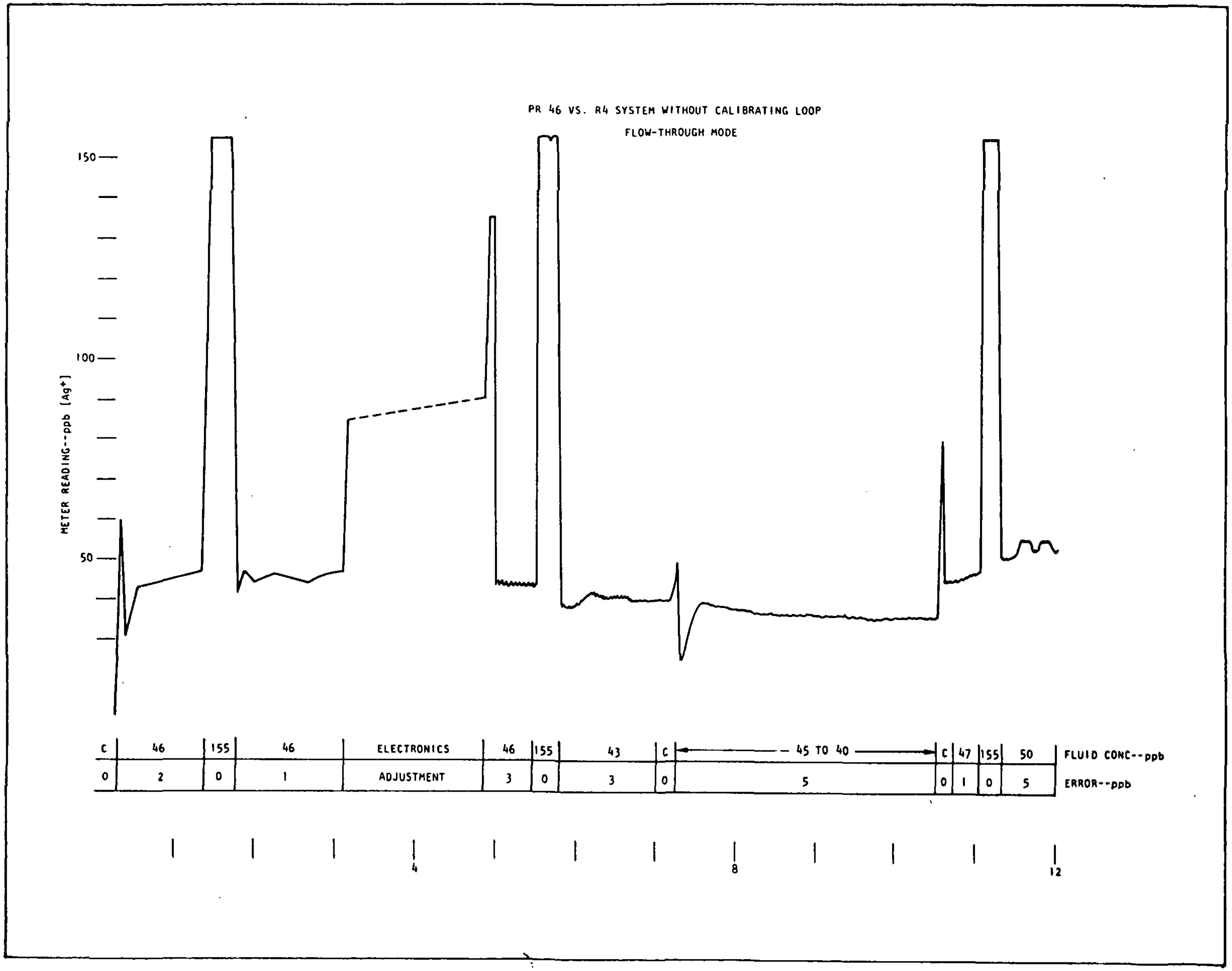


Figure 10-6. Flow-Through Test Data--Calibration Fluid from Reservoir

The test setup was that shown in Figure 10-5 with a slight modification. Reservoir R3 was replaced by the ion exchange column/silver bromide column through which de-ionized water passed during calibration.

The test results are shown in Figure 10-7. A large and varying error was observed with the 50 ppb solution flowing through. With the 150 ppb solution, the system meter appeared to be pegged at 155 ppb.

Since the actual output of the ion exchange/silver bromide column was not known, the test setup was modified slightly by adding an open beaker in the line between the output of the silver bromide column and the solenoid valve. This allowed periodic removal of sample for analysis. The open beaker also allowed observation and removal of bubbles from the column effluent.

A 90-minute test was run with analysis of the effluent of the silver bromide column at 0, 50, and 70 minutes. The test results are shown in Figure 10-8. The errors are very large but appear to be steady. The most apparent cause of the error was a 28 ppb calibration error due to low silver ion concentration in the effluent of the silver bromide column. A less obvious error determined by flow-through test later showed that the adjustments for electrode span and offset potential in the electronics were out of adjustment by a significant amount. Since these two adjustments interact with each other, determination of the individual error due to each was not readily made.

The system was then run in the flow-through mode without the calibration loop using 50, 75, and 150 ppb from the various reservoirs and attempts were made to adjust the span and offset potential controls. These are miniature potentiometers in the electronics package. Span and offset potential adjustments resulted in a temporary matching of meter readings with the concentrations of the solutions but a continuous upward drift was observed. The sensing electrode was beaker tested and found to have a span or sensitivity of 59 mV/decade without drift.

The input amplifiers were changed such that each had a gain of one. The common mode rejection ratio was also increased significantly. However, system tests still showed a continuous upward drift.

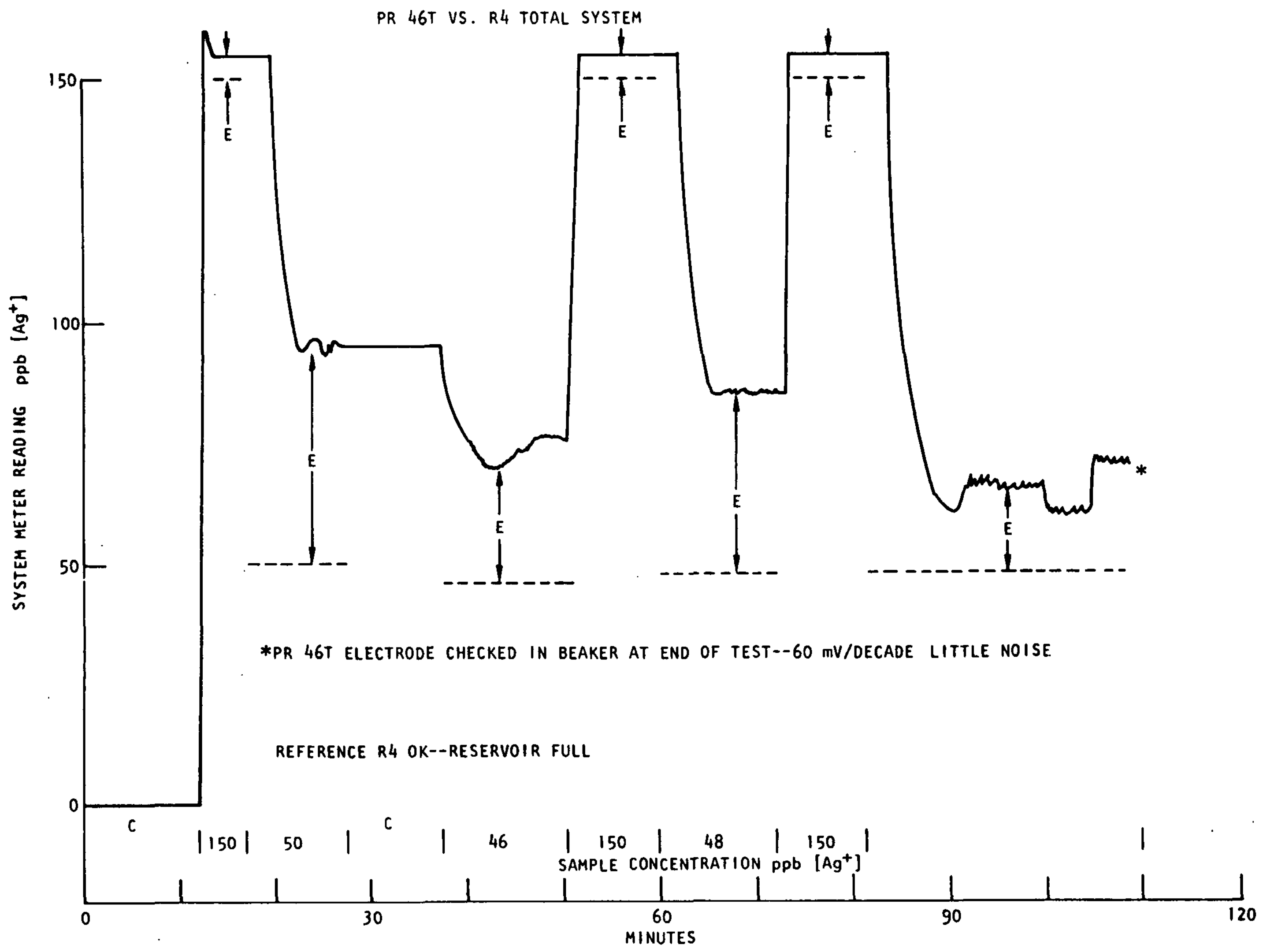


Figure 10-7. Flow-Through Test Results with Total System

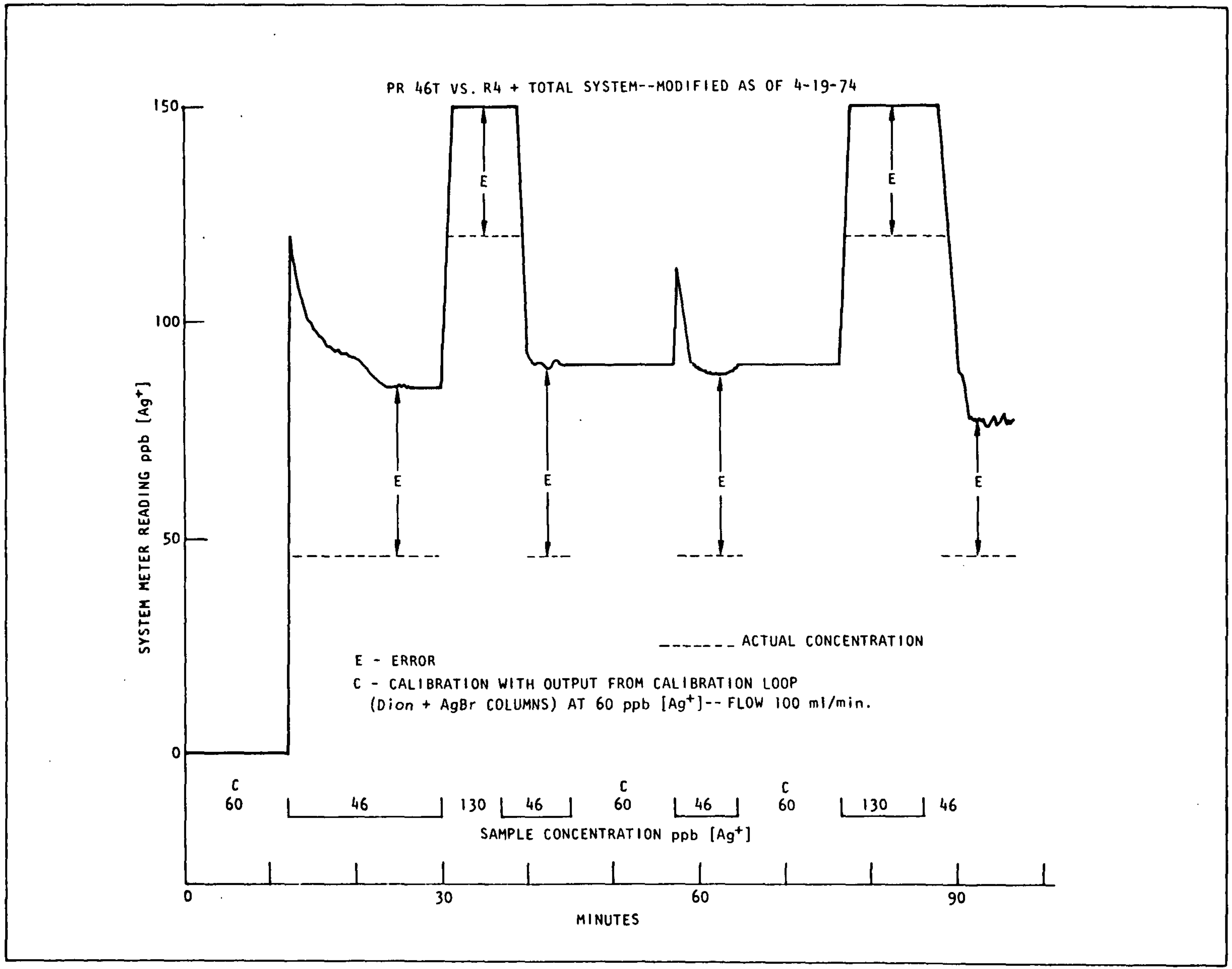


Figure 10-8. Flow-Through Test Results with Effluent of Silver Bromide Column Analyzed

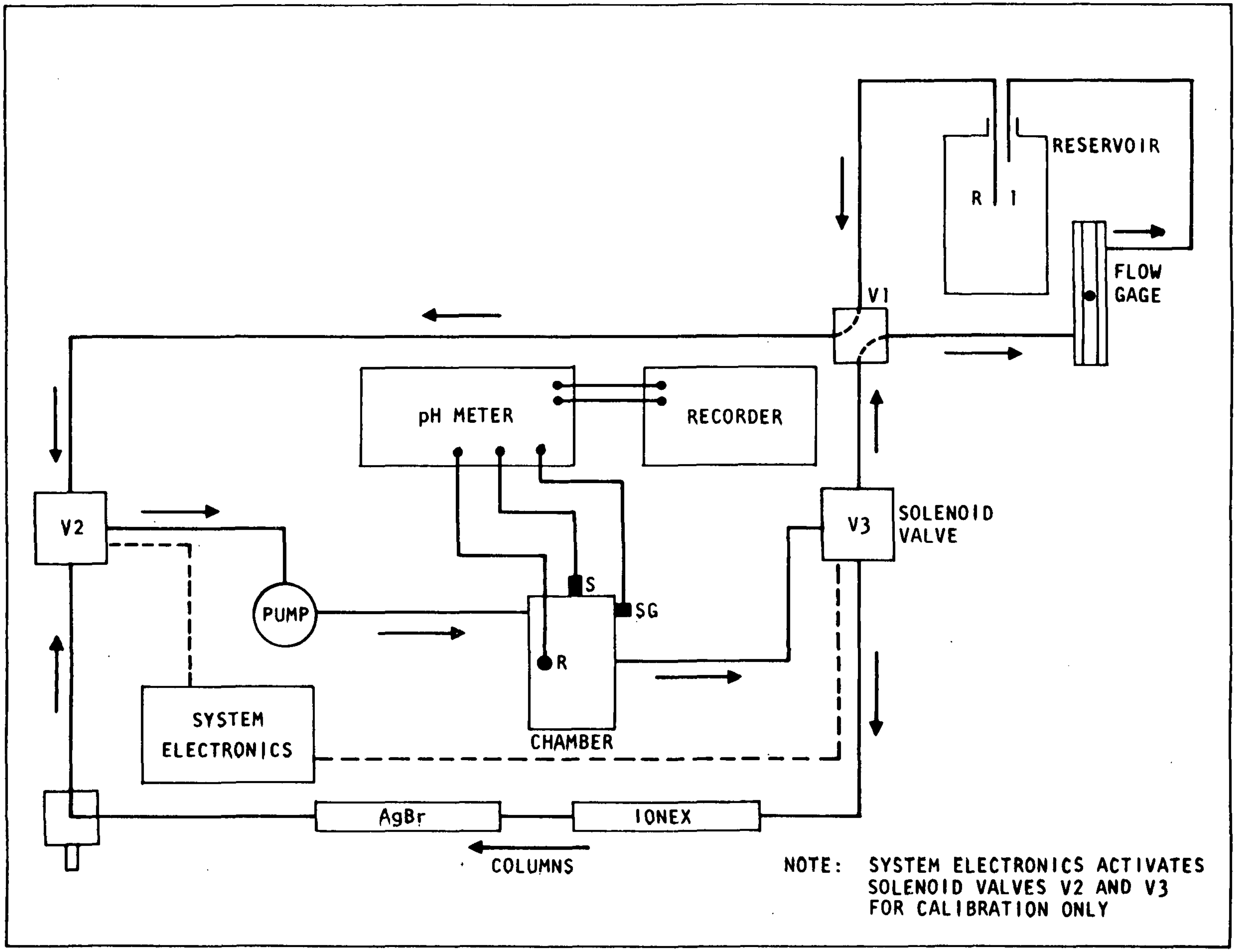
To determine if it was the system electronics or the electrodes and fluid system that were drifting, the preamplifiers were bypassed and the signals from the electrodes were connected to a pH meter (see Figure 10-9). In a 25-hour recirculation test the output of the electrodes was observed to drift, after stabilization, +2 mV or -1 mV at the 50 ppb level. This is shown in Figure 10-10.

Operation of the system in the flow-through mode while making electronic measurements and tests indicated that the thermocompensation for the silver bromide column effluent was malfunctioning. Since the delivery time for a new thermocompensation was six months, the compensating circuit was essentially shorted out. Preliminary short-term tests indicated this action had indeed reduced the drift significantly.

A 16-hour recirculation test was performed recirculating the fluid to an 18-liter reservoir of approximately 50 ppb silver ion solution. The contents of the reservoir were analyzed before and after the test. The fluid was recirculated at 65 ml/min. (8.6 lb/hr) at 25 ±1°C. The test setup was the same as that shown in Figure 10-9 except that the complete electronics were used. The input from the 75 ppb reservoir comes into the system at the same location that the output end of the silver bromide column would connect to the system.

The results of the test are shown in Figure 10-11. The actual silver ion concentration of the recirculating fluid decreased slowly due to silver ion depletion due to deposition on the surface of the system and reservoir (45 ppb at start to 42 ppb at finish, a drop of 3 ppb). The indicated level of silver ion went from 48 ppb at the start to 45 ppb at the finish showing an overall parallel drop of 3 ppb similar to the true concentration.

The cause of the up-down shift or drift is not definitely known. It is very probable that the drift and/or error is due to a combination of phenomenon such as flow variations, bubble interference, electrode drift, electronic drift, and perhaps the buildup and discharge of a streaming potential(s). The offset of 3 ppb from actual concentration could be due to improper adjustment of offset potential or calibration errors.



NOTE: SYSTEM ELECTRONICS ACTIVATES SOLENOID VALVES V2 AND V3 FOR CALIBRATION ONLY

Figure 10-9. Test Setup--Silver Ion Monitor with pH Meter for Flow-Through Test

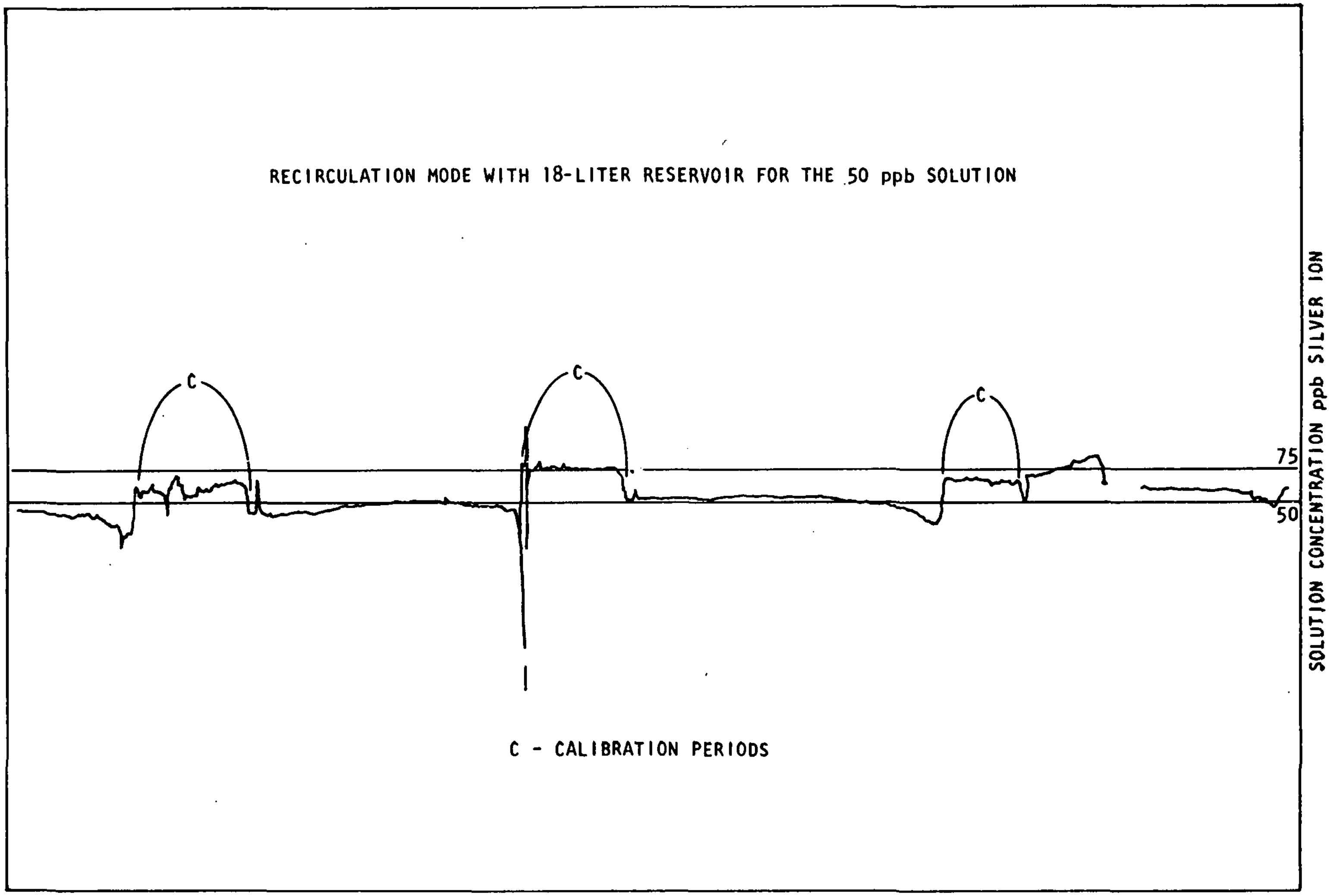
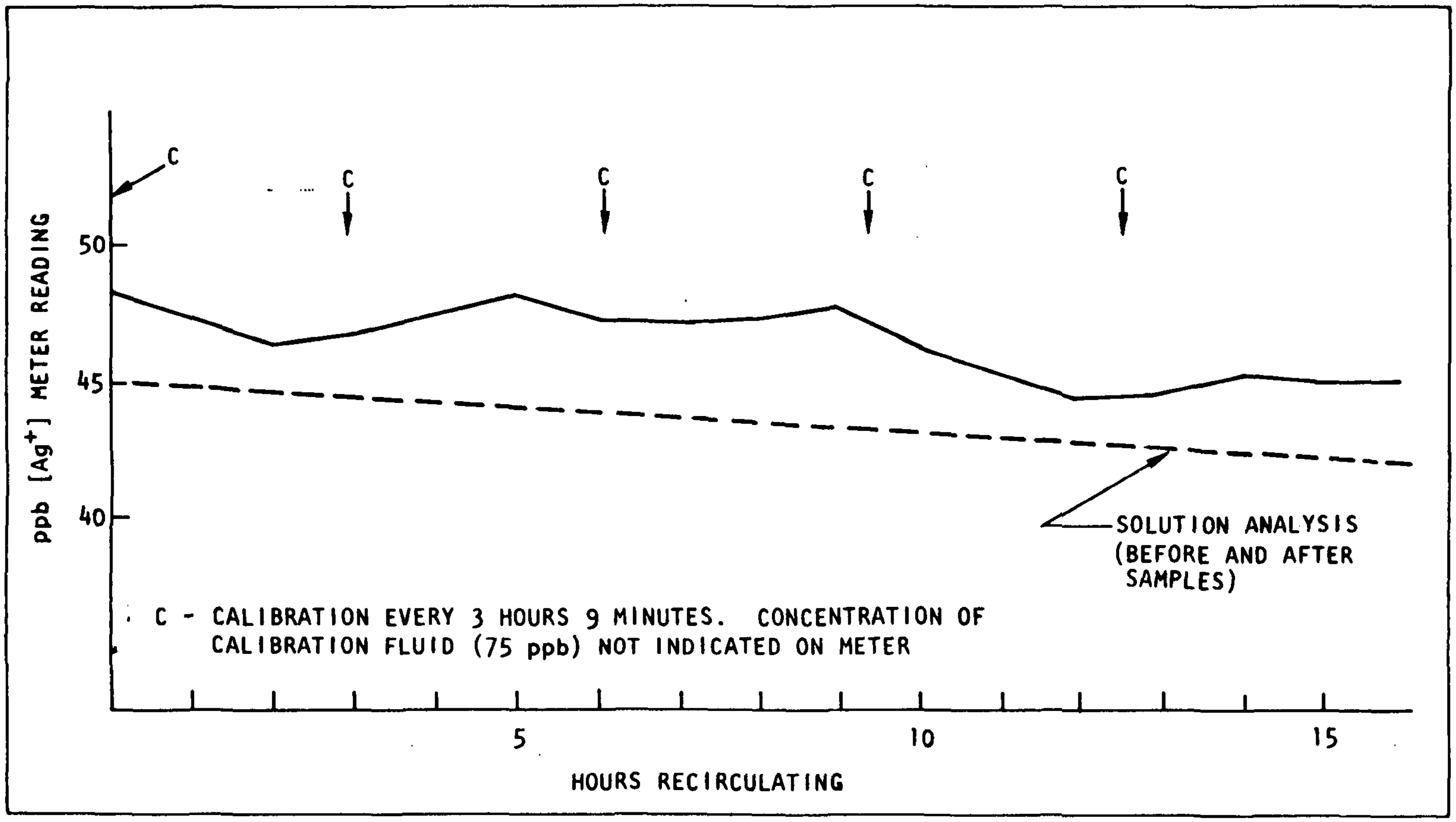


Figure 10-10. Silver Ion Monitoring--pH METER. Manual Calibration--25 Hours



C - CALIBRATION EVERY 3 HOURS 9 MINUTES. CONCENTRATION OF CALIBRATION FLUID (75 ppb) NOT INDICATED ON METER

Figure 10-11. Silver Ion Monitoring System with Electronics Automatic Calibration Using 75 ppb From Reservoir

If a 3 ppb downward shift correction was applied to the meter readout, the largest resulting system error would be 2.5 ppb or within the 5-percent error limit established as a goal.

A 72-hour recirculation test with calibration only at the beginning of the test showed a beginning concentration of 42 ppb. After 72 hours, the indicated level was 40 ppb while the actual was 30 ppb. The up-down variations in drift were again observed. The overall error in this test was 10 ppb at the 30-ppb level or 33.3%. This definitely demonstrates the need for frequent calibration.

The 72-hour test was followed by a 3-day continuous recirculation test with the same test setup. Span and offset adjustments were made to correct meter reading errors and at the same time the differential and common mode voltages were measured. Both the common mode voltages were observed to sporadically and rapidly increase the same amount while the differential voltage, which reflects the response of the electrodes and thus silver ion concentration, indicated a similar change. This showed that there was no drift of the electronics but some undetermined phenomenon within the system was causing the up-down drift and unusual response.

The ion exchange column was cleaned out and repacked with an ion exchange resin mixture prepared exactly in accordance with the Chemtric procedure (see Appendix "C"). A quantity of the IRA-402 resin was received from Chemtric. The silver bromide column was repacked with freshly prepared silver bromide/glass bead mixture in accordance with the Chemtric procedure.

The initial flow-through test resulted in a silver ion concentration in the column effluent of approximately 60 ppb. An additional 15 cm (6 in.) column of silver bromide was added to the calibration loop. The effluent was constant at 76 ppb silver ion at 25°C (77°F) for a flow of 100 ml/min. (12.3 lb/hr) using pressure from the de-ionized water system.

An attempt to test the repacked silver bromide columns as part of the calibration loop showed that there was too great a difference between the pressure drop of the calibration loop and the monitoring loop resulting in a flow difference of about 1 to 3. Such a flow difference resulted in calibration errors greater than 5 ppb.

The degradation of the PR 46 sensing electrode and its backup electrode precluded further testing.

APPENDIX A

TEST DATA ON ADHESIVES AND FABRICATION TECHNIQUES FOR A 65°C USE SENSING ELECTRODE

A-1.0 ADHESIVE AND FABRICATION TECHNIQUE STUDY - SILVER SULFIDE ELECTRODE

A-1.1 Introduction

Under Contract NAS9-12733, an evaluation was performed on solid-state silver sulfide electrodes to be used as a silver ion sensor in a monitoring instrument for silver ions in the Space Shuttle Potable Water System.

Exposure to a 500 ppb silver ion solution at 60°C resulted in degradation of the electrode response. Response became erratic, non-Nernstian or showed continuous drift.

The degraded electrodes were examined and found to have a poor seal between the silver sulfide pellet, the silver ion sensing element, and the electrode housing. The higher temperature or cycling between high and low temperature had apparently caused a failure in the seal allowing the silver ion solution(s) to diffuse or flow between the pellet and housing resulting in an unacceptable response.

Initially the silver ion monitors were to be placed downstream of the shuttle's water heaters and chillers, thus requiring an electrode having an operating range of 4 to 71°C (40 to 160°F).

The purpose of the adhesive and fabrication technique study was to find an adhesive and/or fabricating technique which would produce silver sulfide electrodes having an operating range of 4 to 71°C.

A-1.2 Adhesives and Fabrication Techniques

Three adhesives and three fabrication techniques were chosen for the study. The adhesives were chosen on manufacturer's recommendations and on communication with adhesive consultants. They were as follows:

1. Epoxylite 223 - The EpoxyliteCorp., New York
2. Kenseal 78-05-083 - Kenics Corp., Danvers, Mass.
3. RTV-108 - General Electric Corp.

Three fabrication techniques were studied:

1. Plain fabrication, i.e., no sandblasting or metal ring.
2. Sandblasting the surface of the silver sulfide pellet and adjacent plastic housing.
3. Formation of the silver sulfide pellet in a stainless steel ring which is readily adhered to by adhesives.

For detailed fabrication see paragraph 5.3.2.4, FINAL REPORT, Residual Water Bactericide Monitor Development Program, FR-2639-102, dated 23 March 1973.

A-1.3 Fabrication

All silver sulfide pellets were fabricated in an identical procedure from one batch of silver sulfide powder. Following fabrication, all electrodes were conditioned in 1000 ppb silver solution at 40°C for 72 hours.

A-1.4 Temperature Tests and Results

Each electrode was stabilized at the test temperature for approximately 30 minutes in a 500 ppb silver ion solution. Each electrode was cycled between 50 and 500 ppb silver ion solutions to determine the response characteristics. Exposure to each solution each time was a minimum of 30 minutes. The test solutions were contained in a beaker in a constant temperature bath.

The rationale for testing was based on the observed performance of electrodes and their failure during the previous contract, in which practically all failures occurred at or resulted from exposure to 65°C. It was assumed that electrodes in a flight monitor would be subjected to cycling from low or ambient temperature to a maximum of 65°C. Therefore, the electrodes were tested at 23°C, then at 65°C, and again at 23°C. Whenever an electrode exhibited non-Nernstian response or excessive noise or drift, it was considered a poor electrode and was eliminated from further testing.

The results of the tests are given in Table A-1. Good response was defined as Nernstian ±3 millivolts or at 23°C, 59 millivolts/decade change (50 to 500 ppb) in silver ion concentration with little or no drift or noise.

The configuration of the electrode used for the tests is shown in Figure A-1. The configuration containing the stainless steel sleeve is now shown since the only difference was the addition of the sleeve.

A-1.5 Conclusion

The data in Table A-1 indicates that none of the adhesive and/or fabricating techniques are suitable for consistently preparing wide temperature range silver sulfide electrodes.

TABLE A-1. ELECTRODE TEST DATA - ADHESIVE AND FABRICATION TECHNIQUE STUDY

Electrode Ident.	Adhesive	Fabrication Technique	Test Temp °C	Response
RP-1	RTV-108	Plain	23-65-23	Good
RP-2	RTV-108	Plain	23-65	Poor
RP-3	RTV-108	Plain	23	Poor (1)
RSB-1	RTV-108	Sandblasted	23-65-23	Good
RSB-2	RTV-108	Sandblasted	23-65	Poor
RSB-3	RTV-108	Sandblasted	23-65-23	Good
EP-1	Epoxylite 223	Plain	23	Poor (1)
EP-2	Epoxylite 223	Plain	23-65-23	Good
ESB-1	Epoxylite 223	Sandblasted	23-65-23	Good
ESB-2	Epoxylite 223	Sandblasted	23-65	Poor
KP-1	Kenseal	Plain	23-65-23	Good
KP-2	Kenseal	Plain	23	Poor (1)
KP-3	Kenseal	Plain	23-65	Poor
KSB-1	Kenseal	Sandblasted	23-65-23	Poor
KSB-2	Kenseal	Sandblasted	23-65	Poor
KSB-3	Kenseal	Sandblasted	23	Poor (1)
MA1	RTV-108	Plain	23-65	Poor
MA2	Epoxylite 223	Plain	23	Poor
MA3	Kenseal	Plain	23-65	Good
MB1	RTV-108	Sandblasted	65	Good
MB2	Epoxylite	Sandblasted	23	Poor
MB3	Kenseal	Sandblasted	65	Poor
MS1	RTV-108	SS Sleeve	23	Poor
MS2	Epoxylite 223	SS Sleeve	23-65	Poor
MS3	Kenseal	SS Sleeve	23-65	Poor

(1) Mfg flaw--either poor solder joint or fab technique.

Key to table:

R = RTV-108 a room temperature curing silicone rubber.

P = Plain fabrication technique

SB = Sandblasting of Ag_2S pellet and adjacent electrode housing surface.

E = Epoxylite 223 an epoxy cement.

K = Kenseal an epoxy cement.

M = Second batch of electrodes fabricated at one time which included the stainless steel sleeve type.

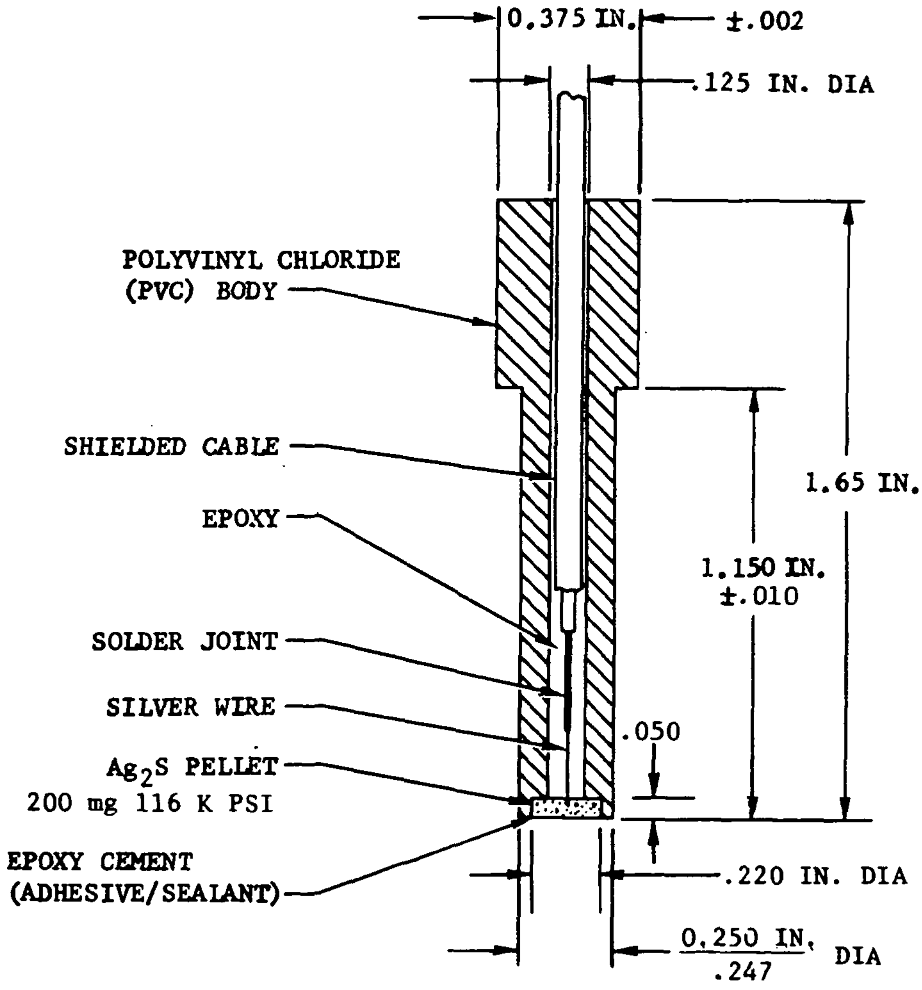


Figure A-1. Solid-State Silver Sulfide (Ag_2S) Electrode

A = Plain fabrication technique as a control, second batch.
B = Sandblasted technique as a control, second batch.
S = Electrodes fabricated with the silver sulfide pellet formed in a stainless steel sleeve.

The test temperature column shows the temperatures at which the electrodes were tested. The last temperature indicated shows the temperature at which the electrode failed or was found to have good response characteristics.

APPENDIX B

PRELIMINARY FAILURE MODE EFFECTS ANALYSIS
SILVER ION MONITOR

A

QCR-2656-501

PRELIMINARY FAILURE MODE EFFECTS ANALYSIS
SILVER ION MONITOR

Contract No. NAS9-13387

18 May, 1973

Prepared for:

National Aeronautics and Space Administration
Johnson Space Center
Houston, Texas 77058

B

1.0 GENERAL

1.1 Introduction

This preliminary report contains the Failure Mode Effects Analysis of the Silver Ion Monitor.

The report is submitted in fulfillment of the National Aeronautics and Space Administration, Johnson Space Center's Contract NAS9-13387 requirement for an informal FMEA analysis.

1.2 Report Summary

The prototype system is non-redundant and therefore all category II failures are single point failures. However, this problem will be solved for the flight designed system by employment of two Silver Ion Monitors as redundant systems.

There are five category I failure modes. All are concerned with gross external leakage. This problem will be solved for flight system by employment of redundant systems and by using a flight qualified manual valve (V1) with a high reliability seal design.

The flight unit requirement is fail operational and fail safe. Fail operational can best be achieved by providing system and subsystem redundancy. Fail safe can be achieved by assuring that in no case will a subsystem failure result in hazard to mission or crew.

2.0 DISCUSSION

The Silver Ion Monitor monitors the silver ion concentration of the Space Shuttle Potable Water Supply System. The silver ions are employed as a bactericide. The monitor is placed upstream of the water heating and cooling apparatus. The Silver Ion Monitor System is composed of the measuring and calibration subsystems.

2.1 Ground Rules Used in Performing FMEA

The following ground rules were used in performing this FMEA:

a. Failures considered were limited to single failure occurrence and their single or multiple failure effects during the mission.

b. Failure classifications were determined by the following criteria:

   1. Failure Classification I - A failure whose occurrence could adversely affect crew safety or other systems.

   2. Failure Classification II - A failure whose occurrence could render the Silver Ion Monitor inoperative.

   3. Failure Classification III - A failure whose occurrence could result in loss of confidence in the monitor readout.

c. Leakage failure modes analyzed were limited to gross leaks.

d. For purposes of analysis the system electronics were broken down into the four basic functions listed in paragraph 6.3.5.2 of "Instrument Package Definition, Silver Ion Monitor, COR-2639-1.

e. Design compensating provisions listed in the FMEA apply to the flight design only, not to the prototype.

FAILURE MODE EFFECTS AND CRITICALITY ANALYSIS

ITEM/FUNCTION	FAILURE MODE	FAILURE EFFECT ON			POSSIBLE FAILURE CAUSE COMPONENT	FAILURE CLASSIFICATION & PROBABILITY OF OCCURENCE	FAILURE DETECTION METHOD	FLIGHT DESIGN ONLY	REMARKS
		LOWEST REPLACEABLE ASSEMBLY/ MODULE	INTRASYSTEM (Silver Ion Monitor)	INTERSYSTEM (Mission)				DESIGN COMPENSATING PROVISIONS	
1. Manual Valve V1/ Servicing	1) Gross External Leakage		Loss of monitoring function due to lack of sample.	Loss or reduction of ship's water supply.	Defective Seal	I		Employ high reliability seal design. Flight qualified valve will not be cycled during flight.	
2. Solenoid Valve V2 or V3/ Calibration	1) Fail in calibration position		Loss of water circulation in the measurement loop.	Loss of monitoring function.	Mechanical actuator failure	III		System Redundancy	
	2) Fail in measurement position.		Loss of water circulation in the calibration loop.	Loss of calibration. Loss of confidence in the monitor readout.	Solenoid electrical failure or mechanical actuator failure	II			
	3) Gross external leakage.		Loss of monitoring function due to lack of sample.	Loss or reduction of ship's water supply.	Defective seal.	I			
3. Pump-Motor Combination/Measurement & Calibration	1) Non-Operative		Loss of Water circulation in measurement and calibration loops. Monitor will not operate.	Loss of monitoring function.	Electrical or mechanical breakdown.	II			
	2) Gross external leakage		Loss of monitoring function due to loss of supply	Loss or reduction of ship's water supply.	Defective seal.	I			
4. Sensor Chamber/ Measurement									
a. Quartz Fiber Junction	1) Plugged		Reference electrode loses contact with the water flow. Monitor will be inoperative.	Loss of or unstable monitoring function.	Drying of KNO_3 electrolyte.	II			

System Silver Ion Monitor

Subsystem ________

PREPARED BY S. S. Moore, Reliability Engineer
DATE May 18, 1973
PAGE 1 OF 6

B-3

FAILURE MODE EFFECTS AND CRITICALITY ANALYSIS

ITEM/FUNCTION	FAILURE MODE	FAILURE EFFECT ON			POSSIBLE FAILURE CAUSE COMPONENT	FAILURE CLASSIFICATION & PROBABILITY OF OCCURENCE	FAILURE DETECTION METHOD	FLIGHT DESIGN ONLY	REMARKS
		LOWEST REPLACEABLE ASSEMBLY/ MODULE	INTRASYSTEM (Silver Ion Monitor)	INTERSYSTEM (Mission)				DESIGN COMPENSATING PROVISIONS	
4. a. (continued)	2) Leakage		Loss of reference electrode. Monitor will be inoperative when KNO_3 is exhausted.	Same as above.	Filter mechanical damage from shock or vibration.	II		System Redundancy	
b. Needle	1) Plugged		Loss of reference electrode.	Same as above.	Septum particle.	II			
c. Electrical Connector on Reference electrode	1) External Leakage		KCl electrolyte could corrode or short the connector contacts. Reference electrode would be lost and monitor would be inoperative.						
d. Rolling Diaphragm	1) Leakage		Reference electrode would be shorted out. Monitor would be inoperative.	Same as above.	Seal leak.	II			
e. Sensing electrode	1) No signal		Loss of the sensing electrode. Ion monitor would be inoperative.	Same as above.	Mechanical damage from shock or vibration.	II			
f. Electrical connector on the sensing electrode.	1) Open or short circuit		Same as above.	Same as above.	Same as above.	II			
g. Thermocompensator sensing thermistor	Open or short circuit		Loss of thermal compensation. Monitor will operate out of tolerance.	Monitor readout is inaccurate. High for open and low for short.	Mechanical damage.	III			

System Silver Ion Monitor

Subsystem __________

PREPARED BY S. S. Moore, Reliability Engineer
DATE May 18, 1973
PAGE 2 OF 6

FAILURE MODE EFFECTS AND CRITICALITY ANALYSIS

ITEM/FUNCTION	FAILURE MODE	FAILURE EFFECT ON: LOWEST REPLACEABLE ASSEMBLY/MODULE	FAILURE EFFECT ON: INTRASYSTEM (Silver Ion Monitor)	FAILURE EFFECT ON: INTERSYSTEM (Mission)	POSSIBLE FAILURE CAUSE COMPONENT	FAILURE CLASSIFICATION & PROBABILITY OF OCCURENCE	FAILURE DETECTION METHOD	FLIGHT DESIGN ONLY: DESIGN COMPENSATING PROVISIONS	REMARKS
h. Thermocompensator electrical connector	Open or short circuit		Same as above.	Same as above.	Same as above.	III		System Redundancy	
j. Chamber inlet and outlet water connections	Gross Leakage		Loss of monitoring due to lack of sample.	Loss or reduction of ships water supply.	Defective seal.	I			
5. Pressure Relief Valve/Measurement	1) Plugged		Sensor chamber may be damaged from over-pressure caused by thermal rise.	Loss of monitoring function.	Contamination or mechanical failure.	II			
	2) Fails to open		Same as above.	Same as above.	Mechanical failure.	II			
	3) Gross leakage internal		Loss of monitor or unstable reading.	Same as above.	Mechanical failure.	II			
	Gross leakage external		Loss of monitoring due to lack of sample.	Loss or reduction of ship's water supply.	Defective seal.	I			
6. Ion Exchange Column/Calibration	1) Plugged		Water would not pass thru the column. Calibration would be lost.	Loss of calibration and loss of confidence in monitor readout.	Contamination	III			
	2) Gross leak external		Loss of calibration function	Same as above	Defective seal or weld.	III			
	3) Channeling (internal leakage)		Calibration error.	Loss of confidence in monitor readout.	Improper assembly.	III			

System Silver Ion Monitor

Subsystem

PREPARED BY S. S. Moore, Reliability Engineer
DATE May 18, 1973
PAGE 3 OF 6

B-5

FAILURE MODE EFFECTS AND CRITICALITY ANALYSIS

ITEM/FUNCTION	FAILURE MODE	FAILURE EFFECT ON			POSSIBLE FAILURE CAUSE COMPONENT	FAILURE CLASSIFICATION & PROBABILITY OF OCCURENCE	FAILURE DETECTION METHOD	FLIGHT DESIGN ONLY DESIGN COMPENSATING PROVISIONS	REMARKS
		LOWEST REPLACEABLE ASSEMBLY/ MODULE	INTRASYSTEM (Silver Ion Monitor)	INTERSYSTEM (Mission)					
7. Silver Bromide Column/Calibration	1) Plugged		Water would not pass thru the column. Calibration may be lost.	Loss of calibration and loss of confidence in the monitor readout.	Contamination	III		System Redundancy	
	2) Gross leakage external		Loss of calibration due to lack of samples	Same as above	Defective seal or weld.	II			
	3) Channeling		Calibration error	Loss of confidence in monitor readout.	Improper assembly.	III			
8. Calibration loop check valve/ Calibration	1) Plugged		Water would not pass thru the columns. Calibration would be lost.	Loss of calibration and loss of confidence in the monitor readout.	Contamination	III			
	2) Fails in the open position.		Silver bromide could leak into the ion exchange column. Premature exhaustion of ion exchange capacity.	Eventual loss of calibration.	Mechanical failure.	III			
9. Calibration loop thermal compensator/calibration	1) Open or short		Loss of temperature compensation. Loss of calibration.	Monitor readout is inaccurate, high for open, low for short.	Mechanical damage.	III			
10. Signal Processing and readout Electronics/Measurement	1) No readout.		Monitor is inoperative.	Loss of monitoring function.	Any of the system failures of items 1 thru 5 of this FMEA, or electronic signals out of tolerance.	II			

System Silver Ion Monitor

Subsystem __________

PREPARED BY S. S. Moore, Reliability Engineer
DATE May 18, 1973
PAGE 4 OF 6

B-6

FAILURE MODE EFFECTS AND CRITICALITY ANALYSIS

ITEM/FUNCTION	FAILURE MODE	FAILURE EFFECT ON LOWEST REPLACEABLE ASSEMBLY/ MODULE	FAILURE EFFECT ON INTRASYSTEM (Silver Ion Monitor)	FAILURE EFFECT ON INTERSYSTEM (Mission)	POSSIBLE FAILURE CAUSE COMPONENT	FAILURE CLASSIFICATION & PROBABILITY OF OCCURENCE	FAILURE DETECTION METHOD	FLIGHT DESIGN ONLY DESIGN COMPENSATING PROVISIONS	REMARKS
10. (Continued)	2) High readout.		Monitor indicates that the silver ion concentration in the water is higher than the actual value.	Possibility that crew members may think the water is sterile when actually non-sterile	Signals out of tolerance.	III		This condition will be detected at calibration.	To endanger the crew two failures would be required. May cause crew to reduce actual silver ion concentration below safe level.
	3) Low readout.		Monitor indicates that the silver ion concentration in the water is lower than the actual value.	Water may contain excessive silver ions and not be detected.	Same as above.	III		Same as above.	Same as above.
11. Logic & Valve Actuation Electronics/Calibration	1) No output.		Calibration cycle will not occur.	Loss of calibration and loss of confidence in the monitor readout.	Electrical failure	III		System Redundancy ↓	
12. Calibration Electronics/Calibration	1) No output.		Same as above.	Same as above.	Same as above.	III		↓	
13. Electronics Integration Components/ Measurement & Calibration.								↓	
3 a. ±15V DC Supply	1) No Output		Preamp & amplifier would not operate. Monitor would be lost.	Loss of monitoring function.	Open or short circuit.	II		↓	
b. +5V DC Supply	1) No output		Op amps timer, logic and calibration electronics would not operate.	Same as above.	Same as above.	II		↓	

System Silver Ion Monitor

Subsystem ______________

PREPARED BY S. S. Moore, Reliability Engineer
DATE May 18, 1973
PAGE 5 OF 6

FAILURE MODE EFFECTS AND CRITICALITY ANALYSIS

ITEM/FUNCTION	FAILURE MODE	FAILURE EFFECT ON			POSSIBLE FAILURE CAUSE COMPONENT	FAILURE CLASSIFICATION & PROBABILITY OF OCCURENCE	FAILURE DETECTION METHOD	FLIGHT DESIGN ONLY DESIGN COMPENSATING PROVISIONS	REMARKS
		LOWEST REPLACEABLE ASSEMBLY/ MODULE	INTRASYSTEM (Silver Ion Monitor)	INTERSYSTEM (Mission)					
c. -5V DC Supply	1) No Output	X	oss of Op amp nd calibration lectronics.	Same as above.	ame as above.	II	X	System Redundancy	
d. -12V DC Supply	1) No Output		oss of timer & oss of calibra- ion.	Loss of confi- dence in the monitor readout.	ame as above.	III		↓	

System Silver Ion Monitor

Subsystem __________

PREPARED BY S. S. Moore, Reliability Engineer
DATE May 18, 1973
PAGE 6 OF 6

APPENDIX C

CHEMTRIC DEIONIZER COLUMN PREPARATION

A

Rec'd from A. Behrend
4-26-74

SILVER HALIDE COLUMNS

1.0 Packing Preparation

Packing preparations for the silver halide columns entails (1) classifying the silver halide granules, (2) cleaning glass beads, and (3) mixing the silver halide and glass beads in the ratio by weight of 1 part silver salt to 1.25 parts glass bead.

1.1 The silver chloride (AgCl) and silver bromide (AgBr) are procured from Fisher Scientific Co., Chicago, Illinois under catalog numbers S-172 AgBr and S-174 AgCl. The reagent grade material "as-received" contains granules ranging from dust sized particles to golf ball sized lumps. Since some degree of uniformity is desirable, the material that passes through a 45 mesh (Tyler) screen should be rejected while material retained by a 6 mesh screen should be further reduced in size by "hammering" with a pestile or by "cutting-up" the lumps with a knife or razor blade. The silver salts can be photoreduced, consequently, care must be taken not to expose them to direct light.

1.2 The glass beads (0.42 - 0.59mm) are procured from Advanced Process Supply Co., Chicago, Illinois 60622, under catalog number 2406-6 coarse.

1.2.1 The "as-received" glass beads should be washed in an aqueous solution of detergent (Alconox or equivalent)

1.2.2 Next the detergent solution should be decanted and the glass beads rinsed with hot tap water several times (at least 5).

1.2.3 Wash the glass beads in concentrated chromic acid; the chromic acid is heated to boiling and allowed to simmer for one hour.

1.2.4 After allowing the chromic acid and glass beads to cool, decant the acid and wash the glass beads repeatedly with deionized water.

1.2.5 Finally, dry the glass beads in an oven for 12 hours at 376^{O}K (217.4^{O}F). Allow the beads to cool to room temperature before use.

1.3 The glass beads and ground silver salts are blended by weight in the ratio of 1.25 parts glass beads to one part silver salt. Once the proper proportions are weighed-out, the ingredients are added to a common container (preferably glass) along with a volume of water just equal to the volume of the ingredients. The ingredients are stirred manually to achieve uniform distribution of glass beads and silver halide particles. For the AgCl column, 312 grams of the dry salt-glass bead mixture are necessary, while 148 grams of the dry AgBr-glass bead mixture fill that column.

2.0 Assembly Preparation

Two Pyrex wool (Owen-Corning Fiberglas Corporation Catalog number 3950 or equivalent) supports for the particulate bed must be prepared.

2.1 A roll of Pyrex wool should be soaked in deionized water and a working surface wet down by deionized water. On the working surface, unroll and fold the wet Pyrex wool into a 1/2 inch thick pile.

2.2 This pile of Pyrex wool should be sandwiched between two 10 x 20 mesh 316 stainless steel retaining screens. The wool is trimmed around the periphery of the screens about 1/16th of an inch in excess.

2.3 A second support bed is prepared for the other end of the column. This is a duplicate of the one from 2.1 and 2.2.

3.0 Assembly

3.1 Insert a support bed assembly of Pyrex wool sandwiched between four screens into the bottom of the canister body.

3.2 Load the canister body, under subdued lighting with the previously prepared packing; see 1.0. Add the packing mixture in 25 to 50 ml increments while tapping the outlet against a hard surface and tapping the canister body with a rubber mallet. When the packing is near completion, gently ram the mixture down with a rubber stopper (smaller in diameter than the canister) affixed to a rod. Do not use any water in loading the canister; if the canister contains water, the silver chloride particles and glass beads will settle to the bottom at different rates resulting in stratification.

3.3 Place the second sandwiched support bed of Pyrex wool on top of the packing.

3.4 The upper sieve is next put in place on top of the Pyrex wool support screens.

3.5 The spring is put into place on top of the sieve.

3.6 The O-ring is positioned on the flange of the canister body.

3.7 The spring is compressed by the canister cover and while holding the cover in its proper position, the V-band clamp is affixed.

3.8 When packing and assembly are complete, connect the canister to a deionized water source and flush at 2 l/min for 10 minutes. Analyze the effluent for silver content and turbidity, to check that the canister is saturating the deionized water with silver ions, and that the "fines" produced during the loading are flushed-out. Repeat flushing until effluent contains no "fines" and Ag^+ content is 1.0 - 1.3 ppm.

4.0 Cartridge Packing

For the PFP tests, cartridges were designed for the silver salt/glass beads mixtures. The cartridges are packed in the same outlined manner outside the column with similar screen and Pyrex wool sandwiches on either end. The cartridge is then slipped into the column and flushed as before. Then, the cartridge can be removed, fresh pyrex wool inserted to replace that which had caught some fines, and the cartridge reloaded into the column.

DEIONIZER COLUMN

1.0 Packing Preparation

Three types of ion exchange resin are used in this column. These resins all manufactured by Rohm & Haas Company of Philadelphia, Pennsylvania are Amberlite IR-120, Amberlite IRA-402, and Amberlite IR-45.

The resins used require very extensive preparation to eliminate manufacturing residues. Previous experience has indicated that the as-received resins are also biologically contaminated - thereby requiring sterilization and decontamination.

1.1 Each resin type is prepared separately. The initial step for IR-120 and IR-45 consists of multiple extractions in boiling, very high quality (2 to 3 megaohm) deionized water. In the above process, a resin quantity of 150 ml IR-45 or 300 ml IR-120 was mixed with at least five volumes of water in a Pyrex glass beaker and heated to boiling. The mixture is boiled for five to ten minutes, after which the container is removed from the heat source and the resins allowed to settle. The supernatant liquid is decanted-off and fresh deionized water added immediately. The resins are again allowed to settle and the water decanted-off and fresh deionized water is added again. The above process is repeated at least ten times or until all traces of color and taste are eliminated.

1.2 For IRA-402 the initial step consists of 3 cycles of exhaustion and regeneration as suggested by the manufacturer. Each cycle is accomplished by exhaustion of 225 ml IRA-402 in a solution of 0.5% sodium chloride and regenerated using 5.0% sodium hydroxide at a level of 1.5 Kg NaOH/cubic meter of resin. The three resins are then ready for mixing.

1.3 Mix the ion exchange resins in a ratio of 200 cm^3 (12.2 in^3) Amberlite IR-120, 150 cm^3 (9.1 in^3) Amberlite IRA-402, and 100 cm^3 (6.1 in^3) Amberlite IR-45. Mix the resins in a container (preferably glass) along with a volume of water just equal to the volume of resins. Stir the mixture manually with a spatula and distribute the resins uniformly.

2.0 Assembly Preparation

Prepare two Pyrex wool support beds for the deionizer column.

2.1 Soak a roll of Pyrex wool in deionized water.

2.2 Wet down a working surface with deionized water, unroll and fold over the wet Pyrex wool into a pile one-half inch thick.

2.3 Sandwich the one-half inch thick wet Pyrex wool pile between two 316 stainless steel retaining screens.

2.4 Trim the Pyrex wool pile with a pair of scissors around the periphery of the screens, about one-sixteenth of an inch larger in radius than the retaining screens.

2.5 Repeat 2.1 - 2.4 for second support bed.

3.0 Packing and Assembly

3.1 Insert the lower Pyrex wool resin support subassembly sandwiched between four retaining screens, two screens on each face of the Pyrex wool disc, into the bottom of the deionizer canister body.

3.2 Load the deionizer canister body with the previously prepared resin mixture; see Section 1.3. Add the resin mixture in 50 to 100 ml increments while tapping the outlet against a hard surface and tapping the canister body with a rubber mallet. When the packing is near completion, gently ram the mixture down with a rubber stopper (smaller in diameter than the canister) fixed to a rod. Do not use any water in loading the canister; if the canister contains water, the Amberlite resins will settle to the bottom at different rates and produce stratification.

3.3 Insert the upper Pyrex wool resin support subassembly sandwhiched between two upper retaining screens and two lower retaining screens on top of the resin bed.

3.4 Place the sieve on top of the Pyrex wool support bed.

3.5 Place the O-ring on the flange of the canister body.

3.6 Center the spring on the sieve.

3.7 Compress the spring with the deionizer column's cover and while maintaining position, position and fasten V-band clamp.

NTIS does not permit return of items for credit or refund. A replacement will be provided if an error is made in filling your order, if the item was received in damaged condition, or if the item is defective.

Reproduced by NTIS
National Technical Information Service
U.S. Department of Commerce
Springfield, VA 22161

This report was printed specifically for your order from our collection of more than 2 million technical reports.

For economy and efficiency, NTIS does not maintain stock of its vast collection of technical reports. Rather, most documents are printed for each order. Your copy is the best possible reproduction available from our master archive. If you have any questions concerning this document or any order you placed with NTIS, please call our Customer Services Department at (703)487-4660.

Always think of NTIS when you want:
- Access to the technical, scientific, and engineering results generated by the ongoing multibillion dollar R&D program of the U.S. Government.
- R&D results from Japan, West Germany, Great Britain, and some 20 other countries, most of it reported in English.

NTIS also operates two centers that can provide you with valuable information:
- The Federal Computer Products Center - offers software and datafiles produced by Federal agencies.
- The Center for the Utilization of Federal Technology - gives you access to the best of Federal technologies and laboratory resources.

For more information about NTIS, send for our FREE *NTIS Products and Services Catalog* which describes how you can access this U.S. and foreign Government technology. Call (703)487-4650 or send this sheet to NTIS, U.S. Department of Commerce, Springfield, VA 22161. Ask for catalog, PR-827.

Name ______________________________
Address ____________________________
____
____
Telephone __________________________

- Your Source to U.S. and Foreign Government Research and Technology.