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FINAL REPORT

RESIDUAL WATER BACTERICIDE MONITOR DEVELOPMENT PROGRAM

Prepared under:

Contract No. NAS9-12733

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BACTERICIDE MONITOR DEVELOPMENT PROGRAM
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Prepared for:

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

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

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ABSTRACT

A bactericidal (silver-ion) monitor is required for the Space Shuttle Potable Water System: potentiometric measurement using an ion-selective electrode appears to be the most feasible of available techniques. During a development program under NAS9-12733, four commercially-available electrodes and a specially-designed, solid-state, silver-sulfide electrode were evaluated for their response characteristics and suitability for space use. The configuration of the solid-state electrode--and its Nernstian response between 10 and 10,000 ppb silver--shows significant promise for use in space.

A pressurized double-junction reference electrode--with a quartz-fiber junction and a replaceable bellows electrolyte reservoir--was designed and verification-tested, paired with a solid-state, silver-sulfide electrode in a test fixture.

Under simulated shuttle water system conditions of temperature (50° to 113°F), pressure (10 to 45 psig) and flow (13 to 60 lb/hr), and silver ion concentrations between 25 and 125 ppb, the electrode pair developed a potential (millivolts) proportional to the logarithm of ionic activity of the silver in solution (Nernstian response) with less than one-percent noise.

Under these simulated conditions, most sensitivity to variations of pressure and flow occurred at a pressure of 25 psig, with a flow of 60 lb/hr at 113°F. These variations amounted to less than 15 percent (18 ppb at a level of 125 ppb), thus confirming the suitability of the technique.

A silver-ion monitoring system which included automatic calibration using a saturated solution of silver bromide as the standard was defined.

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1.0 SUMMARY

The Residual Water Bactericide Monitor Development Program, under Contract No. NAS9-12733, was intended to explore the feasibility of a potentiometric method of analysis for silver ion in the Space Shuttle Potable Water System.

The development program was divided into three tasks:

- Technique Selection
- Technique Testing
- Instrumentation Package Definition

Under Technique Selection, a literature search to determine the current state-of-the-art confirmed the promise of a potentiometric system for this demanding measurement under the difficult conditions envisioned. Four commercially-available ion-selective electrodes (Beckman, Corning, Orion, and NIL silver sulfide) were evaluated on their response characteristics and suitability for zero-gravity use and ability to withstand ±6-g acceleration.

An experimental solid-state, silver-sulfide electrode was designed, fabricated, and evaluated in an effort to eliminate artifacts due to the uncertainties associated with fluid movement in zero g.

The results of the evaluation of the commercial electrodes and the experimental electrode were summarized in a Test Data Matrix. It was established that the liquid-filled construction of the commercial electrodes made them undesirable for space use, while the solid-state construction of the experimental electrode made it ideal.

All the electrodes exhibited Nernstian response with sensitivities down to 50 ppb for silver ion. The solid-state electrode showed better precision than any of the commercial electrodes, but its response time (for 99-percent response) was slower than that of commercial electrodes. The stability of the solid-state electrode was equivalent to the better commercial electrodes.

A Beckman Perma-Probe™ was originally proposed as the reference electrode since it is a solid body reference with a nonflowing electrolyte junction. Such solid construction made it a candidate for zero-gravity use. However, it was found to be incompatible with solutions containing silver ions because of leaching of potassium chloride from the electrode body resulting in precipitation of silver chloride in the immediate vicinity of the reference electrode.

The Test Data Matrix was used to facilitate the comparison of the key parameters of each of the four commercial silver-sulfide electrodes and one

experimental solid-state, silver-sulfide electrode. A trade-off analysis was included. On the basis of the data in the test matrix and the assigned weighting factors, the experimental solid-state electrode was selected for further study and testing in the environmental test fixture.

The Technique Testing task provided for the design and fabrication of a test fixture and flow cell to simulate the conditions of temperature, flow, and pressure in the Space Shuttle Potable Water System. As part of the Technique Testing task, 22 solid-state, silver-sulfide (Ag_2S) electrodes, and 4 gel-filled, silver-sulfide electrodes were fabricated and tested. Seven of the solid-state electrodes exhibited semilogarithmic response from 10- to 1000-ppb silver at room temperature (73°F). Two of these exhibited satisfactory semilogarithmic response at 104°F, but at 140°F the performance of these two electrodes was marginal, although response was semilogarithmic from 25- to 1000-ppb silver ion. Room-temperature response of all electrodes after exposure to 140°F was poor, and all exhibited continuous drift. The drift was found to be due to leakage of the test solutions into the interior of the electrode through a temperature-degraded epoxy seal. New electrodes were made with a change in the epoxy cement and electrode body material in an attempt to correct the seal problem.

A number of fabricating techniques were studied in an attempt to improve the solid-state, silver-sulfide electrode. These included sintering of the silver-sulfide pellet, impregnating the pellet with epoxy, forming the pellet under various pressures, and conditioning by soaking in silver solutions. The conditioning by soaking in silver solutions was the only technique which appeared to improve the response characteristics of the solid-state, silver-sulfide electrodes. Using the other techniques did not provide any detectable improvement.

The four gel-filled, silver-sulfide electrodes were made for a comparison of the response characteristics of the gel-filled vs. solid-state configuration. No significant differences were found. The epoxy seals on these electrodes also failed.

New solid-state, silver-sulfide electrodes made with polypropylene bodies and Armstrong adhesive, followed by a conditioning treatment, yielded a high percentage (13 out of 14) of acceptable electrodes with Nernstian response from at least 25 to 1000 ppb $[Ag^+]$ at 77°F when conditioned for 72 hours in a 1000-ppb silver solution at 104°F. Two of these electrodes were evaluated in the test fixture as part of the System Tests.

Five special gel-filled, nonflowing, double-junction reference electrodes were designed and fabricated for evaluation in the test fixture. All five failed when exposed to 140°F. Swelling of the internal gel electrolyte at the elevated temperature caused failure of the glass body. Modification of this reference electrode to provide better thermal stability resulted in an electrode which was both noisy and sensitive to flow and pressure changes.

A new reference electrode--based on a previous Beckman design for use with an Apollo pH water sensor--was designed and fabricated. It was a pressurized double-junction reference with a quartz-fiber junction having a 1.69 x 10^{-3} fl oz per day (50 microliters) flow. The secondary electrolyte was stored in a bellows reservoir.

In the System Tests, the solid-state, silver sulfide and the new reference were tested under varying conditions of temperature (50° to 149°F), pressure (10 to 45 psig), and flow (13 to 60 lb/hr), with solutions containing 25- to 125-ppb silver ion. The response at 10°, 77°, and 113°F was semilogarithmic with less than one-percent noise. The reference electrode was mildly sensitive to changes in pressure and flow, and exhibited maximum apparent offset of less than 15 percent at 25 psig, 60 lb/hr flow at 113°F.

During the system tests, the orientation of the electrode with respect to the sample flow was shown to be critical. Sample flow between the electrodes--rather than past the electrodes in line--resulted in low noise and optimum electrode response.

The use of a silver-bromide/glass-bead column to provide a calibration standard was shown to be feasible for an automatic calibration system.

Based on the requirements of the Space Shuttle Potable Water System, and the data obtained in the development program, an instrumentation package for a monitoring system was defined.

2.0 INTRODUCTION

Results of the McDonnell Douglas 90-day water measurement tests (MDAC Paper WD 1582, April 1971) show that chemical sterilization or bacteriostasis will be required to maintain the potability of water supplies generated by currently-envisioned systems. These tests showed that significant bacterial contamination occurred at several points, but was especially prevalent at the cold-water ports. The use of bactericidal agents in the water supply system would prevent bacterial multiplication in areas of lowered temperature and in areas of potential stagnation and thus, through the elimination of these "seed" populations, preclude back-contamination of the system.

Silver ion has been proposed as such a bactericidal agent for the Space Shuttle, in which the potable supply will probably be a combination of stored and fuel-cell water. However, this agent, as would any other, would require monitoring to ensure that bactericidal levels are achieved and maintained at critical points in the water-supply system, and also to ensure that excessive levels do not occur due to malfunctions of one or more subsystems.

The intent of the Residual Water Bactericide Monitor Development Program was to explore the feasibility of using a potentiometric method for determining silver-ion concentrations in the Space Shuttle Potable Water System. An instrumentation system definition was included in the program and scheduled to follow the demonstration of feasibility. This final report, therefore, contains the results of the development program and includes the instrumentation definition.

B

3.0 CONCLUSIONS

a. A potentiometric method for silver-ion analysis, using an ion-selective electrode, was demonstrated to be feasible for a Residual Water Bactericide Monitor System for the Space Shuttle Potable Water System.

b. A solid-state silver-sulfide sensing electrode was shown to have response characteristics suitable for the Residual Water Bactericide Monitor.

c. The solid-state configuration of the silver-sulfide electrode makes it ideally suitable for zero-gravity use and ability to sustain ±6-g acceleration.

d. A pressurized, double-junction reference electrode having a quartz-fiber junction and sample-pressure equalization was shown to function independent of orientation.

e. The feasibility of the above sensing and reference electrodes to perform under the varying conditions and restrictions of temperature, flow and pressure of the Space Shuttle Potable Water System was demonstrated.

f. The use of a silver-bromide/glass-bead column was shown to be feasible for supplying a solution of known silver-ion concentration as a standard in an automatic calibration system.

4.0 RECOMMENDATIONS

a. It has been shown that the solid-state, silver-sulfide electrode fails at a temperature somewhere between 115° and 149°F. This failure has been related to the degradation of the adhesive/sealant used to retain the silver-sulfide pellet in the electrode body. Further effort should be made to solve this temperature-related problem by investigating the use of other commercial adhesive/sealants and/or the use of primer to promote better adhesion. The use of mechanical seals, such as O-rings, should also be considered as well as materials having similar coefficients of expansion.

b. The current state-of-the-art in the development of solid-state reference electrodes has not produced any reference electrodes which are compatible with the silver-ion solutions in the low parts-per-billion range. The major problem with the current solid-state reference electrodes is the use of a solid electrolyte which reacts with silver ions. The development of a suitable solid-state reference electrode would significantly reduce the complexity of an electrode pair, and reduce the size and weight of the sample cell of the silver-ion monitor. Therefore, it is recommended that a program be conducted to investigate a solid-state reference electrode with an electrolyte compatible with silver-ion solutions.

c. The use of a potentiometric method of analysis for increasing the residual water bactericide (silver ions) in the Space Shuttle Potable Water System has been clearly demonstrated to be feasible. Therefore, it is recommended that a preliminary flight prototype be designed, fabricated and evaluated as the next logical step towards the realization of a flight qualifiable monitor.

5.0 TECHNICAL DISCUSSION

5.1 Space Shuttle Potable Water System Characteristics and Requirements

The following Space Shuttle Potable Water System characteristics and bactericide monitor design guidelines were considered during the course of this development program.

5.1.1 System Characteristics

The Space Shuttle Potable Water System has characteristics as follows:

• Water Supply	From fuel cells
• Supply Flow Rate	8.7 lb/hr (max) at 10 kW
• Fuel Cell Exit Temperature	150° to 175°F
• System Pressure	15 to 60 psia
• pH	6.5 to 7.5
• Water Delivery Flow Rate	Up to 60 lb/hr
• Water Delivery Temperature	
Hot	150° to 160°F
Cold	40° to 60°F
• Water Delivery Pressure	30 psid at 50 lb/hr

5.1.2 Bactericide Monitor Criteria

- It must be highly sensitive and accurate throughout the silver concentration range of 1 to 500 ppb.
- It must provide rapid measurement.
- It must be reliable and repeatable.
- It must be compatible and fully operable in zero g.
- It must be capable of sustaining up to 6-g acceleration in any axis.
- It must be used in a manner consistent with flight safety requirements and mission objectives.
- It must not affect or degrade the operation of any other spacecraft system (considering EMI, impurities into water system, etc.).
- It must be easily calibrated and specific for silver (i.e., no system interference from other water constituents).

5.1.3 Design Considerations

5.1.3.1 Configuration

The configuration of the bactericidal monitoring system should be such that the following Space Shuttle constraints are taken into account:

- Low weight and volume;
- Minimal power requirements;
- Ease in maintenance;
- High reusability rate (i.e., long life time);
- Low cost (both initial and operational costs);
- Zero-g and ±6-g (any direction) application.

The system configuration also should be compatible with the present Space Shuttle Potable Water System concept.

5.1.4 Application Techniques

During space shuttle flights, the bactericide monitoring system must operate automatically, requiring no crew participation for either normal or off-design operation. The flight unit must be fail operational-fail safe.

5.2 Review of Potentiometric Technology

Continuous potentiometric measurement of ion activities or concentration using ion-selective electrodes has been used for many years, especially in the form of pH measurement of the hydrogen and hydroxyl ions. During the past decade there has been an accelerated interest in this technique with the commercial availability of ion-selective electrodes which respond selectively to a large variety of ionic species. The selective response of the ion-selective electrodes arises from the selective exchange or transport of certain ion species from a sample solution through the electrode membrane in the direction containing the lower activity of the mobile ion. Since ions carry a charge, an electrical potential is set up which opposes further ion migration, and eventually an equilibrium is established in which the potential across the membrane is exactly that required to prevent further net movement of ions.

The potential of an ion-selective (sensing) electrode* cannot be measured by itself. It is necessary to have a second (reference) electrode* in the

---

*The term "electrode" is defined as a device by which an electric current passes into or out of a cell, apparatus, or body. In the case of the galvanic cell formed by electrodes for measuring the activity or concentrations of ions (including pH), this electrochemical procedure is called potentiometry. The terminology for the electrodes is as follows:

- The electrode which responds to the ion species of interest is called the SENSING, INDICATING, or MEASURING electrode, i.e., pH or glass electrode, and ion-selective--such as silver sulfide.
- The other electrode is called the REFERENCE electrode. It provides an electrical contact with the test solution through a liquid-liquid junction, and must be of invariant potential with respect to ionic concentration changes of the solution. In addition, the liquid in the reference electrode which contacts the solution must be chemically nonreactive with any of the ions of the test solution.

solution to complete the circuit through the solution to the measuring instrument. The ion-selective electrode and reference electrode--as a pair in an aqueous solution--form a galvanic cell. The two electrodes are connected to a measuring instrument and the potential (EMF) between the electrodes is measured while minimizing any current flow passing through the system (about 10^{-9} ampere should not be exceeded) to approximate as closely as possible the conditions of thermodynamic reversibility. If the electrodes are polarized by too heavy a current flowing in the system, the cell potential will change.

In contrast to other electrochemical terminology, the electrodes for potentiometric measurements or ion-selective electrode measurements are not called anodes or cathodes. In fact, depending on ion concentration, temperature, and choice of reference, the measuring or indicating electrode may be positive or negative with respect to the reference. Also, during a wide change in concentration, the millivolt output of the electrode pair may go from positive to negative or reverse.

The cell potential is dependent on the concentration, or more exactly, the activity or active concentration of the ionic species in the sample solution. The potential-activity relationship is given by the Nernst equation:

$$E_i = E_i^o + \frac{2.3\ RT}{nF} \log a_i$$

where: E_i = electrode potential in millivolts developed by the system.

E_i^o = electrode potential of unit activity, and depends on the choice of reference electrode and also includes a small potential associated with the liquid-liquid junction between the sample and electrolyte of the reference.

R = gas constant

= 8.3143 joules/°K gram-mole

= 1545.3 ft lb_f/lb mole °R (Rankin)

T = Temperature

= °K

= °R = °F + 459.60

F = Faraday

= 96,486.7 (g equiv of electricity)

= 12,157.9 (lb equiv of electricity)

$\frac{2.3\ RT}{nF}$ = Nernst factor, and has a value of 59.16 millivolts at 77°F for a change of one decade in ion activity.

n = ionic charge

a_i = activity of ionic species in solution

As the ion-selective electrodes respond to activity, calibration curves are required to determine concentration. Since the Nernst equation relates the electrical potential (in millivolts) directly to the logarithm of the activity of the silver ion (equivalent to concentration below 10^{-3} molar silver), calibration curves are plotted on semilog paper. If the response of the electrode at 77°F is Nernstian, a straight line plot will result having a slope of 59 millivolts per decade change in silver-ion activity.

When the total ion of interest is free or chemically active, a predictable relationship exists between the ion activity and concentration:

$$a_i = \gamma_i m_i$$

where: a_i = ion activity

γ_i = activity of the ion of interest

m_i = ion concentration

When only a fraction of the total ion is chemically active, the ion-selective electrode gives a direct measurement of the active ion in solution.

The activity coefficient, γ_i, depends upon the total ionic strength of the solution. In infinitely dilute solutions, the activity coefficient can be considered equal to one; activity is then equal to concentration. In very dilute solutions, the activity coefficient can be calculated by the equation derived from the Debye and Huckel limiting law:

$$\log \gamma_i = AZ_i^2 \sqrt{I}$$

where: A = constant which is a function of the temperature and dielectric constant of the solvent. For an aqueous solution at 77°F, A is equal to 0.511.

Z_i = charge of the ion.

I = ionic strength of the solution defined by Lewis and Randall as

$$I = \frac{1}{2}\sum m_i Z_i^2$$

Ion-selective electrodes are subject to specific interferences, and a response may be obtained for ions other than the specific ionic species for which the electrode is relatively selective. These interferences can arise from two sources. The first type occurs when the interfering ion enters the membrane and contributes to the diffusion process. Interferences of this type do not occur with solid-state crystal electrodes. The strict requirements in the size and shape of the diffusing ion prevent all but the measured ion from moving through the crystal.

A second source of interference occurs when there are surface reactions with interfering ions. In this case, the degree of interference can be generally established by the following equation:

$$E = E_o + \frac{2.303\ RT}{Z_m F} \left[\log a_m + K_i a_i \right]$$

The selectivity constant, K_i, is defined as the ratio of the solubility products, K_{sp}, for the particular salts.

If the above formula were to be applied for the chloride-ion electrode, bromide being the interfering ion, the K_i value would be the ratio of the solubility products for silver chloride over silver bromide, or

$$1.8 \times 10^{-10} / 5.2 \times 10^{-13} = 3.5 \times 10^{2}$$

The value of this solubility constant shows that, in general, the solid-state crystal electrodes cannot be used in solutions containing large amounts of an ion that reacts to form a more insoluble compound than the solid crystal itself.

It is apparent that the degree of interference will increase with the activity and the K value of the interfering ion. Highly-selective electrodes will show very low K values for interfering ions. Thus, when significant specific interferences are present, accurate direct measurements may not be possible unless the K values and the activities of the interfering ions are known and appropriate correction applied.

In the case of the solid-state, silver-sulfide electrode for the measurement of silver ion, the silver-sulfide pellet at the tip of the electrode is the ion-selective or permeable membrane (see Section 5.3.1.3).

The potentiometric cell formed by the silver-sulfide electrode and reference electrode for the measurement of silver ions is:

Ag: Ag_2S/Test Sample/Reference Electrode

The reaction at the silver-sulfide (indicator) electrode surface is:

$$Ag^{+}_{(SOL)} \rightleftharpoons Ag^{+}_{(Ag_2S)}$$

$$Ag^{+}_{(Ag_2S)} + e \rightleftharpoons Ag_{(Solid)}$$

The double arrows indicate reversibility of the reactions as well as equilibrium.

5.3 The Silver-Sensing Electrode

5.3.1 Technique Selection

5.3.1.1 General

Theoretically, a potentiometric method of analysis utilizing solid-state, ion-selective electrodes should be the best candidate for monitoring the silver-ion concentration in the low ppb range in a Space Shuttle Potable Water System. Manufacturers claim sufficient sensitivity--10^{-7} molar (10 ppb)--for silver, using silver-sulfide electrodes. A few authors claimed to have substantiated such claims. To provide NASA with such a potentiometric technique, the answers to two basic questions were needed.

- Would commercially-available, silver-sulfide electrodes actually be capable of detecting silver ions in the 10-ppb level or lower?
- Could solid-state, silver-sulfide electrodes be made which would have electrochemical characteristics equivalent to or better than the commercially-available electrodes?

Favorable answers to these two questions would show the feasibility of potentiometric methods utilizing solid-state, ion-selective electrodes.

The technique selection was divided into three subtasks:

- Establish current state-of-the-art and test commercially-available electrodes;
- Design and fabricate electrodes to extend state-of-the-art;
- Perform screening tests to evaluate functional performance.

All of the above subtasks deal with ion-selective, silver-sensing electrodes. Because the actual performance of these subtasks overlapped or were carried out simultaneously, the following paragraphs are not addressed to each subtask separately but to the variance procedures which provided the selection of a technique.

The selection test program was designed to permit selection of the optimal electrode (silver sulfide) design (or designs) which would be suitable for use in the silver-ion monitoring system for the Space Shuttle Potable Water System.

5.3.1.2 Establishment of the State-of-the-Art

As part of the program to establish the state-of-the-art, a literature review was made which did not add to the information already available in company files, but did locate data establishing the manufacturers' claims of Nernstian response for the silver-sulfide electrodes down to silver-ion concentrations of 10^{-7} molar (10 ppb). The techniques used were generally titration methods. The instability of low ppb silver solutions was well noted in the literature, and the only methods found for stabilizing the low ppb silver solutions were those which complexed the silver ion with organic chelating agents. Such stabilized solutions were not suitable for potentiometric measurements because the silver ions are not free, but bound to the organic molecules.

5.3.1.3 Electrode Configuration

The four commercial electrodes evaluated were the Beckman Sulfide Electrode No. 39610; the Corning Sulfide Electrode No. 476129; the National Instrument Lab (NIL) Direct Reading Sulfide Electrode No. 5-2602; and the Orion Silver/Sulfide Electrode No. 94-16. Each of these electrodes had a silver-sulfide membrane at the tip of the electrode, connected to an internal reference electrode by an internal filling solution (Figure 5-1). The NIL electrode was of the Pungor type and had the silver sulfide dispersed in a rubber-like polymer, while all others used a solid-silver-sulfide pressed pellet or membrane. Such a configuration was not considered suitable for zero-gravity use or ±6-g acceleration because of the filling solution. The construction of the experimental solid-state, silver-sulfide electrode is shown in Figure 5-2a and Figure 5-2b. The solid-state configuration makes it ideally suited for space use.

The literature contained several indications that a composite membrane containing both silver sulfide, Ag_2S, and silver iodide, AgI, and identified as silver sulfide iodide, Ag_3SI, would be more sensitive to silver ions in solution and have faster response than the Ag_2S electrode. A few experiments were made to verify such claims. The solid-state electrodes containing the Ag_3SI pellet exhibited lower sensitivity to silver ions than the commercial electrodes, so evaluation was stopped. For the remainder of the program, only silver-sulfide electrodes were evaluated.

5.3.1.4 Evaluation of the Electrodes

5.3.1.4.1 Introduction

The procedure for evaluation of the electrodes was the same for both the commercial ion-selective electrodes and the experimental electrodes.

The electrodes were first tested for their response characteristics, then assigned a weighting factor as a result of a study of their configuration

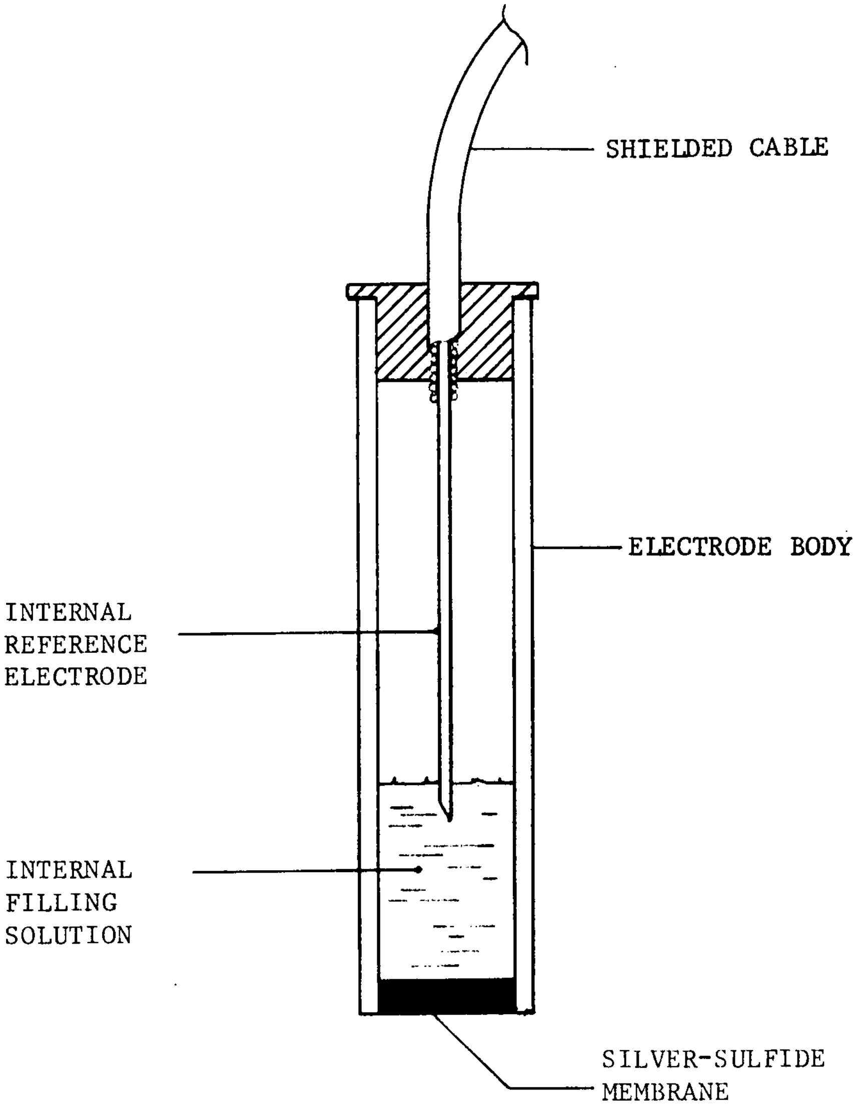
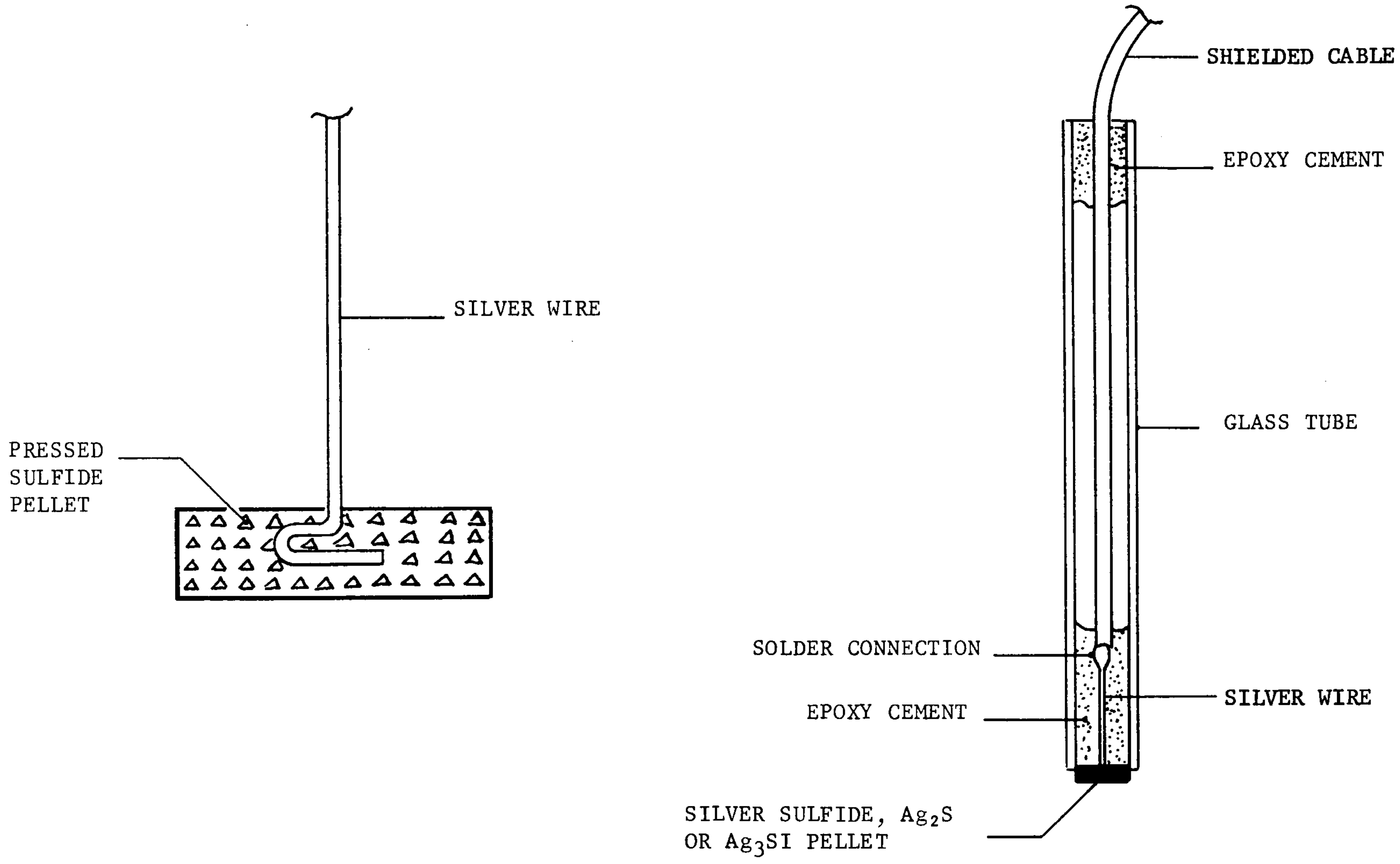


Figure 5-1. Commercial Silver-Sulfide Electrode Showing Internal Filling Solution



a. Cross-Section of Experimental Solid-State Sulfide Pellet and Connecting Wire

b. Construction Detail

Figure 5-2. Solid-State, Silver-Sulfide Electrode in relation to their use in zero gravity and ability to sustain a ±6-g acceleration (Figures 5-1 and 5-2). The response characteristics of interest were:

- Sensitivity
- Accuracy
- Precision
- Response Time
- Specificity

5.3.1.4.2 Test Procedures

The test procedures for all the electrodes were the same. Originally, the procedure as outlined in the Master Test Plan, TM-122T, followed the general laboratory use for ion-selective electrodes as recommended by electrode manufacturers, which included stirring the solution and using a double-junction reference of the sleeve type with a potassium nitrate, KNO_3, solution as the secondary electrolyte. To expedite the testing of four commercial electrodes and a larger number of experimental electrodes, it was proposed to use an electrode switch; this permitted testing four electrodes at a time in the same beaker.

The sleeve-type, double-junction reference caused errors and drift (see Section 5.4). The electrode switch introduced noise and was useless because four electrodes plus a reference in the test solution at one time appeared to cause more rapid absorption of the silver ions than occurred with one electrode and reference. As a result, a downward drift of response occurred in solutions below 100-ppb silver. The original procedure also called for washing the electrode tips with distilled water and blotting with absorbent tissue. This technique also was found to cause errors and drift.

After numerous tests and changes, the final procedure adopted used only one sensing electrode and a reference with a salt bridge having a porous ceramic junction and containing one molar potassium nitrate. Silver-ion solutions containing 100 ppb or lower were prepared by diluting the 1000-ppm silver Atomic Absorption Standard immediately before use. Both electrodes were dip-rinsed with a portion of the next test solution, which was then discarded. Sensitivities on the lower limit of Nernstian response and the lower limit of useful response were determined by performing measurements on silver-ion solutions from 10- to 1000-ppb silver. These data were then plotted on semilog paper; any deviation from a straight line with other than 59 millivolts-per-decade concentration change was interpreted as poor response, poor sensitivity, or both. Accuracy was established using dilutions of the A.A. Standard (HARLECO)* as reference.

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*Silver Standard, 1000 ppm Ag; Salt silver nitrate ($AgNO_3$); HARLECO, 60th & Woodland Avenue, Philadelphia, Pennsylvania

Precision was determined by replicate inter- and intra-daily measurements. The response time was obtained from a strip chart recording of electrode response beginning with the immersion of the electrode pair in the test solution. Dip-rinsing of the electrode between samples was not used for the response-time tests, since it would have resulted in erroneous response times.

All evaluation tests were performed in a glass beaker using a Teflon-coated magnet stirring bar and magnetic stirrer. Temperature was monitored and found to be 75 ±1.8°F.

5.3.1.4.3 Standard and Calibration Solutions

In order to evaluate ion-selective electrodes, a number of standard or calibration solutions covering the range of interest were required. Such solutions must be stable and the concentration of the ion of interest must be accurately known. Thus, standard solutions covering the range of 1- to 10,000-ppb of silver ion were required to evaluate both the commercial silver-sulfide electrodes and the experimental solid-state electrodes.

Initially, a stock solution of $AgNO_3$ containing 500-ppm silver was prepared by standard gravimetric techniques and stored in a brown bottle. The stock solution was kept for five days only, then discarded. Serial dilutions were made of the stock solution covering the range of 1- to 10,000-ppb silver. These solutions were used immediately to measure the electrode response and to prepare a calibration and response plot. After a proper measuring technique was developed, most of the commercial electrodes were shown to exhibit Nernstian or near-Nernstian response between 10,000 and 100 ppb (Figures 5-3 and 5-4). In Figure 5-3 the response data points for the Corning electrode, marked by a square, show two data points not on the response line. The data point for the 5,000-ppb silver-ion concentration was doubtful due to continued shifting of the reading. Thus, that particular data point was discounted and a straight line drawn through the remaining data points in an apparent best fit. Below 100 ppb, the calibration or response plots showed nontypical and doubtful response. The experimental electrode exhibited near-Nernstian response from 10,000 to less than 50 ppb. (The observed nontypical and doubtful response was thought to be due to poor stability of the silver solutions below 100 ppb.) Also, attempts to use these same but fresh, serially-diluted solutions for stability studies and electrode precision studies resulted in data showing a continuously drifting response indicating a rapid depletion of the silver ion from the solution. The use of saturated solutions of silver bromide and silver chloride did not solve the problem since they were temperature-sensitive and gave 73-ppb silver for the saturated solution of silver bromide and 1453-ppb silver for the saturated solution of silver chloride at 77°F.

In an attempt to prepare standard solutions which were both stable and of known silver concentration, the principles of the solubility product constant and common-ion effect were utilized. Solutions containing accurately-measured amounts of potassium bromide, KBr, were saturated with silver bromide, AgBr, by adding an excess of the solid. The silver-ion concentration was calculated using the solubility product constant, or K_{sp}, for silver bromide

$$K_{sp} = \left[Br^-\right] \times \left[Ag^+\right]$$

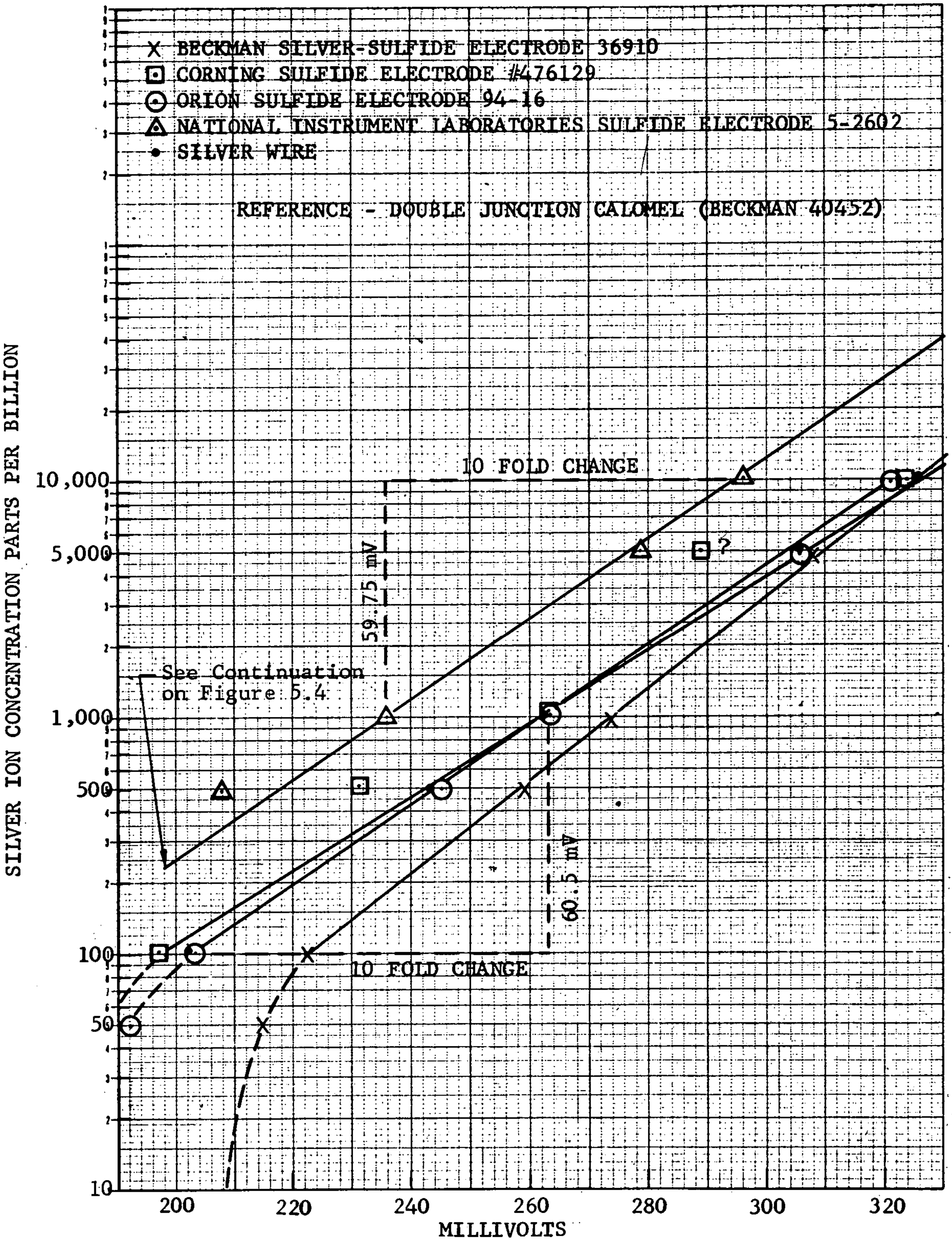

Figure 5-3. Response of Commercial Silver-Sulfide Electrodes Versus Silver-Ion Concentration

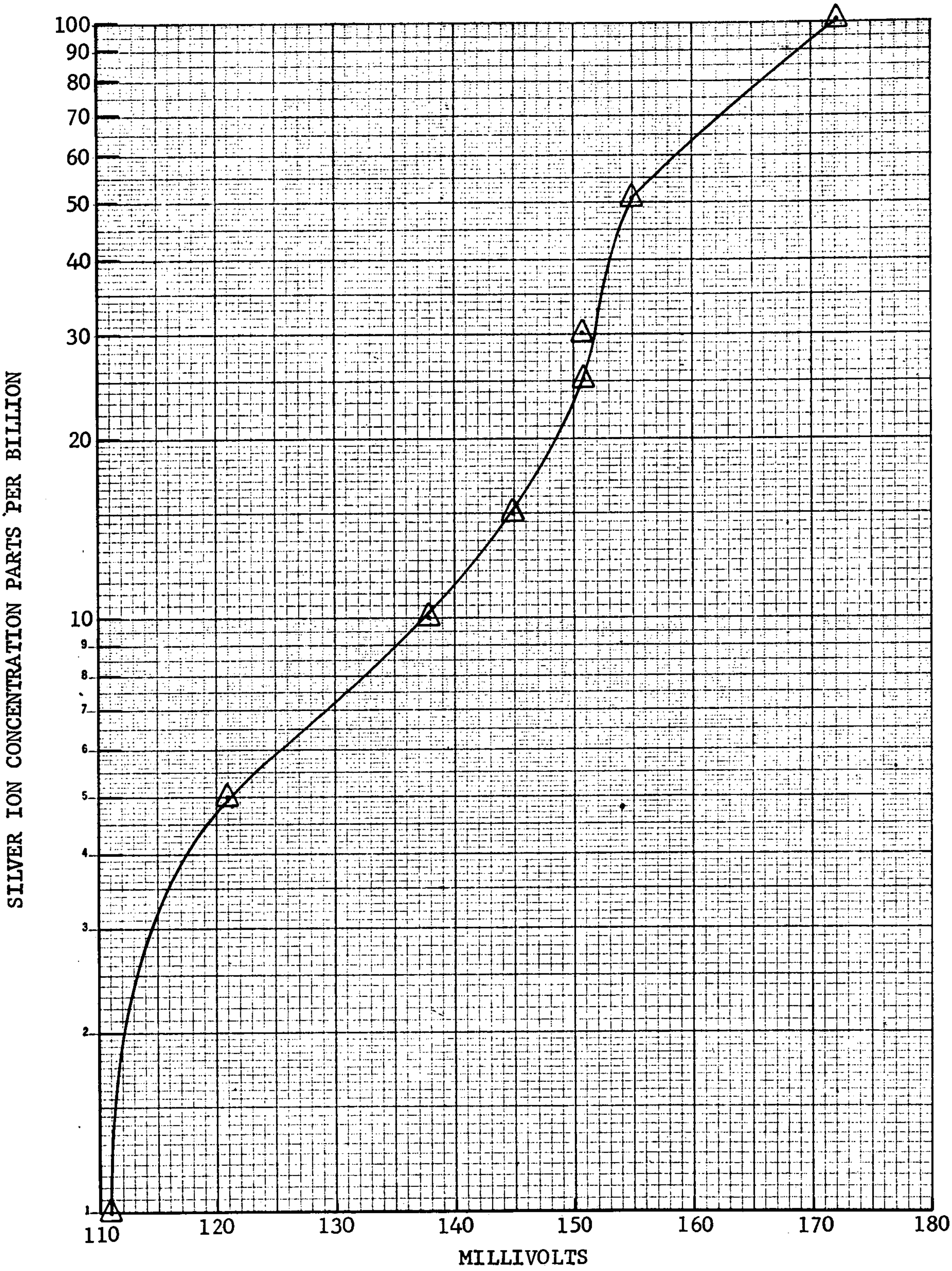

Figure 5-4. NIL Sulfide Electrode Response Versus Silver-Ion Concentration (1 to 100 ppb)

and for the concentration of the silver ion,

$$\left[Ag^+\right] = \frac{K_{sp}}{\left[Br^-\right]}$$

The K_{sp} for silver bromide is listed as 7.7×10^{-13} in the Handbook of Chemistry and Physics. Therefore, a 10^{-6} molar solution of potassium bromide containing an excess amount of solid-silver bromide should contain the bromide, $\left[Br^-\right]$, from the KBr plus the bromide from the solid AgBr which dissolved.

If x is amount of AgBr dissolved,

then $\left[Ag^+\right] = x$

$$\left[Br^-\right] = 10^{-6} + x$$

since $\left[Ag^+\right] \times \left[Br^-\right] = 7.7 \times 10^{-13}$

$$(x)\left(10^{-6} + x\right) = 7.7 \times 10^{-13}, \text{ or}$$

$$x^2 + 10^{-6}x - 7.7 \times 10^{-13} = 0$$

solving the quadratic for x

$$x = +0.51 \times 10^{-6}$$

Thus, the total $\left[Br^-\right] = 1 \times 10^{-6} + .51 \times 10^{-6} = 1.51 \times 10^{-6}$

then $\left[Ag^+\right] = \frac{K_{sp}}{\left[Br^-\right]} = \frac{7.7 \times 10^{-13}}{1.51 \times 10^{-6}} = 5.1 \times 10^{-7}$ molar

or 55-ppb silver. The calculations take into account the amount of bromide ion contributed by the silver bromide which has dissolved.

The stabilized solutions and silver-nitrate solutions were used to prepare a response and calibration plot for each electrode. The observed responses for the electrodes were non-Nernstian but proportional to log of $\left[Ag^+\right]$ activity. However, in most instances, two straight-line, nonintersecting plots for each electrode resulted, one line between 50- and 1000-ppb silver showing the electrode responses in the silver nitrate solutions, and another almost parallel line between 0.55 and 5.5 ppb showing the response of the electrodes in the KBr/AgBr (solid) solutions, as shown in Figure 5-5.

To check the electrode responses, a switch was made to solutions prepared by serial dilution of a 1000-ppm silver Atomic Absorption Standard.

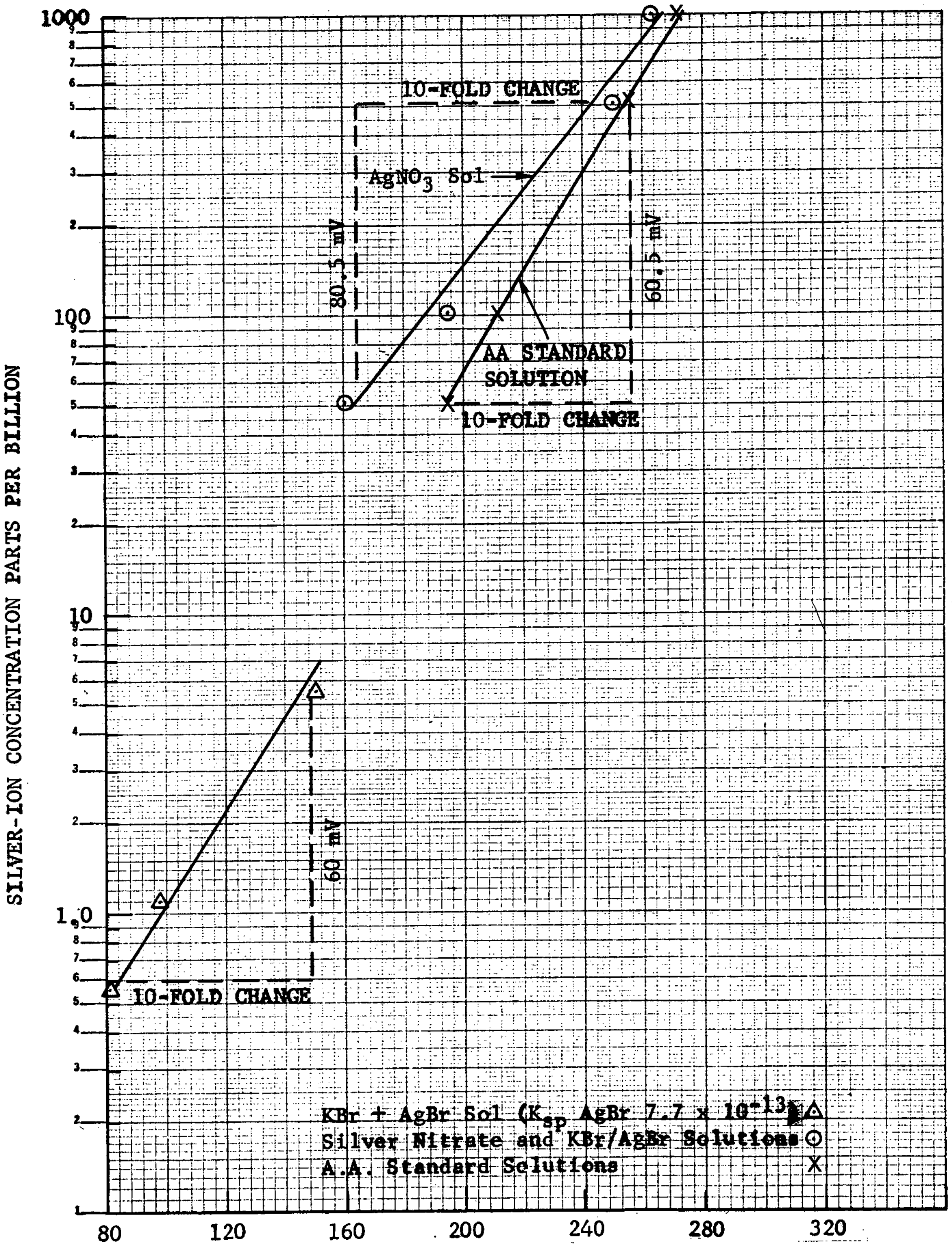

Figure 5-5. Typical Electrode Response (Orion Electrode)

A plot of the electrode responses based on the A.A. Standard solution showed a different response than with the supposedly equivalent silver-nitrate solutions. Two of the commercial silver-sulfide electrodes exhibited Nernstian response between 50 and 1000 ppb. The experimental solid-state electrode 1B also showed Nernstian response in the same range.

The response of the electrodes in the A.A. Standard-based solutions was then plotted, together with the electrode responses in the KBr/AgBr (solid) solutions. Again, two nonintersecting straight lines resulted, each having a slope of 60 mV per decade change in silver-ion concentration (Nernstian response), Figure 5-5. Theoretically, a straight line plot should have resulted from 0.55 to 1000 ppb. The reason for the offset of the KBr/AgBr (solid) solution response line from that of the A.A. Standard response line is not known, but could very likely result from impurities in either or both the KBr and AgBr. Because of this, no attempt was made to connect the lines from both solutions. It is apparent, however, a straight line could be drawn through both sets of data points with reasonable fit. The response of the Beckman electrode in the KBr/AgBr (solid) solutions was almost identical to the responses of other electrodes, which indicated a good possibility that it, too, has Nernstian response between 0.55- and 1000-ppb silver.

The response of the electrodes in the silver-nitrate solutions showed a significant difference from the response obtained with the dilutions of the A.A. Standard, and was thought to be the result of contamination of the distilled water with chlorides causing a reduction of the ionic concentration of silver by forming insoluble silver chloride. However, the same distilled water was used to dilute the A.A. Standard; thus, the reason for this discrepancy remains unclear. Further tests showed that all electrodes exhibited Nernstian response from 50- to 10,000-ppb silver ion when dilutions of the A.A. Standard were used. Therefore, it was decided that all further testing would be made using the A.A. Standard dilutions.

Further attempts were made to determine the reason for the poor correlation between the electrode responses in the silver-nitrate solution and the dilutions of the A.A. Standard. A number of solutions used to determine the electrode responses were sent to a commercial laboratory for analysis for silver. A standard concentration and X-ray fluorescence method was used. The results were not reliable, especially when the results showed less than 1-ppb silver for a saturated solution of silver chloride. Two of the samples submitted were from the same bottle of KBr solution, saturated with AgBr, and showed 13- and 22-ppb silver. The reason for the anomalous results is not clear, since the laboratory which performed the tests has been found to be very reliable over a number of years. Atomic absorption spectroscopy would have been used except that neither the local commercial laboratories nor Beckman's Application Laboratory was set up for low-ppb silver determination.

5.3.1.5 Electrode Evaluation Summary and Configuration Selection

The test data for the evaluation of the four commercial silver-sulfide electrodes and one experimental solid-state, silver-sulfide electrode were summarized in a Test Data Matrix (Table 5-1). The matrix contains actual

	COMMERCIAL SILVER SULFIDE				EXPERIMENTAL
	1	2	3	4	
Electrode Configuration*	Beckman	Corning	Orion	NIL	1B
1. Lower Limit of Nernstian Resp. (ppb)	1 (50)	1 (50)	1 (50)	1 (50)	2 (50-100)
2. Lower Limit of Useful Detectability (ppb)	2 (50)	2 (50)	2 (50)	1 (<50)	2 (50)
3. Precision (C.V. %)					
500 ppb	3 (0.98)	2 (0.72)	4 (1.09)	5 (1.29)	1 (0.23)
100 ppb	5 (4.54)	2 (1.05)	4 (1.8)	3 (1.06)	1 (0.7)
50 ppb	5 (6.92)	3 (2.74)	4 (4.04)	2 (1.54)	1 (0.97)
25 ppb 10 ppb 5 ppb 1 ppb	Questionable Stability and Concentration of Solutions				
4. Response Time, 10-500 ppb (seconds)					
90%	(<3)	(1)	(1.5)	(<1)	(10)
95%	3 (5.5)	2 (5.5)	1 (6)	4 (8)	5 (18)
99%	(18)	(16)	(14)	(20)	(54)
Response Time, 500-10 ppb (seconds)					
90%	(13)	(28.5)	(17)	(5)	(36)
95%	3 (33)	4 (45)	2 (24)	1 (14.5)	5 (81)
99%	(80)	(80)	(54)	(32)	(144)
5. Calibration Stability ±0.5 mV/minutes 50 ppb Solution	4 (36)	2 (60)	1 (72)	5 (20)	3 (48)
6. Zero-g Use	5	5	5	5	0
7. Zero-g Modification Feasibility	2	2	2	5	0
8. ±6-g Use	1	1	1	1	0
9. ±6-g Modification Feasibility	1	1	1	2	0
10. Impedance (Ohms)	4 (11K)	3 (7.0K)	1 (3.5K)	5 (140K)	2 (4.5K)
11. Points Summary[1]	(39)	(30)	(29)	(40)	(22)

*Keyed to Sensor:Reference Pair.

1 - Lowest Total Points Indicates Electrode with Best Feasibility for Zero Gravity Use.

Table 5-1. Test Data Matrix--Silver-Ion Detection by Potentiometric Electrodes test data values in parentheses and a weighted numerical figure derived in conjunction with NASA for each test of each electrode. The assignment of a weighting factor for each test was made such that the sum of the weighted figures for each electrode would indicate a relative order of feasibility for the five electrodes. Therefore, the electrode with the lowest total points would be most feasible for the intended use.

A brief explanation of the individual tests and assignment of a weighting factor for each is given in the following paragraphs.

5.3.1.5.1 Lower Limit of Nernstian Response

The electrode with lowest ppb Nernstian response was assigned a value of 1; that electrode with highest ppb response was given a value of 5, since five electrodes were evaluated. Other electrodes were assigned intermediate values. Data were based on using A.A. Standard solutions, serially diluted.

5.3.1.5.2 Lower Limit of Use (Non-Nernstian but Linear) Detectability

The electrode with lowest ppb reliable detectability was assigned a value of 1, while that electrode with least sensitive (or highest ppb) detectability was given a value of 5. Other electrodes were assigned appropriate intermediate values.

5.3.1.5.3 Precision

The electrode exhibiting lowest coefficient of variation (C.V.) for six separate samples of three concentrations (500, 100, and 50 ppb) was assigned a value of 1, while that electrode exhibiting the highest coefficient of variation was assigned a value of 5. Electrodes with intermediate coefficients were given intermediate values. Separate samples of each concentration were used for each measurement.

5.3.1.5.4 Response Time

Electrodes were tested for response times under two conditions:

- 50-ppb silver solution to 500-ppb;
- 500-ppb silver solution to 50-ppb.

Between solutions, the electrode pair (reference and sensing) were lightly blotted to remove excess sample before immersing in the next solution. Again, values 1 through 5 were assigned, with the fastest response time being assigned a value of 1.

5.3.1.5.5 Calibration Stability

Since the 50-ppb silver-ion solution was the lowest concentration which appeared to have both stability and apparently reliable known concentration, it was used for stability tests. Each of the test pairs was immersed in this solution and electrode response recorded until a drift of ±0.5 mV was noted following stabilization. At the 50-ppb level, 0.5 mV was equivalent to 1-ppb silver. The electrode with the longest recorded stability time was assigned a value of 1, the shortest stability time a value of 5, and the others assigned appropriate intermediate values.

5.3.1.5.6 Zero-Gravity Use

From the known and manufacturer's published physical configuration data, each electrode was evaluated as to its zero gravity use in terms of yes or no. Since the reliable application of any chosen electrode in zero gravity is of prime consideration, a yes answer was assigned a value of 0, while a no answer was assigned a value of 5.

5.3.1.5.7 Zero-Gravity Modification Feasibility

The feasibility of modifying existing electrodes was considered. Again, the importance of zero-gravity application was indicated by a 0 for that electrode(s) not requiring modification for zero-gravity use, a 2 for those considered practical for modification, and a 5 for those believed not feasible for modification due to specific physical properties. The Beckman, Corning, and Orion commercial electrodes were assigned a value of 2 by reason that the plastic body could be modified and a gel could replace the liquid filling solution. The NIL electrode was assigned a value of 5 since the body was glass and the rubber matrix containing the silver-sulfide membrane would not likely be suitable for the temperatures and pressures required in the bactericide monitor.

5.3.1.5.8 ±6-g Use

The same provisions and assignment of values used for zero-gravity use were utilized for the ±6-g use. A value of 0 was assigned if electrode configuration was suitable for ±6-g use, and a 1 was assigned if configuration was not suitable for ±6-g use.

5.3.1.5.9 ±6-g Use Modification Feasibility

The electrodes requiring no modification for ±6-g use were assigned a value of 0; those electrode configurations which could possibly be modified by use of gel and modification of plastic body were assigned a value of 1; the electrode having a poor modification feasibility was assigned a value of 2.

5.3.1.5.10 Electrode Impedance

The very low silver-ion concentrations anticipated in the potable water system in conjunction with the purity of the water would result in a liquid system having a very high impedance or low conductivity. Whenever a potentiometric electrode measuring system is used in such a high impedance system, a certain amount of noise is inherent in the system with the impedance of the electrode system contributing to the overall noise.

Thus, as a factor in the evaluation of a silver-sensing electrode system, the impedance of both the sensing and reference electrodes should be considered.

The impedance or resistance of each of the silver-sulfide electrodes has been measured. The higher the impedance, the higher the assigned value. The measured impedance for each electrode is given in ohms in parentheses in Table 5-1.

5.3.1.5.11 Summary

The selection of an electrode configuration was preceded by an evaluation of the data presented in the Test Data Matrix. The Points Summary of the matrix was found to be an effective means of rating the electrodes in relation to their feasibility for the intended use.

The characteristics of the electrodes were reviewed in relation to the order of importance assigned by NASA. In descending order, these were:

1. Zero gravity use
2. Calibration stability
3. Precision
4. Lower limit of useful detectability
5. Response time

On the basis of the weighted scores (Points Summary), the solid-state, silver-sulfide electrode was selected as the sensing electrode for further testing in the environmental test fixture.

5.3.2 Technique Testing

5.3.2.1 Electrode Configuration

The solid-state, silver-sulfide electrode was chosen as the configuration for further testing. The solid-state construction requirements are very simple and yield a very reliable, rugged electrode with very few restrictions on the physical configuration.

The sensing electrode consists of a silver-sulfide pressed pellet with a section of the connecting silver wire as an integral part of the pellet. The exposed portion of the silver wire is soldered to a suitable shielded cable. The pellet and adjacent cable were sealed into a polyvinyl chloride (PVC)* body with epoxy cement. Figure 5-6 shows the configuration as well as the dimensions of the silver-ion sensing electrode. The diameter of the silver-sulfide pellet for the previously reported experimental electrode was 0.35 inch, while the diameter for the test fixture design was reduced to 0.21 inch. The response of the silver-sulfide electrode is not a function of its exposed surface.

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*The configuration of the solid-state, silver-sulfide electrode at the completion of the contract included a polypropylene body.

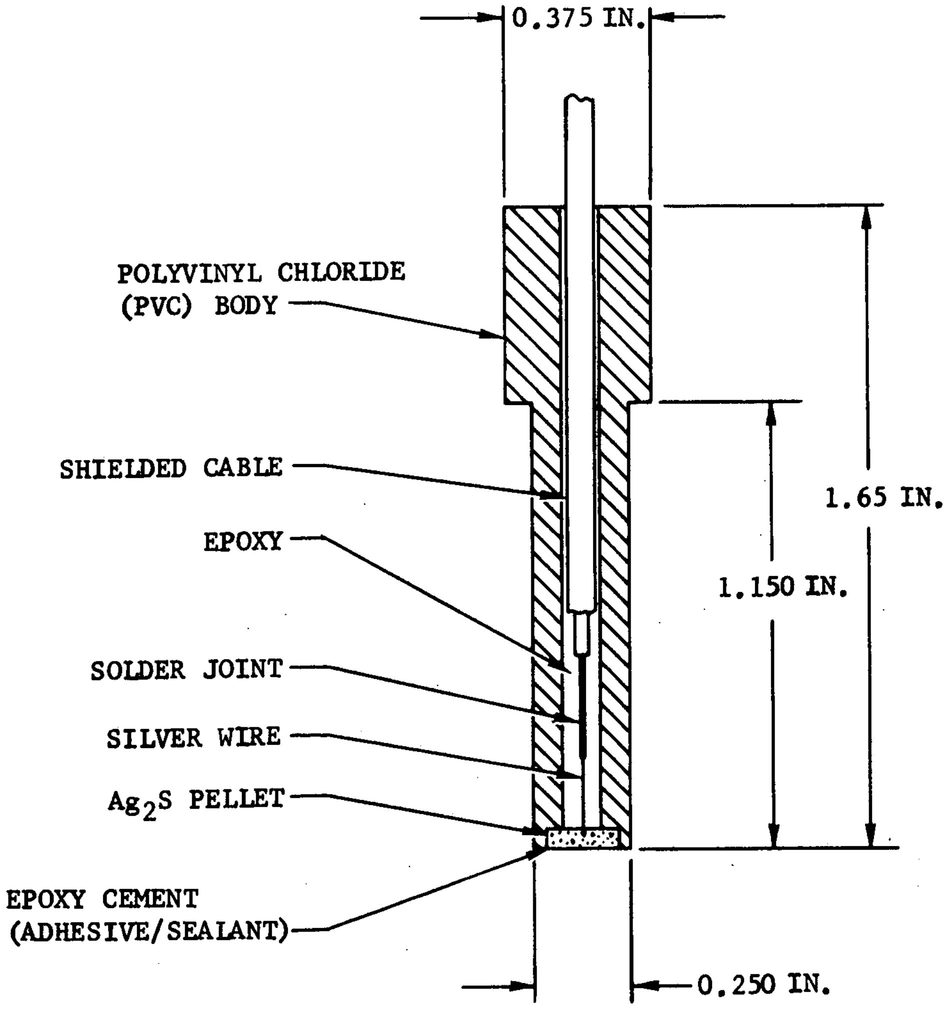

Figure 5-6. Solid-State Silver-Sulfide (Ag_2S) Electrode

5.3.2.2 Baseline Parameters

To obtain a more complete set of key parameters against which subsequent procedures could be evaluated, the initial portion of technique selection established system parameters under ideal laboratory conditions at a constant ambient temperature. Parameters which were studied are:

- Sensitivity--established by performing measurements on serial dilutions from 500-ppb silver ion to the lower limit of detection;
- Accuracy--established by use of a silver Atomic Absorption Standard;
- Precision--established by replicate inter- and intra-daily series;
- Response Time--as defined by response to a change in concentration at the sensor.

5.3.2.3 Electrode Response vs. Fabrication Technique

Beckman has been concerned with the development and fabrication of pellet-type electrodes for several years, being one of the leading innovators in the field. Drawing upon these years of experience, the fabrication techniques employed to obtain the initial electrodes proved to be highly successful and demonstrated the promise of this type of sensor. However, these early electrodes were obtained on a low-yield basis and it was thought that certain additional procedures in the fabrication process might enhance the yield of the electrodes as well as their overall sensitivity and Nernstian range. A number of these procedures were studied as summarized in the following sections. Since they are largely independent of one another, the order in which they are presented does not necessarily represent a sequential development process. In the interests of time conservation, several of the modifications were evaluated in parallel.

In most cases two or more electrodes were fabricated and/or conditioned and tested as a group or in an identical manner in an attempt to eliminate errors in evaluation due to spurious electrode responses.

The C series was fabricated first, using fabrication parameters known to be satisfactory in the fabrication of similar configured electrodes. Electrodes C1 through C5 exhibited different sensitivities (slope in mV per decade change in silver-ion concentration) and a wide range of offset potentials (see mV response at 1000 ppb). The responses of these electrodes were non-Nernstian, and the lower limit of acceptable response was 100 ppb or higher for C2 through C5. Refer to Table 5-2.

A number of reports on various types of pH and ion-selective electrodes indicated that numerous types of electrodes require a conditioning treatment in a solution containing the ion(s) of interest. The conditioning treatment facilitates the achievement of equilibrium of the ions within the sensitive part of the electrode and usually results in a change-of-response characteristics such as: greater sensitivity; a shift-of-response slope to Nernstian or near-Nernstian; and greater stability (less noise and drift.) Electrodes C6 through

				RESPONSE AT ROOM TEMPERATURE (73°F)							RESPONSE AT 104°F								RESPONSE AT 140°F							
																	RESPONSE AT 73°F AFTER 104°F								RESPONSE AT 73°F AFTER 140°F	
ELECTRODE IDENTIFICATION	TYPE (1) SOLID STATE-FILLED	PELLET FORMING PRESS. X 10^3 PSIG	SPECIAL PELLET TREATMENT OR ELECTRODE TREATMENT	TRIAL	SLOPE (2) mV/DECADE	REFERENCE ELECTRODE (3)	SEMI-LOGARITHMIC RANGE PPB $[Ag^+]$	mV FOR 1000 PPB $[Ag^+]$	REPEATABILITY (4)	RESPONSE CURVE SHAPE	TRIAL	SLOPE mV/DECADE	REFERENCE ELECTRODE	SEMI-LOGARITHMIC RANGE PPB $[Ag^+]$	mV FOR 1000 PPB $[Ag^+]$	RESPONSE CURVE SHAPE	SLOPE	SEMI-LOGARITHMIC RANGE PPB $[Ag^+]$	TRIAL	SLOPE mV/DECADE	REFERENCE ELECTRODE	SEMI-LOGARITHMIC RANGE PPB $[Ag^+]$	mV FOR 1000 PPB $[Ag^+]$	RESPONSE CURVE SHAPE	SLOPE	SEMI-LOGARITHMIC RANGE PPB $[Ag^+]$
C1	SS	116	KI SOLUTION SOAK AFTER EXPOSURE TO AgBr	1 2	54 81	R1 R1	30-1000 25-10.000	178 179	- P	STRAIGHT STRAIGHT	-	---	--	---	---	---	SLOPE CHANGES AFTER EXPOSURE TO AgBr					---	--	---	--	---
C2	SS	116	NONE	1	66	R1	100-10.000	315	-	ANGLED	-	---	--	---	---	---	NON-LINEAR RESPONSE BELOW 100 PPB AT 73°F						--	---	--	---
C3	SS	116	NONE	1	72	R1	500-10.000	323	P	ANGLED	-	---	--	---	---	---	NON-LINEAR RESPONSE BELOW 500 PPB AT 73°F						--	---	--	---
C4	SS	116	NONE	1	72	R1	500-10.000	324	P	ANGLED	-	---	--	---	---	---	NON-LINEAR RESPONSE BELOW 500 PPB AT 73°F						--	---	--	---
C5	SS	116	NONE	1	84	R1	250-10.000	187	-	ANGLED	-	---	--	---	---	---	NON-LINEAR RESPONSE BELOW 250 PPB AT 73°F						--	---	CONTINUOUS DRIFT (5)	
C6	SS	116	16 HRS IN 1000 PPB $[Ag^+]$ BEFORE 73°F TEST	1 2	67 67	R1 R1	10-1000 20-1000	293 301	F	STRAIGHT STRAIGHT	-	---	--	---	---	---	--	---	-	--	--	---	--	---	CONTINUOUS DRIFT (5)	
C7	SS	116	16 HRS IN 1000 PPB $[Ag^+]$ BEFORE 73°F TEST	1 2	65 65	R1 R1	10-1000 10-1000	237 235	G	STRAIGHT STRAIGHT	1	?	PP	POOR		ERRATIC	59	100-1000	-	--	--	---	--	---	CONTINUOUS DRIFT (5)	
C8	SS	116	1 HR IN 1000 PPB $[Ag^+]$ BEFORE 73°F TEST	1	55	R1	250-10.000	282	-	ANGLED	-	---	--	---	---	---	NON-LINEAR RESPONSE BELOW 250 PPB AT 73°F						--	---	--	---
C9	SS	116	1 HR IN 1000 PPB $[Ag^+]$ BEFORE 73°F TEST	1 2	57 54	PP PP	100-1000 50-1000	465 495	F	STRAIGHT STRAIGHT	1	61	R1	50-1000	339	STRAIGHT	57	10-1000	1	77	R2	25-1000	315	STRAIGHT	ERRATIC-DRIFTING	
C10	SS	116	AFTER 104°F TEST - 3 HRS AT 140°F IN 1000 PPB $[Ag^+]$	1 2	48 52	PP PP	25-1000 10-1000	455 459	F	STRAIGHT	1	98	R1	100-1000	320	BENT	58	25-1000	1	--	R2	ERRATIC	--	---	CONTINUOUS DRIFT	
C11	SS	116	AFTER 104°F TEST - 4 HRS AT 140°F IN 1000 PPB $[Ag^+]$	1 2	59 74	PP PP	10-1000 10-1000	457	P	STRAIGHT STRAIGHT	1	73	R1	25-1000	295	CURVED	58	10-1000	-	--	--	---	--	---	CONTINUOUS DRIFT (5)	
C12	SS	116	AFTER 104°F TEST - 4 HRS AT 140°F IN 1000 PPB $[Ag^+]$	1 2	63 54	PP PP	10-1000 25-1000	443 442	P	STRAIGHT STRAIGHT	1	116	R1	---	382	CURVED	48	10-1000	-	--	--	---	--	---	CONTINUOUS DRIFT (5)	
C13	SS	116	AFTER 104°F TEST - 4 HRS AT 140°F IN 1000 PPB $[Ag^+]$	1 2	54 54	PP PP	100-1000 10-1000	393 393	G	ANGLED STRAIGHT	1	121 75	R2	50-250 250-1000	304	ANGLED	41 55	10-100 100-1000	-	--	--	---	--	---	CONTINUOUS DRIFT (5)	
F1	SS	116	PELLET IMPREGNATED WITH EPOXY	1 2	50 72		10-100 100-1000	-- --	G	ANGLED	-	---	--	---	---	NOT TESTED ABOVE 73°F BECAUSE OF ABNORMAL RESPONSE							--	---	--	---
F2	SS	116	PELLET IMPREGNATED WITH EPOXY	1	69		10-1000	365	G	STRAIGHT	1	58	R2	10-500	200	STRAIGHT	61	10-1000	1	95	R2	50-1000	197	STRAIGHT	55	25-500
G1	F	116	NONE					---	-	---	-	---	--	---	---	---	--	DEFECTIVE ELECTRODE			--	---	---	---	--	---
G2	F	116	NONE	1	68	PP	25-1000	280	F	STRAIGHT	1	88	R2	50-1000	122	STRAIGHT	NOT DONE		1 1	56 70	R2 R2	10-250 250-1000	89	ANGLED	61	25-1000
G3	F	116	AFTER 73°F TEST - 140°F 4 HRS IN 1000 PPB $[Ag^+]$	1	54	PP	10-1000	312	G	STRAIGHT	-	---	--	---	---	---	--	---	-	--	--	---	---	---	CONTINUOUS DRIFT (5)	
G4	F	116	AFTER 73°F TEST - 140°F	1	58	PP	10-1000	315	G	STRAIGHT	-	---	--	---	---	---	--	---	-	--	--	---	---	---	CONTINUOUS DRIFT (5)	
P1050	SS	29	PELLET FORMING PRESSURE VARIED												DEFECTIVE ELECTRODE - NO RESPONSE TO CHANGE OF SILVER-ION CONCENTRATION											
P2100	SS	58	PELLET FORMING PRESSURE VARIED	1	62	PP	50-500	394	F	ANGLED						HI AND LOW CONC. IN FAR NON-LINEAR REGION										
P3150	SS	87	PELLET FORMING PRESSURE VARIED	1	24	PP	---	303	-							POOR SENSITIVITY - NOT TESTED ABOVE 73°F										
S4	SS	116	PELLET HEATED 297°F 3 HRS IN N_2 ATMOS.	1 2	61 74	R1 R1	100-1000 25-1000	147 136	P	--						POOR RESPONSE AFTER EXPOSURE TO AgBr										
S2-16	SS	116	PELLET HEATED 392°F 16 HRS IN N_2 ATMOS.	1	15	R1	---	234	-							VERY POOR SENSITIVITY										
S4-6	SS	116	PELLET HEATED 815°F 6 HRS IN N_2 ATMOS.	1	51	R1	250-10.000	162	-	ANGLED						NON-LINEAR RESPONSE BELOW 250 PPB AT RT										
S6-3	SS	116	PELLET TEMP. RAISED TO 1112°F OVER 3 HRS - N_2 ATMOS.	1	52	R1	500-10.000	220	-	ANGLED						NON-LINEAR RESPONSE BELOW 500 PPB AT RT										

(1) SS - SOLID STATE (Ag_2S) FIGURE 5-6
F - GEL FILLED FIGURE 5-7

(2) SLOPE = MILLIVOLTS (MV) CHANGE PER 10 FOLD CONCENTRATION CHANGE

(3) PP = PERMA PROBE WITH 1M KNO_3 SALT BRIDGE
R1-R2 = SPECIAL DOUBLE JUNCTION REFERENCE

(4) P = POOR
F = FAIR
G = GOOD

(5) THESE ELECTRODES EXPOSED TO 1000 PPB $[Ag^+]$ AT 140°F FOR FOUR HOURS AFTER THE 73°F OR 104°F TEST FOR THERMAL STABILITY TEST. AS NOTED IN TEXT ALL FAILED.

Table 5-2. Silver-Ion Electrode Evaluation Data

C13 were subjected to various conditioning treatments after fabrication, in the same manner as electrodes C1 through C5, and tested at 63°, 104°, and 140°F. Response of electrodes generally indicated that as a result of exposure to 1000-ppb silver solution at room temperature for 16 hours, or 104°F for 1 to 4 hours, the response characteristics improved, i.e., became essentially Nernstian (58 mV/decade), or the low ppb portion of the semilogarithmic response line became straight. Note 73°F response after exposure to 104°F for electrodes C7, 9, 10, and 11 in Table 5-2. However, all these electrodes failed when exposed to 140°F due to adhesive/sealant degradation. These tests indicated that a conditioning process significantly enhances electrode response characteristics. The conditioning parameters (silver-ion concentration time and temperature) did not appear to be critical.

A parallel development effort considered the effects of pellet porosity on electrode response time. The solid-state silver-sulfide pellets made for the majority of the sensing electrodes described in this report were formed under very high pressure--116,000 psig. However, porosity could slow the response time of the electrode by retaining a portion of a previous liquid sample which would need to be replaced by the new sample before proper response could be obtained. Some porosity always exists, and it was thought that perhaps porosity effects could be minimized by impregnating the silver-sulfide pellet with wax or epoxy cement. To test this theory, two electrodes were fabricated in the identical manner as the C series electrodes, with the exception that the silver-sulfide pellets were vacuum impregnated with an epoxy cement which was allowed to cure for 24 hours.

After conditioning in 1000-ppb silver at 104°F, one of the epoxy-impregnated electrodes exhibited abnormal response which could not be explained. The other electrode exhibited Nernstian response (58 mV per decade), but its response time, as well as all other characteristics, was essentially the same as the C series electrodes. These epoxy-impregnated electrodes are identified in Table 5-2 as F1 and F2.

The use of a gel electrolyte in place of a liquid electrolyte in a silver-sulfide electrode was considered as a means of making the electrode independent of orientation and capable of sustaining a ±6-g load. Such electrodes were investigated in a parallel effort. Figure 5-7 shows the configuration of the gel-filled electrodes. The gel-filled electrodes G2 through G4 exhibited essentially the same characteristics as the solid-state electrodes. Electrode G2 exhibited semilogarithmic response from 25- to 1000-ppb silver ion, but the slope was 9 millivolts per decade above theoretical at room temperature, while at 104°F the response was 25 millivolts per decade above theoretical. At 140°F, the response of G2 was non-Nernstian and had two response slopes (56 mV for 10- to 250-ppb silver-ion concentration, and 70 mV for 250- to 1000-ppb silver ion). It should be noted that after the 140°F test, the room-temperature response had changed to near theoretical (61 mV per decade) from 25- to 1000-ppb silver ion.

The electrodes of the P series were made using silver-sulfide pellets formed at 25-, 50-, and 75-percent of the standard pressure (116,000 psig). The variation of pressure was investigated because certain proprietary documents

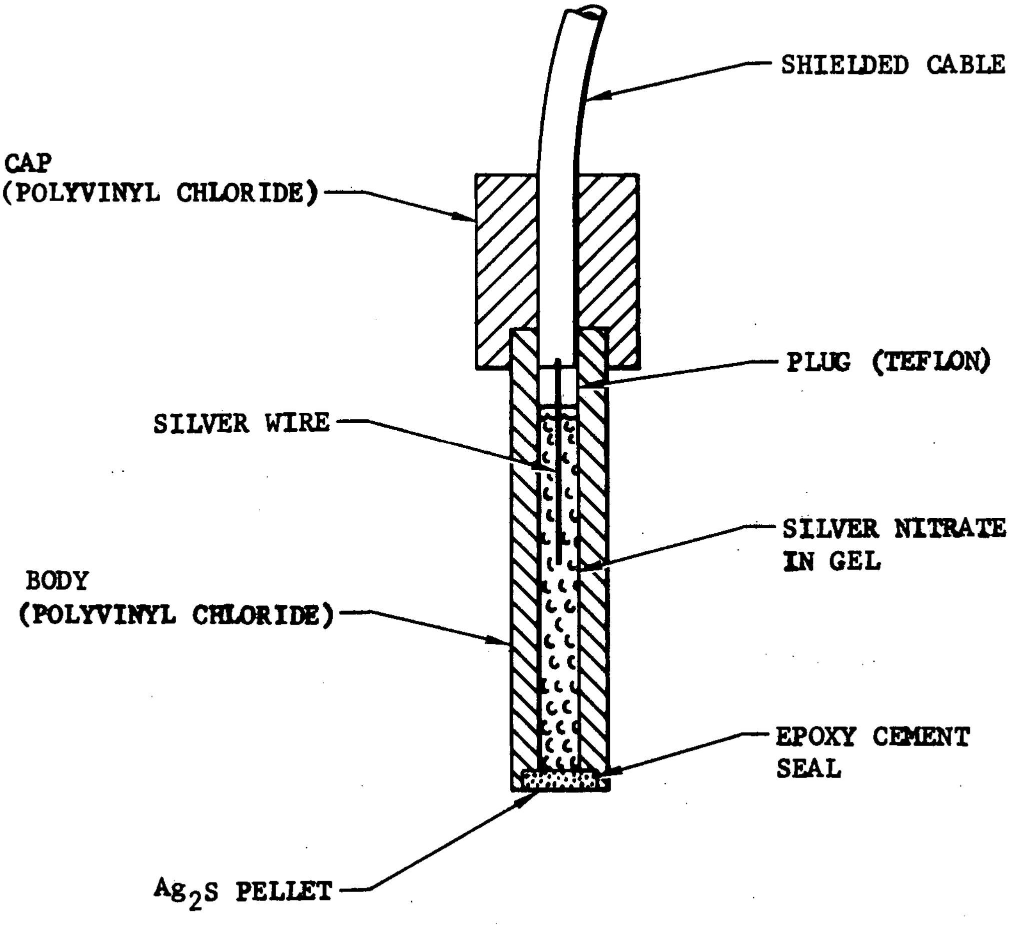

Figure 5-7. Gel-Filled Silver-Sulfide (Ag_2S) Electrode

indicated that certain kinds of pressure-formed pellets exhibited optimum electrical characteristics over a specific range of forming pressures, and this is usually not the highest attainable forming pressure. These lower pressures yielded electrodes with unsatisfactory responses.

Another fabrication technique investigated in parallel was the heat treatment or sintering of the silver-sulfide pellet after pressing (identified as the S series electrode in Table 5-2), based on instructions given in a paper by H. Hirata and K. Higashiyama.* These authors claimed better sensitivity and stability due to the heat treatment. It is a known fact that in the fabrication of the silver-sulfide pellet, severe stresses are built up in the pellet and silver wire by the very high pressure used (116,000 psig), which could be responsible for the high offset potential observed (compare the millivolt response at 1000 ppb for C, F, and G series electrodes with the S series electrodes in Table 5-2). The lower millivolt responses of the S series indicated that the heat treatment did relieve the stress within the silver wire and pellet.

Although the four S electrodes were fabricated at the same time with apparently identical materials and techniques, except for the heat treatment, a variety of responses was observed. One electrode exhibited an initial near-Nernstian response, 61 mV per decade, but changed to 74 mV per decade with semilogarithmic response from 25- to 1000-ppb silver ion. Two others exhibited semilogarithmic response between 250 or 500 ppb with a 52 mV-per-decade sensitivity. The fourth electrode exhibited very poor response with 15 mV-per-decade sensitivity.

Electrodes which, at 73°F, exhibited a sensitivity to silver ion of 100 ppb or lower with semilogarithmic response were also tested at 104° and 140°F. With the exception of electrodes F2 and G2, all those electrodes tested at 140°F were found to have failed due to the thermal degradation of the adhesive/sealant (Epoxylite 8751) used to retain the silver-sulfide pellet in the body of the electrode. The electrode failure was indicated by their erratic and/or continuous drift of response when retested at 73°F. Physical examination as well as sectioning and microscopic study showed that the adhesive/sealant failed at the interface of the polyvinyl chloride (PVC) electrode body and the silver-sulfide pellet. The failure of the epoxy cement permitted the silver test solutions to seep into the interior of the electrode, thus interfering with the development of the potential across the permeable membrane, the silver-sulfide pellet. In addition, the solution which had seeped into the electrode probably emerged slowly and mixed with subsequent silver solutions at the surface of the electrode, causing drift.

The fact that two electrodes (F2 and G2) did not fail at 140°F showed that occasionally a satisfactory seal could be made between the polyvinyl chloride body and silver-sulfide pellet by using Epoxylite 8751 cement. However, the data clearly indicate that reliable combinations of such materials cannot be expected.

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*TALANTA, Vol. 391-398, 1972

The evaluation of the C series electrodes indicated that the general technique used to fabricate these electrodes was satisfactory, but that a conditioning procedure was required to obtain optimum response (Nernstian response, 59 mV-per-decade change in silver-ion concentration, with sensitivity to 10 ppb or lower). The other fabrication techniques evaluated did not provide any definite improvement in the response characteristics or the stability of the electrode.

A revised fabrication technique was developed, based on the data and experience obtained during the evaluation of the electrodes just described. The new technique included the following:

- A change of electrode body material from polyvinyl chloride to polypropylene which was given a chromic acid etch to provide a better bonding surface;
- Adhesive/sealant changed from Epoxylite 8751 to Armstrong A-12;
- Silver-sulfide pellet solvent cleaned just prior to cementing in electrode body;
- Exactly-defined procedures for each fabrication step;
- A conditioning treatment, following fabrication, which consisted of soaking in 1000-ppb silver-nitrate solution at 104°F for 72 hours.

  The conditioning treatment parameters were empirically selected.

Two batches of electrodes were fabricated using the new technique. These electrodes were designated as the D and H series, with the only difference between them being the date of fabrication. Fourteen electrodes were fabricated and all but one exhibited Nernstian or very near Nernstian response at 77°F. Six exhibited semilogarithmic sensitivity from 10 to 1000 ppb $[Ag^+]$, while seven had a sensitivity range of 25 to 1000 ppb $[Ag^+]$. One failed to respond to the conditioning treatment. Two of these electrodes were used in the evaluation test in the test fixture in combination with the QJPE reference electrode. Figure 5-8 shows a typical plot of the electrode response of the D and H series electrodes before and after conditioning.

5.3.2.4 Electrode Fabrication Technique

1. Prepare fresh silver-sulfide powder. (Beckman proprietary information.)
2. Prepare silver wire, 0.025-inch diameter by 0.5 inch. (Beckman proprietary information.)
3. Place wire in 0.215-inch-diameter pellet die.
4. Weigh out 200, ±5 milligrams silver sulfide and place in pellet die.
5. Place ram in die.
6. Place die in hydraulic press and attach die connector to vacuum pump.

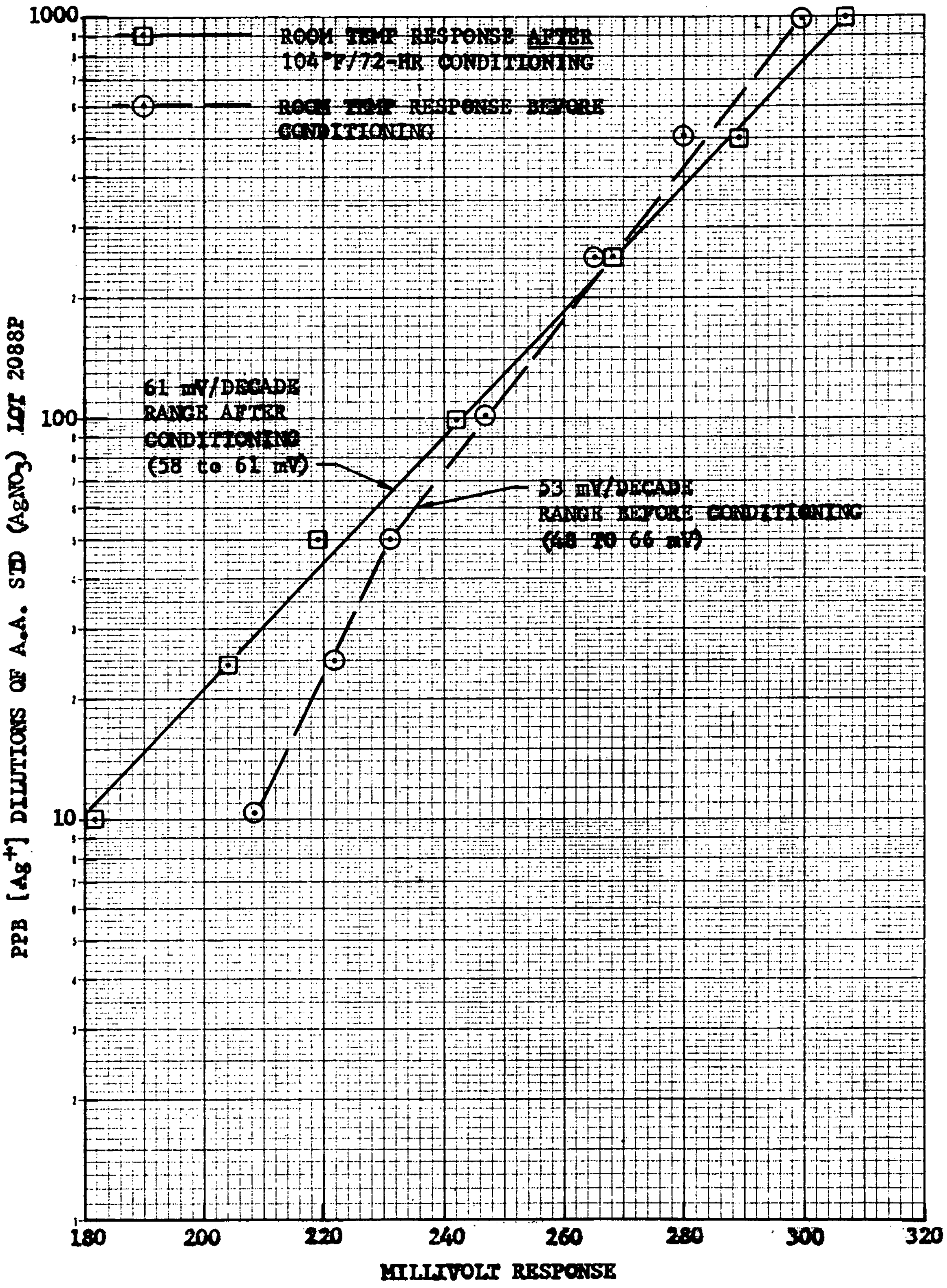

Figure 5-8. Typical Response of "D" and "H" Series Solid-State Silver-Sulfide Electrodes Before and After Conditioning

7. Apply vacuum, minimum 25 in. Hg.

8. Build up pressure to a maximum of 116,000 psig over a period of 5 seconds.

9. After 2.5 minutes, release vacuum.

10. Release pressure after 5 minutes.

11. Remove formed pellet with integral silver wire from die.

12. Clean pellet and wire in reagent-grade acetone.

13. Prepare polypropylene electrode body as follows:

    a. Etch in chromic acid 3 hours at room temperature;
    b. Wash in distilled water;
    c. Soak in distilled water 3 hours with 3 changes of water;
    d. Dry overnight at 100°F.

14. Prepare shielded cable, Belden 8216 RG-174/U, as shown in Figure 5-9:

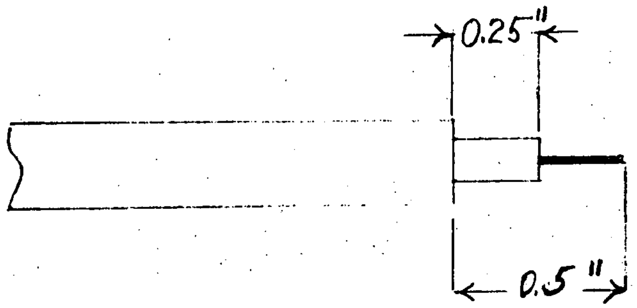

Figure 5-9. Shielded Cable Preparation

    a. Remove 0.5-inch outer covering and braided shield.
    b. Expose 0.25 inch of inner conductor, as shown.

15. Solder silver wire, exposed above the silver-sulfide pellet, to the exposed inner conductor of the cable.

16. Protect solder joint from contamination, moisture, etc. (Beckman proprietary information.)

17. Cement silver-sulfide pellet in electrode body with appropriate adhesive/sealant.*

18. Cure adhesive/sealant as per manufacturer's instructions.

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*Epoxy Cements, Epoxylite 8751, and Armstrong A-12, found unsatisfactory above 115°F for this application.

19. Condition electrode in 1000-ppb silver nitrate ($AgNO_3$) solution for 72 hours at 104°F.

20. Cool to room temperature, then rinse with distilled water.

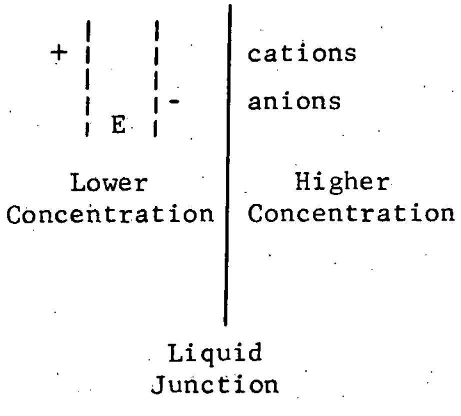
21. Check sensitivity between 10- and 1000-ppb silver ion. Should be between 58 and 61 mV per decade at 77°F.

5.4 The Reference Electrode

5.4.1 Function

The primary function of a reference electrode is to provide an invariant electrical connection with the liquid sample. It completes the electrical circuit from the solution to the measuring instrument. It establishes a reference potential against which the indicator or sensing electrode is measured. The reference electrode must have a stable, constant potential. Its potential must not change when placed in different sample solutions. It must equilibrate rapidly with different solutions.

To keep the potential constant, the reference electrode must be surrounded by a solution having a constant silver-ion concentration. If this is done, the solution around the reference electrode differs from that around the indicator solution. A liquid-to-liquid contact must be established between these two solutions. This is known as a <u>liquid junction</u>. Because ions are electrically charged and have differing diffusion mobilities, an electrical potential can arise at a liquid junction. This is referred to as liquid-junction potential. The origin of liquid-junction potential is shown schematically in the sketch below.



The driving force for ions to diffuse is the concentration gradient. The net diffusion of ions is from the higher to lower concentration. If the cations move faster than the anions, there is a net separation of charge with the lower-concentration solution becoming positive with respect to the higher-concentration solution. This potential will tend to slow down the diffusion cations and speed up the diffusion of anions until at equilibrium the potential balances out the differing driving forces of cation and anion. This is expressed by the equation for liquid-junction potential for a uni-uni valent salt:

$$E_{e.j.} = \frac{RT}{F} (t_+ - t_-) \ln \frac{C_2}{C_1}$$

where t_+ and t_- are the fraction of electricity carried by the cation and anion, respectively, and

C_1 and C_2 are the lower and higher concentrations, respectively.

It can be seen that any fluctuations in the concentration gradient (e.g., by stirring) will cause fluctuation in liquid-junction potential.

One of the ways to minimize liquid-junction potentials is to use, as the electrolyte surrounding the reference electrode, a high concentration of a salt having equal mobilities of cation and anion (e.g., potassium chloride or potassium nitrate). If the concentration of this salt is high compared with that of the sample, most of the electrical charge across the liquid junction will be carried by the ions of the reference electrode. Since the mobilities of cation and anion in this solution are about equal, the separation of charge and liquid-junction potential is minimized. To minimize contamination of sample solution with reference electrode electrolyte, the liquid junction is made as small as possible. A small, pore-size opening at the liquid junction also minimizes fluctuations in liquid-junction potential when the sample solution is mixed.

5.4.2 Originally-Proposed Reference Electrode

The Beckman Perma-Probe reference electrode was originally proposed for the silver-ion monitoring system because it is a solid-state, nonflowing reference and ideally suited to zero-gravity application. However, the active tips of the electrode contain solid potassium chloride, KCl, which can be leached very slowly from its matrix when in contact with a solution. Although the amount of potassium chloride which can be leached at one time is very small, there is, apparently, an adequate amount of soluble chloride to react with silver ions forming insoluble silver chloride. When in contact with low ppb silver-ion solution, the amount of potassium chloride available would react with the silver and significantly reduce the level of ions.

In order to isolate the KCl from the test solution, the Perma-Probe was tested using a 1M potassium nitrate (KNO_3) salt bridge (Figure 5-10). This configuration exhibited a high impedance which resulted in noise in excess of 2 mV in silver solutions below 100 ppb. Consequently, a Beckman 49052 double-junction calomel reference with 1M KNO_3 in the outer bridge was used with the silver-sulfide electrodes on the general recommendation of manufacturers of such electrodes. Until recently, it was believed that this reference was suitable for the application. However, after observing continuous electrode

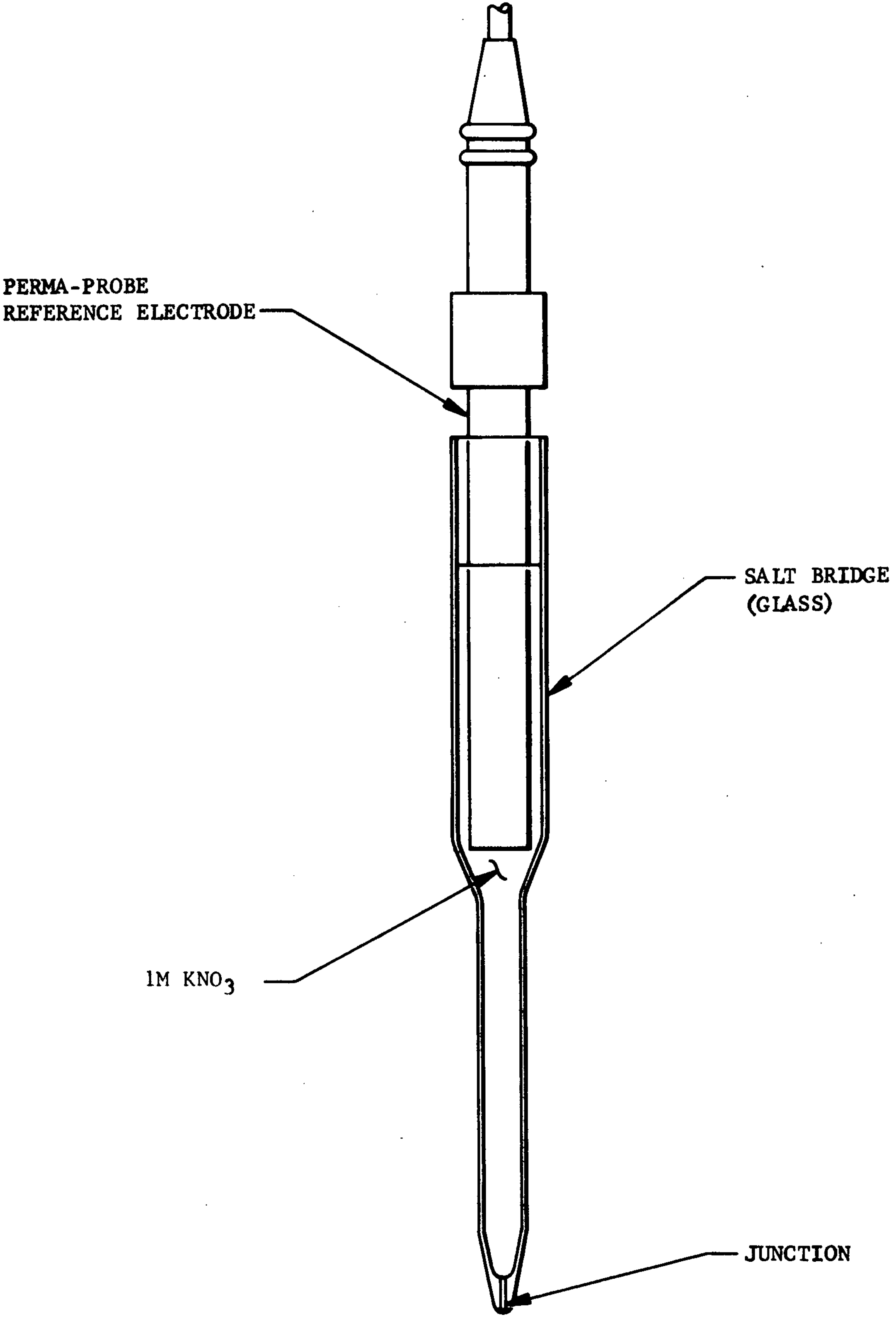


Figure 5-10. Perma-Probe Reference Electrode and Salt Bridge

response drift in stabilized silver solutions, further experiments were conducted as described below.

A silver-sulfide electrode and a standard calomel reference in a 1M KNO_3 salt bridge were immersed in a continuously stirred 50-ppb silver solution. After the response of this pair had reached a stabilized reading, the tip of an electrically-isolated Beckman 40452 double-junction reference was immersed in the solution. Immediately, the response of the measuring pair went from 163 millivolts to 152 millivolts, or an indicated change of 12-ppb silver at the 50-ppb silver level.

A second experiment allowed the double-junction reference electrode to remain in the solution while the stability of the measuring electrode pair was recorded. A continuous drift was observed.

Five reference electrode configurations were then evaluated on the basis of two key parameters:

- Effective impedance in 50-ppb silver solutions--a low impedance is required to avoid excessive noise;
- Minimum liquid-junction flow or leaching of electrolyte--required to minimize contamination of sample with electrolyte which can immediately alter the ionic concentration of the sample.

Two liquid junctions were evaluated, each having a 0.375-inch-diameter coarse frit and backed up with an agar gel containing either silver chloride or potassium chloride. Although these junctions were nonflowing, the chloride electrolyte was readily leached from the agar.

Two variations of the salt bridge shown in Figure 5-10 were evaluated. These utilized two varieties of ceramic frit and provided very low flow, but exhibited very high impedances when used with standard reference electrodes. The high observed impedances resulted from the long path between liquid junction and reference.

The third configuration, which was satisfactory for a beaker test, is shown in Figure 5-11. This configuration utilized a very small, low frit junction with a very short distance between the junction and the reference, thus reducing the electrical impedance yet providing very low sample contamination.

5.4.3 A Reference Electrode for the Test Fixture

5.4.3.1 Original Double-Junction Reference Test Fixture Configuration

A double-junction reference electrode suitable for zero-gravity use was designed for use in the test fixture. The reference was essentially a silver/silver-chloride electrode within a second housing. In place of the normal liquid electrolyte, the electrolyte in both sections was in the form of a gel. The outer housing electrolyte was a saturated potassium nitrate gel. The liquid junctions between the inner and outer housings and the outer housing and the sample liquid were porous ceramic rods. The housing of

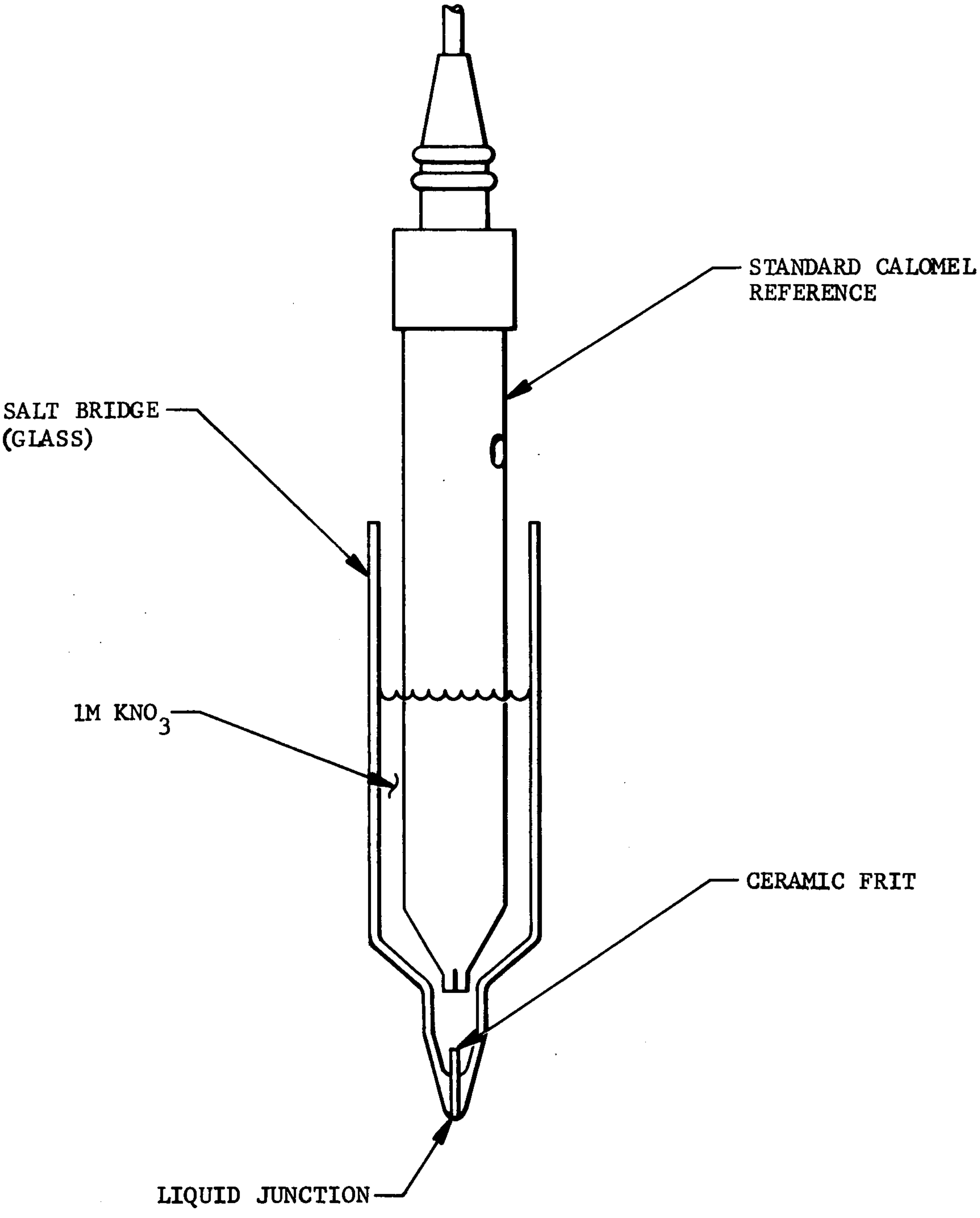


Figure 5-11. Configuration of Third Salt Bridge and Reference Configuration

this electrode was glass, but it is feasible to make the housing out of a strong plastic in the interest of reliability and safety. Figure 5-12 shows the configuration and the dimensions of the reference electrode.

Initial evaluation of this reference electrode indicated a very noisy electrode which was also sensitive to changes in sample flow or stirring if in a beaker. The noise may be described as mixing noise at the liquid-liquid junction between the sample and electrode internal electrolyte. The total ionic concentration of the solution being measured also had an effect on the observed noise. The higher the total ionic concentration (lower specific resistance), the lower the noise level or effect of flow changes.

In order to reduce the mixing noise at the liquid junction, a fine mesh nylon cloth was placed over the tip of the reference electrode. This modification reduced both noise and sensitivity to stirring rate changes (Figures 5-13a and 5-13b).

Since the main purpose of the nylon mesh was to reduce liquid mixing at the liquid-liquid junction, while maintaining low impedance liquid contact, it was believed that a thicker but coarser weave cloth would perform better. Thus, a 5/16-inch-diameter disc of 0.05-inch-thick coarse weave, glass cloth was cemented on the tip of the reference. This modification significantly reduced the potential offset change due to stirring rate changes, but did not reduce the noise any more than did the nylon mesh. This is illustrated in Figures 5-13b and 5-13c.

To determine the effect of the modification of the reference in reducing noise and sensitivity to actual flow changes, the electrode pair was placed in the test fixture and the following test performed. The flow rate of the test fluid--saturated silver-bromide solution--was varied from slow flow (17.5 lb/hr) to near maximum flow (52.5 lb/hr) at constant temperature and pressure (73°F and 10 psig). A maximum of a 3-percent or 4.2-millivolt change was observed which corresponds to an error of approximately 8-ppb silver at a 75-ppb silver level due to flow changes. The recorded data are shown in Figure 5-13d. The wide trace indicates a high-frequency instrument noise equal to about 3-ppb silver concentration. Proper grounding and shielding of leads reduced this noise to an insignificant level prior to performing the regular test-fixture tests.

Five of these double-junction reference electrodes were fabricated and utilized during the evaluation of the solid-state, silver-sulfide electrodes dicussed earlier in this report. These electrodes were identified as R1 through R5.

All five electrodes functioned satisfactorily at room temperature and 104°F, but on exposure to 140°F, four of the electrodes failed as a result of the outer housing breaking and completely falling away from the inner electrode. Electrode R2, however, survived several hours at 140°F but eventually cracked, resulting in very noisy and erratic electrode-pair response.

The failure of these reference electrodes was attributed to the swelling of the two filling gels at the elevated temperature of 140°F without sufficient allowance for the expansion.

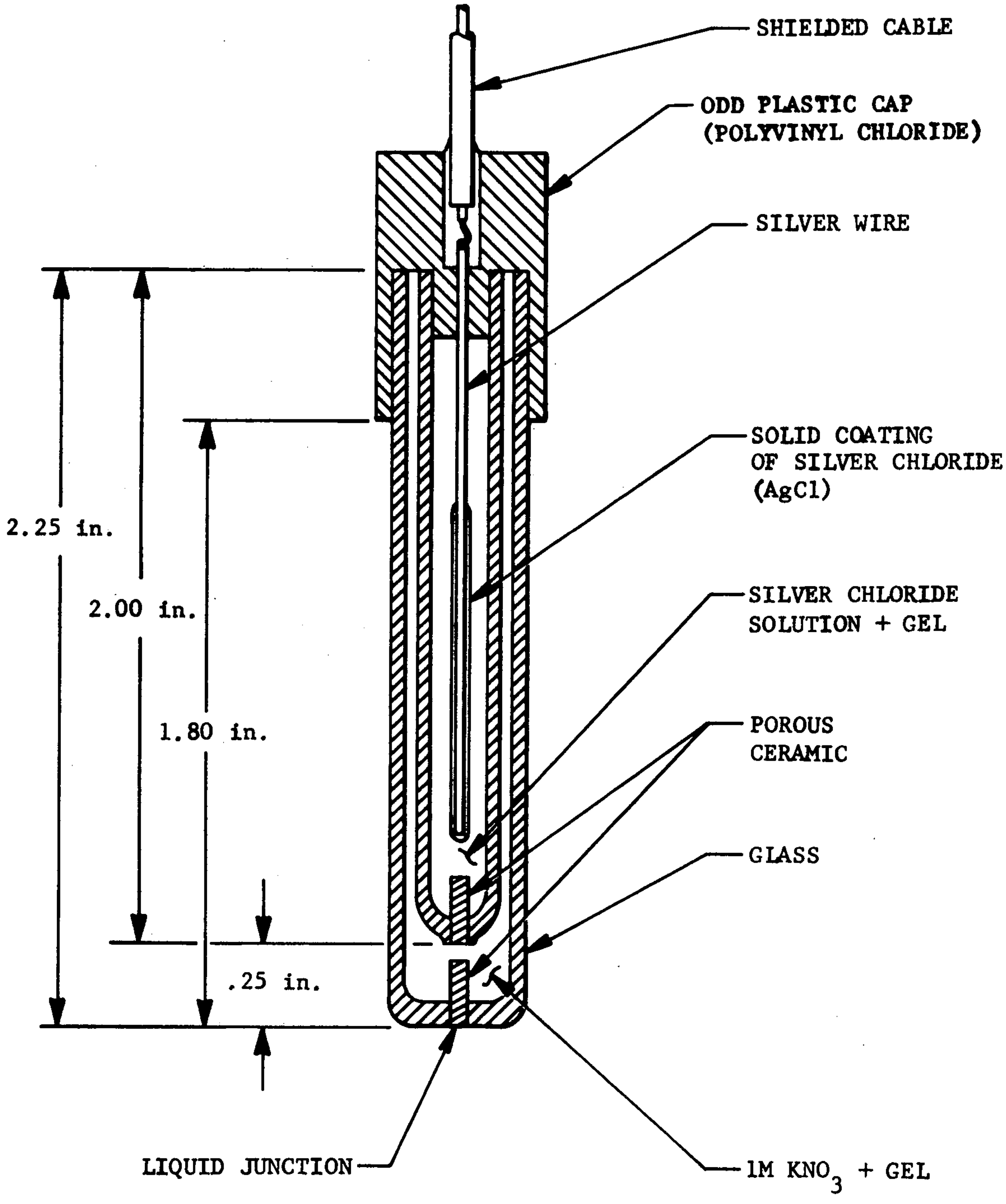
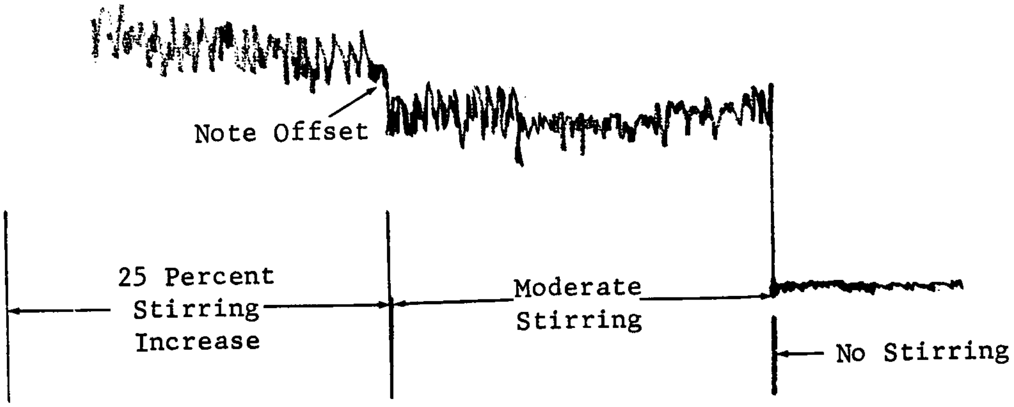
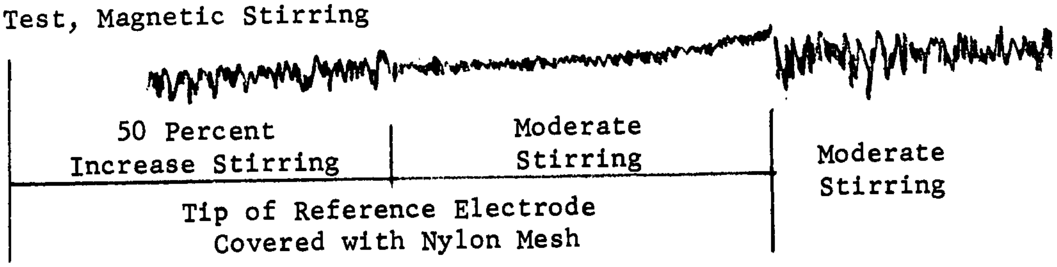


Figure 5-12. Double-Junction Reference Electrode

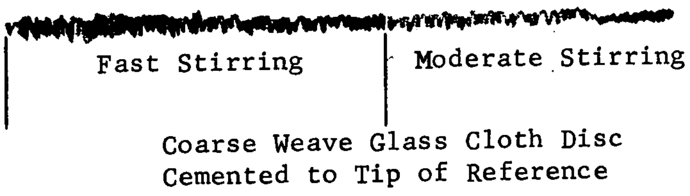
a. Beaker Test, Magnetic Stirring



b. Beaker Test, Magnetic Stirring



c. Beaker Test, Magnetic Stirring



d. Test Fixture Test

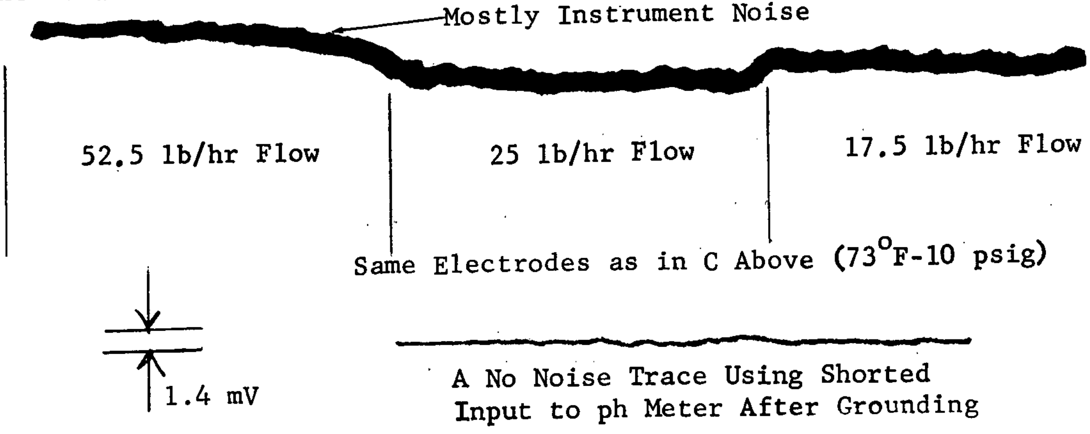


Figure 5-13. Noise and Stirring Effects Before and After Modification of Reference Electrode

5.4.3.2 Modified Double-Junction Provision for Gel Expansion and Contraction

Three new modified reference electrodes, having provision for expansion and contraction of the gels, were designed and fabricated.

Figure 5-14 shows a cross-section of this modified double-junction reference electrode. All three references were found to be extremely sensitive to changes in pressure and flow. That is, changing the flow of the 50-ppb $[Ag^+]$ solution from 20 lb/hr at 10 psig to 60 lb/hr at 20 psig resulted in roughly an 80-mV change equivalent to greater than 1000-ppb $[Ag^+]$ error. These reference electrodes were also very noisy in spite of using the glass cloth over the liquid junction area. One of these new references, when tested at 50°F, became very noisy and erratic. Upon returning to 77°F, the response of this reference was satisfactory. It was believed that the cooling of the gel caused a sucking action at the liquid junction, thus partially filling the porous ceramic rod with a test solution having a very high resistivity in place of the low resistivity KNO_3 electrolyte which would result in a very noisy, erratic, and nonreproducible reference.

A new reference electrode was designed, based on a previous Beckman design for an Apollo pH Water Sensor. The new reference electrode contained a pressurized, quartz-fiber, flowing liquid junction, having an estimated flow rate of 1.69×10^{-3} fl oz (50 microliters) per day. This estimate is based on tests performed on the original Apollo pH Water Sensor. A flow of 1.69×10^{-3} fl oz (50 microliters) per day of a 1-molar potassium nitrate (1M KNO_3) into the water system would not be detectable by taste nor by most analytical methods or instrumentation. With careful fabrication of the quartz fiber junction and a bellows/reservoir containing approximately 1/2 fluid ounce (15 ml) of electrolyte, a reference electrode--based on the principles of the new reference--would operate for approximately 7 to 10 months without requiring replenishment of the electrolyte.

5.4.3.3 Quartz-Fiber Junction, Pressure-Equalizing Reference (QJPE)

The new design reference also incorporated a means of equalizing the system pressure on both sides of the quartz-fiber junction (liquid junction) such that regardless of the system pressure, the differential pressure seen by the junction would be only that supplied by the low-rate (approximately 2 pounds compression) spring pressing on the bottom of the bellows. A cross-section of the quartz-fiber junction, pressure-equalizing reference is shown in Figure 5-15. This reference has been given the abbreviated identification of QJPE reference.

The QJPE reference was somewhat larger than the ordinary reference. However, the design met the following physical criteria:

- A reference that would fit into the flow cell of the test fixture without modification of the flow cell;
- A reference capable of rapid fabrication with on-hand parts and materials;

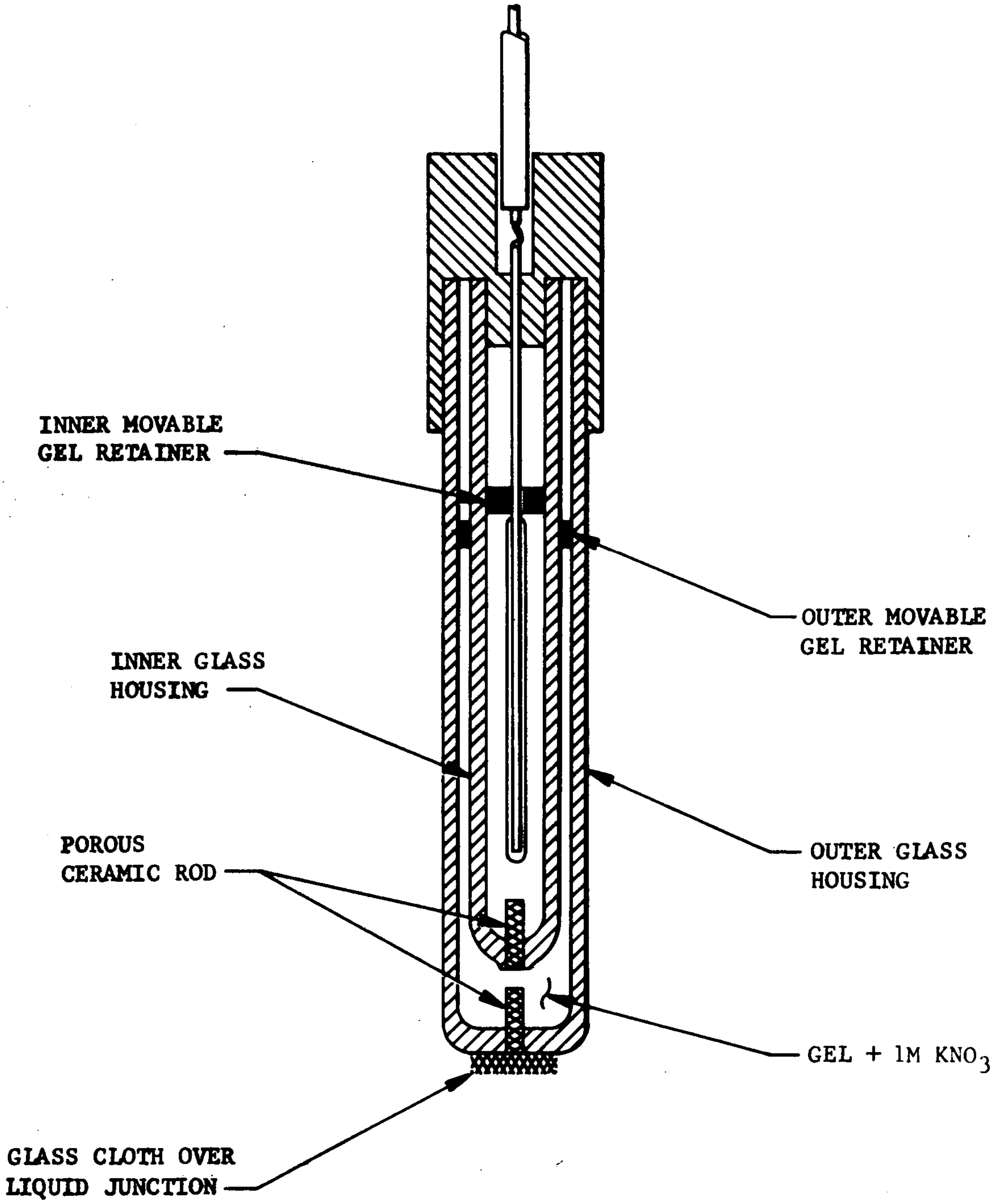


Figure 5-14. Modified Double-Junction Reference Electrode

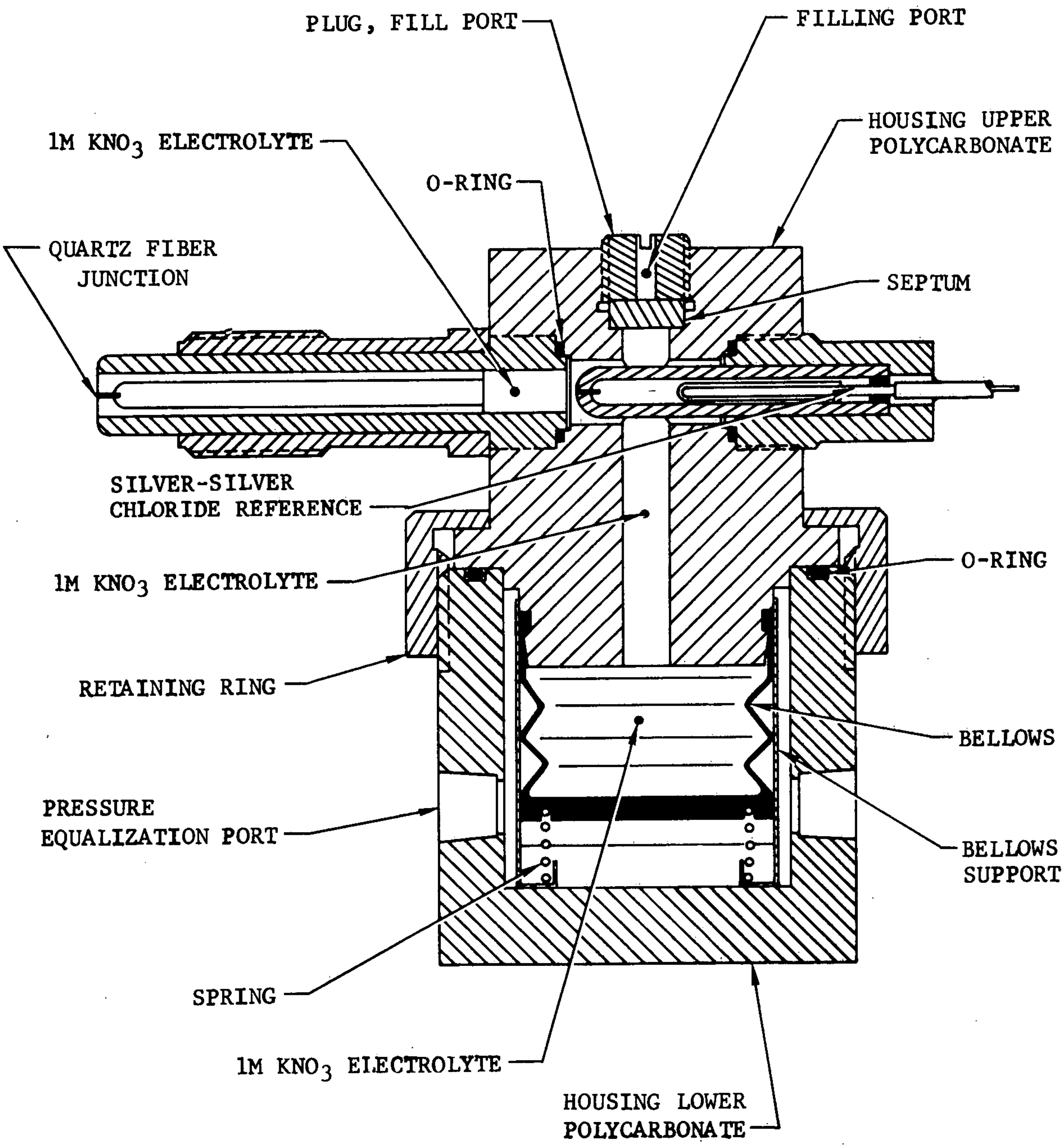


Figure 5-15. Cross-Section of New Quartz Fiber Junction--Pressure Equalizing Electrode (QJPE)

- A reference construction permitting rapid change of critical parts as necessitated by degradation or breakage of parts.

The mating of the QJPE reference with the flow cell of the test fixture is shown in Figure 5-16.

It should be understood that the configuration shown was that of an experimental breadboard setup. The configuration of the flow cell and QJPE reference do not represent or approximate the configuration of the flow cell or sensor to be designed for the shuttle water system.

An initial checkout of the QJPE reference--paired with a final configuration sensing electrode, H3, and tested at room temperature using a beaker and magnetic stirring assembly with a pH meter--yielded a response curve of 59 mV-per-decade change of silver-ion concentration with practically no sensitivity to rate of stirring.

5.5 The Test Fixture and Flow Cell

5.5.1 The Purpose of a Test Fixture

The development and evaluation of any component or system for space use must include testing under conditions of simulating as near as practical, those of eventual use. The development of a monitor for residual water bactericide--silver ions in parts per billion--required a test fixture which could simulate the conditions of a Space Shuttle Potable Water System. The conditions to be simulated were those of a very pure water system containing various levels of silver ions in the 10- to 100-ppb range in which flow, pressure, and temperature could be independently varied. The test fixture described in the following paragraphs provided for such simulated testing.

5.5.2 Design and Fabrication

The design of the test fixture was based on the following requirements necessary to simulate space shuttle potable water system conditions:

System Pressure:	15-60 psia
Water Delivery Temperature	
Hot:	150°-160°F
Cold:	40°-60°F
Water Delivery Pressure:	30 psia
Water Delivery Flow Rate:	To 60 lb/hr

In addition, the materials used in construction of the test fixture should be those which would be used in the potable water system and also be compatible with silver $\left[Ag^+\right]$ and bromide $\left[Br^-\right]$ ions.

Since the test cell and electrodes were the only components of the monitoring system likely to be affected by a change in gravity environment, these components must be demonstrated to be suitable for zero-gravity application.

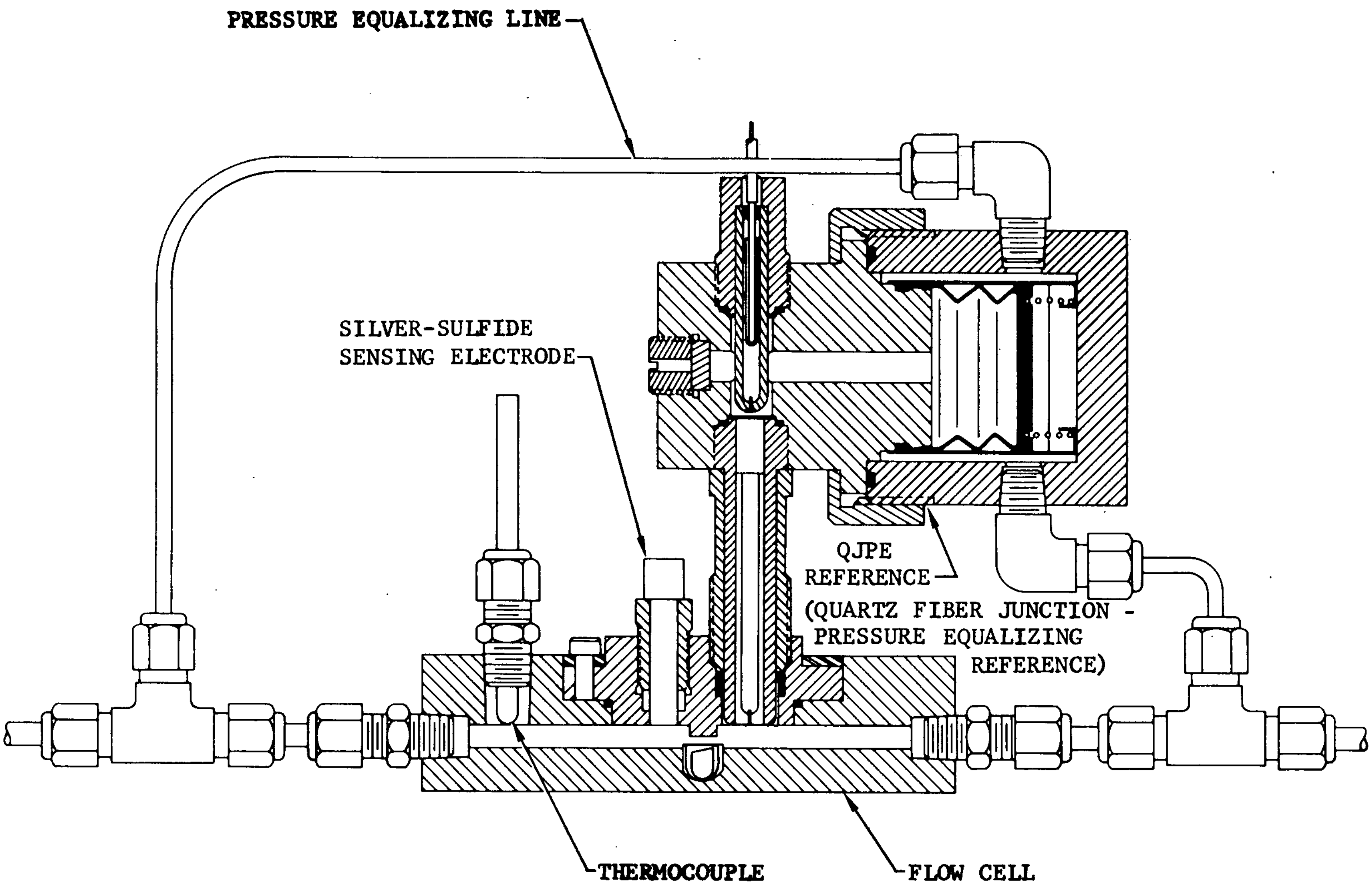


Figure 5-16. Mating of New QJPE Reference With Flow Cell of the Test Fixture

The most critical components of a potentiometric monitoring system required to operate in a zero-gravity environment are the electrodes which normally require vertical positioning because of internal filling solutions, and liquid junctions requiring gravity flow. Since specially-designed electrodes were fabricated to demonstrate their suitability for zero-gravity application as well as meeting the other requirements of the monitoring system, the test fixture should provide a means of demonstrating such suitability. Simulation of zero-gravity conditions were provided in test fixture experiments by mounting in a horizontal position in the flow cell of the test fixture to show that the electrodes did not depend upon gravity for flow or positioning of internal solutions. In addition, it is obvious that the solid-state construction of the electrode would permit operation in any orientation. A block diagram of the system is shown in Figure 5-17.

Figure 5-18 shows a layout drawing of the test fixture. The circled numbers identify the components which are given in the component list, Table 5-3. Most of the components were mounted on a plywood panel which was back-mounted on a semiportable, low-temperature water bath. Behind the plywood panel was the constant-temperature bath in which the heat transfer coil was immersed.

Figure 5-19 is a photograph of the test fixture.

With the exception of the flow cell, the two electrodes and the glass tube of the flowmeter, all components contacting the fluid were 316 stainless steel. The connecting tubing and the Swagelok fittings were 316 stainless steel. The flow cell was Teflon and the electrodes were mainly glass and plastic.

The test fixture was provided with a 1.1-gallon (4-liter) stainless-steel reservoir and a silver-halide canister connected to a variable pressure gear pump through a three-way valve. The output from the pump passed through a 15-foot by 1/4-inch stainless-steel heat transfer coil which was immersed in a constant-temperature bath, then past the pressure gage to the flow (test) cell. After leaving the flow cell, the fluid passed through the flowmeter, then to a three-way valve, permitting the fluid to be routed to the reservoir, the halide canister, or to waste. The flowmeter contained a needle valve for controlling the flow rate

5.5.3 Flow Cell

A detailed cross-section drawing of the flow cell is shown in Figure 5-20, while Figure 5-21 shows a top view of the flow cell. The circled numbers identify the components listed in Table 5-4.

The flow cell body and cover were Teflon. The cover was easily removable and rotatable for purposes of modification or changing the orientation of the electrodes with respect to the flow path of the water sample.

The flow cell was provided with a stainless, sheathed, thermocouple, mounted via a Swagelok fitting, for measuring fluid temperature in the immediate area of the silver-ion monitoring electrodes.

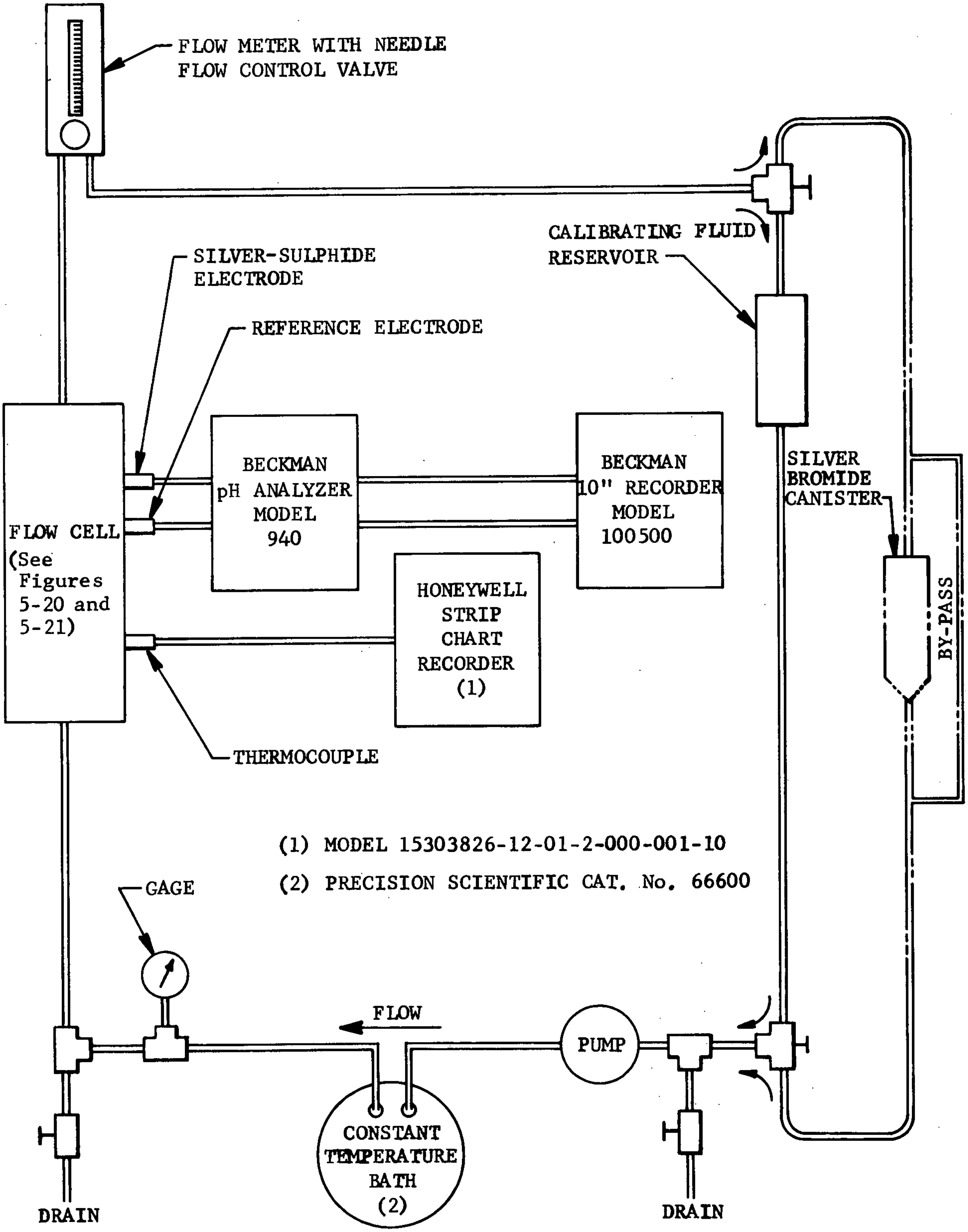


Figure 5-17. Block Diagram of Environmental Test Fixture

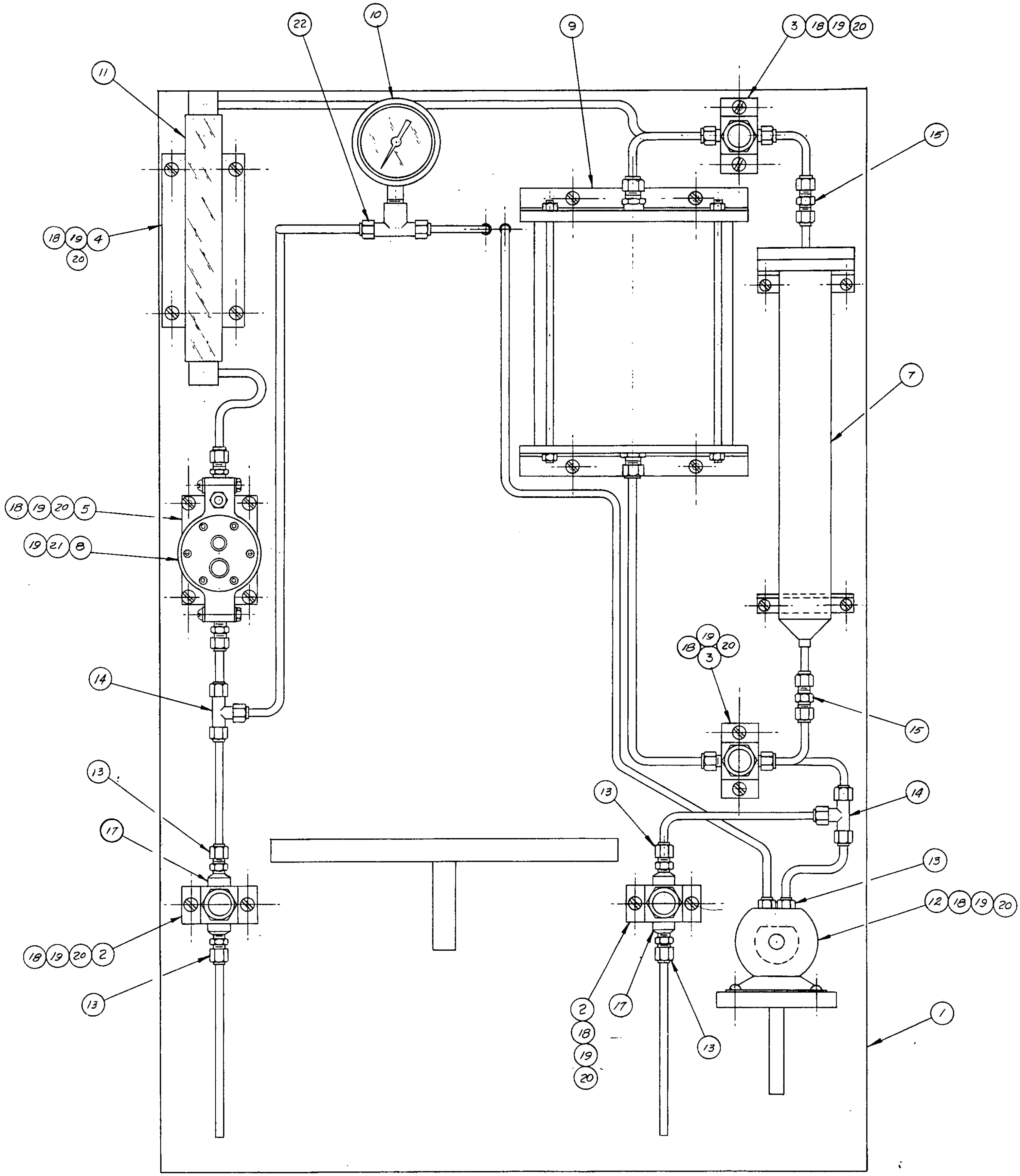


Figure 5-18. Test Fixture Layout

Number	Component
1	3/4-inch Plywood Support
2	Valve Mounting Bracket
3	Three-way Valve, Whitey Ball Valve, #43XS4, 316 Stainless Steel
4	Flowmeter Mounting Bracket
5	Flow Cell Mounting Bracket
6	--
7	Silver-Bromide Canister
8	Flow Cell--Teflon
9	Reservoir 1.1 gallon (4-liter), 316 Stainless Steel
10	Pressure Gage--0 to 60 psig, Marshalltown #188 Stainless Steel
11	Flowmeter, Brooks Model 1355-FIAAA with tube #R-6-15-A
12	Gear Pump, Variable Pressure, Micro Pump #12-41-316-759
13	Swagelok Tube to Pipe Fitting
14	Swagelok Tee
15	Swagelok Union
16	--
17	Drain Valve, Whitey Ball Valve, Two-way, #43F2 316 Stainless Steel
18	Swagelok Nut
19	Swagelok Ferrule, Front
20	Swagelok Ferrule, Rear
21	Flow Cell Cover--Teflon
22	Swagelok Tube to Pipe Tee

Table 5-3. Component List for Test Fixture

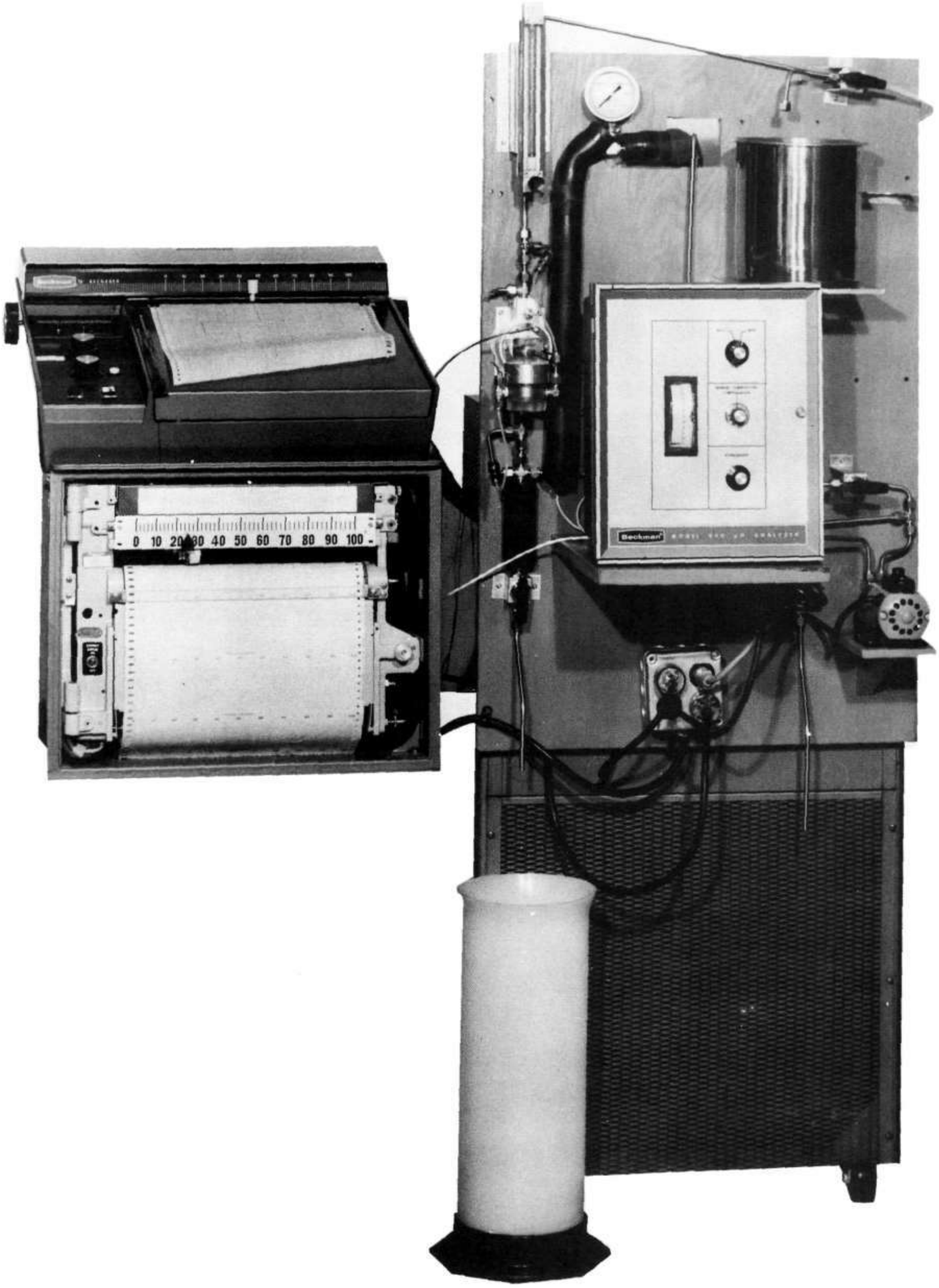


Figure 5-19. Photograph of Test Fixture

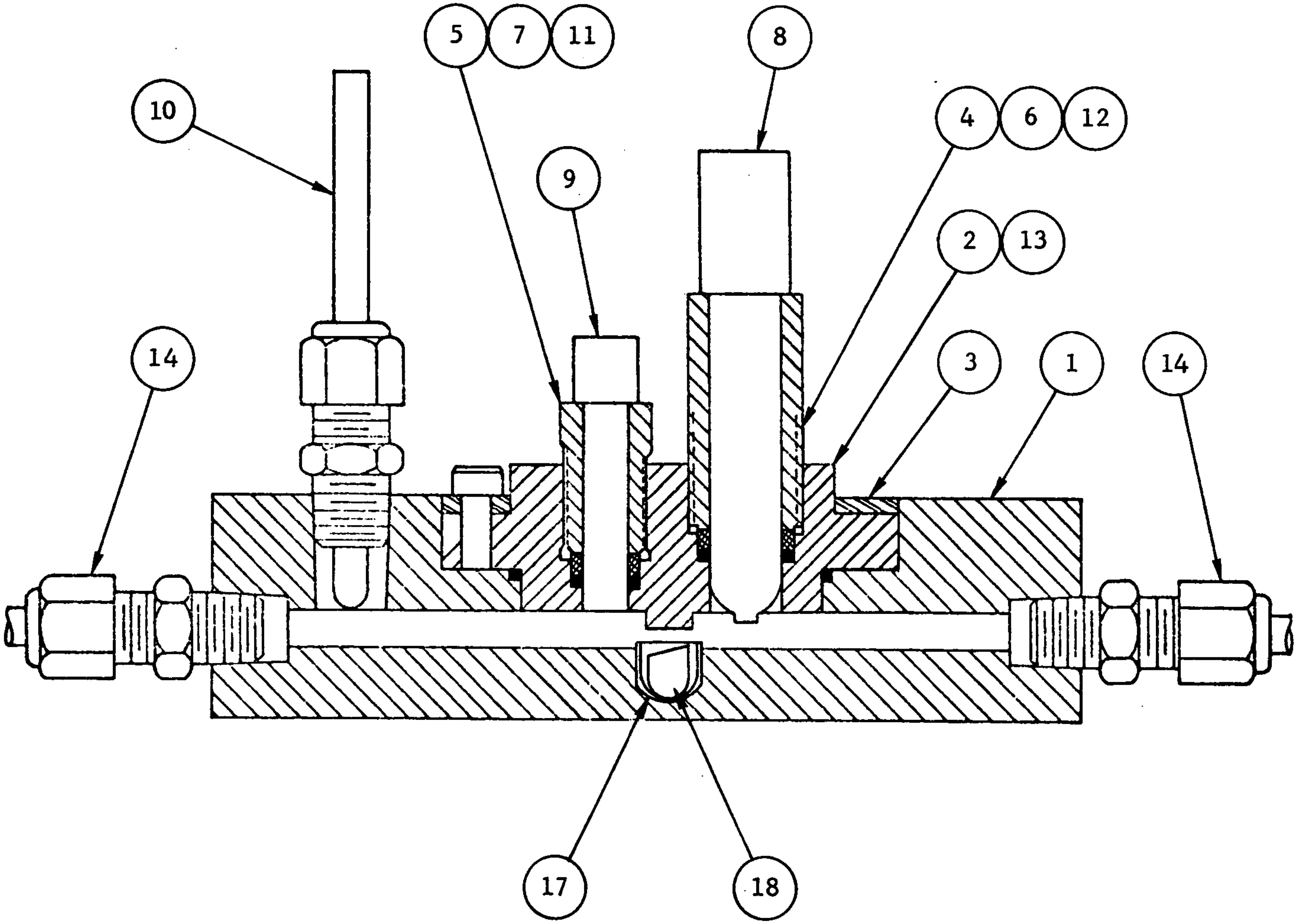


Figure 5-20. Flow Cell, Cross-Section

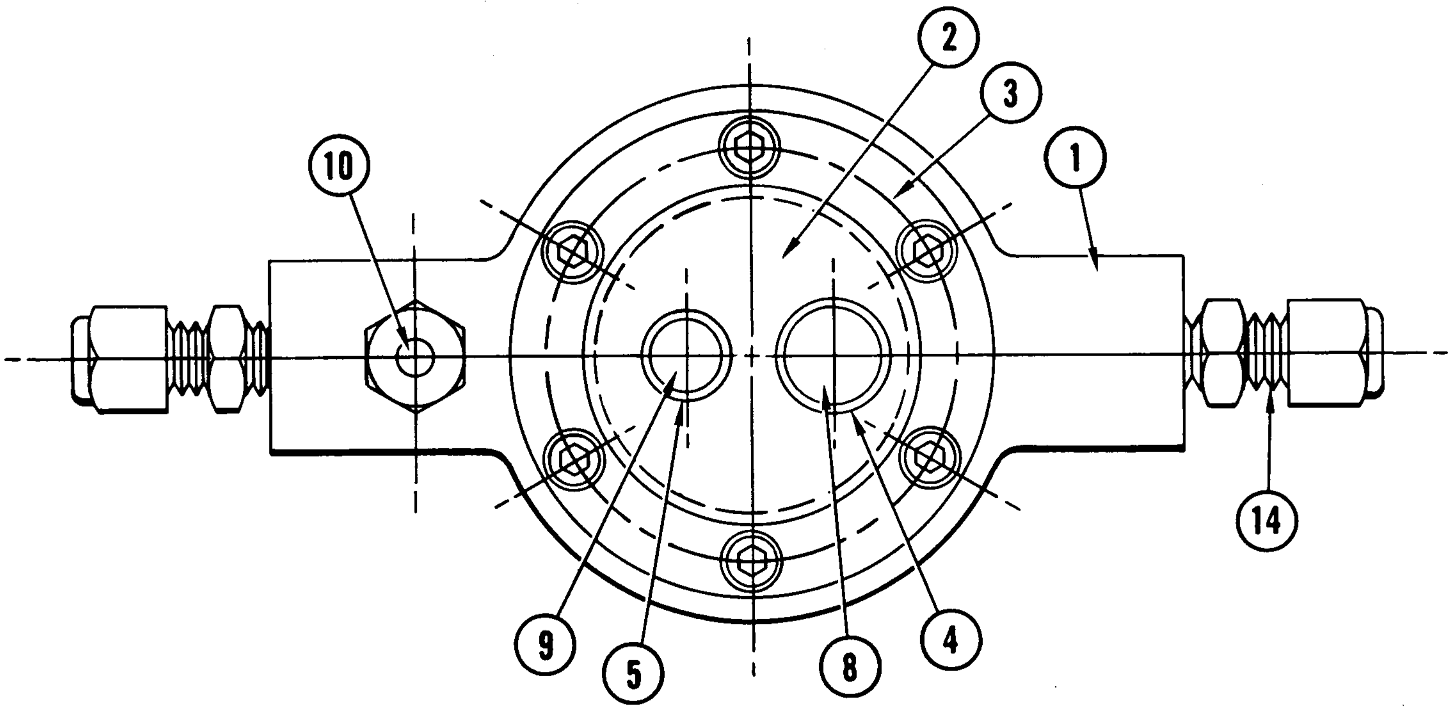


Figure 5-21. Flow Cell, Top View

Number	Component
1	Flow Cell Body--Teflon
2	Flow Cell Cover--Teflon
3	Flow Cell Cover Retaining Ring
4	Reference Electrode Retainer--Stainless Steel
5	Sensing Electrode Retainer--Stainless Steel
6	Bushing--Stainless Steel
7	Bushing--Stainless Steel
8	Reference Electrode
9	Sensing (Solid-State, Silver-Sulfide) Electrode
10	Sheathed Thermocouple (Fenwal, Inc.) 3/16" Dia. x 3" Long--200 to 400°F
11	O-Ring, Sensing Electrode Sealing, Viton A
12	O-Ring, Reference Electrode Sealing, Viton A
13	O-Ring, Cover Sealing--Teflon
14	Swagelok, Pipe to Tube Fitting, Stainless Steel
15	--
16	--
17	Cavity for Teflon-Coated Magnetic Stirring Bar
18	Teflon-Coated Magnetic Stirring Bar

Note: Not shown in Figure 5-20 is the magnet and drive motor behind the flow cell used to translate rotational motion to the stirring bar.

Table 5-4. Component List for Flow Cell

The flow cell contained a Teflon-covered stirring bar magnet to permit stirring of the fluid in the vicinity of the electrode during periods of nonfluid flow. A magnet mounted on the shaft of a small dc motor, positioned behind the flow cell, transferred movement to the stirring bar magnet. This capability was found not to be necessary since measurements were always made in a flowing system.

5.5.4 The Silver-Bromide Canister

The silver-bromide canister was fabricated according to the design data given in Chemtric Final Report 3097, Potable Water Bactericide Agent Development, Contract NAS9-12104, dated July 1972. The pertinent data for the canister is repeated here for the convenience of the reader.

The sizing of this component was based upon previous experience gained by Chemtric in evaluating a silver-halide column developed by Melpar. This unit consisted of a cylindrical column containing silver-bromide granules in mixture with glass beads. The column provided an effective bed diameter of 1.5 inches, and a bed length of 7.5 inches; it contained 0.359 lb (162 grams) of AgBr particles, and 0.449 lb (204 grams) of glass beads.

The function of the glass beads was to retard agglomeration of the silver-bromide particles into a single large mass during quiescent periods, to reduce pressure drop across the bed and to effectively increase the surface area of the silver-bromide particles by keeping them separated.

The canister contained the following, in sequence from the outlet (back end) to the inlet:

a. A perforated metal disc welded to the end cap which, in turn, was welded to the cylindrical body;

b. Four discs of 10-mesh, 316-stainless steel screen, followed by a layer of pyrex wool 1/8- to 1/4-inch thick, and a single disc of the same screen; this combination of screens and pyrex wool retained the particulate contents of the canister and provided a lower pressure drop than pyrex wool alone;

c. The media (silver bromide-glass bead mix) was packed into the canister on top of the above items;

d. The inlet particle retainer was similar to b., above, but the order was reversed--that is, a screen disc was placed on top of the media followed by pyrex wool and 4 screen discs;

e. A stainless-steel, doughnut-shaped disc backed up the above items. The disc provided on O-ring seal between the disc periphery and the cylinder ID; the center of the ring was covered with a perforated metal disc, tack-welded in place; a ridge of the periphery of the center hole served to locate the media compression spring;

f. A spring fabricated from 18-8 stainless steel was trapped between the above disc and the removable end cap; the spring provided a compressive load on the media to retard media particle movement which could result in particle disintegration and/or channeling;

g. The end cap provided for centering the spring and an O-ring seal between the end cap and the flange welded to the canister body; the end cap was held in place by 4 screws.

The design effort on the canister emphasized control of potential corrosion sites. Tubing nipples welded from the inside of the end cap were used to eliminate threaded connectors on the canister body. The fixed end cap was butt-welded as opposed to a lap-type union. The canister was heat treated and annealed to minimize the potential for intergranular corrosion. Finally, all canister parts were passivated. Subsequent cleaning and decontamination procedures were executed, without the use of abrasives, to preserve the integrity of the passivated surface.

The type 316 stainless-steel tubing selected for the canister had a 1.750-inch OD and a wall thickness of 0.049 inch. Therefore, the ID was 1.652 inches, and a length of 12.8 inches was selected to accommodate 450 ml (27.5 in.^{3}) of resin. The resultant L/D ratio was 7.8.

The selected spring provided 6.6 lbs of force per inch of length, from 2.34 inches (free length) to 0.44 inch at which point the spring was solid; the target compressive load (8 lbs) was applied when the spring was squeezed down to 1.125 inches. The spring was fabricated from 0.080-inch OD, type 18-8 stainless-steel wire. Other characteristics were as follows:

Mean Coil Diameter = 1.24 inches
Number of Active Coils = 4
Total Number of Coils = 5-1/2
Free Length = 2.34 inches

The overall length of our canister was modified to a total length of 13 inches and used two identical springs, fabricated according to the above data, and an extra perforated metal disc to provide extra versatility in case an ion-exchange column was required to provide a zero or background silver-ion fluid for calibration reference.

5.5.5 Test Fixture Capabilities

The capabilities of the test fixture are:

Fluid Volume: 260 in.^{3}
Reservoir Volume: 240 in.^{3}
Fluid Flow: 0-66 lb/hr, H_2O
Fluid Pressure at Maximum Flow: 0-62.7 psia (48.7 psig)
Temperature Range Capability at Maximum Flow: 39° to 165°F
Temperature Measurement: 0° to 212°F
Temperature Recording: Continuous (Honeywell Recorder)
Silver Ion Monitoring: Meter readout and continuous recording (Beckman 940 pH Analyzer and Beckman 10-inch Recorder)
System Calibration: Manual

5.5.6 Preliminary Test Fixture Checkouts

After the final assembly, 0.5 gallon of distilled water was placed in the reservoir and the pump started. At 10 psig, severe leaks were observed around both the wells in the flow cell cover for the reference and sensing electrodes. The originally-proposed Teflon O-rings did not provide sufficient compression and deformation to provide a seal around the electrodes. Viton-A O-rings were substituted for the Teflon O-rings and proved satisfactory at maximum conditions of pressure and flow.

A temperature stability test was run for 18 hours with a saturated silver-bromide solution, obtained from a freshly prepared silver-bromide canister, as the test fluid. Pressure was set for less than 2 psig and flow at 25 lb/hr. Temperature and millivolt response of monitoring electrodes were continuously recorded. These data are given in Table 5-5. The data shows that for an 18-hour continuous test under the conditions listed, a temperature variation of +0.9°to -1.35°F was recorded while a sensor of +7.5 mV was noted for the C2 electrode. The saturated solution of silver bromide, AgBr, with excess solid AgBr, should deliver a stable silver-ion concentration to the electrodes, if the temperature remained constant. However, the temperature was observed to vary +0.9° and -1.35°F. This would change the solubility of the silver bromide such that the silver-ion concentration would increase or decrease by ±2 ppb and would account for a minor contribution to the observed sensor response change.

The electrode response variations observed were greater than expected for the indicated temperature variations. As was seen in subsequent tests of the C2 electrode, the response of this electrode was not optimal. The electrode had not received any conditioning treatment which was subsequently found to be necessary for optimum response. Subsequent tests of C2 and other C-series electrodes are discussed in Section 5.3.2.3. The conditioning treatment is also covered in this section.

Also, as discussed in Section 5.7.3, extended pretreatment of the silver-bromide canister was required before stable conditions were achieved. This test, however, did illustrate that reasonable temperature control could be exercised with the test fixture.

It was determined that due to the rapid loss of silver ions, $[Ag^+]$, from solutions containing 500 ppb $[Ag^+]$ or less, an accurate evaluation of the electrode system could not be made while recycling silver-nitrate solutions in the test fixture. Saturated solutions of silver halides could be used by recycling the test solution through a bed of silver halide and glass beads, but such a source of silver ion was limited by temperature and flow effects. The saturated silver-halide source would not supply accurately-known test solutions ranging from 20 to 500 ppb at each of the chosen test temperatures of 50°, 77°, 113°, and 149°F. Therefore, the test solutions were made up in 0.53-gallon (2 liters) to 1.1-gallon (4 liters) batches just prior to passing through the test fixture. Each batch was made up by diluting a known quantity of a HARLECO Atomic Absorption Silver Standard and each batch was analyzed by a silver-sulfide electrode set up independent of the test fixture and calibrated within six hours of use.

Time (Hours)	Temperature (°F)	Sensor Response (Millivolts)	Time (Hours)	Temperature (°F)	Sensor Response (Millivolts)
0.5	40.5	221	10.5	40.5	205.5
1.0	40.5	214	11.0	40.5	210
1.5	40.5	206	11.5	40.5	210
2.0	40.1	206	12.0	40.5	210
2.5	39.6	203	12.5	40.1	209
3.0	39.6	200.5	13.0	40.1	207
3.5	39.15	200	13.5	39.6	206
4.0	39.15	202	14.0	39.6	205
4.5	38.7	203.5	14.5	39.15	205.5
5.0	38.7	205	15.0	39.15	206
5.5	38.25	211	15.5	40.5	205.5
6.0	38.25	215	16.0	40.5	204
6.5	38.25	213	16.5	40.5	200
7.0	39.15	209	17.0	40.5	201.5
7.5	39.15	209	17.5	40.1	203
8.0	38.7	208.5	18.0	39.6	204
8.5	38.25	207			
9.0	38.25	208.5			
9.5	38.25	208.5			
10.0	40.1	204.5			

Test Conditions

Temperature Set--39.6	Test Fluid--AgBr (Sat. Solution)
Pressure--<2 psig	Fluid Flow--25 lb/hr
Sensing Electrode--C2	

Recorded Variations

Temperature	Sensor Response
+0.9°F	±7.5 mV
-1.35°F	

Table 5-5. Results of 18-Hour Test Fixture Stability Tests--Temperature and Electrode Response

F

A standard Beckman laboratory pH meter was used in the initial test with the test fixture. A high noise level was observed, 14 mV or 11 ppb at a 50-ppb silver-ion level. Since the test fixture was similar to a small process loop in a water treatment or chemical plant, a Beckman process pH Analyzer, Model 940, was used with the system. The use of the 940 pH Analyzer considerably reduced the noise to the point that below 40 lb/hr there was no noticeable noise observed. At the higher flow rate and pressure--60 lb/hr at 45 psig--the noise was nearly 6 mV (equivalent to 5 ppb $[Ag^+]$ at the 50-ppb $[Ag^+]$ level). By substituting air pressure in place of the pump, it was established that the ac/dc variable speed pump motor was contributing about 75 percent of the noise, while the gear-type pump was adding mechanical noise to the system through pulsations and also some cavitation at the higher pump rates.

The prime feature of the Beckman Model 940 pH Analyzer was the differential input measuring circuit which virtually eliminates errors due to the high common-mode noise rejection of the differential input stage.

Standard laboratory pH meters do not have such a noise-reducing differential input, but merely amplify with respect to solution ground.

Using the 940 pH Analyzer, and making the changes shown below, reduced the detectable noise level to between 1.5 to 3.0 mV as the maximum noise at any combination of flow and pressure. The changes were:

- Electrical isolation of the ac/dc motor and adding a capacitor across the motor leads;
- Mechanical filtering of the liquid after leaving the pump by inserting a 1.25- by 12-inch fine glass bead column between the pump and the heat transfer coil;
- Optimizing of ground connections for the total system;
- Adjustment of the spring rate of the QJPE reference to obtain a liquid junction with minimum noise and minimum electrolyte flow;
- A change of the pressure equalization connection to the reference from a dead-ended "T" connection to a flow-through arrangement.

5.5.7 Tests with Variations of Flow, Pressure, and Temperature

Following the preliminary tests, a series of tests was made while varying the pressure, flow, and temperature. During these tests, it was observed that the reference electrode was sensitive to variations in flow and pressure, while later modifications of the reference were found to be unstable for use at temperatures other than ambient. (A discussion of the reference electrode, its problems, and subsequent solutions and development is contained in Section 5.4).

Subsequent test-fixture tests at 149°F revealed that the adhesive/sealant used to fabricate the solid-state, silver-sulfide electrode failed at this temperature. The development of the solid-state, silver-sulfide electrode is described in Section 5.3.

5.5.8 Modification of the Flow Cell

In the original design of the flow cell, the sample flowed past the reference electrode, then past the silver-ion sensing electrode. The original flow path is shown in Figure 5-22. The 77°F tests yielded good electrode response. After reducing the noise by switching to the 940 pH Analyzer and modifying the reference electrode, the maximum noise observed was less than 2.0 millivolts, usually at 25 psig and 40 lb/hr.

However, at 113°F, the noise at 25 psig and 40 lb/hr was greater than 18 millivolts, while the noise at 25 psig and 60 lb/hr was of such frequency and magnitude it could not be recorded on a conventional strip chart recorder. Figure 5-21b shows an actual section of the strip chart recording of the electrode response at 113°F, 25 psig at both 20 and 40 lb/hr. Note the large increase in noise when changing flow from 20 to 40 lb/hr. The noise problem was discussed with members of other departments--in particular those responsible for designing flow cells for process instrumentation. The result of these discussions and several experiments was the modification of the flow cell so that the sample flowed mainly <u>between</u> the reference and sensing electrodes. Figure 5-23a shows the sample flow path through the modified cell, and Figure 5-23b shows an actual recording of the electrode response at 113°F, 25 psig, and flows of 20, 40, and 60 lb/hr after the modification. The displacement or upward offset and slight upward drift was the result of the sudden change in sample flow which disturbed the liquid junction of the reference. The small spikes shown for 40 and 60 lb/hr flow usually disappeared as the system returned to equilibrium, at which time the drift had stopped and the offset due to flow change had been reduced. The time required for the electrode response to reach equilibrium after a rapid change in pressure or flow was dependent on the magnitude of the change, the temperature, the silver-ion concentration, the characteristics of the individual electrode, the sample volume of the flow cell, and the total sensing system of which the electrodes were a part.

A comparison of the noise shown in Figure 5-22b and 5-23b illustrates the critical effect of flow cell design. The wider the required range of such parameters as pressure, flow, temperature, and ion concentration, the more critical becomes the design of the flow cell. The frequency and rate of change of the parameters must also be considered.

In most applications, the rate of flow through the cell is relatively unimportant, as long as the sample is always representative of the solution in the main line or tank. In the determination of pH of high purity water or slightly buffered solutions, sample agitation or flow is necessary to avoid incorrect results. This is also true of solutions of low ionic concentrations, such as silver ions in the low ppb (e.g. 100 ppb) range. Also, the optimum rate of flow of these solutions appears to vary with the design of the flow cell. One important consideration for process electrode applications is to avoid high fluctuating flows which disturb the liquid junction.

Again, it must be stressed that the requirements for the Residual Water Bactericide Monitor are such that the design of the flow cell is very critical.

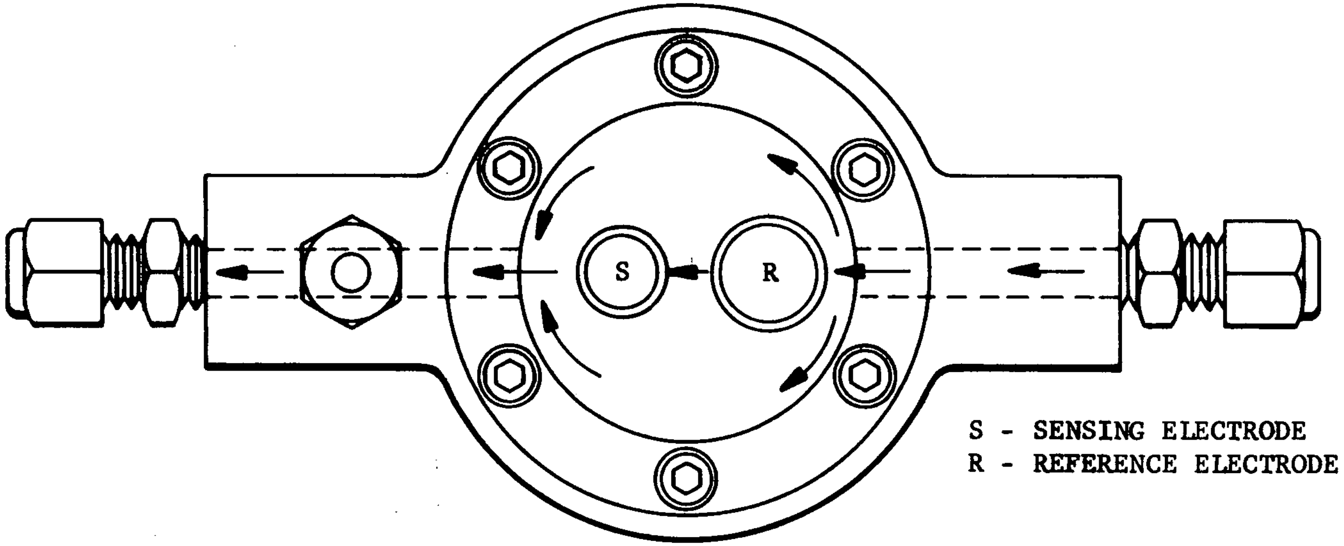


Figure 5-22a. Sample Flow for Original Design of Flow Cell

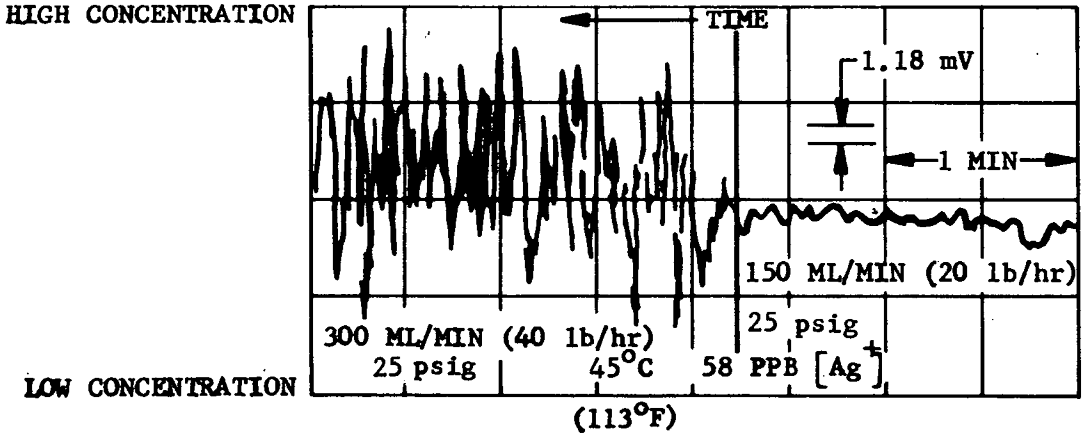


Figure 5-22b. Noise Level at 113°F With Original Design Flow Path

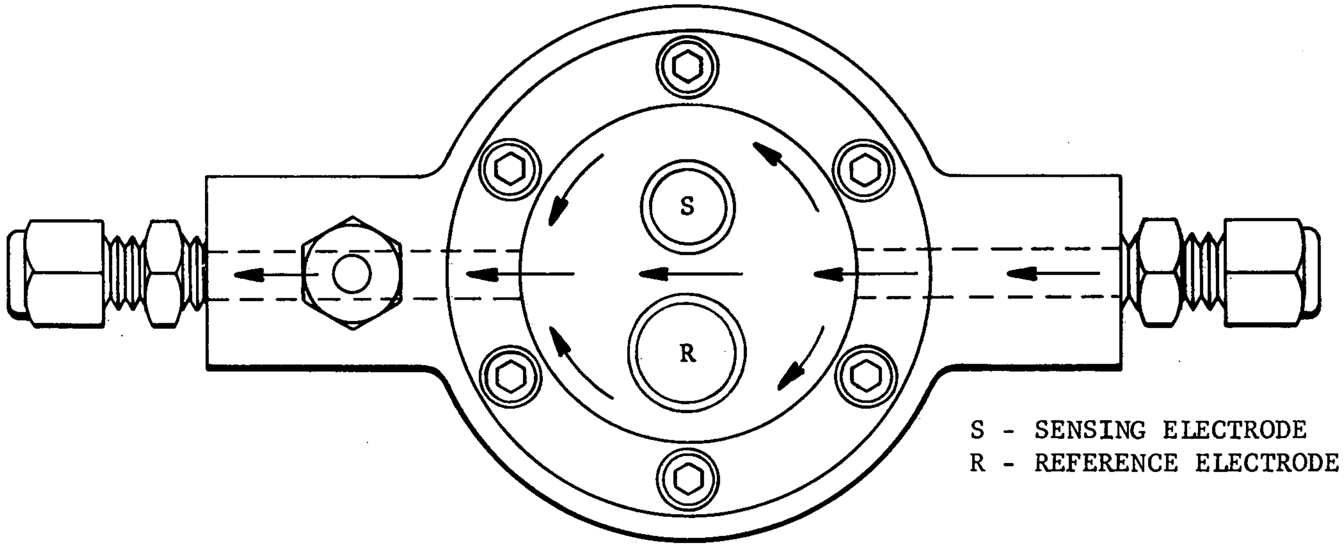


Figure 5-23a. Sample Flow After Flow Cell Modification

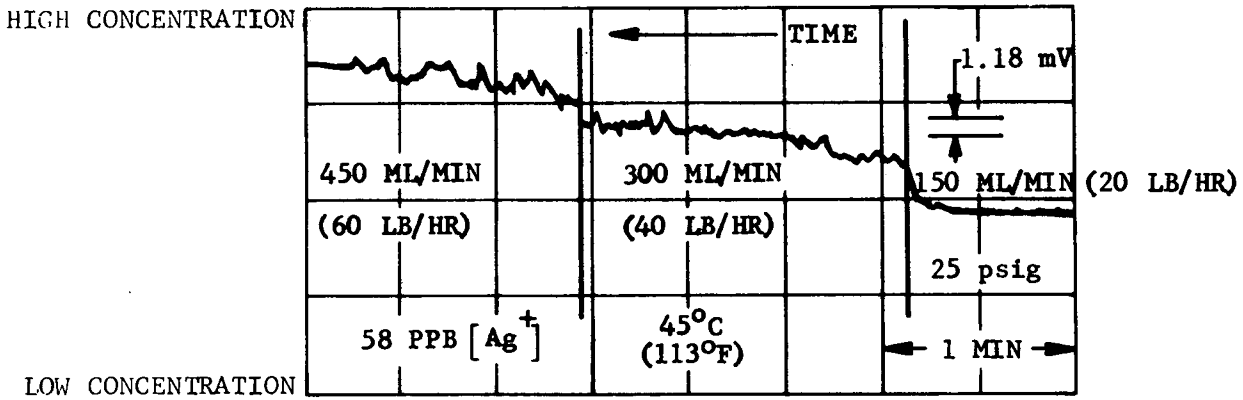


Figure 5-23b. Noise Level at 113°F After Flow Cell Modification

5.6 Results of System Tests

The complete system used for the tests consisted of the test fixture, the flow cell and electrodes, a Beckman 940 pH Analyzer, a Beckman 10-inch Recorder, and a Honeywell temperature recorder (see Figures 5-18 and 5-19). Each of these instruments is on a scheduled calibration program. However, to assure that each was functioning properly when connected to the system, they were checked as follows: the thermocouple was connected to the temperature recorder and the combination checked against an accurately calibrated thermometer; the 940 pH Analyzer, recorder, and electrode input connections were assembled and checked by injecting known voltages from a precision voltage source into the electrode connections over the range of interest, and rechecked with a digital voltmeter. An 18-hour stability check of the 940 pH Analyzer and recorder, with the electrode connections to the analyzer shorted, showed a drift of less than 1 millivolt, e.g. at 50 ppb this would be less than approximately 1 ppb.

The test fluids were made up in batches of 0.53 and 1.1 gallons by diluting an Atomic Absorption Standard (HARLECO). A sample of each batch was immediately analyzed for silver-ion concentration by a silver-sulfide electrode setup independent of the test fixture.

The setup used to analyze the silver-ion concentration of the test fluids consisted of a Beckman Century SS™ pH Meter, Model 076009; a solid-state, silver sulfide electrode of the H series, and a double-function reference electrode with 1M potassium nitrate as the second electrolyte; a Beckman 10-inch Recorder, Model 100500, and a Sargent Hot Plate-Magnetic Stirrer Model H. The system was calibrated 73°F with accurately made dilutions of Atomic Absorption Silver Standard (HARLECO) just before use. The test fluids were also analyzed at 73°F. Both calibration and test fluids were stirred at the same rate using a Teflon-covered magnetic stirring bar and the Sargent Magnetic Stirrer.

Periodically, a sample of the test fluid was analyzed after passing through the flow cell to confirm the test fixture reading by an independent measurement. Unbiased results were assured since different operators, electrode pairs, and test setups were used.

The stability of the low ppb silver-ion solution was such that the solutions would show a continuous loss of silver ion when recirculated in the test fixture. Because of the poor stability of the solution, preparation of the proper dilution of the standard immediately before passing the solution through the test fixture was necessary. The only time any solution was recirculated through the system was during the warm-up periods prior to temperature stabilization.

To detect any adverse effects of the test fixture upon the electrode responses, a comparison was made between the electrode responses in a constant-temperature cell and the responses in the test fixture. The comparison was made at 50° and 77°F over the silver-ion concentration range of 25 to 100 ppb. The comparisons are shown as part of Figures 5-24 and 5-26. The excellent agreement between

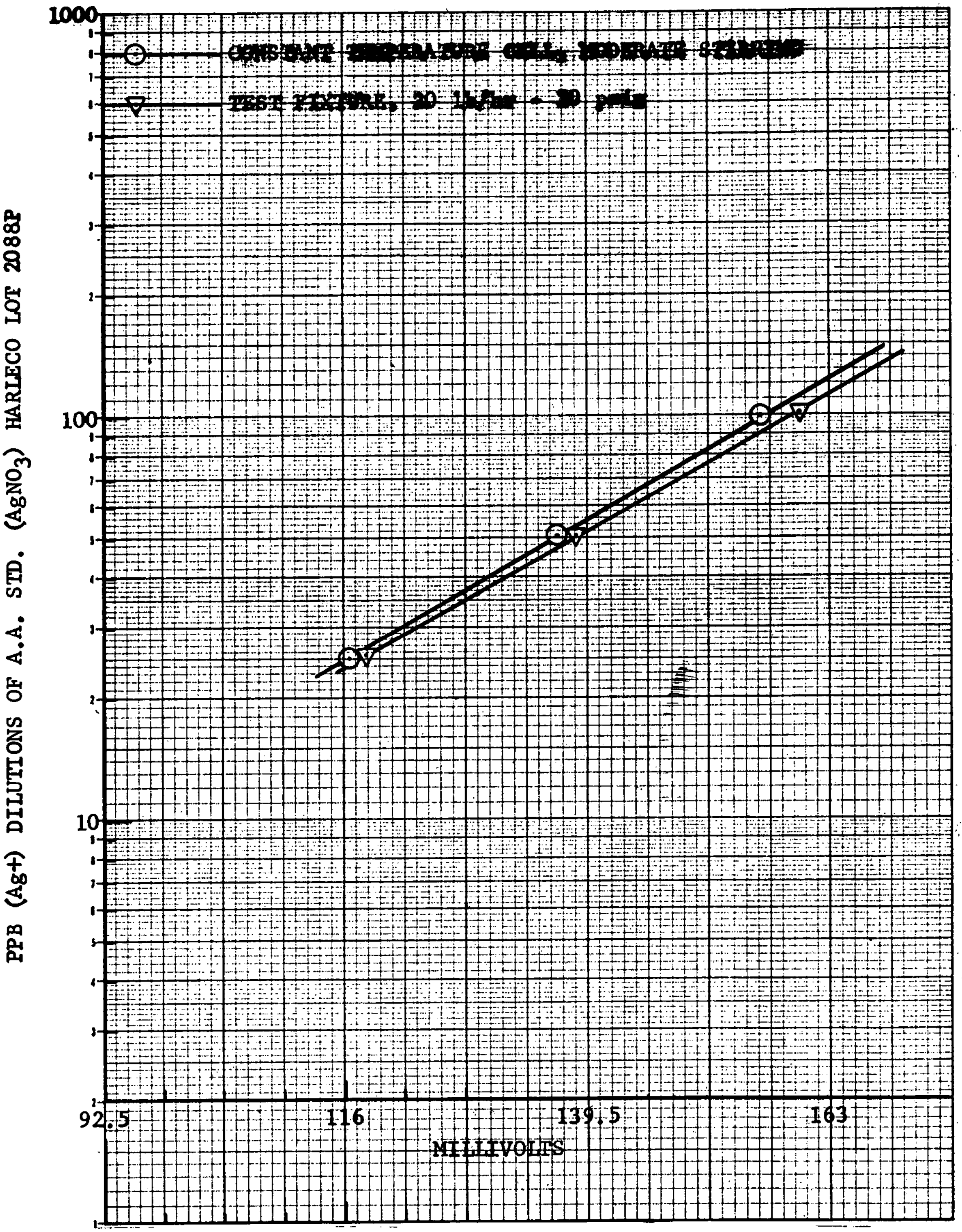


Figure 5-24. Response of QJPE/H3 Electrode Pair at 50°F

the test fixture results and that of the constant temperature cell should be noted. Figures 5-24 and 5-26 are also calibration curves for the 50° and 77°F pressure and flow variation tests.

The necessity of rapidly making large batches of test solutions and immediately pouring some into the reservoir of the test fixture resulted in solutions which did not contain an exact level of silver ion. An analysis of the solutions, described above, gave the actual silver-ion concentration of the solutions as mixed and after flowing past the electrodes. Hence, Tables 5-6, 5-7, and 5-8 contain data on 48, 88, and 125 ppb silver-ion levels.

In addition to determining the effects of flow and pressure at each temperature level, a three-point response check was also made at these temperatures.

Table 5-6 gives the results of the 50°F test for effects of pressure and flow. At 20 and 40 lb/hr, the effects were minimal. At a flow of 60 lb/hr, the apparent offsets averaged 11.4 percent (10 ppb at 88-ppb $[Ag^+]$). However, these data are for a breadboard system and such effects of pressure and flow were estimated to be less than 2-percent maximum in a properly engineered system such as defined in the Instrument Package Definition, Section 6.0.

Figure 5-24 gives the response of the electrodes to changes in silver-ion concentration at 50°F. The responses in the test fixture and in a constant-temperature cell were both semilogarithmic and exhibited excellent agreement. Table 5-7 gives the results of the 77°F test for effects of pressure and flow. At all levels of pressure and flow, the electrode system exhibited only a very small offset error due to such changes.

Figure 5-25 shows the recorded response of the electrode pair at 77°F. Data for Table 5-7 were taken from this recorded response. The sudden downward shift was due to a sudden change of pressure and flow which might have been equivalent to opening a water port or valve next to the flow cell containing the electrodes. Such a sudden change in flow and/or pressure disturbed the very sensitive liquid-liquid junction of the reference electrode. However, the pressure equalizing ability of the QJPE reference rapidly re-established equilibrium at the liquid-liquid junction and the offset error was corrected in less than one minute.

Figure 5-26 shows the response of the electrode pair at 77°F in both the test fixture and in a constant-temperature cell. Again, agreement is excellent.

The data given in Table 5-8 for the effect of pressure and flow at 113°F shows that at 60 lb/hr flow the largest range of apparent offset errors are observed which range between 3 and 18 ppb at a concentration of 125-ppb $[Ag^+]$. These data illustrate that the higher the operating temperature, the greater the effects of flow and pressure or any other changes likely to disturb the equilibrium of the liquid-liquid junction of the reference electrode. Such changes at 113°F resulted in an average offset error of approximately 8 ppb, or 6.4 percent at 125-ppb silver ion.

Apparatus:	Test Fixture Beckman 940 pH Analyzer Beckman 10-inch Recorder
Electrodes:	Reference--Quartz Fiber Junction, Pressure Equalizing Sensing --Solid-State Silver Sulfide H3

Test Solution 88 ppb $[Ag^+]$

Flow lb/hr	Pressure psig	Indicated $[Ag^+]$ Conc ppb	Apparent Error $[Ag^+]$ ppb	Noise mV(1)
20	10	88	0	<0.5
	25	86	-2	<0.5
	45	85	-3	<0.5
40	10	87	-1	0.5
	25	82	-6	<0.5
	45	84	-4	<0.5
60	10	78	-10	<0.5
	25	79	-9	<0.5
	45	77	-11	<0.5

Table 5-6. System Test Data--Pressure and Flow Effects at 50°F

Apparatus: Test Fixture
Beckman 940 pH Analyzer
Beckman 10-inch Recorder

Electrodes: Reference--Quartz Fiber Junction, Pressure Equalizing
Sensing --Solid-State Silver Sulfide H3

Flow lb/hr	Pressure psig	Indicated $[Ag^+]$ ppb	Apparent Error ppb	Noise mV
Test Solution - 25 ppb $[Ag^+]$				
20	10	25	0	1.0 max
	25	25	0	1.0 max
	45	23.5	-1.5	1.0 max
40	10	24.5	-0.5	1.0 max
	25	25.5	+0.5	1.0 max
	45	24	-1	1.0 max
60	10	24	-1	1.0 max
	25	25	0	1.0 max
	45	24	-1	1.0 max
Test Solution - 48 ppb $[Ag^+]$				
20	10	45	-3	1.0 max
	25	46	-2	1.0 max
	45	48	0	1.0 max
40	10	44	-4	1.0 max
	25	48	0	1.0 max
	45	47	-1	1.0 max
60	10	48	0	1.0 max
	25	49	+1	1.0 max
	45	48	0	1.0 max

Table 5-7. System Test Data--Pressure and Flow Effects at 77°F

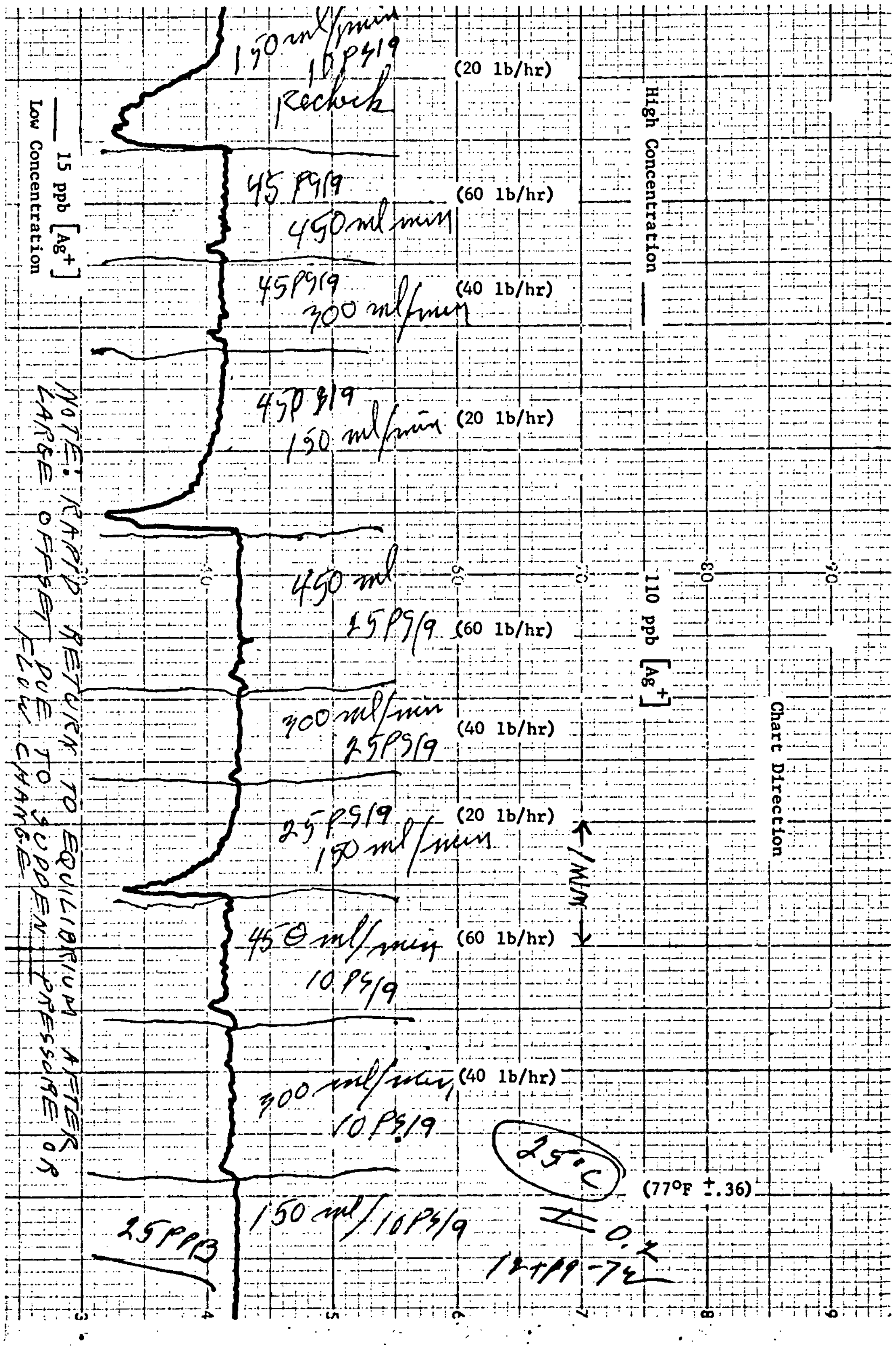


Figure 5-25. Recorded Response of QJPE/H3 Electrode Pair at 77°F and 25 ppb [Ag+] - Pressure and Flow Varied

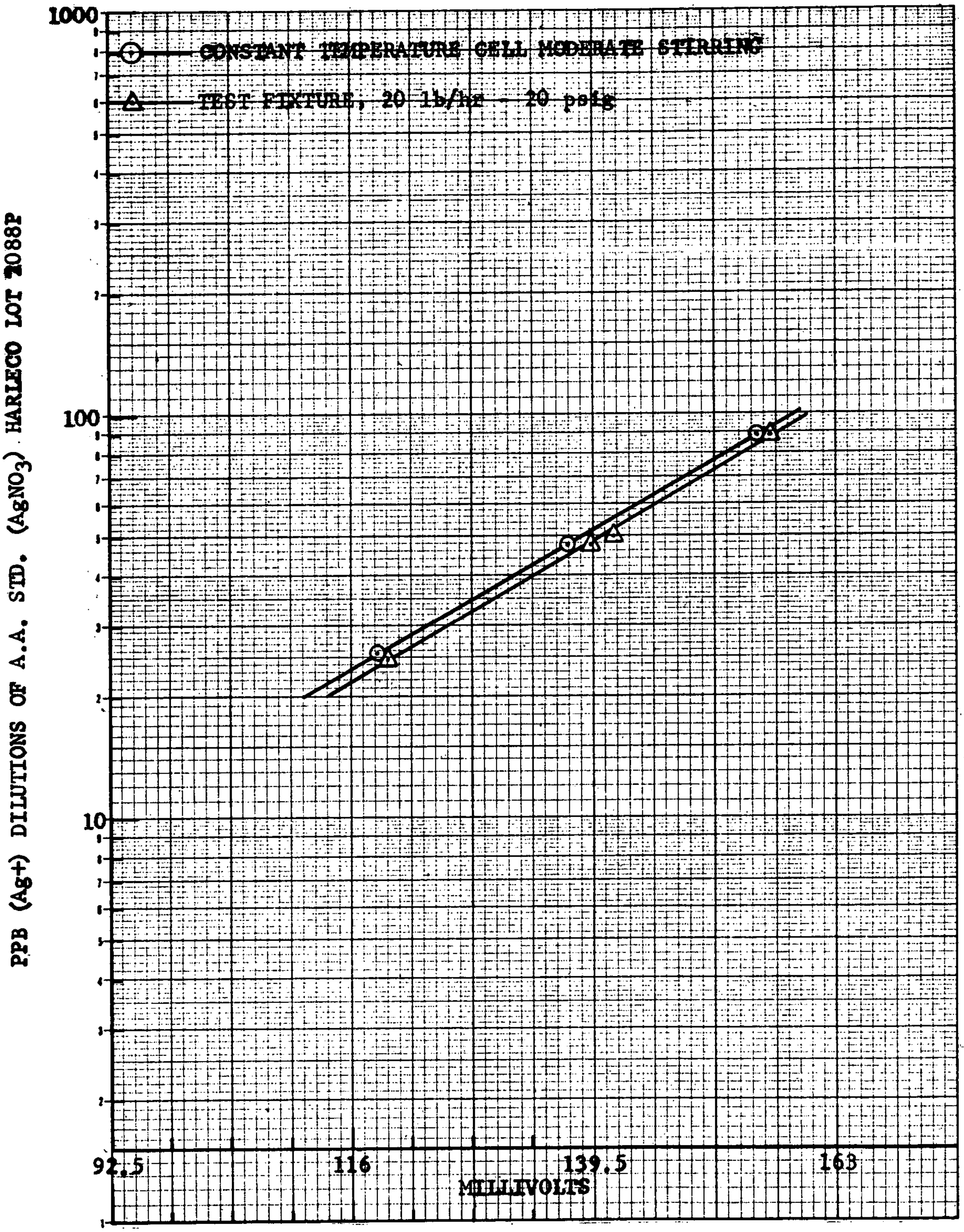


Figure 5-26. Response of QJPE/H3 Electrode Pair at 77°F

Apparatus: Test Fixture
Beckman 940 pH Analyzer
Beckman 10-inch Recorder

Electrodes: Reference--Quartz Fiber Junction, Pressure Equalizing
Sensing --Solid-State Silver Sulfide H3

Test Solution 125 ppb $[Ag^+]$

Flow lb/hr	Pressure psig	Indicated $[Ag^+]$ Conc ppb	Apparent Error $[Ag^+]$ ppb	Noise mV
20	10	125	0	1.0 max
	25	139	+14	1.0 max
	45	122	-3	1.0 max
40	10	140	+15	1.0 max
	25	135	+10	1.0 max
	45	128	+3	1.0 max
60	10	132	+8	1.0 max
	25	143	+18	1.0 max
	45	128	+3	1.0 max

Table 5-8. System Test Data--Pressure and Flow Effects at 113°F

The response curve for changes in silver-ion concentration at 113°F is given in Figure 5-27. Again, semilogarithmic response was observed between 25- and 125-ppb silver ion. Figure 5-27 does not contain a line for the response of the electrodes in the constant temperature cell due to the fact that the test fluids below 100-ppb silver ion began to show a loss of silver ion before the fluid became thermally stabilized at the required temperature.

This phenomenon was not observed in the test fixture since the test fluid was brought to temperature very rapidly as it passed through the heat-exchange coil.

Table 5-9 presents the effects of pressure of a flow at 149°F. The accuracy and validity of such data are questioned since such data points were obtained from readings which were in a constant state of drift and instability. Although the 77°F response tests following the 149°F tests showed a stable semilogarithmic response between 25- and 100-ppb silver ion, an examination of the silver-sulfide electrode H3 revealed a failure or separation of the adhesive/sealant at the interface of the adhesive and the silver-sulfide pellet. Tests on other silver-sulfide electrodes from the same batch as the H3 electrode also showed adhesive/sealant degradation after exposure at 149°F for 4 hours or more.

5.7 Calibration System

5.7.1 Calibration System Requirements

The calibration of any system requires the use of a standard solution of known concentration which must be stable and compatible with the measurement system. The value or concentration of the standard should be near to that anticipated for the unknown being analyzed. In addition, a means must be provided for storage, transportation, and introduction of the standard into the measuring system in a manner which does not affect in any way the standard or measuring system. Also, the standard, its properties and method of use, should be well understood.

The choice of a standard and method of calibrating the Residual Water Bactericide Monitoring System was severely restricted by the very low parts-per-billion range of silver ion required, the stringent requirement that the standard and method not contaminate the space shuttle water system, and the zero-gravity environment.

Since the calibration of a potentiometric measuring system requires that both sample and standard pass through the same measuring cell, the choice of silver material for the standard was limited to silver bromide and silver chloride to avoid contaminating the water system.

The stability of low parts-per-billion solutions of both these salts is very poor. On the other hand, methods to automatically and accurately dilute stable solutions of silver salts--e.g., 1000 ppm silver nitrate, $AgNO_3$, down to 50 ppb--are not reliable and would require a complex system.

In addition to the above requirements, the monitor system must provide for automatic calibration.

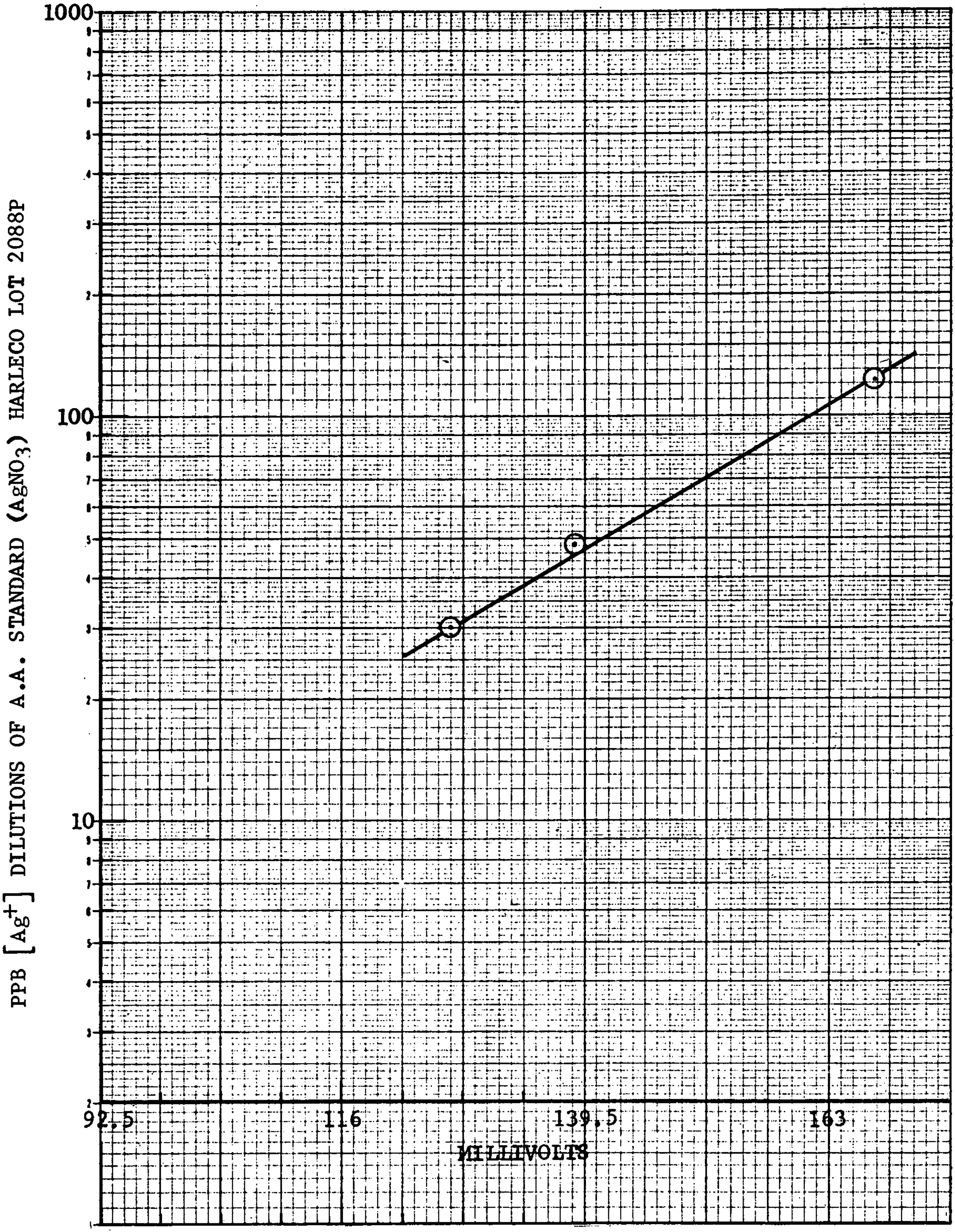


Figure 5-27. Response of QJPE/H3 Electrode Pair at 113°F, 20 lb/hr Flow at 20 psig

G

Apparatus: Test Fixture
Beckman 940 pH Analyzer
Beckman 10-inch Recorder

Electrodes: Reference--Quartz Fiber Junction, Pressure Equalizing
Sensing --Solid-State Silver Sulfide H3

Test Solution 100 ppb $[Ag^+]$

Flow lb/hr	Pressure psig	Chart Div Reading	Indicated $[Ag^+]$ Conc ppb	Apparent Error $[Ag^+]$ ppb	Noise (mV)
20	10	80	?	?	2.5 mV with spike
	25	72	?	?	
	45	59	?	?	
40	10	93	?	?	
	25	82	?	?	
	45	67	?	?	
60	10	98	?	?	
	25	90	?	?	
	45	79	?	?	

All readings unstable and drifting.

No calibration or span check possible.

After rechecking response at 77°F, electrode was sectioned and adhesive/sealant observed to have failed at interface of silver-sulfide pellet and electrode body.

Table 5-9. System Test Data--Pressure and Flow Effects at 149°F

5.7.2 A Calibration Standard--Theoretical Approach

The solubility of silver bromide in water at ambient temperature is about 100 ppb, which is close to the required concentration of silver ions needed for bactericidal action. Thus, a source of saturated solution of silver bromide would fulfill the requirements for the standard needed to calibrate the Residual Water Bactericide Monitor.

The saturated solution of silver bromide can be provided by passing deionized water through a silver-bromide/glass-bead column. A calibration loop consisting of an ion exchange resin column, followed by a silver-bromide/glass-bead column, would provide the saturated solution which then would be pumped through the measuring cell.

Since the solubility or saturation of silver bromide changes rapidly with temperature changes near ambient, a means must be provided to correct for such variations to provide accurate calibration. Enclosing the silver-bromide column and associated tubing within a heating jacket and providing thermostatic control would add complexity to the system. It is believed that a thermocompensator--such as used in pH systems--can be placed in the silver-bromide column, and its change in resistance due to changes in temperature of the column would automatically adjust the electronic output of the calibrating system for silver-bromide solubility changes due to temperature changes.

5.7.3 Verification Testing of the Theoretical Approach

The use of a column of silver bromide to provide a reliable calibration standard was investigated. A silver-halide canister was filled with a mixture of glass beads and fine powdered silver bromide, in accordance with the data given in the Chemtric report. Distilled water was passed through the column at room temperature, then measured for silver-ion concentration with the silver-sulfide electrode system. In order to achieve saturation of the water with the silver bromide, it was found necessary to recirculate the water through the column for at least one hour. At saturation, a level of 75- to 77-ppb silver ion was measured at room temperature. To be applicable to our proposed calibration method, the silver-bromide column must saturate a water sample flowing through the column at a rate of up to 40 lb/hr on a single pass.

Chemtric confirmed the data given in their final report that saturation was achieved with the silver-bromide column at flow rates up to 60 lb/hr at room temperature. Their analysis of the water for silver-ion concentration, using an atomic absorption method, gave a silver-ion concentration of 80 ppb at saturation. This is in excellent agreement with our analysis at saturation of 75- to 77-ppb silver ions.

Further study of the problem of obtaining saturation on a single pass revealed that the silver bromide used in our column was contaminated. This was confirmed by comparing the color of a sample of silver bromide of known purity with that used in the column. The known sample had a very light yellow color while that used in the column had a deep orange-yellow color.

An empty halide canister was shipped to Chemtric where it was filled with a mixture of their quality of silver bromide and glass beads. Upon return to Beckman, the column was installed in a modified version of the Test Fixture. The test assembly is shown schematically in Figure 5-28.

It was necessary to condition the column for 18 hours with several changes of distilled water recycled through the canister. A total of 18 gallons of distilled water was used as the silver-ion concentration dropped from 1000 ppb to below 100 ppb.

The reason for the conditioning requirement is not completely understood. However, since the increased silver levels were detected with the potentiometric system, it is unlikely that the material was silver-bromide fines which would be subject to the same solubility limitations (76 ppb saturated at 73°F) but, rather, that it was due to some highly soluble silver contaminant(s). This condition has also been experienced by Chemtric.*

A bench system was calibrated at 73 ±0.36°F using dilutions of a Silver Atomic Absorption Standard (HARLECO). The silver-bromide canister, in series with the output of the constant-temperature heat exchanger, was maintained at 73.4°F throughout the test. Results of the flow tests are given in Table 5-10. The silver-ion concentration measurements noted in the table were made on individual water samples taken after a single pass through the canister.

Flow[1] lb/hr	Concentration ppb $[Ag^+]$
13	76
26	76
40	78
13 for 2 days	76 ±2

[1] At 10 psig

Table 5-10. Silver-Ion Concentration vs. Flow for the Silver-Bromide Canister

The literature values for the solubility of silver bromide at various temperatures vary such that at 77°F, silver-ion concentrations of from 70- to 100-ppb may be calculated.

The important thing at the present time is the demonstrated stability of the silver-bromide canister as a source of a calibration fluid.

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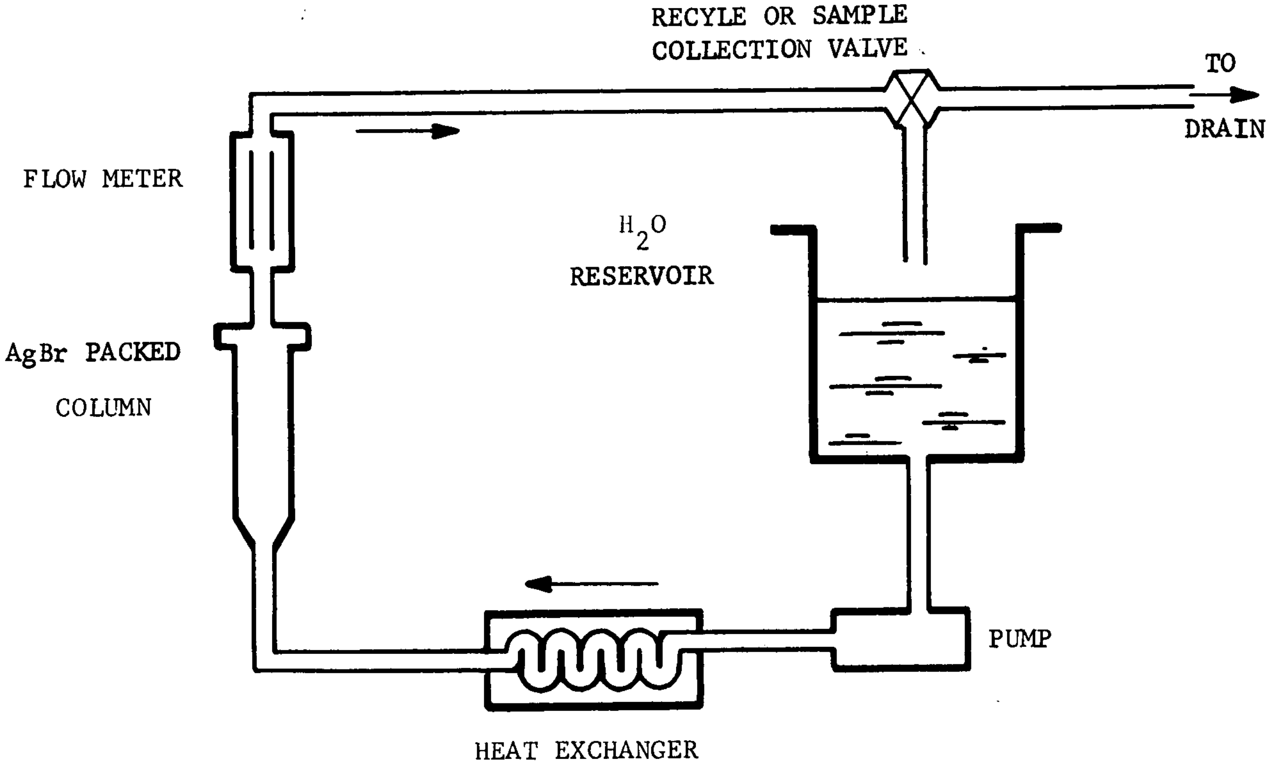
*Personal communication--W. Jasionowski



NOTE: SYSTEM WAS MAINTAINED AT 10 psig FOR ALL FLOWS.

Figure 5-28. Schematic of Test Assembly for Verification Testing of the Calibration Method

6.0 INSTRUMENT PACKAGE DEFINITION

6.1 Introduction

Based upon the knowledge gained during the technique selection and testing phases of the program, it was possible to derive a preliminary design of a silver-ion monitoring instrument package that would be compatible with the characteristics of the Space Shuttle Potable Water Supply System.

The constraints of low weight and volume were given prime consideration during the instrument definition stage. However, the volumes and weights given for the conceptual system are estimated maximums and do not represent the probable lower volumes and weights obtainable from a detailed design.

6.2 Technical Approach

6.2.1 System Design Philosophy

The basic philosophy of the approach to the instrument package definition 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 would not burden a program with the high cost of the qualified components during a prototype flight unit development.

6.3 Monitoring System Definition

6.3.1 General

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

In the monitoring mode, the sample would flow from the potable water system of the shuttle through the system isolating valve, V1, through valve V2, then through the pump and sensor chamber. This would provide an almost constant flow of sample to the sensor chamber. The effluent from the sensor chamber would return to the water system through valves V3 and V1. As the water sample passed through the sensor chamber, the concentration of the silver ion

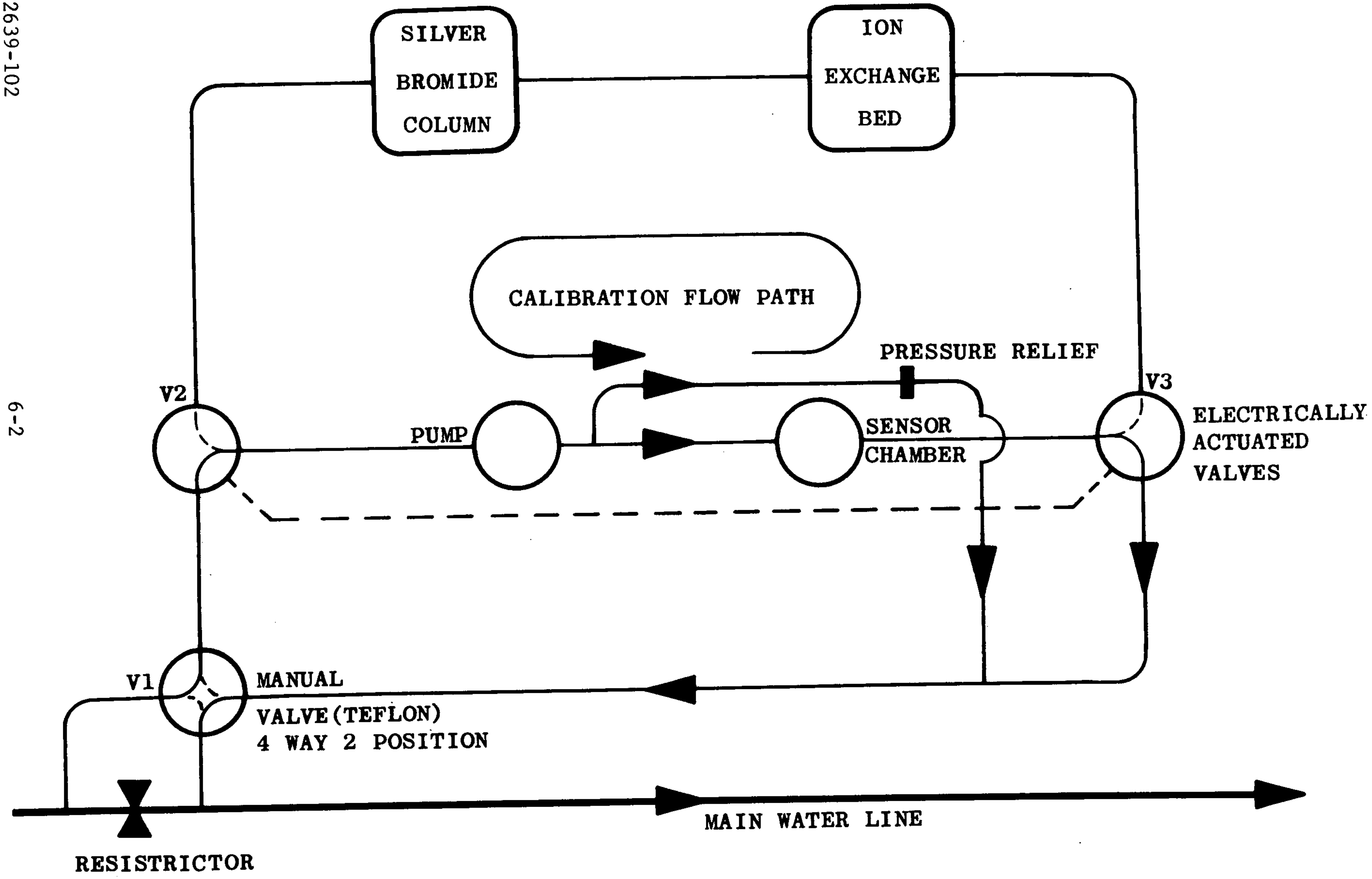


Figure 6-1. Flow Diagram--Residual Water Bactericide Monitor

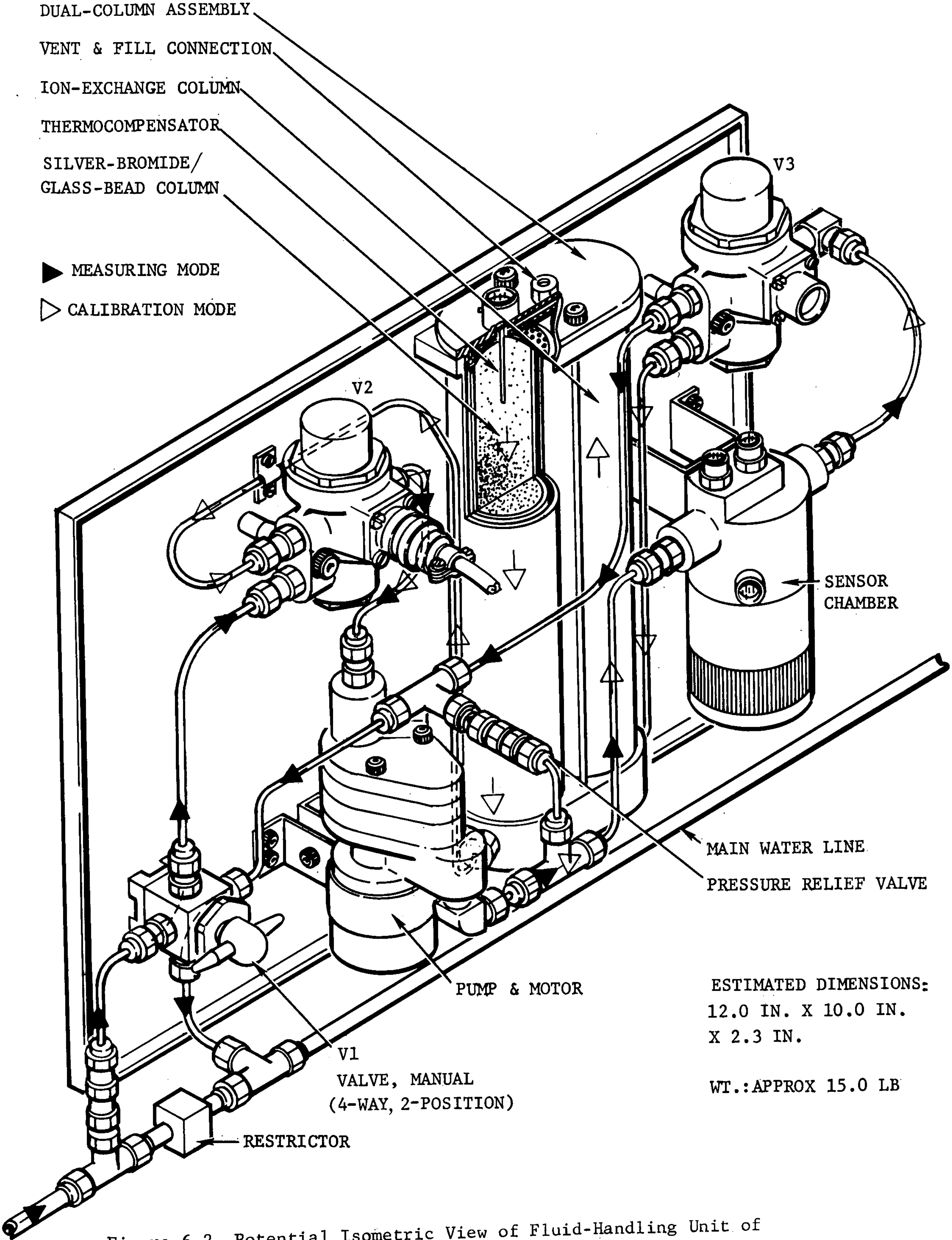
in the water would be detected by the potentiometric electrodes. The signal from the electrodes would be processed by the electronics package and the concentration of the silver ion in the water sample indicated on a meter. During periods in which water in the main water line would not be flowing, the 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.

In the automatic calibration mode, a timer circuit in the electronics package would initiate the calibration sequence approximately once every 20 hours. Solenoid valves V2 and V3 would be activated, and place the pump and sensor chamber in a closed loop with the dual column, thus forming the calibration loop. The pump would circulate the water in the line through valve V3 and into the deionizer chamber of the dual column where the ion exchange resins would remove all of the silver and bromide ions. The deionized water would then be routed through a check valve to the silver-bromide chamber. The silver-bromide chamber would be filled with a mixture of glass beads and fine powdered silver bromide, AgBr. Water passing through the silver-bromide column would become saturated with silver bromide at a concentration defined by the solutions coefficient of the AgBr at the ambient temperature of the system. This would be the calibration fluid which would be passed through valve V2 and pumped to the sensor chamber where the concentration of the silver ions would be detected. The automatic calibration electronics would compare the output of the electrodes with a known value and adjust the readout accordingly.

Physically, the silver-ion monitoring system would consist of two units, a fluid handling unit and an electronic package which would include the readout meter.

6.3.2 The Fluid Handling Unit

A concept of the fluid handling unit is shown in Figure 6-2, Potential Isometric View of Fluid Handling Unit of Silver Monitor. The major components of this unit would be the sensor chamber which houses the electrodes, the pump which circulates the water sample and calibrating fluid, the dual column assembly which would contain the ion exchange resin column and the silver-bromide column, and the valves. The components would be mounted approximately as shown on an aluminum supporting frame. All components would be mounted to the frame directly or by brackets. Ample space would be provided to service the sensors and replaceable electrolyte cartridge. Replacement of the cartridge would not require any other mechanical or electrical disassembly. The dual-column assembly would contain two expendable cartridges that could be replaced by removing the lid of the assembly and lifting the used cartridges out. After replacement of the cartridges, 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 would be provided for this purpose. The entire assembly would be enclosed with an aluminum cover. Each of the components will be defined in the following paragraphs and their function(s) explained.



ESTIMATED DIMENSIONS:
12.0 IN. X 10.0 IN.
X 2.3 IN.

WT.:APPROX 15.0 LB

Figure 6-2. Potential Isometric View of Fluid-Handling Unit of Silver-Ion Monitor

6.3.2.1 Components

6.3.2.1.1 Manual Valve

The system would use a Teflon, manual, 4-way, 2-position valve that would be used only when the sensor cell or silver-ion generator or deionizer were to be serviced. The valve chosen for this purpose would be 2-1/8 inches high, and the body would be a 1-inch cube, plus fittings for the 1/8-inch-diameter, stainless-steel tubing. This would be a commercial valve manufactured by Fluorocarbon Company of Anaheim, California, P/N SC P2-12-4C.

6.3.2.1.2 Fluid Pump

The fluid pump would be a fixed-displacement, motor-driven gear pump. Its purpose would be to provide a constant flow of sample water to the sensor cell during sensing and calibration. The gear pump which has been chosen is a qualified, flight-approved component. The flow rate would be a function of outlet pressure. At a 65-psig outlet pressure, the flow rate would be 0.11 gpm. The motor that would drive the pump would be a synchronous, 110 Vac, 400-Hz motor chosen for low electrical noise requirements. A synchronous ac motor would be safe to operate in oxygen-enriched atmospheres. The power consumption would be approximately 30 watts at 70°F, and the motor would weigh 2.75 pounds. The pump housing would be stainless steel with Delrin gears for long life and quiet operation. The pump would be approximately 2-1/4 inches in diameter, 2-3/4 inches long. It would weigh approximately 1.25 pounds. The pump is manufactured by Hydro-Aire of Burbank, California.

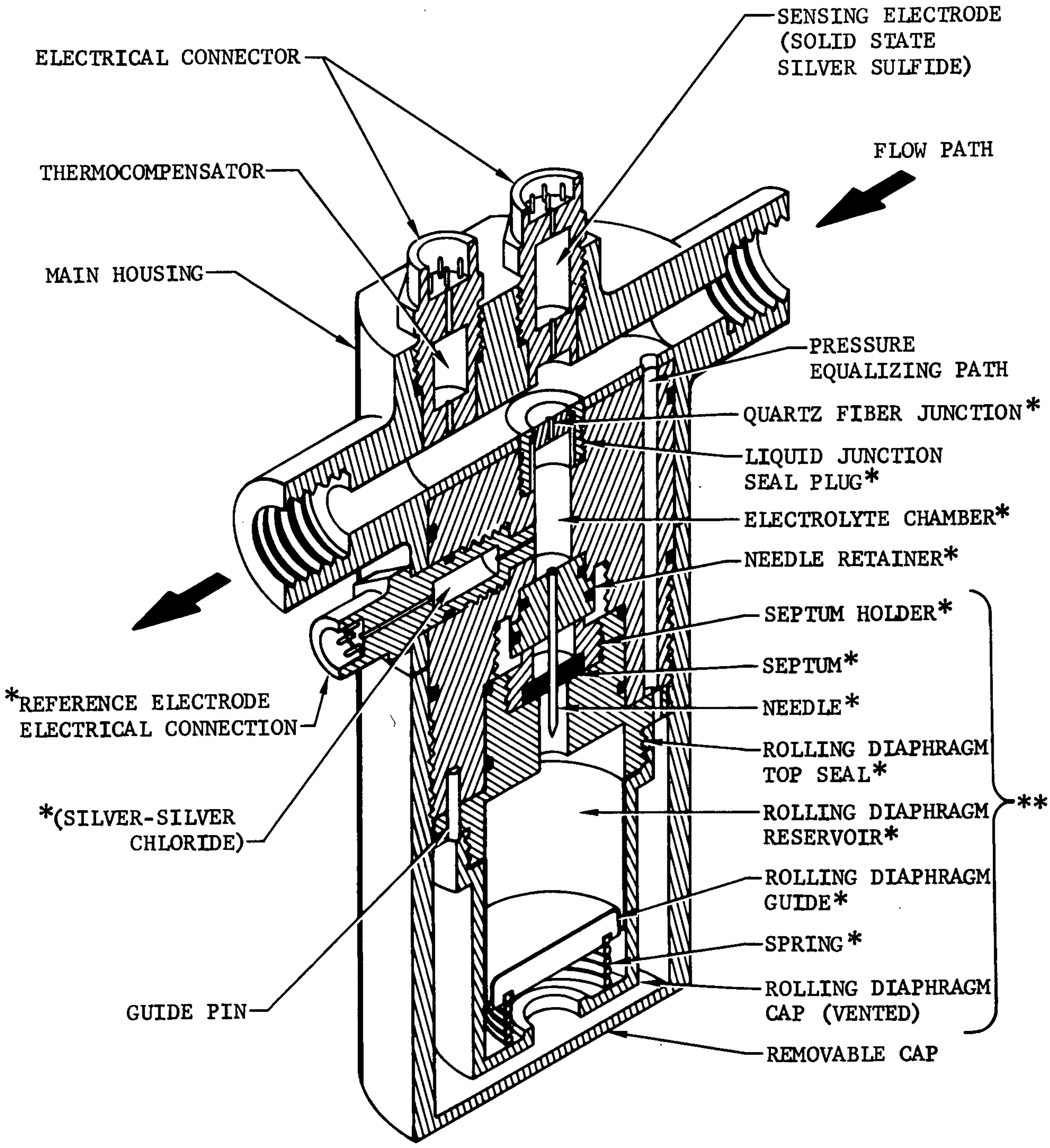
6.3.2.1.3 Sensor Chamber

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

The sensor chamber would be designed to be cylindrical in shape and contain the silver-ion sensing electrode, the reference electrode, the electrolyte chamber, quartz fiber junction, and the replaceable electrolyte cartridge. A thermocompensator also would be mounted in the chamber. The chamber would provide a straight flow-through path for the water sample along which would be located the sensors (Figure 6-3).

Within the sensor chamber there would be three flow paths:

- A straight-through flow path for the water sample. As the sample flows through the chamber, it would pass between the sensing electrode and the quartz junction of the reference, then past the thermocompensator. Previous studies have shown the straight flow path provides optimum electrode response with low noise.
- A pressure-equalizing sample path. A portion of the water sample would flow into the cavity occupied by the rolling diaphragm and apply system pressure on the diaphragm in addition to the spring



*COMPONENTS OF REFERENCE ELECTRODE

**ELECTROLYTE CARTRIDGE

SIZE: APPROX 2" DIA. x 5" LONG
WT: APPROX 0.8 LB

Figure 6-3. Half-Section of Sensor Chamber pressure. Equalizing the pressure on both sides of the quartz junction with system pressure would be required to minimize sensitivity of the reference to pressure changes.

- Electrolyte flow path. The electrolyte which would be stored in the rolling diaphragm reservoir would flow 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 1.69 x 10^{-3} fl. oz (50 microliters) per day. The concept of a replaceable rolling diaphragm reservoir is proposed to simplify maintenance and increase reliability. (The replaceable reservoir was described in paragraph 6.3.3.2.4.)

The sensor chamber would be connected to the monitoring system as shown in Figures 6-1 and 6-2. All parts should be AN 10050-2 or -4. The electrical connections between the sensor chamber and electronics subassembly would utilize Bendix or other approved electrical disconnects.

The sensor chamber is estimated to measure 2 inches in diameter and 5 inches in length. Its estimated weight is 0.8 pound.

6.3.2.1.4 Sensor Chamber and Pump Interface With Calibration Loop

The sensor chamber and pump would be connected to the calibration loop whenever the two electrically-operated solenoid valves, V2 and V3, would be activated (Figure 6-1). These valves would be automatically activated during the short calibration sequence which would be controlled by the calibration electronics.

6.3.2.1.5 Materials and Subsystem Compatibility

All items in contact with the potable water should be stainless steel or Kel-F, with the exception of the sensors. No materials in contact with the potable water should affect or be affected by the condition of the water.

6.3.2.1.6 Solenoid Valves

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

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

6.3.2.1.7 Pressure Relief Valve

A small relief valve would be 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.

6.3.3 The Electrodes

6.3.3.1 The Silver-Ion Sensor

The silver-ion sensor would be a solid-state, silver-sulfide electrode which was shown to exhibit Nerstian response at least to 10 ppb of silver ion. The active part of the electrode would consist of a dense silver-sulfide pellet or membrane fabricated with a silver wire as an integral part of the pellet. The inner wire of a shielded cable would be soldered to the exposed portion of the silver wire. The silver-sulfide pellet and a small portion of shielded cable would be sealed in an electrode housing or body. The electrode would develop a millivolt (potential) output as a result of exchange or transport of silver ions from a sample solution through the pellet or membrane. The millivolt output would be proportional to the silver-ion activity in the sample solution.

Under the present contract, this electrode configuration was shown to be suitable as the sensing electrode for a silver-ion monitor for the space shuttle water system and the physical characteristics of the silver-sulfide pellet make it readily adaptable to a wide configuration of sizes and shapes. Thus, any new design of the sensing electrode would be made to be representative of a flight component.

The sensing electrode body would be fabricated from a NASA-acceptable material such as polypropylene. The sensing electrode would be mounted in the sensor chamber body by a threaded connection with the sensitive silver-sulfide pellet exposed to the flowing sample.

6.3.3.2 Reference Electrode

A variety of reference electrode designs were evaluated during the technique testing phase. The final configuration which 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 design is shown as part of Figure 6-3 and described in the following paragraphs.

The reference electrode subsystem would consist of the following components all contained within the sensor chamber.

- A silver-silver chloride 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 (1M KNO_3);

- A quartz fiber junction having a flow of approximately 1.69×10^{-3} fl oz (50 microliters) per day of electrolyte;
- A replaceable electrolyte cartridge;
- A needle to connect the secondary electrolyte chamber with the reservoir.

6.3.3.2.1 Silver-Silver Chloride Electrode

The silver-silver chloride electrode would have a glass body or spacecraft approved plastic mounted in a plastic cap through which the electrical connections would be made to the internal silver wire. The internal silver wire would be coated with silver chloride and surrounded by a saturated solution of potassium chloride. A porous ceramic rod would provide diffusing liquid junction with the 1M KNO_3 solution, or secondary electrolyte.

6.3.3.2.2 Quartz Fiber Junction

The quartz fiber junction would consist of a quartz fiber(s) held in a glass or other spacecraft approved nonmetallic disc. The disc would be held in place and the periphery sealed with a threaded cap. The quartz-fiber junction would be replaceable through the mounting port of the sensing electrode.

6.3.3.2.3 Secondary Electrolyte Chamber

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

6.3.3.2.4 Electrolyte Cartridge

The replaceable electrolyte cartridge would contain approximately 0.5 fluid ounce of 1M KNO_3, which would be expended in approximately 7 to 10 months when installed in the sensing unit. The cartridge body would be Kel-F and contain a rolling silicone rubber diaphragm. A spring would be provided to press on the diaphragm and produce a constant electrolyte pressure on the quartz-fiber junction. A portion of the water from the sample stream would be 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 would be that supplied by the spring. The cartridge would be prefilled, and have an estimated shelf life of greater than 2 years.

6.3.3.2.5 Electrolyte Needle

The electrolyte cartridge would be designed to be sealed by means of a silicone rubber septum. When installed in the sensor chamber, a hypodermic-type needle would pierce the septum, allowing the electrolyte to enter the secondary electrolyte chamber. The electrolyte cartridge would be intended for ground replacement, however. The weight of the electrolyte cartridge is estimated to be less than 0.55 lb. The outer case would be a CRES alloy that would act as an electrical shield for the electrode.

6.3.3.2.6 Thermocompensator

The thermocompensator will consist of a specially-designed resistor whose electrical characteristics vary with temperature in such a manner as to electrically compensate for response changes of the sensing electrode due to temperature variation. The thermocompensator would be located in the main flow path of the water sample within the sensor chamber.

The thermocompensator would mount in the sensor chamber via a threaded connection and would readily be replaceable.

6.3.4 Calibration System

6.3.4.1 Theoretical Design

The proposed approach for accurate calibration would be 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 would circulate water through an ion exchange column where any silver ions would be removed, then through a silver-bromide/glass-bead column where the water would be saturated with silver bromide. The saturated solution would pass through the pump, then through the sensor chamber where the silver ions would be detected by the electrodes. The automatic calibration electronics would compare the output of the electrodes with the known value and perform an electronic compensation accordingly. Since the solubility of the silver bromide in water would vary significantly with small changes in temperature, a means of compensating for the change in solubility would be required. A thermocompensator, located in the silver-bromide column and connected to the calibrating electronic circuit, would provide the necessary correction. The calibration loop is shown as part of Figure 6-1.

6.3.4.2 Mechanical Design

During the calibration mode, both three-way, two-position solenoid valves would be energized, providing a closed loop of fluid for circulation through the silver-ion sensor cell. The water would first go through an ion-exchange chamber where the anions and cations would be removed. The fluid would then pass through a check valve, which would prevent backward flow of the silver ions, then enter the second chamber where the silver bromide would saturate the fluid with 70-80 ppb $[Ag^+]$.

6.3.4.3 Interface Design

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

C2

6.3.4.4 Dual-Column Design

The dual-column assembly would contain two replaceable cartridges--the deionizer cartridge and the silver-bromide cartridge--as well as a check valve. Each type of cartridge would be of a different diameter to prevent incorrect assembly of the two cartridges. The purpose of the check valve would be to prevent silver and bromide ions from migrating backwards into the deionizer from the silver-bromide column. The lid would be O-ring sealed to the cartridge housing. The lid would contain a cross-connection flow path with a cartridge check valve between the two chambers. A fill and vent valve would be located on the lid to purge the calibration loop of air during servicing. The dual-column is shown in Figure 6-4.

6.3.4.4.1 Deionizer Cartridge

The cartridge would contain anionic type IR-45 and cationic type IR-120 ion-exchange resins placed in separate layers to prevent mixing of acid and basic chemicals. These resins would remove all silver and bromide ions in the calibration fluid. The deionized water would then be routed through the check valve to the silver bromide chamber. The volume of the deionizer cartridge is estimated to be approximately 7.63 in^3.

6.3.4.4.2 Silver-Bromide Cartridge

As the calibration water would pass through the bed of silver bromide/glass beads, it would become saturated with silver bromide. The 0.441 lb of 50-micron glass beads increases the surface area of the 0.353 lb of silver bromide. The replaceable cartridge would be approximately 1.75 inches in diameter by 9 inches long. There would be suitable screens and filtration material at the outlet to prevent loss of the glass beads.

6.3.4.4.3 Fill and Bleed Valve

Provisions would be made to add water and bleed any trapped air when the deionizer cartridge or silver-bromide cartridge would be replaced.

6.3.5 Monitor Electronics

6.3.5.1 General

The monitor electronics should 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 ions;

b. Automatically compensate for temperature variations in the solution and system;

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

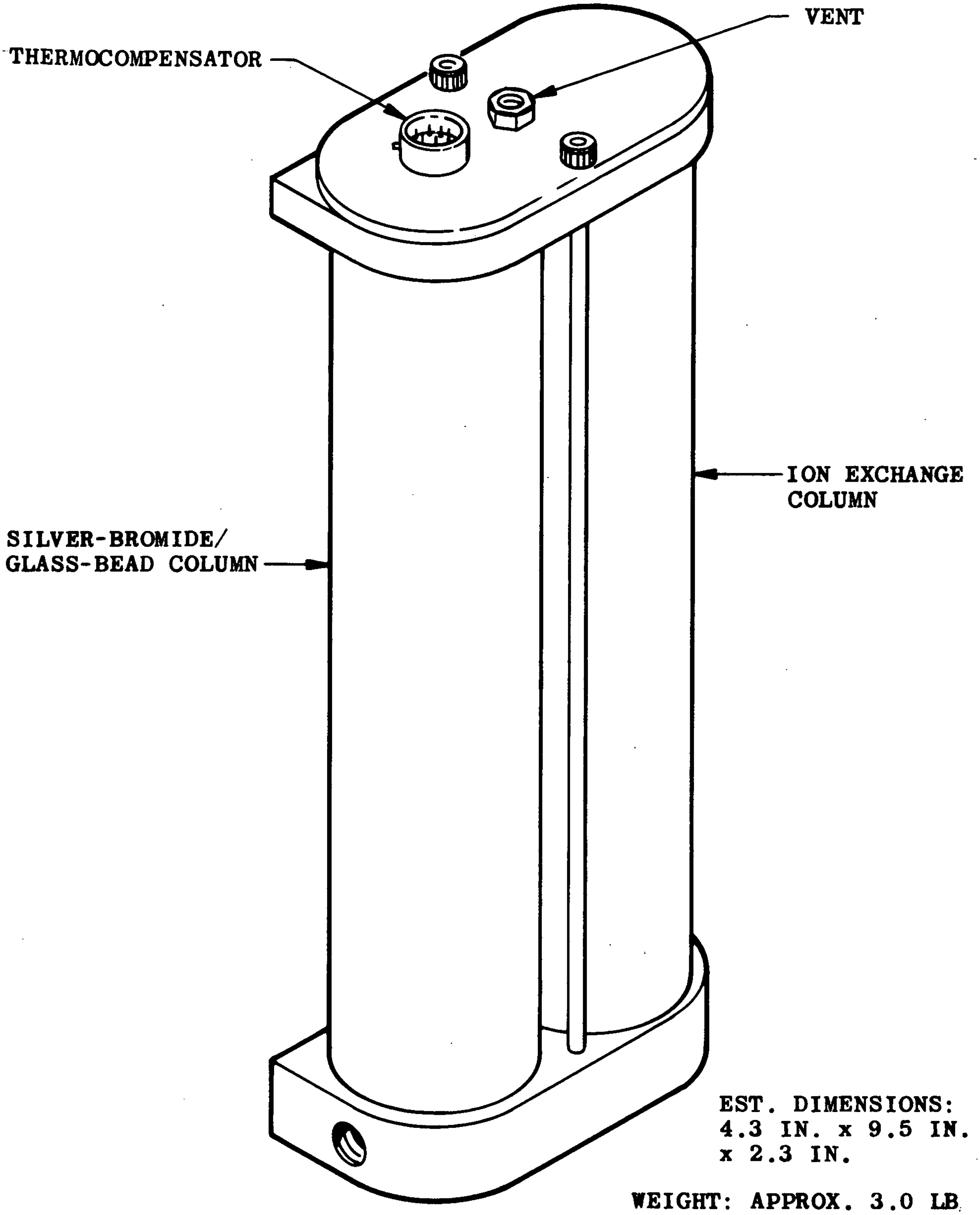

Figure 6-4. Dual-Column Assembly

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.

Figure 6-5 shows the indicators and controls which would be required for the sensor electronics. The general block diagram for the electronics is shown in Figure 6-6.

The electronics should have the following criteria:

- Eventual utilization of NASA flight-approved parts;
- Small size and weight;
- Low power consumption;
- Fail-safe performance;
- Ease of accessibility and maintenance;
- Compatibility with other systems--lack of RFI and EMI, etc.

6.3.5.2 Electrical Design

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

- Logic and Valve Actuation

    a. Sequencer
    b. Logic
    c. Valve and relay drivers
    d. Valves and relays

- Calibration Electronics

    a. Comparators
    b. Logic
    c. Directional relay drivers
    d. Directional relays
    e. Motor
    f. Calibration pot

- Signal Processing and Readout

    a. Buffers
    b. Instrumentation amplifier
    c. Sample-and-hold circuit
    d. Readout meter

- Electronic Integration Components

    a. Power conditioning dc-dc converter and regulators
    b. Wiring harness
    c. Front panel

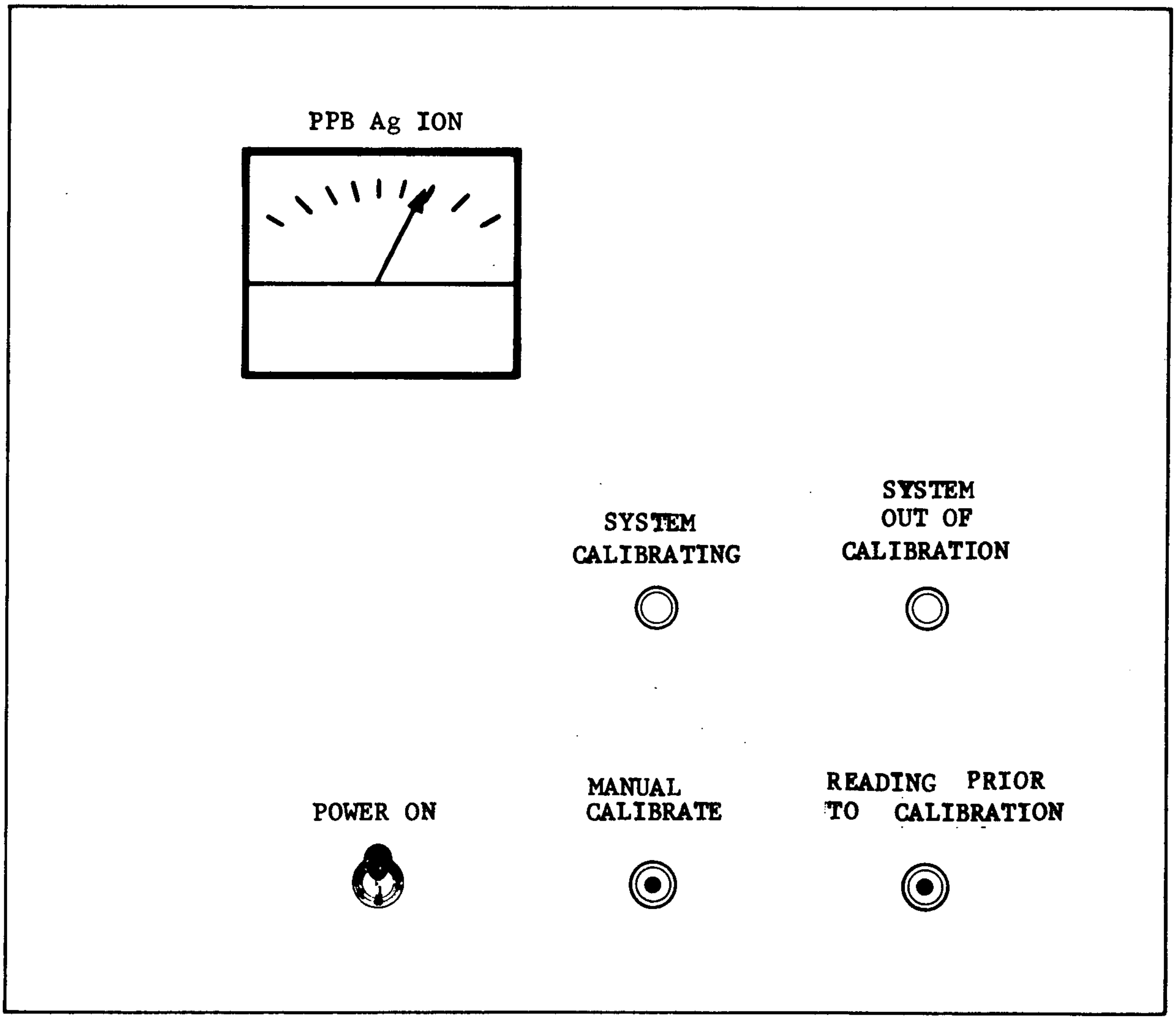

Figure 6-5. Electronic Controls and Indicators

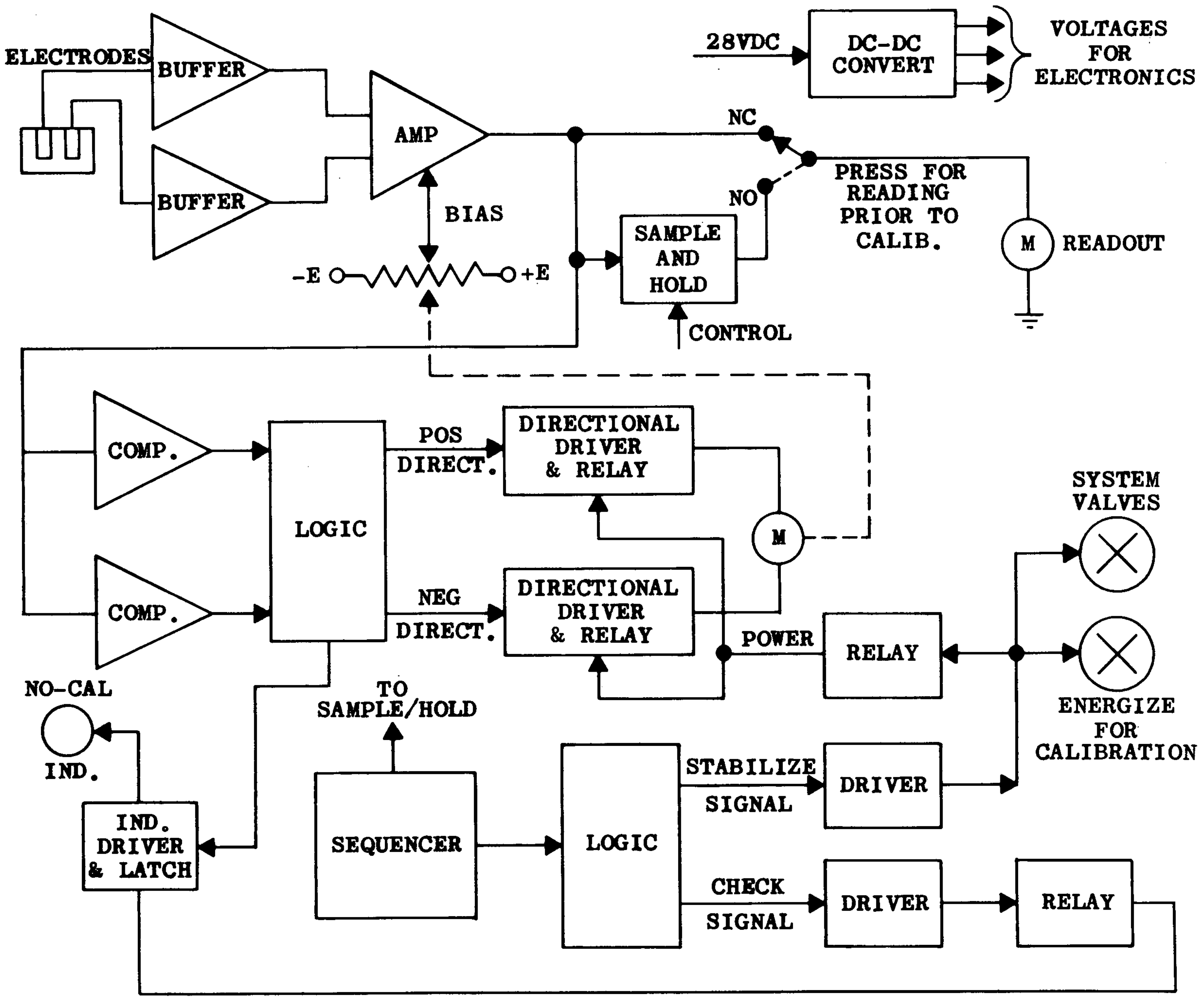

Figure 6-6. **Electronic Block Diagram**

6.3.5.2.1 Logic and Valve Actuation

A detailed block diagram of the logic and valve actuation system is shown in Figure 6-7. The unit would consist of a clock oscillator, a base divider, a divider chain, logic, and drivers.

Figure 6-8 shows the waveforms (logic would be positive). The clock oscillator would consist of a Mostek MK5009P timer circuit and produce a clock signal which would be a 1.33×10^{-2} Hz square wave. A second Mostek MK5009P is employed as a divider. It would divide the clock by 1000 to produce the base clock, a square wave with a period of 20.8 hours. Each time the base clock would go positive, the differentiator circuit would produce a positive spike which would reset the divider chain of three flip-flops.

The three-flip-flop divider chain and its associated logic would form a "hang-up" counter. After reset, the divider chain would start to respond to clock pulses and count, as shown by A, B, and C in Figure 6-7. The divider's clock, however, would be gated by the logic output expression ABC. If the count should be anything but seven, the clock pulses would be gated through and operate the divider chain. When the count reached seven, the gate would allow no more pulses to pass through to the divider chain, so the divider would stay "hung-up" in the seven state, until the base clock produced another spike, in approximately 20.8 hours.

The logic would also produce additional expressions. $\overline{ABC}$ operates the driver which would energize the system valves and a relay which would place the unit in the calibration mode. ABC would operate the driver which would energize the calibration check relay.

If a manual initiation of a calibration cycle would be desired at any time, the operator would depress the manual calibration initiate switch. This would not interfere with the automatic sequence of calibration, except that pushing the manual calibration switch during a calibration interval would reset the divider chain and restart the calibration interval.

6.3.5.2.2 Calibration Electronics

The calibration electronics would respond to the signal from the logic every 20.8 hours, or whenever the calibration sequence would be manually initiated. The "stabilize system" signal would be on for seven count periods. This would amount to 8.75 minutes.

Figure 6-9 shows a block diagram of the calibration electronics.

During the calibration period, the "stabilize system" command would pull in the calibration relay. The contacts would apply power to the directional drivers and relays. The comparator outputs would have the characteristics shown in Figure 6-10. If, during the stabilization period, the instrumentation amplifier output should be in the dead zone, no power would be applied to the motor. Should the amplifier output be too low, the low comparator output would go high,

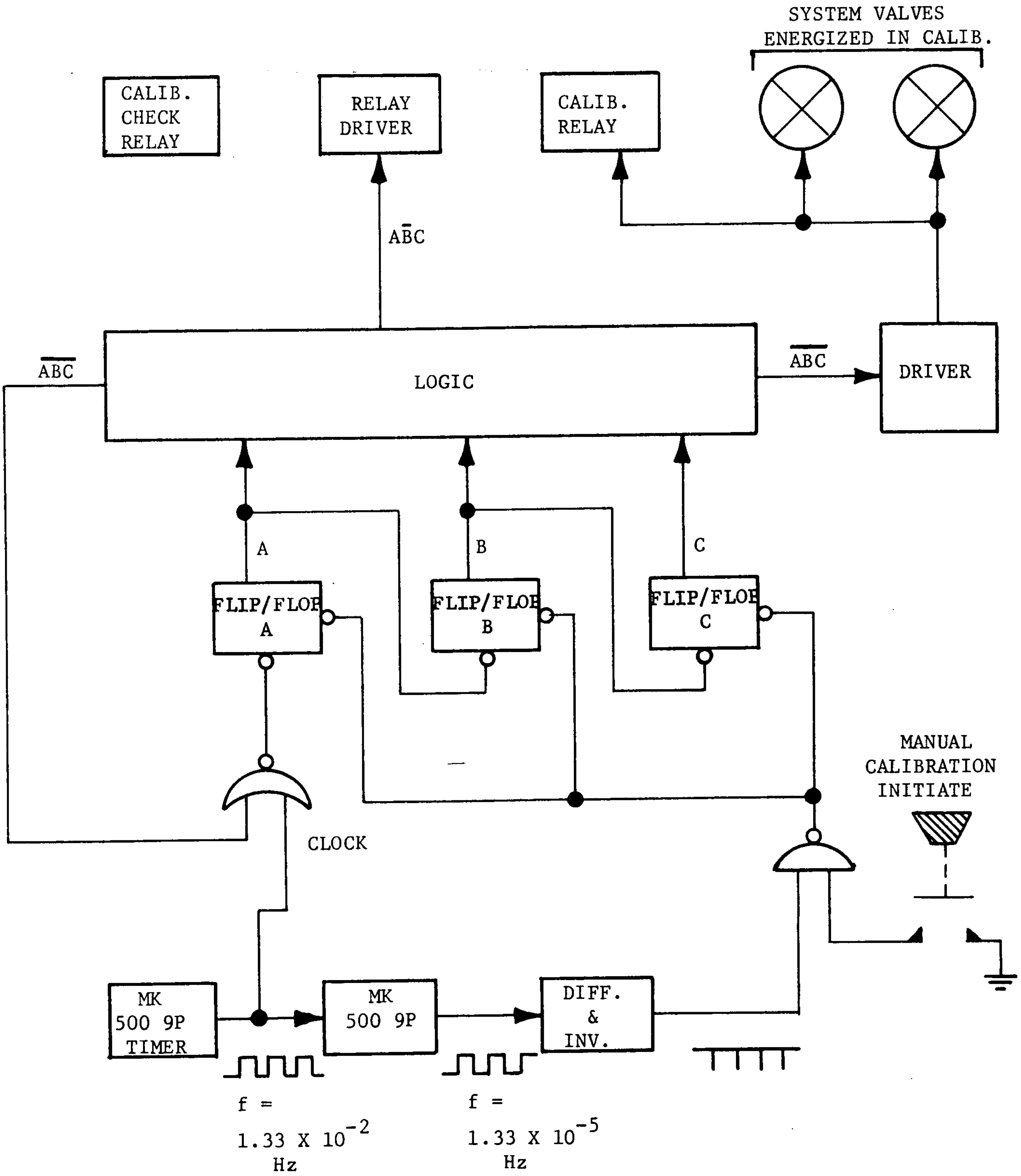

Figure 6-7. Logic and Valve Actuation--Block Diagram

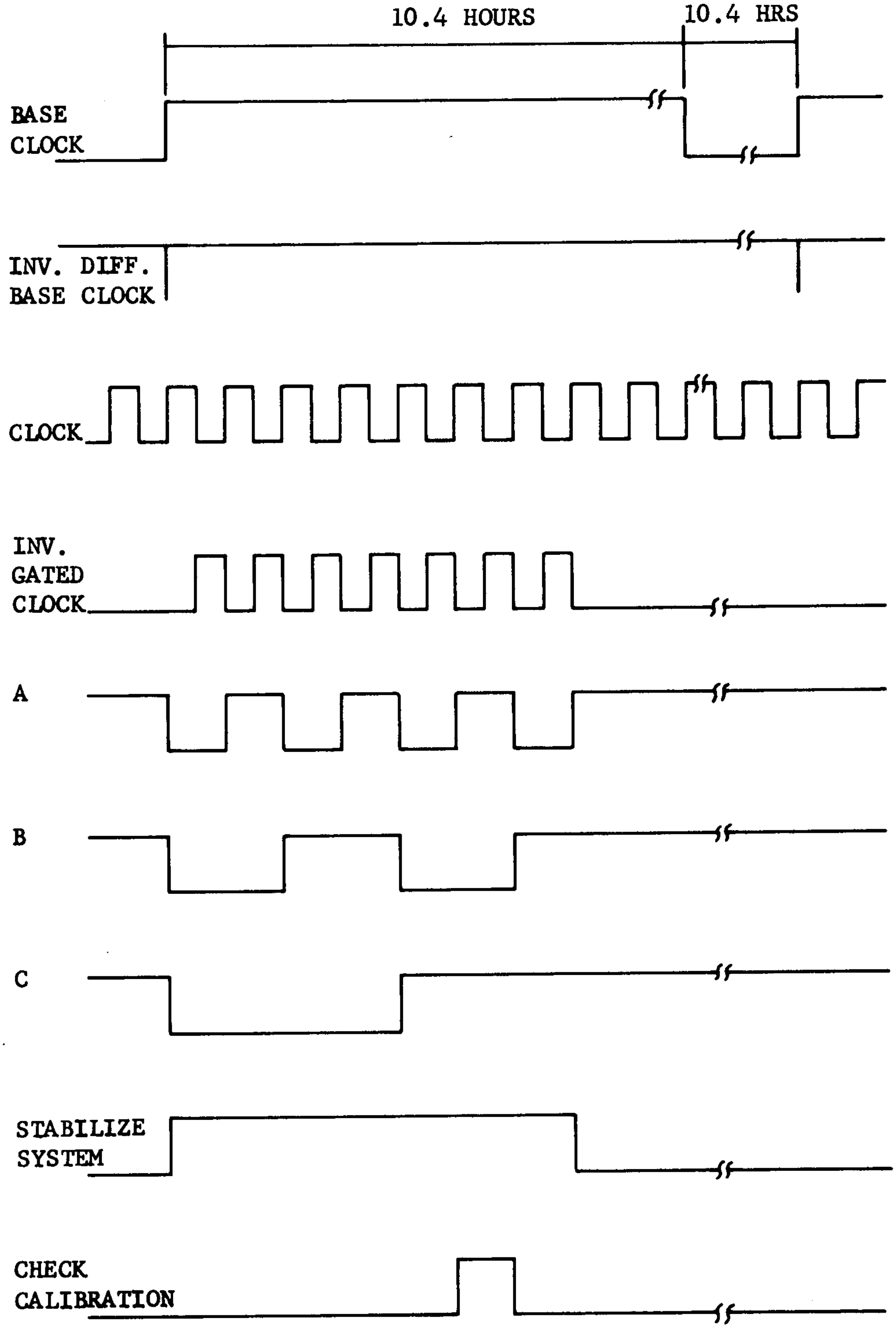

Figure 6-8. Logic Waveforms

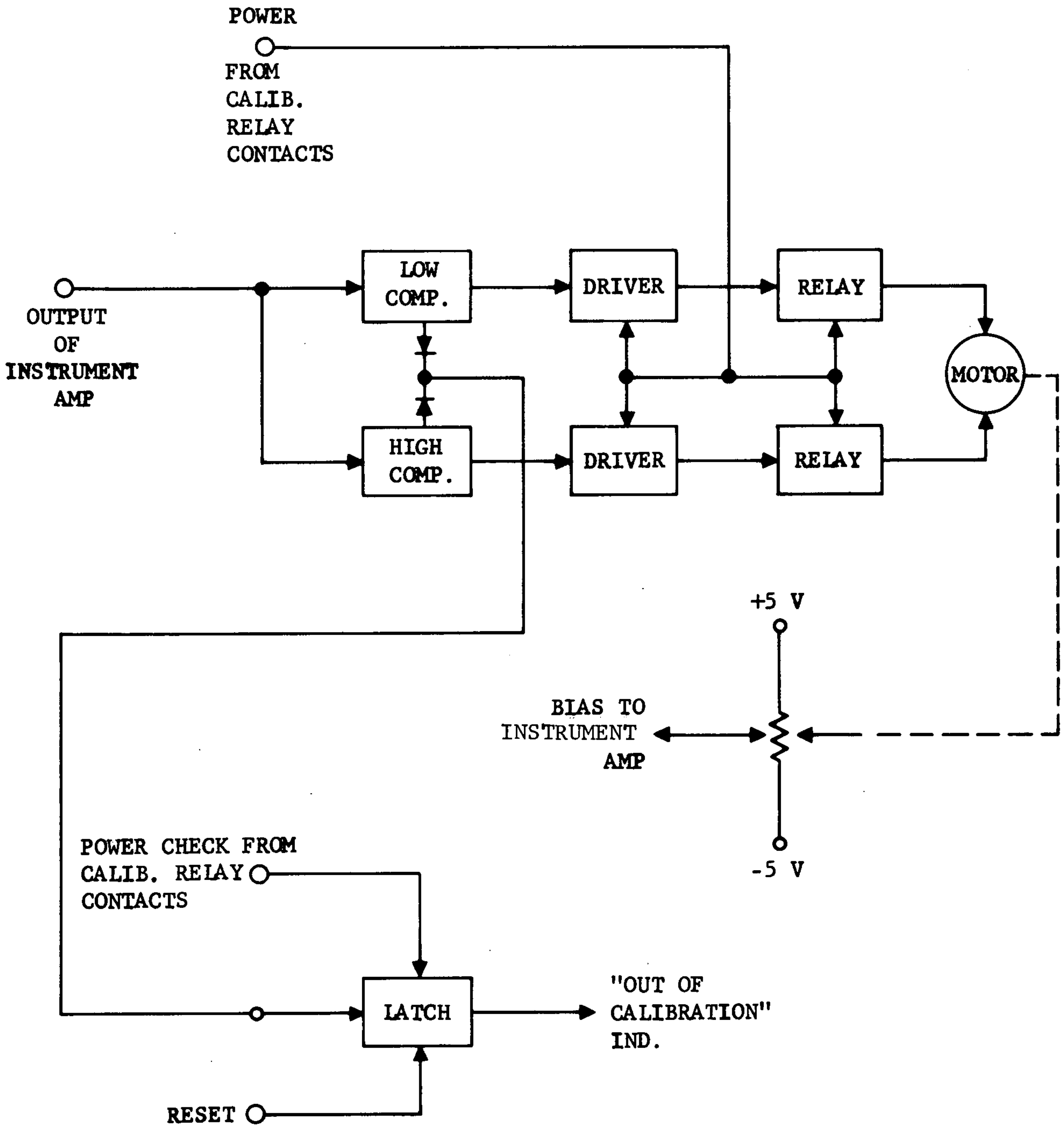

Figure 6-9. Calibration System--Block Diagram

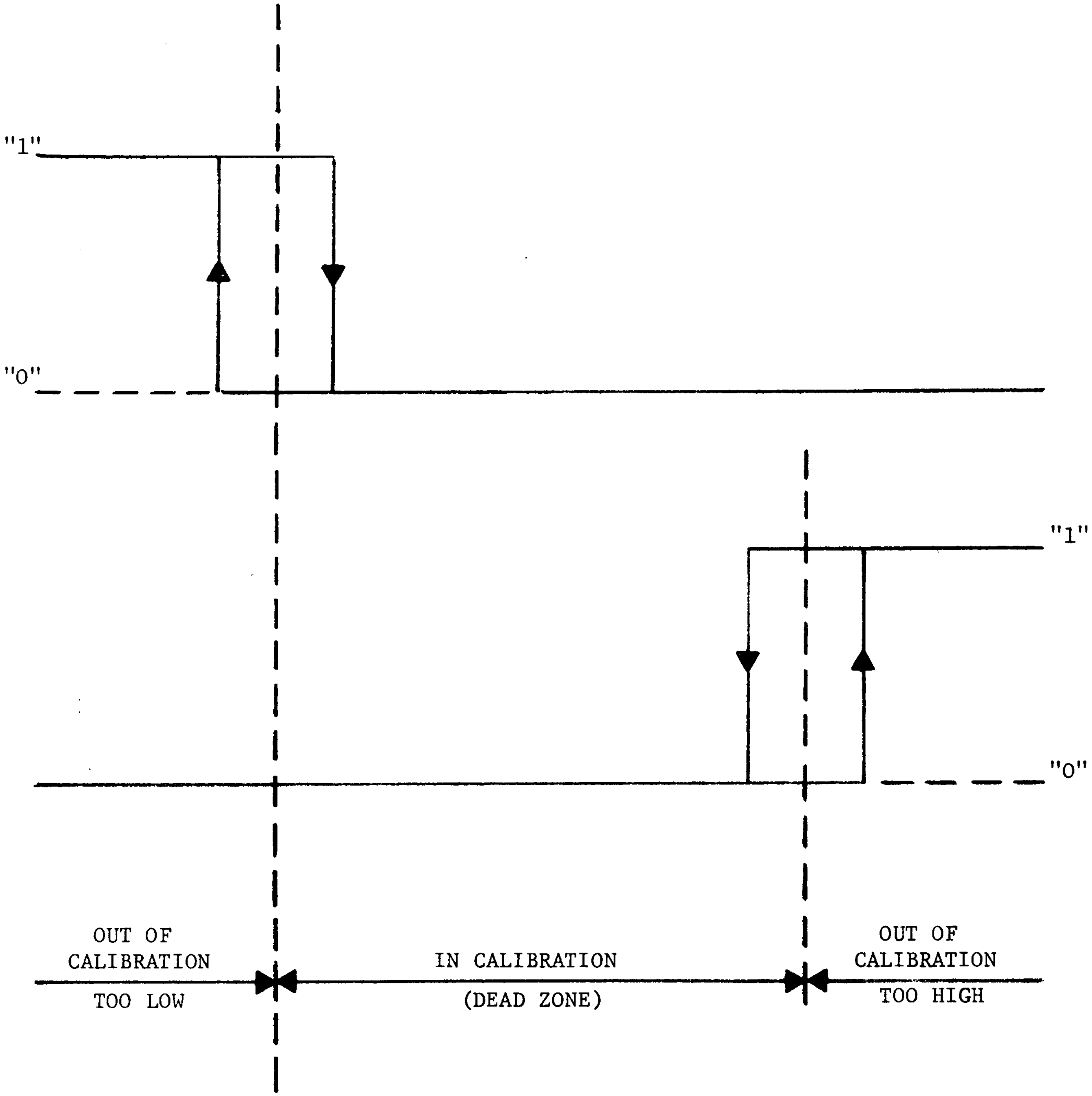

Figure 6-10. Calibration Comparator Characteristics

activating the correct driver and relay, the contacts of which would turn the motor (a reversible synchronous type) in the correct direction. The motor would turn a pot, which would apply a bias signal to the instrumentation amplifier. The motor would continue to turn the pot until the amplifier output falls back within the dead zone, at which time the comparator output would drop to zero, de-energizing the relay and shutting off the motor.

Should the amplifier output be too high, the high comparator would come on, activating its relay and causing the motor to turn in the opposite direction. Figure 6-11 shows how the motor direction relays would operate.

The center of the dead zone would correspond to the correct amplifier output reading which should be present when the calibrating solution would be circulating through the system.

During the five count, the "check calibration" command would operate the check calibration relay, which would enable the latch circuit. Should either comparator output still be in the "1" state, it would mean that the system would be unable to achieve proper calibration during the first 5 minutes of the sequence. If so, then the latch circuit would latch up and turn on the "out of calibration" indicator. The indicator would stay on until the start of the next calibration period, at which time the latch circuit would be reset, and the system would be recalibrated and rechecked.

During the normal operating mode, the pot would sit in the last position it was rotated into and would feed a bias correction signal to the instrumentation amplifier.

During the calibration interval, the output meter would read out the amplifier output, which should be the calibration reading. This could be bypassed to show the sample reading just prior to calibration. (This is described in the next paragraph.) A compensating thermistor would be placed in the system to compensate for variations in the concentration of the calibrating solution due to temperature.

6.3.5.2.3 Signal Processing and Readout

Figure 6-12 is a block diagram of the signal processing and readout system.

The system electrodes would feed two buffer amplifiers, which would be FET-input amplifiers and would have an input impedance on the order of 10^{15} ohms. The prototype would actually use the two preamplifier cards from the 940 Process Analyzer, since they are already developed and would be readily available.

The difference between the two buffer outputs would be amplified by a differential amplifier. The output of the first differential amplifier would then be amplified, with respect to solution ground, by a second amplifier. These two amplifiers would be the two halves of a 747-type IC operational amplifier (a dual amplifier package consisting of two 741 chips). The last stage would also have a bias correction input, as previously explained. The output would be. . . .

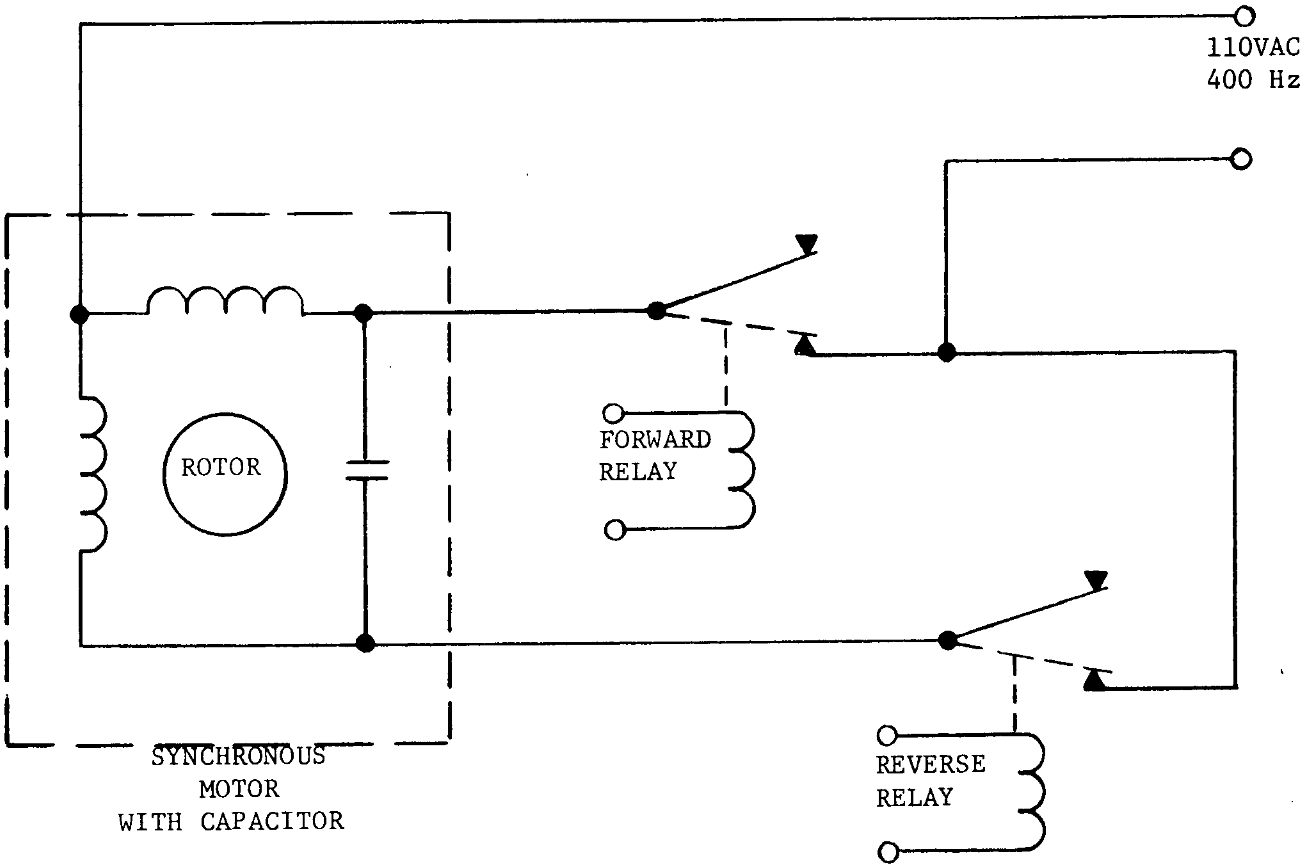

Figure 6-11. Motor Direction Control Calibration Potentiometer

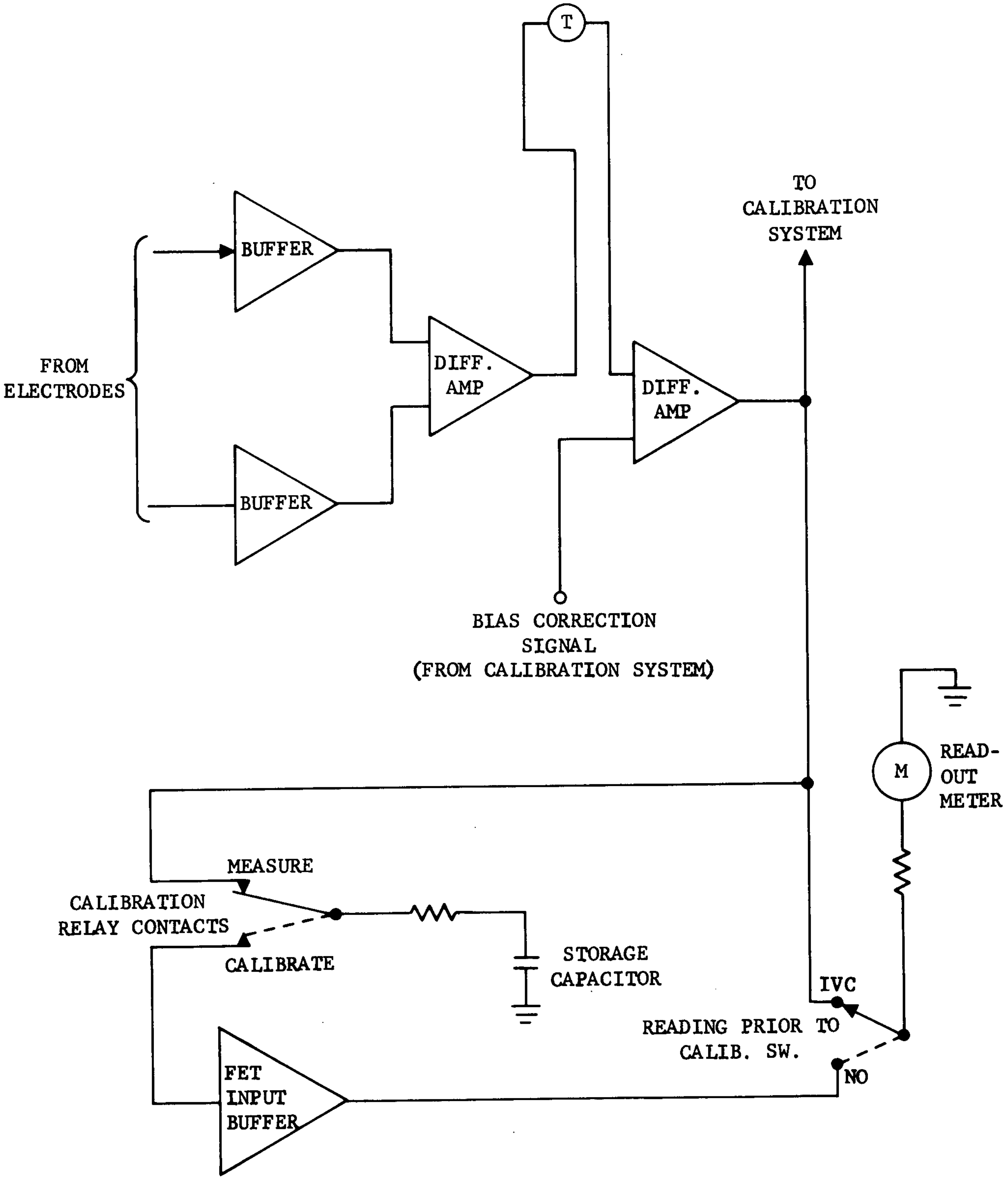

Figure 6-12. Signal Processing and Readout

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connected through a resistor to a micro- or milliammeter, which would be the output meter.

During the normal mode of operation, the output signal would also be routed through the NC contacts of the calibration relay to a high quality, low leakage capacitor, i.e., Teflon, polystyrene, polycarbonate, or Mylar dielectric material. During the calibration interval, the calibration relay would switch the capacitor from the amplifier output to the input of a FET-input operational amplifier, connected as a unity voltage gain buffer. Should an AD503-type amplifier be used, the input impedance would be 10^{11} ohms or better. Should the storage capacitor be one microfarad, the time constant for the capacitor discharge would be 10^5 seconds, which would be about 28 hours. This would be much more than sufficient to store the charge for the calibration interval of approximately 9 minutes. The capacitor, then, would store the last amplifier reading prior to calibration, during the calibration interval. If this previous reading would be desired, the operator would press the PRIOR READING switch and momentarily read that instead of the calibration reading from the amplifier.

A thermistor in the amplifier input would compensate for variations in the solution temperature.

6.3.5.2.4 Electronic Integration

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

  110 Vac 400 Hz - Pump and Calibration Pot Motors
  +28 Vdc - Valves and Relays
  +15 Vdc - Preamp and Amplifier
  +5 Vdc - Op Amps, Timer, Logic, and Cal Pot
  -5 Vdc - Op Amps and Cal Pot
  -12 Vdc - Timer
  -15 Vdc - Preamp and Amplifier

Power at 110 Vac, 400 Hz would be obtained from the spacecraft supply as would +28 Vdc, from which the remaining dc voltages would be derived. Figure 6-13 shows the power distribution and conditioning system. Protection would be offered by circuit breakers (which would also double as on/off switches), input fusing resistors, and a 30-V zener diode on the dc input line.

Dc-dc converters should be used wherever possible, due to the small size and low power dissipation. If required, additional regulation could be added to the outputs.

- EMI/RFI. EMI/RFI filters should be included on the +28 Vdc input lines to prevent interference from the system being fed back onto the main power bus.

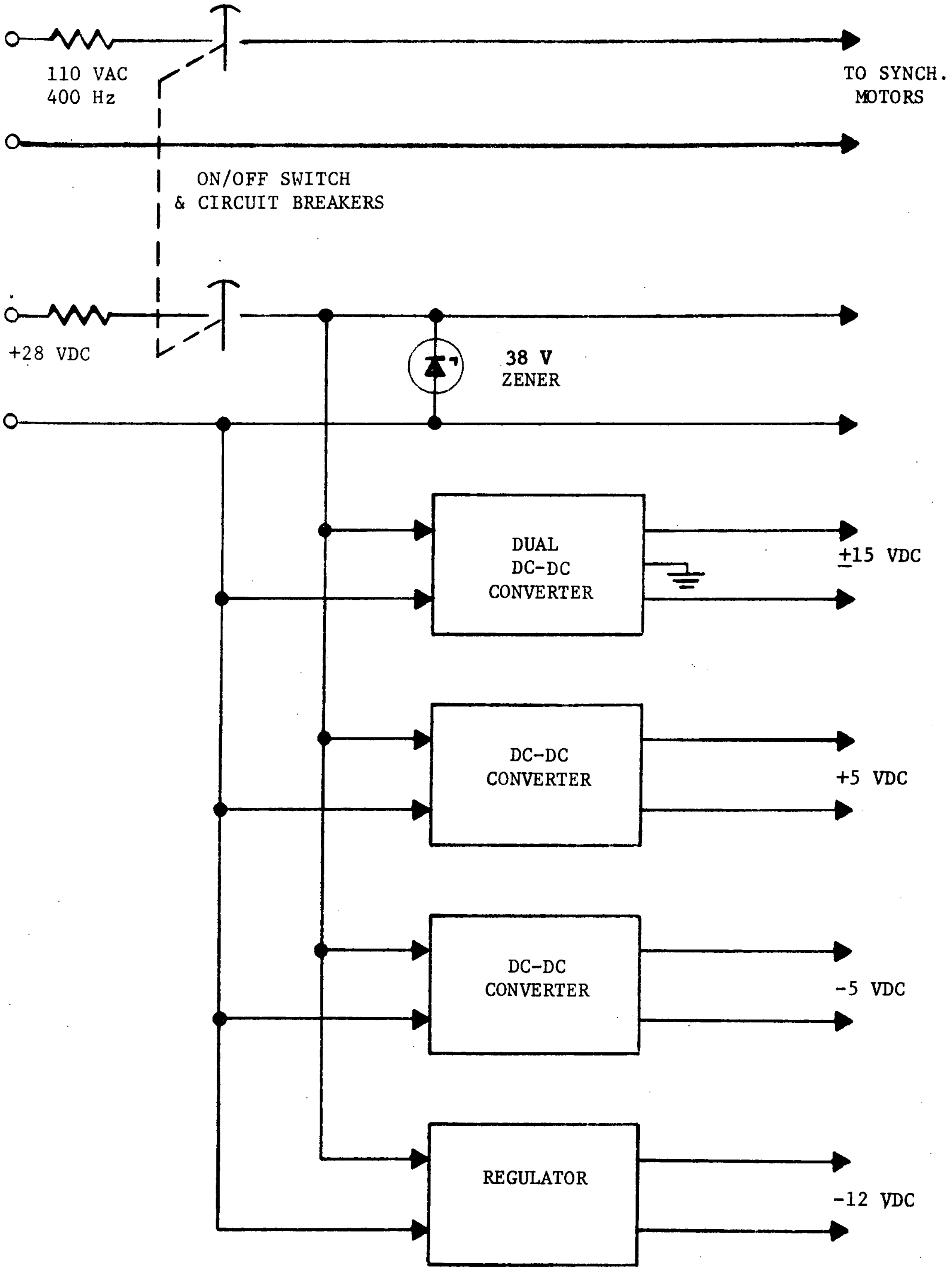

Figure 6-13. Power Conditioning

- Packaging and Interconnections. The preamp buffers would be in a separate shielded package. The balance of the electronics, less the pump motor and valves, should be on a printed circuit board. This would greatly simplify the wiring. A harness would be required to interconnect the following items:

  1. Indicators and controls on panel
  2. Preamp can
  3. Electronics PC board
  4. Valves
  5. Pump motor
  6. Input power lines
  7. Electrodes
  8. Thermistors in system

6.3.6 Material

In addition to the materials used in the sensor chamber, the following materials would be used in the system: the supporting frame, cover, and brackets would be aluminum; all tubing would be 1/4- or 1/8-inch stainless steel; the solenoid valve would be aluminum and the manual valve would be Teflon; the electronic housing would be aluminum; all MS fittings would be stainless steel; the ion-exchange assembly would be fabricated from stainless steel.

6.3.7 Finishes

All aluminum parts shall be anodized per MIL-A-8625, and all stainless-steel parts passivated per MIL-S-5002 or electropolished.

6.3.8 Interface Requirements

The silver-ion monitoring system would require the following interface requirements with the space shuttle vehicle:

- An electrical connection would be required for 28 Vdc and 110 Vac, 400 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 would be required, one on each side of a low percent restrictor. 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 would be removed from the main line. The quick disconnect would be a commercial component--Swagelok P/N 400QC-6.

6.3.9 Quality Assurance

During the study of the Residual Water Bactericide Monitor Development, the Quality Assurance activities included studies for ease of manufacture, quality problems related to hardware, and the inspectability of both in-house manufactured parts and items procured from vendors.

The sensor chamber, which would be the most complex mechanical part, would be well within our abilities to both machine and assemble. Because a large portion of our business is research and development for space programs, inspection equipment is available to assure compliance to drawings and specifications.

AN fittings, which are NASA-approved hardware, have been used for standardization to provide ease of assembly and inspectability. This eliminates the probability of assembly errors and increases the ease of maintenance.

Electronic components have been analyzed and can be procured to military specifications or JAN-type parts.

There are no identifiable problems which could be seen which may impact the quality of the equipment.

6.3.10 Reliability

Throughout the development program, reliability techniques were utilized as design and study tools.

In keeping with the concept that a system of simple design and capable of performing its intended function is more reliable than a more complex system, this system would meet that criteria. The system requires few electromechanical devices, and the electronics used would be of proven discrete and integrated circuit component types. These devices and components were chosen so that during any follow-on effort, they could be selected from NASA-preferred parts lists and thus easily qualify for space-flight applications.

In addition, the materials selected for the construction of the components in the system would be from (or could easily be changed to) NASA-preferred materials lists and could also be qualified for space-flight applications.

The design of the system would be of such a nature that during any follow-on effort a detailed reliability program could be applied efficiently. A failure-modes-and-effects analysis and reliability predictions could be performed during tradeoff studies to insure equipment reliability and long-life performance. Also, single failure points could be identified for possible corrective design efforts.

6.3.11 Safety

During the study of the Residual Water Bactericide Monitor Development, the safety activities included studies for the identification of deficiencies that would impact safety of personnel and equipment, and ground-testing operations.

The chemistry was studied to see if it would have a corrosive effect on the equipment as well as handling hazards for personnel. One molar potassium nitrate would be used in the reference electrode at a volume of 1.69×10^{-3} fl oz (50 microliters) per day. Potassium nitrate is not a harmful or corrosive material. Complete failure of the quartz-fiber junction of the reference electrode, which would be highly unlikely, would allow a maximum of approximately 0.5 fluid ounce of one molar potassium nitrate, $1M\ KNO_3$, to be slowly injected into that particular section of the potable water system connected to the silver-ion monitor. The rate would be dependent upon the extent of failure of the junction but would also be restricted by the maximum flow allowed by a small-pore hypodermic needle connecting the electrolyte reservoir with the secondary electrolyte chamber. Solid silver bromide would be used in the dual column assembly to produce a concentration of 70-80 ppb at ambient temperature, which would be very low concentration, not corrosive and not hazardous to personnel. In order to have greater assurance these chemicals would not affect the flow path corrosively, the instrument would be designed so the path material would be either 316 stainless steel or Kel-F.

The displacement pump would operate on 110-Vac, 400-Hz power. Since pumps of this nature have been designed to operate in a 100-percent enriched oxygen atmosphere, there would be no foreseeable problems. The remainder of the electronics would operate at a safe range of 28 Vdc.

The compactness and layout of the system would enable the design to be free of any sharp corners which could cause a safety hazard. In all cases, spacecraft and personnel safety were considered key objectives throughout this design.