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FINAL REPORT

HEAT STERILIZABLE pH ELECTRODES

Contract No. NAS 2-4388

A. Kaplan
Beckman Instruments, Inc.

April 1969

Prepared for:

National Aeronautics and Space Administration
Ames Research Center
Moffett Field, California 94035

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1.0 INTRODUCTION

The Voyager Spacecraft to Mars will carry experiments for the purpose of detecting extraterrestrial life. One of the experimental methods being considered is the measurement of pH changes due to the metabolic rate of bacteria. To prevent contamination of the Martian environment, the spacecraft will be sterilized. Therefore, the spacecraft subsystems must be designed to withstand the effects of dry-heat sterilization and decontamination in ethylene oxide.

The purpose of this project has been the development of the glass and reference electrodes for pH measurement that meet the Voyager's sterilization specifications. The requirements are that the pH and reference electrode assemblies perform satisfactorily after six heat sterilization cycles and six cycles of decontamination in ethylene oxide. One heat sterilization cycle is defined as 92 hours at 135° C. One decontamination cycle is defined as 30 hours in a mixture of 12 percent ethylene oxide in freon 12 at 50° C.

2.0 SUMMARY

The important parameters that describe the characteristics of pH electrodes are span or sensitivity, impedance, and response time. Considering that the test requirements of this project called for repetitive sterilization of glass and reference electrodes, it was also necessary that these parameters either remain constant during the sterilization tests or change in a predictable manner. The design goals were maximum sensitivity to pH changes as determined by calibration with standard buffer solutions of pH4 and pH10; a response time of one minute or less; a maximum impedance of 1000 megohms for the glass electrode; and an impedance of 5,000 ohms for the reference electrode.

Upon conclusion of the Design Verification Tests (DVT), we fabricated and delivered to NASA/Ames three glass electrode assemblies and three reference electrode assemblies. These units were built to the specifications of the DVT assemblies. The DVT data are included in Appendix B of this report.

The test results show that the electrodes were useful for pH measurements after each of the six heat sterilization and six decontamination cycles. The design goals, however, were not reached for each design parameter. The pH sensitivity of sterilized electrodes varied during each sterilization cycle. The average pH span varied from 5.22 to 6.04 pH units, with the extreme values showing a greater variation.

The electrode impedance generally increased after each heat cycle. Two groups of glass electrodes fabricated at different times produced significantly different results in impedance. Group A averaged 1800 megohms and Group B 750 megohms at the end of the DVT. The variations in pH span and response time for the two groups of electrodes were similar despite the difference in impedance. The design goal for the glass electrode impedance was originally specified to assure compatibility with state-of-the-art flight qualified amplifiers. This goal is met even with electrodes having higher impedances than those tested because amplifiers with an input impedance of 10^{14} ohms or greater are available.

The reference electrodes were designed to provide seven days' operation. The electrode impedance design goal was chosen to assure a reliable flow of electrolyte through the electrode junction. The reference electrode impedance averaged 5000 ohms at the end of the DVT. The impedance was as high as 12,500 ohms after the first heat cycle, but this caused no problem in electrolyte flow and response time.

The response time of the glass electrodes varied from 5 to 10 minutes to reach the final reading. The time to respond to within 0.3 pH units of the final reading was two minutes. The reference electrode response time was one minute. Since the actual experimental conditions will not produce drastic or rapid changes in pH, a response time of several minutes appears adequate for this purpose.

One problem not related specifically to pH measurement was encountered during this program and not satisfactorily solved. The use of elastomers as seals to store liquids during the sterilization tests has not afforded adequate reliability. The test units began to leak at various stages of the testing. Several different elastomers were tested without success. This problem will be common to any experiment in which O-rings are used to contain liquids in reservoirs during sterilization. The elastomer problem should receive immediate emphasis to find a solution.

3.0 EXPERIMENTAL WORK

The experimental work was conducted to measure the effects of sterilization on the performance of the electrode assemblies. The parameters measured were the sensitivity of the electrodes to standard buffer solutions, impedance of the electrodes, and electrode response time.

These parameters were measured during the course of the sterilization procedure specified in the Jet Propulsion Laboratory Specification VOL-50503-ETS with the exception that the heat sterilization was performed in ambient air rather than in dry nitrogen. This specification requires that parts be heat-sterilized for 92 hours at 135° C, and that this cycle be repeated six times. The parts were then tested for compatibility in ethylene oxide for 6 cycles of 30 hours each at 50° C. These tests were performed and after each cycle electrodes were tested for pH sensitivity, response time, and impedance.

The impedance of the reference electrodes indicates the flow rate of electrolyte through the asbestos fiber junction. The electrode was selected to provide one week's operation using about 1 milliliter of saturated KCl. The impedance of the glass electrodes determines the requirements of the electronic amplifier, with the minimum input impedance increasing as higher impedance electrodes are used.

3.1 Reference Electrode Assembly

The reference electrode assembly was designed to operate for one week at a pressure of one earth atmosphere. It is an integral unit consisting of a water reservoir and transfer assembly, and an electrode containing crystalline potassium chloride (Figure 3-1). The filling solution reservoir is isolated from the electrode by a spool-type valve and a piston. After sterilization and immediately before a pH measurement is required, the filling solution is transferred to the electrode by actuating the valve and piston with gas from a supply at 100 psi.

Table 3-1 shows the actuating pressure required by the transfer mechanism before and after sterilization. The required actuation pressure rose from 25 psi before sterilization to 90 psi after sterilization. The heat cycling had caused the O-rings on the valve and piston to adhere to the walls of the transfer assembly. The O-rings used were a copolymer of ethylene-propylene compound #E515-8, manufactured by the Parker Seal Company.

Some of the DVT assemblies suffered a loss of electrolyte during the course of the heat cycling. Other units retained some of the filling solution, but transfer of the solution to the electrode was unsatisfactory because of the pressurizing gas leaking past the O-rings. This either prevented complete actuation of the piston, or, as happened in one unit, the leakage of gas past the O-rings was so severe that the gas expelled the solution from the electrode.

The reference electrode is constructed of a glass tube and an asbestos fiber junction through which saturated KCl flows. Except for the size of the

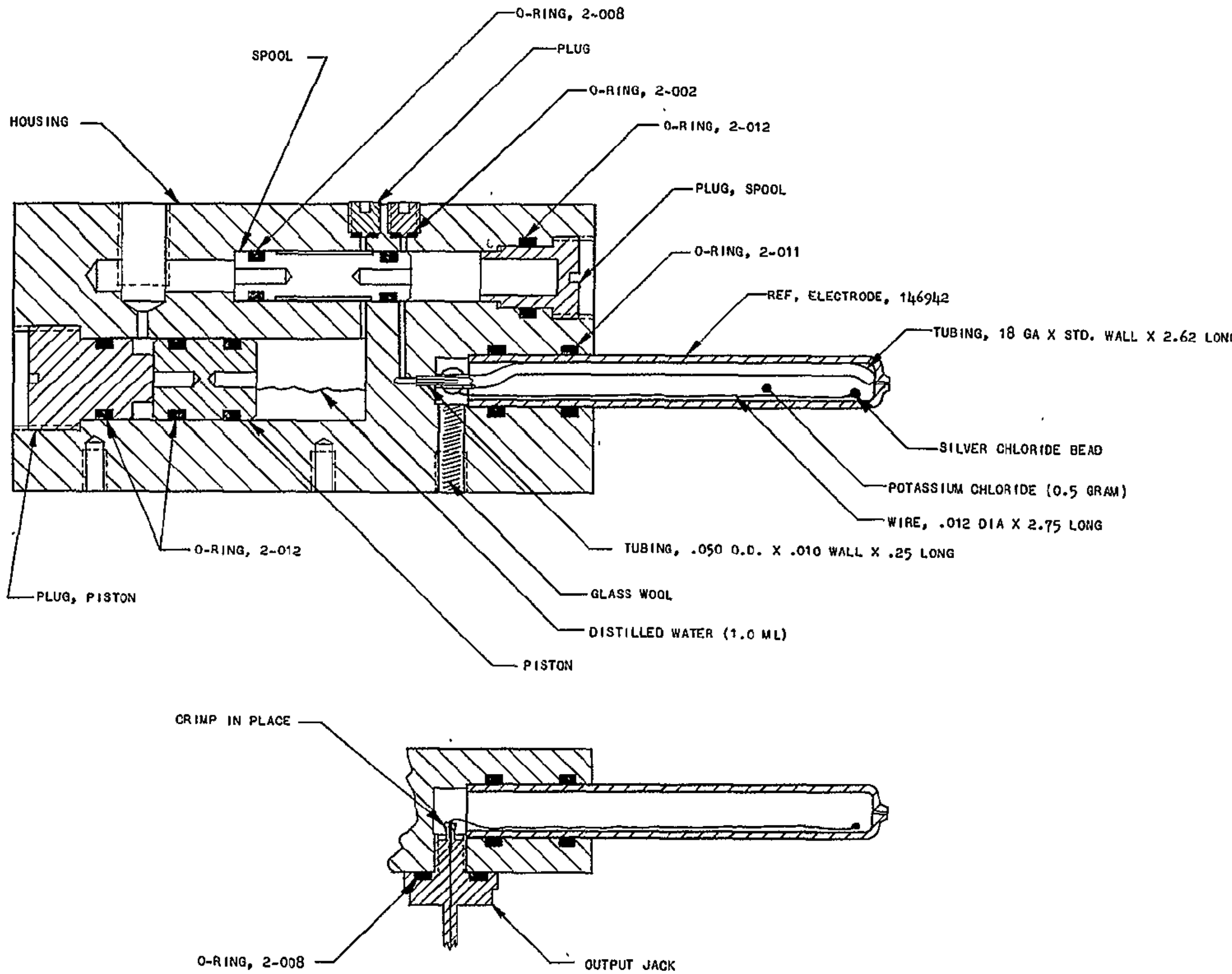

Figure 3-1. Reference Electrode Assembly

DVT	1	2	3
Activation Pressure			
Before Sterilization	23 psi	25 psi	20 psi
After 2 Heat Cycles	90 psi (1)		
After 6 Heat Cycles		90 psi (2)	
After 6 Heat Cycles and 6 ETO Cycles		.	85 psi (3)

(1) Piston could not complete travel to the bottom of the cylinder because of a plug of lubricant in the flow path.

(2) Valve actuated at 55 psi; piston actuated at 90 psi, but did not travel to the bottom of the cylinder because of O-ring leak.

(3) There was a slow leak of gas past the O-rings, but the valve and piston were completely actuated.

Table 3-1. Reference Electrode Assembly - Effect of Sterilization on Transfer Assembly electrode, the fabrication is the same as for a commercial reference electrode. The design goal for the reference electrode was that it have an impedance of 3000 ohms after sterilization to assure a reliable flow of electrolyte. At the conclusion of the design verification tests, six reference electrodes had an average impedance of 4000 ohms.

Figure 3-2 shows the effect of sterilization on impedance and on pH span of the electrode when tested with a commercial glass electrode. The graph shows the average and extreme values obtained during the testing.

During one period of developmental testing, several reference electrodes that had been sterilized suffered a change in impedance from several thousand ohms to several megohms. It had appeared that the junction had dried out and was not wettable after being filled with the filling solution. Several of these electrodes were boiled in water in an effort to reprime the junction. This procedure was partially successful in that the electrodes showed a decrease in impedance, but not to the original level. A new group of electrodes was tested and compared to several electrodes made with porcelain junctions. The performance of the asbestos fiber junction was superior to that of the porcelain junction and since the impedance problem never recurred, the asbestos fiber junction was used in all subsequent work.

3.2 Glass Electrode Assembly (Figure 3-3)

The glass electrode assembly uses the same design concept as the reference electrode assembly, the only exception being the use of the glass electrode

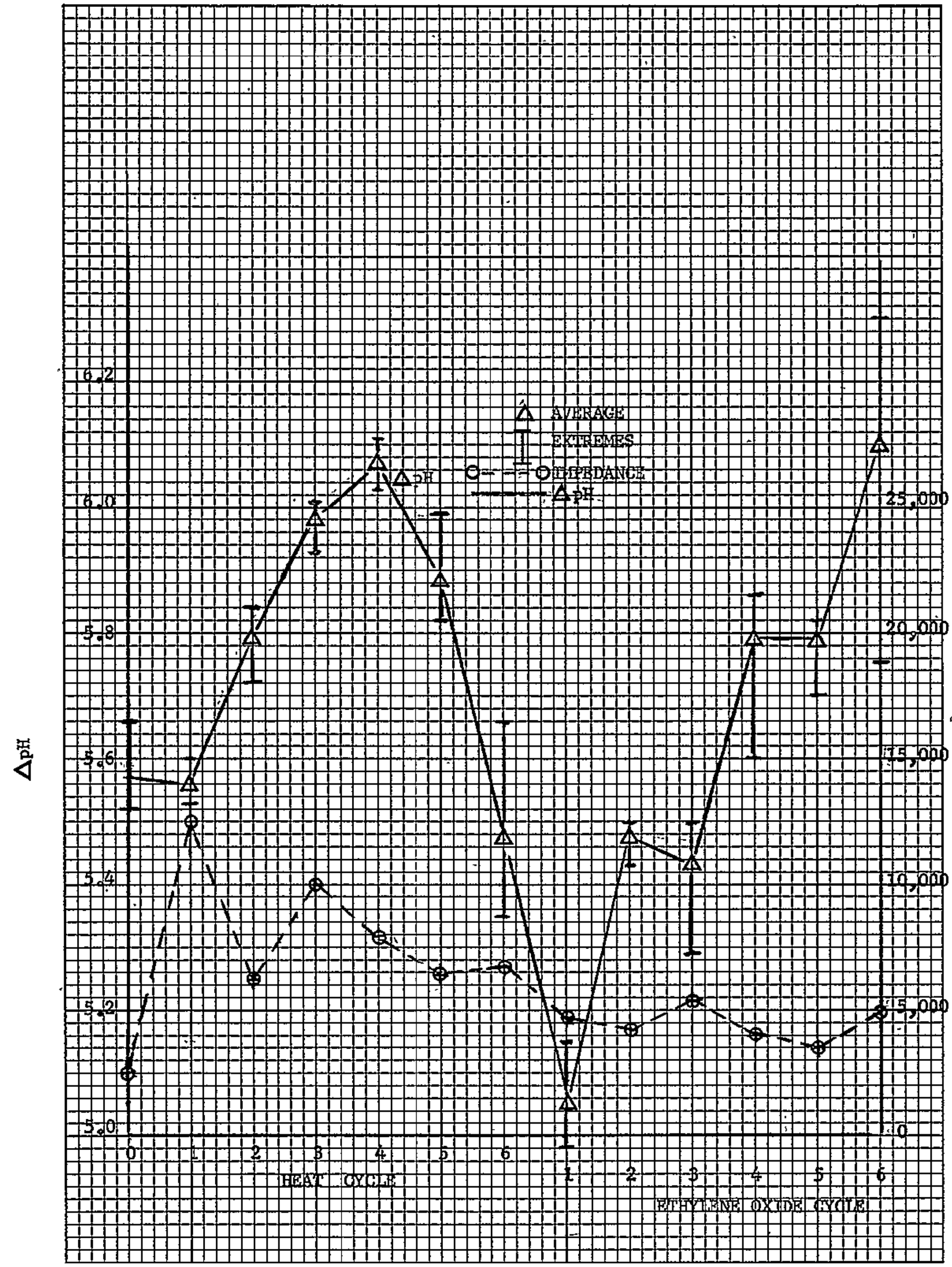

Figure 3-2. Reference Electrodes pH Span and Impedance Vs. Sterilization

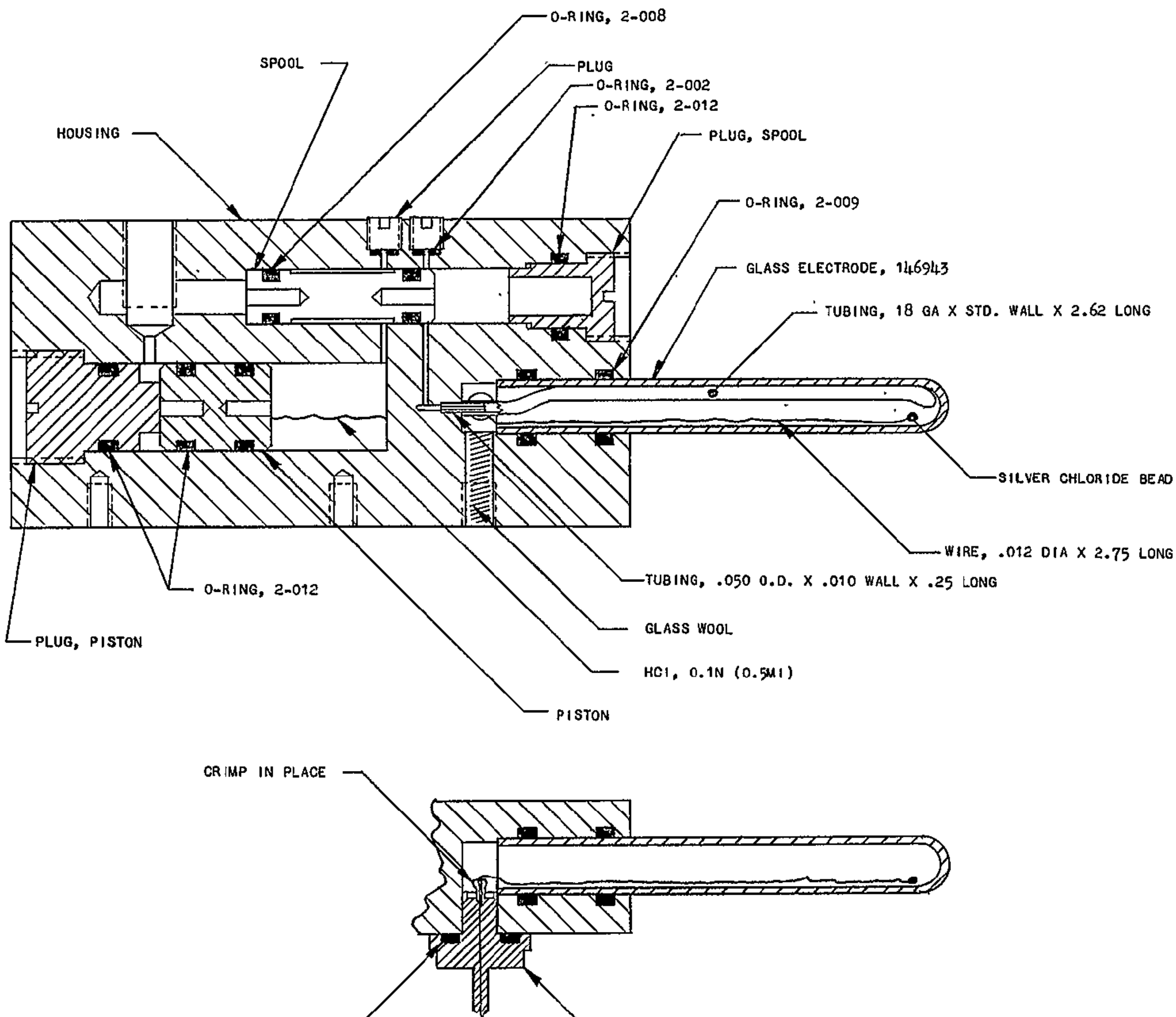

Figure 3-3. Glass Electrode Assembly

and a filling solution of 0.1N HCl. The operation is the same, with the filling solution stored in the reservoir during the sterilization cycles. The performance of the glass electrode assembly was comparable to that of the reference electrode assembly.

Table 3-2 shows the effect of sterilization on the actuation of the transfer assembly. Before sterilization, 20 to 25 psi was required to actuate the valve and piston. At the various stages of sterilization, the DVT assemblies required from 80 to 85 psi for actuation. The same problems of leakage were encountered in the testing of the glass electrode assembly due to leaks through the O-rings.

Before designing the glass electrode assembly, several glass electrodes were fabricated using conventional techniques as used for commercial electrodes. The electrode contained the filling solution and was hermetically sealed. The seal was annealed to relieve the stress at the glass-to-platinum joint. The filling solution had been developed and tested in a previous program. This program had required that the electrodes be sterilized for 24 hours and repeated four times. The current requirements of four-day cycles repeated six times proved too severe for the electrode.

Sterilization caused two problems which could not be corrected. The glass membrane became very thin with a concurrent drastic increase in impedance and severe fragility of the glass membrane. Another unfavorable result of the heat sterilization was the failure of the glass-to-platinum hermetic seal. The platinum wire extended from the silver/silver chloride half-cell through

DVT	1	2	3
Actuation Pressure			
Before Sterilization	25 psi	20 psi	25 psi
After 2 Heat Cycles	80 psi (1)		
After 6 Heat Cycles		(2)	
After 6 Heat Cycles and 6 EtO Cycles			85 psi (3)

(1) O-rings allowed gas to leak into electrode, causing loss of the filling solution.

(2) O-rings allowed severe leakage of pressurizing gas, and valve and piston would not actuate.

(3) Reservoir was dry; gas leaked after valve and piston were actuated.

Table 3-2. Glass Electrode Assembly - Effect of Sterilization on Transfer Assembly the glass for connection to an amplifier. Repeated heat sterilization caused this seal to crack.

In the absence of satisfactory solutions to these problems, it was decided to apply the design of the reference electrode assembly for use in the glass electrode. The same design was used, with a glass electrode replacing the reference electrode. The filling solution used was 0.1N HCl. Since the glass electrode operates without a flow of electrolyte, a small quantity of filling solution was required than used in the reference electrode, and the glass electrode assembly (Figure 3-3) was made slightly smaller than the reference electrode assembly.

3.3 Materials

3.3.1 KEL-F

KEL-F was chosen for construction of the filling solution storage and transfer assembly. Both electrode assemblies use this material as the main housing, and for the valve and piston. KEL-F was used because of its reported properties of chemical inertness and high-temperature resistance. These objectives were realized with all of the DVT units showing no degradation at the conclusion of the sterilization program. Earlier prototype testing did reveal a problem which was subsequently corrected before fabricating the DVT units. This problem is described in the Materials Report on Sterilizable Electrodes and is summarized here.

KEL-F is available as a raw material that has either been molded or extruded. The molded material will be crystalline if it is annealed in the mold, or it will be amorphous if it is quick-quenched during the molding process. Although the amorphous form is generally more desirable, its use led to failure of the part during this application. The quick-quenched, or amorphous KEL-F, cracked during the heat cycling. This was apparently the result of a nonuniform structure and high stresses that developed in the thick cross sections being used. On the other hand, the annealed form provided a uniform structure free from the molding stresses and resulted in a much more stable end product. Extruded shapes also had high residual stresses which caused parts to crack. For this reason, molded rod stock was used for the fabrication of the piston and valve.

3.3.2 Glass Electrode

The glass electrode is made from Beckman GP glass and has a 6-mm diameter stem and an 8-mm diameter bulb. These dimensions were chosen so as to require a minimum volume of filling solution and a minimum sample volume.

As in the reference electrode assembly, a Teflon tube is used to transfer the filling solution directly to the bottom of the electrode to avoid trapping air in the pH-sensitive glass bulb. During the design verification testing, several glass electrodes were tested for sensitivity to pH after each sterilization cycle. The results are shown in Section 3.4, Design Verification Tests.

3.3.3 Elastomers

O-rings were required to seal the reagents in the reservoirs during sterilization and to seal a piston that is actuated by gas pressure after sterilization. The DVT assemblies had O-rings made from ethylene-propylene. These assemblies leaked at various stages of the sterilization program.

Previous to this test, O-rings had been tested that were made of Viton A, Butyl 318-7, and Buna N. Buna N was the least satisfactory. Severe shrinkage after one heat cycle caused the loss of resiliency during the heat cycling. During prototype testing the butyl compound appeared satisfactory. It failed, however, during subsequent testing. The ethylene-propylene, recommended for use at high temperature applications where low porosity is also required, was then tested. The ethylene-propylene also appeared to be satisfactory during the prototype test, but did not withstand the severity of the design verification testing.

This problem has not been solved. Greater attention should be directed to the development of a suitable elastomer to meet the sterilization and decontamination requirements. There are several Voyager experiments which will require O-rings as seals to store reagents in valves. A satisfactory elastomer is not currently available.

3.4 Design Verification Tests

The design verification tests (DVT) were performed on three glass electrode assemblies, three reference electrode assemblies, and several of the glass electrode and reference electrode subcomponents. The effects of sterilization were expected to be more significant in the case of the electrode subcomponents than for the filling mechanism, and a greater number of these were tested to obtain statistically more meaningful data. The DVT report is included as Appendix B to this report.

4.0 CONCLUSIONS

The sterilization specifications proved far more severe on the electrodes than was anticipated at the start of the program. The materials problems were solved with the exception that we did not have a satisfactory elastomer for O-rings at the end of this program. Presuming that a suitable elastomer will be developed in the near future to meet the sterilization requirements, the electrode assemblies will have the capability of being sterilized and still retain the properties needed for pH measurement.

The impedance of an electrode does not indicate its sensitivity to changes in pH. Low impedance electrodes afford faster response time. In the work discussed in this report, pH measurements were made with a commercial Beckman pH meter (Model 7600) and response times were about two minutes. Faster response times are possible using amplifiers designed with a higher input impedance and lower input capacitance. This may not be required, however. At this time, it is necessary for the project experimenters to establish specifications for response time, pH sensitivity and stability, and the measurement range based on data from experiments such as the Wolf Trap.

The pH sensitivity varied during the sterilization procedure, but the electrodes and the pH meter required no special provisions for recalibration after each sterilization cycle. The sensitivity was determined using two standard buffer solutions. In actual practice the electrodes will require calibration immediately before use. Variations during sterilization, therefore, do not introduce a new problem and do not increase the complexity of the calibration procedure. These tests show that pH electrodes can withstand the sterilization conditions and be used on the bacterial detection experiment.

5.0 RECOMMENDATIONS

The greatest limitation imposed on the design of the sterilizable electrodes was the failure to find a suitable elastomer for use in the O-rings. Since other Voyager experiments will also require the use of O-rings, it is apparent that a more comprehensive effort is required to solve this basic problem. Although there is a continuing Materials Evaluation Program conducted at the Jet Propulsion Laboratory, we were not able to find a satisfactory solution to this problem either through a review of the JPL reports or through personal communications with JPL. In addition to testing other elastomers, other types of seals such as diaphragms or Bal-Seals should be considered in place of the simpler O-rings.

The evaluation of the glass electrodes revealed two inconsistencies in performance. During the design verification tests, the design parameter that showed the greatest variations was the electrode impedance. The greatest variation was evident in comparing one lot of electrodes to another. The variations in impedance, however, did not seem to limit the use of the electrodes. There was no apparent correlation between impedance variations and changes in pH sensitivity. It would still be desirable to be able to more closely predict the performance of the electrode and it is, therefore, recommended that other pH-sensitive glasses be evaluated for use in the electrode. The specifications for impedance, response time, and sensitivity should be re-evaluated and based on system requirements of the proposed application. Sensitivity and stability are the most important parameters in specifying the electrode performance.

There were also variations in the pH sensitivity during the course of the sterilization procedure. This does not present a significant limitation, however, since it would be necessary to calibrate the electrodes before use regardless of the effects of sterilization.

Long-term stability tests were not performed because of funding limitations caused by several unanticipated problems early in the program. These tests should be made and can be done using the electrode subcomponent of the electrode assemblies. Twenty-two of each electrode were delivered to NASA/Ames for further testing. Since there is no significant difference in performance after two heat cycles as compared to six cycles, future work can be expedited by evaluating the electrodes after two heat cycles and two decontamination cycles.

APPENDIX A

OPERATING INSTRUCTIONS FOR THE HEAT STERILIZABLE ELECTRODES

(P/N 146944 - Glass Electrode, P/N 145617 - Reference Electrode)

A.1 OPERATING PROCEDURE

The Electrode Assemblies have been supplied ready for sterilization or for use. When the assemblies are to be used, perform the following procedure:

1. Mount each assembly upright with the electrode facing down.
2. Install a 5/16-24 x 1/8 tube fitting in the side of the KEL-F block for connection to a 100 psi gas supply.
3. Open the gas supply to the assembly to actuate the valve and piston. This transfers the solution from the reservoir to the electrode.
4. Operate the assembly in an upright position to avoid spilling the electrode filling solution.
5. Connect a cable with either a clip lead or a tip jack to the silver connector on the side of the assembly and to a high input impedance amplifier. A commercial pH meter is suitable for use with the electrode assemblies.

A.2 CLEANING AND RECHARGING PROCEDURE

NOTE

Refer to assembly drawings 146944 (Glass Electrode) or 145617 (Reference Electrode).

1. Remove each of the following parts:
   a. Piston Plug (Item 5)
   b. Piston (Item 6)
   c. Spool Plug (Item 4)
2. With the spool valve (Item 2) in the open position, flush the electrode through the transfer flow path, using distilled water. The water will empty from the 0.161 diameter vent hole.

3. When the assembly is clean, add the required filling solution to the reservoirs:

   a. 0.5 ml of 0.1N HCl for the glass electrode assembly;

   b. 1.0 ml of distilled water to the reference electrode assembly.

   This should be done with the assembly held with the vent hole down to avoid having the filling solution flow into the electrode.

4. Insert the piston, being careful not to drive the solution out of the reservoir.

5. Insert the piston plug.

6. Close the spool valve by pushing it to the stop.

7. Insert the spool plug.

8. For the Reference Electrode Assembly (145617), add 0.5 mg of crystalline KCl to the electrode. This can be done by adding the KCl through the vent hole and tapping or shaking the assembly to cause the KCl to fall into the electrode .

9. Insert a small piece of glass wool to prevent the KCl from spilling out the vent hole.

APPENDIX B

DESIGN VERIFICATION TEST REPORT

(IR-2495-103)

CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

1.0 INTRODUCTION

The data in Section 2.0 were taken during Design Verification testing of heat sterilizable glass and reference electrodes. The electrodes were tested after heat sterilization and ethylene oxide decontamination as described in the Sterilizable Electrode Design Verification Test Plan.

2.0 SUMMARY OF TEST RESULTS

2.1 Filling Solution Storage and Transfer Assembly

One pair of DVT assemblies was tested after two heat sterilization cycles. The glass electrode assembly actuated at 80 psi, but most of the filling solution was lost from the electrode because of gas leaking through the O-rings. There was enough filling solution transferred to the electrode to make a pH measurement. The reference electrode assembly actuated at 90 psi. Not all of the water in the reservoir was transferred to the electrode because of a plug that formed in the flow-path. Enough water was transferred, however, to dissolve the potassium chloride crystals in the electrode to form the saturated solution used in the reference electrode. The two electrode assemblies were used as an electrode pair to measure pH, using standard buffers of pH 4 and pH 10. There was a pH span of 5.5 pH units.

The second pair of DVT assemblies was tested after the 6th heat sterilization cycle. The glass electrode assembly would not actuate because of severe leakage of the pressurizing gas around the O-rings. This leakage caused the complete loss of electrolyte during the sterilization. The reference electrode assembly actuated at 85 psi, but the piston did not travel to the bottom of the reservoir. This was also due to O-ring leaks. Some of the water was transferred to the electrode. It was still necessary to add unsterilized filling solutions to the electrodes to make the pH measurements.

This was done and using the standard buffers of pH 4 and pH 10, a pH span of 5.65 units was obtained. At this time, the glass electrode assembly had an impedance of 2650 megohms.

The third pair of DVT assemblies was tested after the 6th ethylene oxide decontamination cycle. Each of the assemblies actuated at 85 psi. The glass electrode assembly had no filling solution remaining in it, and gas leaked through the O-rings after actuation of the valve and piston. The reference electrode assembly had some water remaining in the reservoir that was transferred to the electrode. There was some leakage through the O-rings after actuation, as evidenced by gas bubbling in the electrode. There was, however, sufficient water to dissolve the potassium chloride crystals and form a saturated solution needed for the pH measurements. The measurement was made after adding unsterilized filling solution to the glass electrode assembly. This electrode pair had a response of 5.4 pH units between buffers of pH 4 and pH 10.

2.2 Spare Glass Electrodes

Two lots of glass electrodes were fabricated and tested concurrently with the DVT assemblies. Glass electrode Group A consisted of three electrodes that were sterilized and two that were used as controls. Group B consisted of eight electrodes that were sterilized and two that were used as controls. Group A was tested through six heat sterilization and six ethylene oxide decontamination cycles, while Group B was tested concurrently, but with four heat sterilization and six ethylene oxide decontamination cycles. The pH response of the two groups of electrodes was fairly similar. At the conclusion of the design verification testing, the pH response of Group A averaged 5.9 pH units. This was the highest reading obtained throughout the design verification tests.

Figures 2-1 through 2-4 show the variation of pH response and impedance during the design verification testing. At the end of the test program, the Group B glass electrodes had an average response of 5.7 pH units.

Although similar in response, the two groups of electrodes were quite different in impedance. Group A averaged about 2200 megohms, while Group B averaged 850 megohms at the conclusion of the Design Verification Test. The response time of the glass electrodes, as measured to the final reading on the pH meter, is from 5 to 10 minutes. However, the pH reading comes to within 0.3 pH unit of the final reading in about two minutes. Tables 2-1 and 2-2 show the averages of the total measurements made and data recorded in Tables 2-3 and 2-4.

2.3 Reference Electrodes

Six reference electrodes were sterilized for six heat sterilization and six ethylene oxide decontamination cycles. At the conclusion of the DVT, the pH span for the six electrodes averaged 5.8 pH units. The electrode impedance averaged 3500 ohms. The average impedance of the electrodes was at its highest after the first heat sterilization cycle, and tended to decrease after each subsequent cycle. Variations were observed in the pH span, but do not appear to have been related to the variation in impedance. As an indication of the electrolyte flow rate through the junction of the reference electrode, the variations in impedance do not appear to be significant.

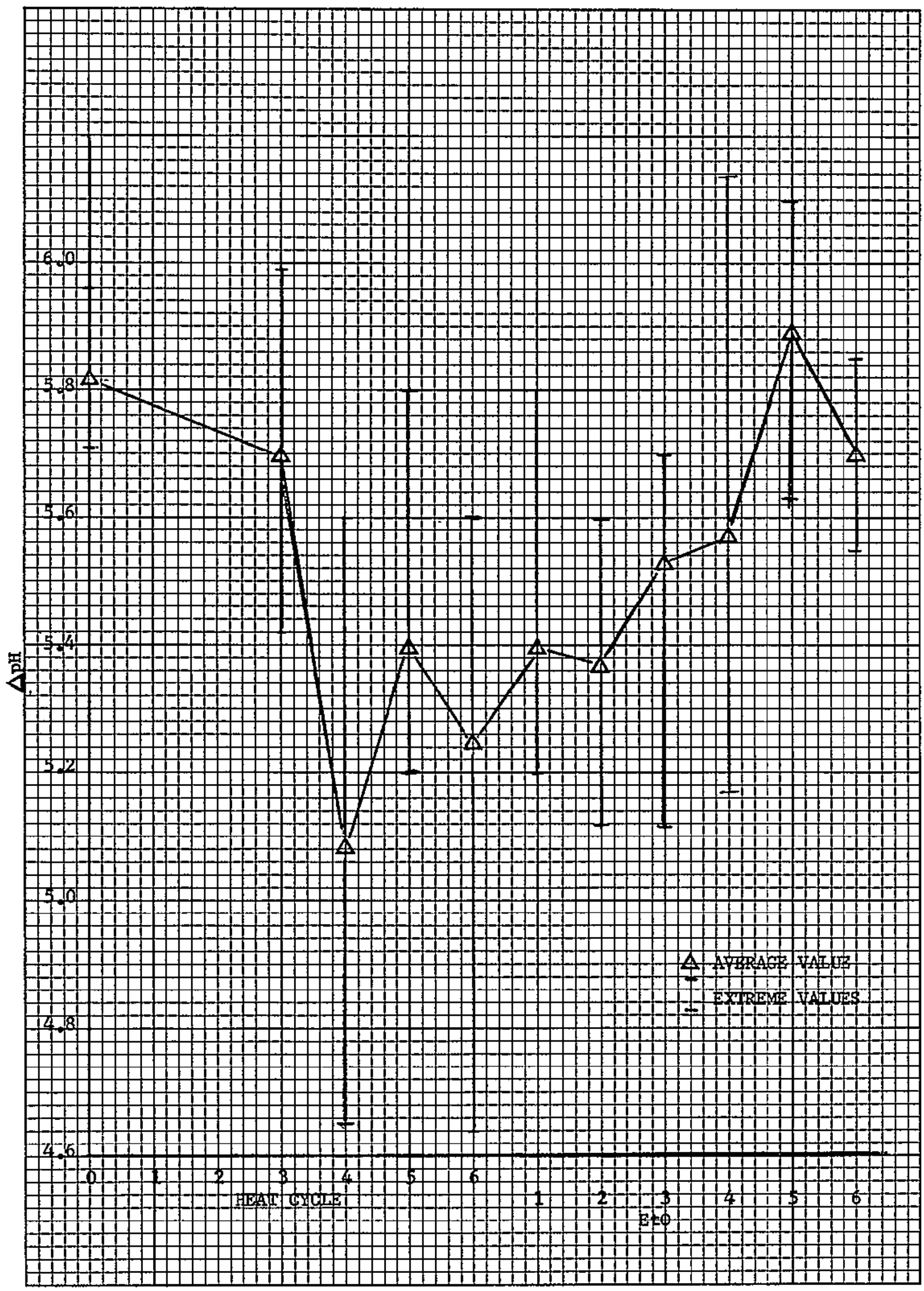

Figure 2-1. Glass Electrode Group A--pH Span Vs. Sterilization Time

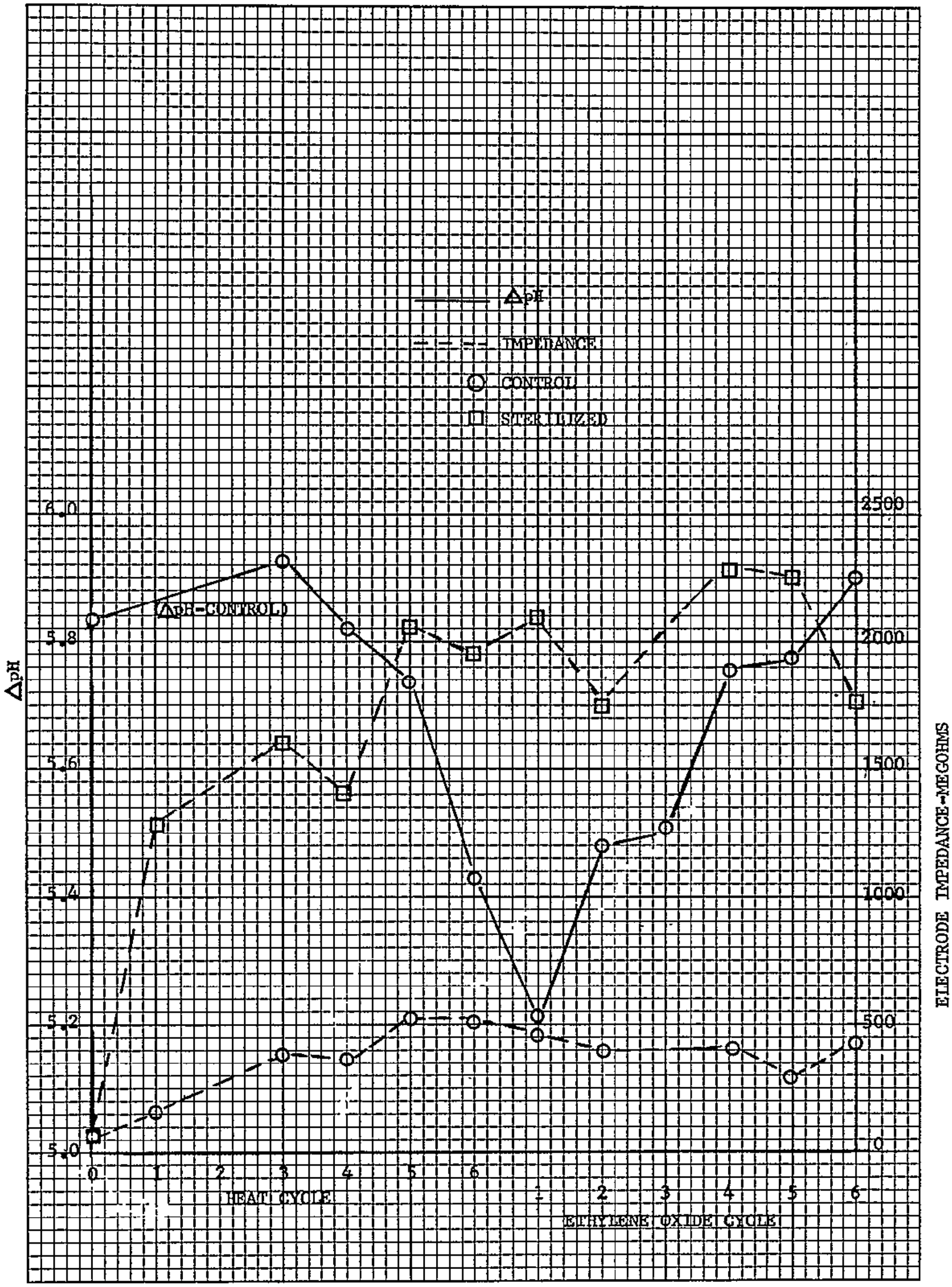

Figure 2-2. Glass Electrode Group A--pH Span and Impedance Vs. Sterilization Time

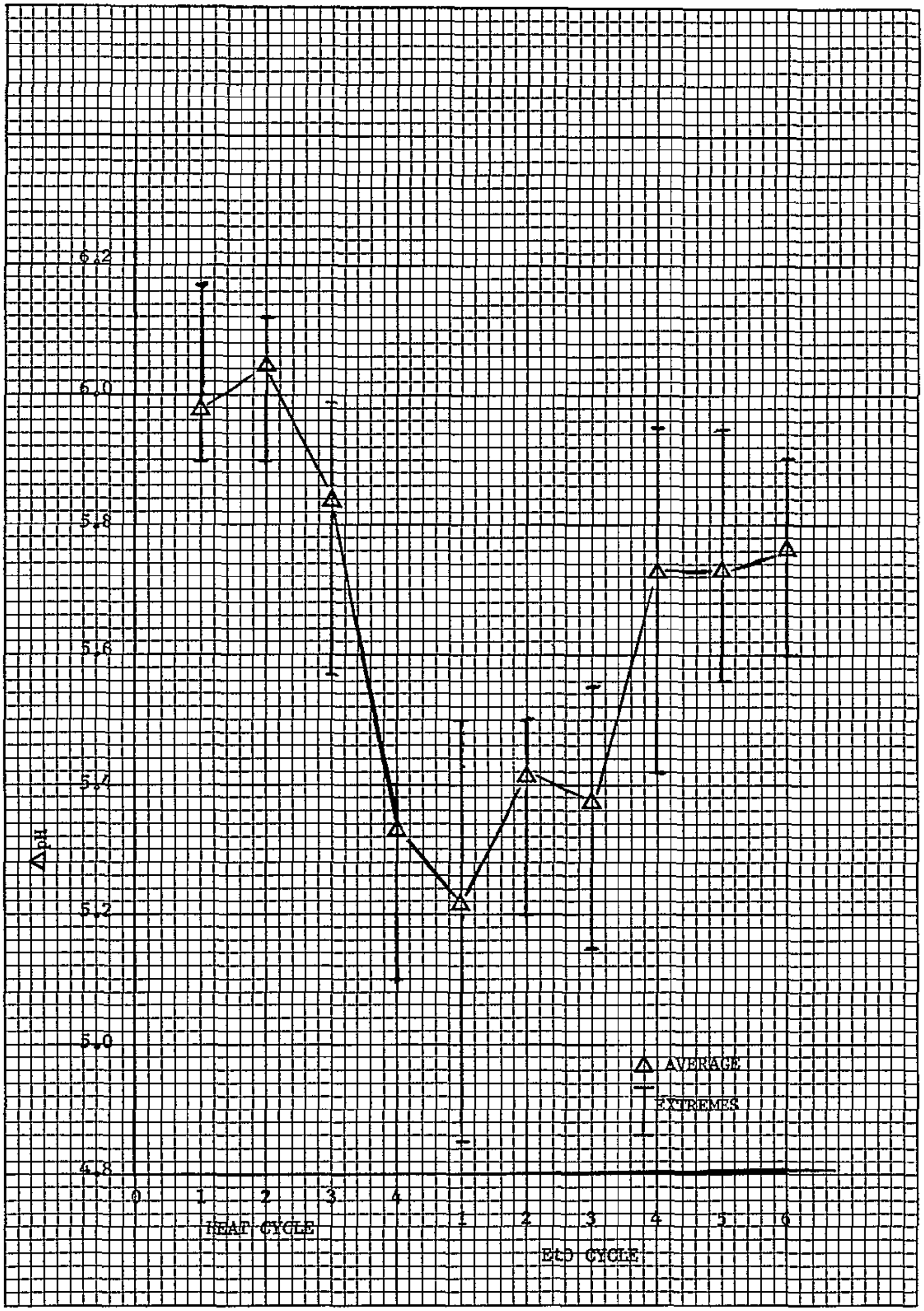

Figure 2-3. Glass Electrode Group B--pH Span Vs. Sterilization Time

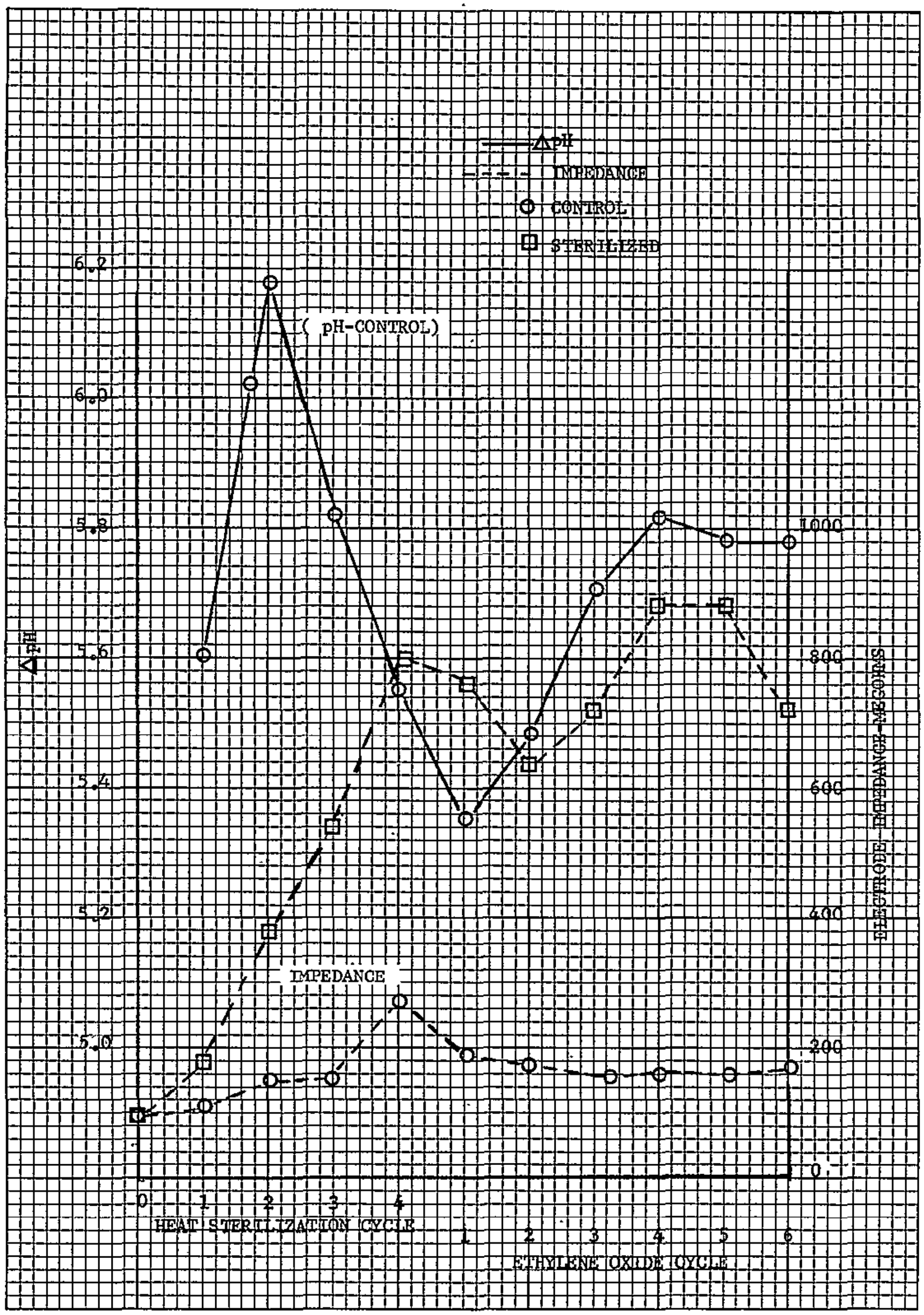

Figure 2-4. Glass Electrode Group B--pH Span and Impedance Vs. Sterilization Time

Sterilization Cycle	Sterilized Electrode ΔpH	Sterilized Electrode Impedance (Megohms)	Control Electrode ΔpH	Control Electrode Impedance (Megohms)
0	5.82	56	5.83	53
1	(1)	1284	(1)	163
2	(3)	(2)	(3)	(2)
3	5.70	1610	5.93	394
4	5.07	1400	5.82	365
5	5.40	2070	5.74	535
6	5.24	1960	5.43	518
Decontamination Cycle				
1	5.40	2090	5.21	478
2	5.37	1760	5.48	393
3	5.53	2070	5.50	402
4	5.57	2300	5.76	427
5	5.89	2260	5.77	294
6	5.70	1770	5.90	440

(1) Sensor Nos. 9 & 10 used as controls: NOT STERILIZED.

(2) Sensor Nos. 1-3 used in DVT assemblies.

(3) Response not measured because meter read offscale.

Table 2-1. Glass Electrode Group A--Analysis of measurements Made in Table 2-3

Sterilization Cycle	Sterilized Electrode ΔpH	Sterilized Electrode Impedance (Megohms)	Control Electrode ΔpH	Control Electrode Impedance (Megohms)
0	"8.34"(1)	97	"8.40" (1)	90
1	5.97	180	5.60	110
2	6.04	380	6.18	150
3	5.84	543	5.82	155
4	5.33	807	5.55	275
Decontamination Cycle				
1	5.21	767	5.35	195
2	5.50	634	5.48	174
3	5.37	722	5.70	157
4	5.73	881	5.82	165
5	5.73	883	5.78	158
6	5.76	713	5.78	168

(1) Error in measurement

Table 2-2. Glass Electrode Group B--Analysis of Measurements Made in Table 2-4

	DESCRIPTION		GLASS ELECTRODES, GROUP A										LIMITS OF ACCEPTABILITY or UNITS OF MEASUREMENT
			1	2	3	4	5	6	7	8	(1) 9	(1) 10	
1	IMPEDANCE BEFORE STERILIZATION		44	60	65	57	59	56	56	61	63	42	50 (Megohms)
2	RESPONSE BEFORE HEAT STERILIZATION	pH4	4.69	4.64	4.62	4.70	4.67	4.65	4.71	4.70	4.70	4.61	pH Units
		pH10	10.40	10.60	10.52	10.51	10.50	10.44	10.49	10.46	10.50	10.47	pH Units
3	STERILIZATION TEMP. 1ST CYCLE (135 ± 1°C)												
4	IMPEDANCE AFTER 1ST HEAT CYCLE		NOTE (2)	NOTE (2)	NOTE (2)	1010	1147	1225	853	1187	172	154	(Megohms)
5	RESPONSE AFTER 1ST HEAT CYCLE	pH4				(3) →							
		pH10				(3) →							
6	STERILIZATION TEMP. 2ND CYCLE (135 ± 1°C)												
7	IMPEDANCE AFTER 2ND HEAT CYCLE					(NOTE) (4) →							
8	RESPONSE AFTER 2ND HEAT CYCLE	pH4				2.71	(NOTE) (5)	3.18	(5)	3.90	2.67	2.66	pH Units
		pH10				10.92	(5)	11.12	(5)	11.02	10.89	11.41	pH Units
9	RESPONSE OF DVT PAIR NO. 1 AFTER 2ND HEAT CYCLE		5.5 pH Units										Theoretical Maximum = 6.0 pH Units
10	STERILIZATION TEMP. 3RD CYCLE (135 ± 1°C)												

(1) Sensor Nos. 9 & 10 used as controls: NOT STERILIZED.
(2) Sensor Nos. 1-3 used in DVT assemblies.
(3) Response not measured because meter read offscale.
(4) No readings taken.
(5) Broken due to handling.

Table 2-3. Glass Electrodes Group A Test Data (1 of 4)

	DESCRIPTION		GLASS ELECTRODES, GROUP A 1	2	3	4	5	6	7	8	(1) 9	(1) 10	LIMITS OF ACCEPTABILITY OR UNITS OF MEASUREMENT
11	IMPEDANCE AFTER 3RD HEAT CYCLE					1630	---	1650	---	1040	162	625	1500 (Megohms)
12	RESPONSE AFTER 3RD HEAT CYCLE	pH4				4.20	---	5.40	---	5.76	4.42	4.48	pH Units
		pH10				10.21	---	11.11	---	11.18	10.30	10.45	pH Units
13	STERILIZATION TEMP. 4TH CYCLE (135 ± 1°C)												
14	IMPEDANCE AFTER 4TH HEAT CYCLE					1460	---	1440	---	1300	270	460	(Megohms)
15	RESPONSE AFTER 4TH HEAT CYCLE	pH4				4.00	---	5.03	---	5.75	3.98	3.12	pH Units
		pH10				9.60	---	10.40	---	10.40	9.35	9.40	pH Units
16	STERILIZATION TEMP. 5TH CYCLE (135 ± 1°C)												
17	IMPEDANCE AFTER 5TH HEAT CYCLE					2550	---	2020	---	1640	510	560	(Megohms)
18	RESPONSE AFTER 5TH HEAT CYCLE	pH4				4.20	---	5.20	---	5.88	4.12	4.28	pH Units
		pH10				10.00	---	10.40	---	11.08	9.90	9.98	pH Units
19	STERILIZATION TEMP. 6TH CYCLE (135 ± 1°C)												
20	IMPEDANCE AFTER 6TH HEAT CYCLE					2310	---	2080	---	1510	401	635	(Megohms)
21	RESPONSE AFTER 6TH HEAT CYCLE	pH4				3.60	---	3.70	---	5.00	3.30	3.35	pH Units
		pH10				9.10	---	9.30	---	9.64	8.80	8.70	pH Units

Table 2-3. Glass Electrodes Group A Test Data (2 of 4)

	DESCRIPTION		GLASS ELECTRODES, GROUP A										LIMITS OF ACCEPTABILITY OR UNITS OF MEASUREMENT
			1	2	3	4	5	6	7	8	(1) 9	(1) 10	
22	RESPONSE OF DVT PAIR NO. 2 AFTER 6TH HEAT CYCLE			5.65 pH Units									pH Units
23	EtO DECONTAMINATION TEMP. 1ST CYCLE (50°C)												
24	IMPEDANCE AFTER 1ST EtO CYCLE					2325	---	2210	---	1750	349	608	(Megohms)
25	RESPONSE AFTER 1ST EtO CYCLE	pH4				3.80	---	390	---	4.50	3.43	3.68	pH Units
		pH10				9.00	---	9.50	---	9.90	8.82	8.70	pH Units
26	EtO DECONTAMINATION TEMP. 2ND CYCLE (50°C)												
27	IMPEDANCE AFTER 2ND EtO CYCLE					1850	---	1730	---	1690	291	496	(Megohms)
28	RESPONSE AFTER 2ND EtO CYCLE	pH4				3.30	---	4.00	---	4.15	3.14	3.70	pH Units
		pH10				8.90	---	9.15	---	9.50	8.80	9.00	pH Units
29	EtO DECONTAMINATION TEMP. 3RD CYCLE (50°C)												
30	IMPEDANCE AFTER 3RD EtO CYCLE					2530	---	1950	---	1740	299	504	(Megohms)
31	RESPONSE AFTER 3RD EtO CYCLE	pH4				3.40	---	2.70	---	4.38	1.60	1.81	pH Units
		pH10				9.10	---	8.40	---	9.53	7.00	7.40	pH Units

Table 2-3. Glass Electrodes Group A Test Data (3 of 4)

	DESCRIPTION		GLASS ELECTRODES, GROUP A 1	2	3	4	5	6	7	8	(1) 9	(1) 10	LIMITS OF **ACCEPTABILITY** OR UNITS OF MEASUREMENT
32	EtO DECONTAMINATION TEMP. 4TH CYCLE (50°C)												
33	IMPEDANCE AFTER 4TH EtO CYCLE					2590	---	2250	---	2050	319	535	(Megohms)
34	RESPONSE AFTER 4TH EtO CYCLE	pH4				1.25	---	2.08	---	1.90	1.57	2.12	pH Units
		pH10				7.39	---	7.25	---	7.30	7.40	7.80	pH Units
35	EtO DECONTAMINATION TEMP. 5TH CYCLE (50°C)												
36	IMPEDANCE AFTER 5TH EtO CYCLE					2640	---	2180	---	1970	296	292	(Megohms)
37	RESPONSE AFTER 5TH EtO CYCLE	pH4				1.65	---	1.77	---	2.75	1.48	2.52	pH Units
		pH10				7.60	---	7.87	---	8.38	7.25	8.30	pH Units
38	EtO DECONTAMINATION TEMP° 6TH CYCLE (50°C)												
39	IMPEDANCE AFTER 6TH EtO CYCLE					1860	---	1720	---	1740	355	526	(Megohms)
40	RESPONSE AFTER 6TH EtO CYCLE	pH4				1.60	---	1.90	---	2.50	1.90	1.40	pH Units
		pH10				7.45	---	7.60	---	8.05	7.70	7.40	pH Units
41	RESPONSE OF DVT PAIR NO. 3 AFTER 6TH EtO CYCLE				5.5 pH	Units							

Table 2-3. Glass Electrodes Group A Test Data (4 of 4)

	DESCRIPTION		GLASS ELECTRODES, GROUP B 1	2	3	4	5	6	7	8	(1) 9	(1) 10	LIMITS OF ACCEPTABILITY or UNITS OF MEASUREMENT
1	IMPEDANCE BEFORE STERILIZATION		75	110	90	100	130	95	80	100	90	90	50 (Megohms)
2	RESPONSE BEFORE HEAT STERILIZATION	pH4	2.71	2.80	2.62	2.63	2.70	2.70	2.70	2.63	2.60	2.60	pH Units
		pH10	11.02	11.08	11.00	11.01	10.99	11.07	11.02	11.00	11.00	11.00	pH Units
3	STERILIZATION TEMP. 1ST CYCLE (135 ± 1°C)												
4	IMPEDANCE AFTER 1ST HEAT CYCLE		240	210	160	260	180	130	120	160	110	110	(Megohms)
5	RESPONSE AFTER 1ST HEAT CYCLE	pH4	4.60	4.50	4.47	4.35	4.48	4.47	4.38	4.48	4.31	4.31	pH Units
		pH10	10.50	10.07	10.46	10.41	10.40	10.40	10.38	10.44	10.38	10.45	pH Units
6	STERILIZATION TEMP. 2ND CYCLE (135 ± 1°C)												
7	IMPEDANCE AFTER 2ND HEAT CYCLE		396	430	370	260	370	340	365	510	120	180	(Megohms)
8	RESPONSE AFTER 2ND HEAT CYCLE	pH4	3.52	3.54	3.52	3.60	3.48	3.50	3.43	3.40	3.27	3.20	pH Units
		pH10	9.60	9.55	9.58	9.50	9.52	9.58	9.43	9.52	9.39	9.43	pH Units
9	STERILIZATION TEMP. 3RD CYCLE (135 ± 1°C)												

(1) Controls: Not Sterilized

Table 2-4. Glass Electrodes Group B Test Data (1 of 4)

	DESCRIPTION		GLASS ELECTRODES, GROUP B 1	2	3	4	5	6	7	8	(1) 9	(1) 10	LIMITS OF ACCEPTABILITY OR UNITS OF MEASUREMENT
10	IMPEDANCE AFTER 3RD HEAT CYCLE		920	590	770	590	770	590	590	360	150	160	(Megohms)
11	RESPONSE AFTER 3RD HEAT CYCLE	pH4	4.30	3.90	3.91	3.96	3.83	3.97	3.88	3.90	3.90	3.88	pH Units
		pH10	9.87	9.77	9.84	9.82	9.82	9.80	9.82	9.69	9.69	9.72	pH Units
12	STERILIZATION TEMP. 4TH CYCLE (135 ± 1°C)												
13	IMPEDANCE AFTER 4TH HEAT CYCLE		863	700	833	677	868	765	740	1015	234	315	(Megohms)
14	RESPONSE AFTER 4TH HEAT CYCLE	pH4	3.70	3.86	3.80	3.65	3.48	3.55	3.90	3.25	3.40	3.30	pH Units
		pH10	9.10	9.25	9.10	8.90	8.95	8.65	9.30	9.10	8.89	8.90	pH Units
15	EtO DECONTAMINATION TEMP. 1ST CYCLE (50°C)												
16	IMPEDANCE AFTER 1ST EtO CYCLE		405	765	790	730	---	765	825	1095	196	195	(Megohms)
17	RESPONSE AFTER 1ST EtO CYCLE	pH4	3.95	3.90	3.85	3.60	---	3.85	3.65	3.50	3.51	3.30	pH Units
		pH10	8.80	9.20	9.10	8.80	---	8.90	8.97	9.00	8.70	8.80	pH Units
18	EtO DECONTAMINATION TEMP. 2ND CYCLE (50°C)												
19	IMPEDANCE AFTER 2ND EtO CYCLE		665	595	600	575	---	683	665	663	196	152	(Megohms)

Table 2-4. Glass Electrodes Group B Test Data (2 of 4)

	DESCRIPTION		GLASS ELECTRODES, GROUP B 1	2	3	4	5	6	7	8	(1) 9	(1) 10	LIMITS OF ACCEPTABILITY OR UNITS OF MEASUREMENT
20	RESPONSE AFTER 2ND EtO CYCLE	pH4	3.50	3.32	3.60	3.70	---	3.40	3.20	3.60	3.50	3.30	pH Units
		pH10	9.00	8.72	9.10	9.15	---	8.60	8.60	9.10	8.92	8.85	pH Units
21	EtO DECONTAMINATION TEMP. 3RD CYCLE (50°C)												
22	IMPEDANCE AFTER 3RD EtO CYCLE		676	711	704	710	---	728	723	802	165	152	(Megohms)
23	RESPONSE AFTER 3RD EtO CYCLE	pH4	3.51	3.40	3.60	3.50	---	3.35	3.40	3.55	1.55	1.14	pH Units
		pH10	8.85	8.85	9.05	8.80	---	8.90	8.75	8.70	7.00	7.10	pH Units
24	EtO DECONTAMINATION TEMP. 4TH CYCLE (50°C)												
25	IMPEDANCE AFTER 4TH EtO CYCLE		858	813	874	815	---	913	865	998	171	158	(Megohms)
26	RESPONSE AFTER 4TH EtO CYCLE	pH4	1.60	1.88	1.80	1.50	---	1.50	1.35	1.60	1.60	1.65	pH Units
		pH10	7.30	7.30	7.50	7.45	---	7.15	7.20	7.47	7.40	7.50	pH Units
27	EtO DECONTAMINATION TEMP. 5TH CYCLE (50°C)												
28	IMPEDANCE AFTER 5TH EtO CYCLE		873	876	875	815	---	880	848	1015	161	154	(Megohms)
29	RESPONSE AFTER 5TH EtO CYCLE	pH4	1.53	1.50	1.68	1.57	---	1.61	1.61	1.60	1.50	2.00	pH Units
		pH10	7.45	7.45	7.35	7.22	---	7.28	7.29	7.16	7.30	7.76	pH Units

Table 2-4. Glass Electrodes Group B Test Data (3 of 4)

	DESCRIPTION		GLASS ELECTRODES, GROUP B 1	2	3	4	5	6	7	8	(1) 9	(1) 10	LIMITS OF ACCEPTABILITY OR UNITS OF MEASUREMENT
30	EtO DECONTAMINATION TEMP° 6TH CYCLE (50°C)												
31	IMPEDANCE AFTER 6TH EtO CYCLE		725	670	754	809	---	681	695	659	194	143	(Megohms)
32	RESPONSE AFTER 6TH EtO CYCLE	pH4	1.75	1.70	1.65	1.60	---	1.55	1.50	1.75	1.50	1.60	pH Units
		pH10	7.45	7.45	7.55	7.20	---	7.40	7.40	7.40	7.30	7.25	pH Units

Table 2-4. Glass Electrodes Group B Test Data (4 of 4)

Figure 2-5 shows the variation of pH response and impedance to reference electrodes during the design verification testing.

The response time for the reference electrode is much faster than for the glass electrode, with final readings obtained in about one minute. Table 2-5 shows the averages of the total measurement made and data recorded in Table 2-6.

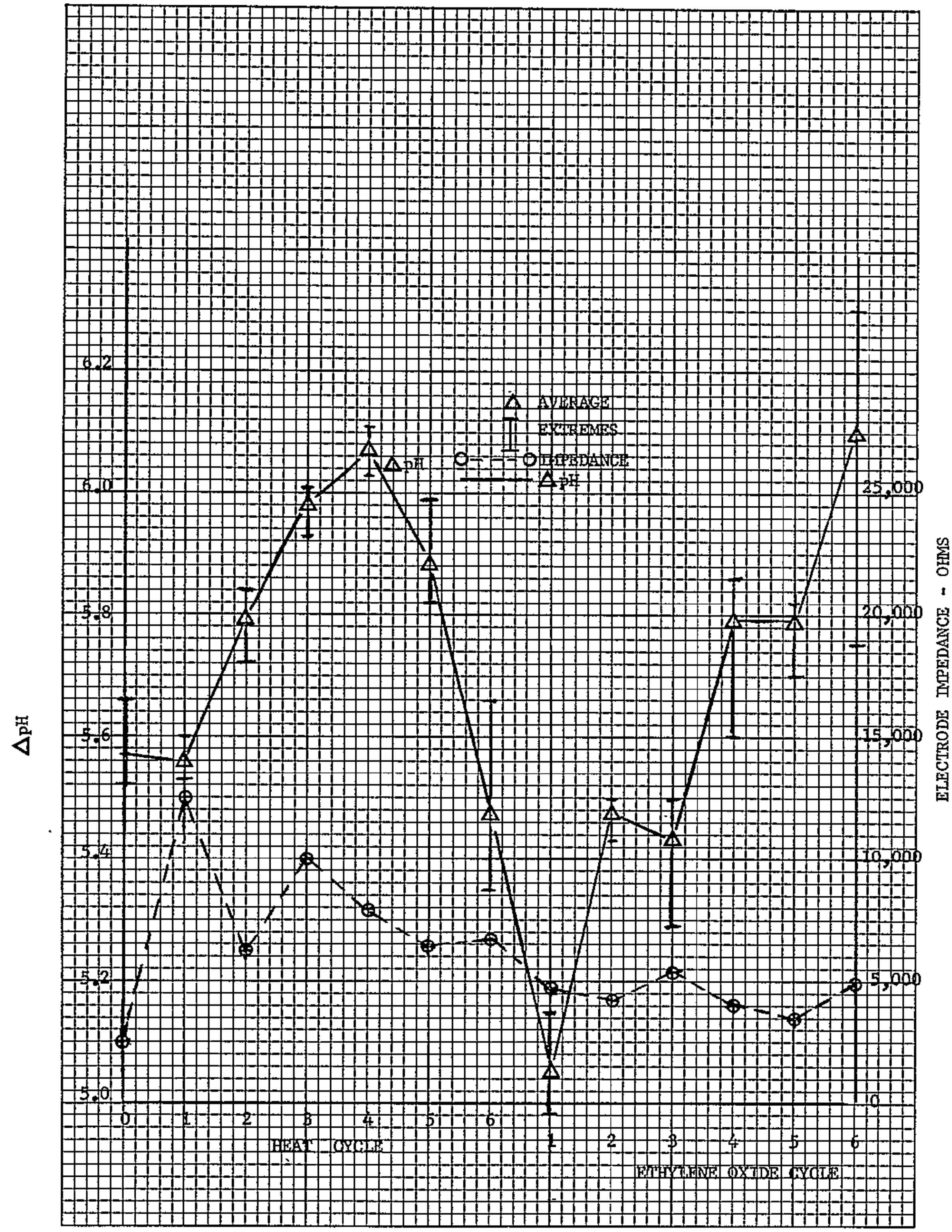

Figure 2-5. Reference Electrodes pH Span and Impedance Vs. Sterilization

Sterilization Cycle	ΔpH	Impedance (ohms)
0	5.57	2,470
1	5.56	12,500
2	5.79	6,200
3	5.98	10,000
4	6.07	7,900
5	5.88	6,400
6	5.47	6,740
Decontamination Cycle		
1	5.05	4,700
2	5.48	4,250
3	5.47	5,400
4	5.79	4,010
5	5.79	3,500
6	6.10	4,900

Table 2-5. Reference Electrodes--Average of Measurements Made in Table 2-6

	DESCRIPTION		REFERENCE ELECTRODES 1	2	3	4	5	6	7	8	9	10	LIMITS OF ACCEPTABILITY or UNITS OF MEASUREMENT
1	IMPEDANCE BEFORE STERILIZATION		2750	1300	2000	3400	3020	1950	1980	2600	2820	2900	5000 Ohms
2	RESPONSE BEFORE HEAT STERILIZATION	pH4	3.12	3.17	3.21	3.20	3.19	3.18	3.19	3.19	3.18	3.20	pH Units
		pH10	8.78	8.74	8.76	8.72	8.75	8.73	8.74	8.76	8.77	8.79	pH Units
3	STERILIZATION TEMP. 1ST CYCLE (135 ± 1°C)												
4	IMPEDANCE AFTER 1ST HEAT CYCLE		NOTE (1)	NOTE (1)	NOTE (1)	11,600	6000	24,000	37,000	17,200	4180	4650	(Ohms)
5	RESPONSE AFTER 1ST HEAT CYCLE	pH4				3.48	3.49	3.50	3.48	3.46	3.46	3.45	pH Units
		pH10				9.04	9.03	9.03	9.05	9.06	9.03	9.04	pH Units
6	STERILIZATION TEMP. 2ND CYCLE (135 ± 1°C)												
7	IMPEDANCE AFTER 2ND HEAT CYCLE					6300	7600	8500	4100	4700	3500	13,000	15,000 Ohms
8	RESPONSE AFTER 2ND HEAT CYCLE	pH4				3.30	3.12	3.10	3.17	3.12	3.09	3.79	pH Units
		pH10				9.04	8.92	8.94	8.89	8.92	8.91	8.89	pH Units
9	RESPONSE OF DVT PAIR NO. 1 AFTER 2ND HEAT CYCLE		5.5 pH Units										Theoretical Maximum = 6.0 pH Units
10	STERILIZATION TEMP. 3RD CYCLE (135 ± 1°C)												

(1) Sensor Nos. 1-3 used in DVT assemblies.

Table 2-6. Reference Electrodes Test Data (1 of 4)

	DESCRIPTION		ELECTRODES 1	2	3	4	5	6	7	8	9	10	LIMITS OF ACCEPTABILITY OR UNITS OF MEASUREMENT
11	IMPEDANCE AFTER 3RD HEAT CYCLE					10,200	9700	10,900	11,800	8000	13,000	---	15,000 Ohms
12	RESPONSE AFTER 3RD HEAT CYCLE	pH4				3.20	3.15	3.12	3.11	3.18	3.10	---	pH Units
		pH10				9.13	9.14	9.11	9.12	9.17	9.10	---	pH Units
13	STERILIZATION TEMP. 4TH CYCLE (135 ± 1°C)												
14	IMPEDANCE AFTER 4TH HEAT CYCLE					8100	8800	7100	8600	7000	9100	-----	(Ohms)
15	RESPONSE AFTER 4TH HEAT CYCLE	pH4				3.24	3.22	3.27	3.22	3.23	3.21	---	pH Units
		pH10				9.30	9.30	9.30	9.33	9.30	9.29	---	pH Units
16	STERILIZATION TEMP. 5TH CYCLE (135 ± 1°C)												
17	IMPEDANCE AFTER 5TH HEAT CYCLE					11,300	6600	6500	4600	3300	4000	---	(Ohms)
18	RESPONSE AFTER 5TH HEAT CYCLE	pH4				3.25	3.20	3.20	3.28	3.23	3.23	---	pH Units
		pH10				9.20	9.08	9.10	9.15	9.11	9.10	---	pH Units
19	STERILIZATION TEMP. 6TH CYCLE (135 ± 1°C)												
20	IMPEDANCE AFTER 6TH HEAT CYCLE					13,000	3900	3100	10,500	3400	3300	---	(Ohms)
21	RESPONSE AFTER 6TH HEAT CYCLE	pH4				3.52	3.56	3.42	3.50	3.56	3.40	---	pH Units
		pH10				8.92	8.92	9.08	9.10	8.91	8.90	---	pH Units

Table 2-6. Reference Electrodes Test Data (2 of 4)

	DESCRIPTION		ELECTRODES 1	2	3	4	5	6	7	8	9	10	LIMITS OF ACCEPTABILITY OR UNITS OF MEASUREMENT
22	RESPONSE OF DVT PAIR NO. 2 AFTER 6TH HEAT CYCLE			5.65 pH Units									pH Units
23	EtO DECONTAMINATION TEMP. 1ST CYCLE (50°C)												
24	IMPEDANCE AFTER 1ST EtO CYCLE					4800	5600	3600	4800	4600	4800	---	(Ohms)
25	RESPONSE AFTER 1ST EtO CYCLE	pH4				4.15	4.20	4.25	4.25	4.30	4.20	---	pH Units
		pH10				9.30	9.30	9.25	9.25	9.28	9.30	---	pH Units
26	EtO DECONTAMINATION TEMP. 2ND CYCLE (50°C)												
27	IMPEDANCE AFTER 2ND EtO CYCLE					4000	5100	3100	5400	3900	4000	---	(Ohms)
28	RESPONSE AFTER 2ND EtO CYCLE	pH4				3.57	3.50	3.50	3.55	3.55	3.50	---	pH Units
		pH10				9.00	9.00	9.00	9.00	9.03	9.00	---	pH Units
29	EtO DECONTAMINATION TEMP. 3RD CYCLE (50°C)												
30	IMPEDANCE AFTER 3RD EtO CYCLE					5100	6500	3900	6500	5300	5200	---	(Ohms)
31	RESPONSE AFTER 3RD EtO CYCLE	pH4				3.64	3.63	3.63	3.68	3.68	3.81	---	pH Units
		pH10				9.11	9.13	9.10	9.12	9.11	9.10	---	pH Units

Table 2-6. Reference Electrodes Test Data (3 of 4)

	DESCRIPTION		ELECTRODES 1	2	3	4	5	6	7	8	9	10	LIMITS OF ACCEPTABILITY OR UNITS OF MEASUREMENT
32	EtO DECONTAMINATION TEMP. 4TH CYCLE (50°C)												
33	IMPEDANCE AFTER 4TH EtO CYCLE					4100	5100	3100	5000	4300	4500	---	(Ohms)
34	RESPONSE AFTER 4TH EtO CYCLE	pH4				4.35	3.55	3.55	3.55	3.60	3.65	3.80	pH Units
		pH10				9.40	9.41	9.40	9.41	9.42	9.40	---	pH Units
35	EtO DECONTAMINATION TEMP. 5TH CYCLE (50°C)												
36	IMPEDANCE AFTER 5TH EtO CYCLE					3000	3800	2500	3500	3200	3400	---	(Ohms)
37	RESPONSE AFTER 5TH EtO CYCLE	pH4				3.49	3.50	3.50	3.53	3.51	3.60	---	pH Units
		pH10				9.30	9.32	9.30	9.34	9.30	9.30	---	pH Units
38	EtO DECONTAMINATION TEMP° 6TH CYCLE (50°C)												
39	IMPEDANCE AFTER 6TH EtO CYCLE					4800	5500	3400	5600	5000	5300	---	(Ohms)
40	RESPONSE AFTER 6TH EtO CYCLE	pH4				3.80	3.70	3.27	330	3.25	3.23	---	pH Units
		pH10				9.55	9.45	9.55	9.60	9.52	9.50	---	pH Units
41	RESPONSE OF DVT PAIR NO. 3 AFTER 6TH EtO CYCLE				5.5 pH	Units							

Table 2-6. Reference Electrodes Test Data (4 of 4)